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CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.

SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.

JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.

AND

WILLIAM FRANCIS, F.L.S.

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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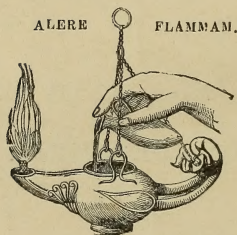
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"Meditationis est perscrutari occulta ; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

———————

——" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

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NUMBER CCXXXVI.—AUGUST.

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PLATES.

ERRATUM.

For formula on page 212, line 11, read

$$K_w = C_v + T \frac{\partial p}{\partial T}\bigg|_v \frac{ds}{dT}.$$

I. *Light Absorption and Fluorescence.*—VI. *Atomic and Molecular Energy Quanta.* By E. C. C. BALY, *Grant Professor of Inorganic Chemistry in the University of Liverpool* [*].

IN the present paper it is proposed to consider the quantitative relationships between the various frequencies exhibited by a substance in the light of the energy quantum theory. These relationships have been detailed in various papers [†], and they would seem to offer a very definite opportunity for the application of this theory. Many attempts have been made to apply the quantum theory, but it must be confessed that the results have not always proved to be very convincing. There is no doubt that any attempts to make use of this theory can only be justified if the results obtained are exact. Confidence in the theory cannot be fostered if the arguments lead to exact deductions from which the observations differ in a marked degree. For example, the Bjerrum theory of molecular rotational frequencies [‡] is a case in point, since this leads to the conclusion that a given substance will exhibit a series of frequencies in the infra-red, the series

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[*] Communicated by the Author.

[†] Phil. Mag. xxvii. p. 632 (1914), xxix. p. 223, xxx. p. 510 (1915); Baly and Tryhorn, Phil. Mag. xxxi. p. 417 (1916); Baly and Garrett, Phil. Mag. xxxi. p. 512 (1916); Garrett, Phil. Mag. xxxi. p. 505 (1916).

[‡] Nernst, *Festschrift*, p. 90 (1912).

having a constant frequency difference. The observed frequencies, however, are not exact, the difference between the extreme values of any one frequency being equal to the difference between two consecutive mean values. Then again there is the formula given by Bjerrum [*] for the molecular heat of hydrogen, $Cv = 5R/2 + R\phi(2\cdot0\,\mu)$, which involves the function of a definite wave-length supposed to be characteristic of hydrogen. It is well known, however, that hydrogen exerts no measurable absorption of energy of this wave-length, and consequently it is difficult to understand how the quantum theory is likely to gain more than discredit from such a case.

On the other hand, the quantitative relations between the various frequencies possessed by a given set of molecules are exact within the highest limit of accuracy reached in observation. Unless therefore the energy quantum theory is capable of explaining the relationships with an equal accuracy, it cannot claim to justify its application.

The relationships which exist may be briefly stated as follows :—

1. Every elementary atom possesses one or more frequencies which are characteristic of the element.

2. When atoms of different elements enter into combination the resulting molecule is endowed with a new frequency which is the least common multiple of the frequencies of the atoms it contains. This may be called the true molecular frequency.

3. The central features of all absorption-bands—that is, those frequencies for which the absorptive power is greatest—are molecular frequencies characteristic of the molecules, since these alone persist when the substance is cooled to low temperatures.

4. The molecular frequencies in the visible and ultra-violet regions are exact multiples of a molecular frequency in the short-wave infra-red, which may be called the infra-red fundamental frequency.

5. The infra-red fundamental frequency is an exact multiple of the true molecular frequency.

6. The breadth of an absorption-band as observed at ordinary temperatures is due to the combination of the molecular central frequency with subsidiary frequencies.

7. Each observed absorption-band consists of a series of sub-groups symmetrically arranged round a central sub-group. If M be the central molecular frequency, the frequencies of the central lines of the sub-groups will be

[*] *Zeitsch. Elektrochem.* xvii. p. 731 (1911), xviii. p. 101 (1912).

given by M $\pm n$I, where $n = 0$, 1, 2, 3, etc. and I is the least common multiple of the frequencies of a group of atoms within the molecule. This may be called an intra-molecular frequency.

8. Each sub-group consists of a central line with series of lines symmetrically arranged round it. If F be the frequency of the central line, then the series of lines will have frequencies given by F $\pm n$A$_1$, F $\pm n$A$_2$, etc., where again $n = 0$, 1, 2, 3, etc., and A$_1$, A$_2$, etc. are those atomic frequencies the least common multiple of which is equal to I.

The first question which arises is the meaning of the characteristic atomic frequencies which are the fundamental constants from which the whole system of frequencies shown by a molecule are derived. Presumably they are connected with the shift of an electron from one stationary orbit to another—a change which must require a definite amount of energy depending upon the electromagnetic force field of the atom. Indeed, it would seem that if the possibility be allowed of the shift of an electron from one stationary orbit to another, it becomes necessary at once to accept the conclusion that a definite and fixed amount of energy is evolved in the change. I therefore propose to start from this assumption, that in any elementary atom it is possible to shift an electron from one stationary orbit to another, that a definite amount of energy is required to effect the change, and that this fixed quantity of energy is connected with the frequency by the relation

$$\frac{\text{Fixed Quantity of Energy}}{\text{Constant}} = \text{Frequency}.$$

This is readily to be understood if the constant involves a function of the time taken in the actual operation, which is the same for every atom and is a universal constant.

This elementary quantum of energy involved in the electron shift is, I believe, the basis of the whole energy quantum hypothesis as applied to absorption and radiation; for I hope to show that the whole can be built up from the original assumption of the elementary quantum as a specific property of the atom. For the sake of convenience only it will be necessary to make use of a value for the constant, and the most recent value for this, based on Planck's theory, is $6 \cdot 56 \times 10^{-27}$. Using this value, the elementary quanta already calculated—namely, those of hydrogen, oxygen, and sulphur—lie between $5 \cdot 25 \times 10^{-16}$ and $1 \cdot 65 \times 10^{-15}$ erg, corresponding with frequencies between $8 \cdot 19 \times 10^{10}$ and $2 \cdot 54 \times 10^{11}$.

The first fact to be dealt with is that when two or more atoms unite together, the resulting molecule becomes endowed with a new frequency, which is the least common multiple of the frequencies characteristic of the atoms. Leaving on one side the cause of the chemical combination, the energy lost in the process may be considered. The simplest possible assumption to make is that in the synthesis of any one molecule each of the component atoms contributes an equal amount of the total energy lost. An elementary atom *ex hypothesi* can only gain or lose energy in elementary quanta, and, further, can only enter into chemical combination if it already contains energy that can be evolved. Let the case be considered of two elementary atoms, the characteristic frequencies of which are 9×10^{10} and $1 \cdot 5 \times 10^{11}$, or in wave numbers $(1/\lambda)$ 3 and 5. The smallest equal amounts of energy that the two atoms can lose is five elementary quanta at the frequency 9×10^{10}, and three elementary quanta at the frequency $1 \cdot 5 \times 10^{11}$. These two amounts are equal to one quantum measured at the frequency $4 \cdot 5 \times 10^{11}$, which is the least common multiple of the two atomic frequencies. In this is doubtless to be found the key to the first problem—namely, that the true molecular frequency is the least common multiple of the frequencies of the atoms in the molecule.

Further, the gain or loss of energy by a molecule as a whole must be equally shared in by the component atoms. When a molecule absorbs or loses energy as a whole, it must do so by means of the elementary quanta characteristic of its atoms. In the case of the molecule specified above, the smallest amount of energy it can gain or lose as a whole is the sum of five quanta at the frequency 9×10^{10} and three quanta at the frequency $1 \cdot 5 \times 10^{11}$. This minimum amount of molecular energy is two quanta at the true molecular frequency, and in this again is to be found an explanation of the fact that the true molecular frequency is the least common multiple of the atomic frequencies.

It is evident, therefore, that, starting from the conception of the elementary energy quantum required to shift one electron, and making the simple assumption that the combining atoms share equally in the energy loss on combination and in the future energy changes of the resulting molecule, we arrive at the conception of molecular quanta, and hence molecular frequency, the latter being the least common multiple of the atomic frequencies.

It can be shown that when molecules under normal conditions are dealt with, one of the most important frequencies

they possess is the infra-red fundamental frequency, which is an exact multiple of the true molecular frequency. In the case of sulphur dioxide the infra-red fundamental is 14 times the true molecular frequency, and in the case of water it is 8 times the true molecular frequency. It was stated above that the smallest possible equal amounts of energy which two or more atoms can evolve when combining together is equal to one quantum measured at the frequency which is the least common multiple of their atomic frequencies. It does not follow, of course, that the reacting atoms only evolve this smallest possible amount of energy. They may evolve an amount of energy which is 2, 3, 4, etc. times this smallest quantity, with the result that the smallest frequency truly characteristic of the molecule may be a multiple of the true molecular frequency. Indeed, it would seem that the infra-red fundamental is the frequency which is truly characteristic of the freshly-synthesized molecule.

At the commencement the simplest possible case was considered of the combination of two atoms, each characterized by a single elementary quantum. There is no necessity to restrict the conditions in this way, and it is to be expected that, at any rate in the atoms of some elements, there will exist more than one possibility of shift of the electrons, and that there will be elementary quanta of different sizes associated with such atoms. It has already been found that two different elementary quanta are associated with the atom of oxygen in the water molecule and with the atom of sulphur in the molecule of sulphur dioxide.

Whilst the establishment of molecular quanta, and hence of molecular frequency, is a simple deduction from the conception of elementary atomic quanta, it cannot be denied that the molecule will also exhibit those frequencies which are characteristic of its component atoms. Although these atoms have united together to form the molecule, there is no reason to expect that they have thereby lost their individuality as far as their powers of absorbing or radiating energy are concerned. The conception of the molecular quantum is based on the assumption that the component atoms can gain or lose elementary quanta when in combination. In addition to this, there is definite evidence that the molecule exhibits the specific frequencies of its atoms, since, although these atomic frequencies have not yet been observed in the long-wave infra-red, they are found in combination with the molecular frequencies as subsidiary

frequencies within the absorption-band groups in the infra-red, visible, and ultra-violet regions. The question then arises as to the course of events when a molecule is exposed to radiation of a frequency that is the same as one of its characteristic atomic frequencies which must be active in the extreme infra-red. Let it be supposed that the molecule formed by the combination of two elementary atoms having the characteristic frequencies 9×10^{10} and $1 \cdot 5 \times 10^{11}$ is exposed to monochromatic radiation of the frequency 9×10^{10}. The atom having this frequency will absorb this energy in elementary quanta of $9 \times 6 \cdot 56 \times 10^{-17}$ erg ; and, further, let it be supposed that this atom absorbs five such quanta. The total quantity of energy now absorbed is equal to the minimum quantity of energy which that atom evolved when combining with the atom with characteristic frequency $1 \cdot 5 \times 10^{11}$, and is equal to one molecular quantum at the true molecular frequency. If the postulate made at the beginning as to the combination of atoms be accepted, then it would seem to follow as a natural consequence that the total energy absorbed by the atom can be transferred to or taken over by the whole molecule as exactly one true molecular quantum. In fact the molecule can obtain one true molecular quantum by the absorption of a whole number of elementary quanta by its atoms, the whole number being, of course, determined by the frequencies of the other atoms in the molecule and the least common multiple of all the atomic frequencies. Further, there is no reason against this process being continuous in the sense that a molecule will be able to gain more true molecular quanta than the single one by absorption of the specified number of elementary quanta by its atoms.

Again, this process will be reversible : that is to say, a molecule will be able to radiate one or more true molecular quanta in the form of the specified number of elementary quanta characteristic of one of its atoms.

It will be seen that this leads to the conception of critical amounts of energy associated with elementary atoms in combination, the critical amount of energy of an atom being a whole number of elementary quanta, characteristic of that atom, which in their sum equal one true molecular quantum characteristic of the molecule of which that atom forms a part. When an atom is exposed to radiation of a frequency equal to its own frequency, it can absorb its elementary quanta until its critical quantity is reached when this critical quantity becomes merged into the molecular energy content as one true molecular quantum.

Amongst the quantitative relationships detailed at the beginning of this paper was mentioned the fact that the central frequencies of all absorption-bands—that is to say, all molecular frequencies—exhibited by a molecule in the visible and ultra-violet are exact multiples of the infra-red fundamental. It is therefore evident that one molecular quantum absorbed at one of the molecular frequencies in the visible or ultra-violet is equal to an exact number of quanta at the infra-red fundamental. If a molecule absorbs one quantum at one of these higher frequencies, this amount of energy can be radiated again as a whole number of quanta at the infra-red fundamental, or partly as quanta at this frequency and partly as elementary atomic quanta. This, as I have shown in previous papers, is the process underlying the phenomenon of phosphorescence or fluorescence, and in this particular case the phosphorescence emission will be in the form of infra-red quanta. Further, it is obvious that the phosphorescence emission need not of necessity be evolved as a whole number of molecular quanta at the infra-red fundamental, but may be radiated as one molecular quantum at a molecular frequency which is a multiple of the infra-red fundamental, the remainder being radiated as molecular quanta at the infra-red fundamental or as elementary atomic quanta. For example, if the molecule absorbs one molecular quantum at the frequency which is ten times the infra-red fundamental, this energy may be evolved as one quantum at the frequency which is nine times the infra-red fundamental and one quantum at the infra-red fundamental itself. In such a case the phosphorescence will be in the visible or ultra-violet region of the spectrum. The factors governing these various alternatives are determined by the conditions under which the molecules exist, but the consideration of these must be postponed. It will be seen from this that a molecule can acquire one or more molecular quanta at the infra-red fundamental in three different ways : by exposure to radiation equal to its atomic frequencies, by exposure to radiation of frequency equal to the infra-red fundamental, or by exposure to radiation of a frequency which is an exact multiple of the infra-red fundamental. Great stress must be laid on this deduction, for it is of paramount importance in connexion with the chemical properties of the molecule.

The next point to be considered is the structure of the absorption-bands—that is to say, the system of subsidiary frequencies which are always found associated with the

true molecular frequency when the absorbing or radiating power of molecules is examined at ordinary temperatures. Two important points must be discussed : first, the formation of the subsidiary frequencies; and, second, the course of events when a molecule absorbs energy at one of these subsidiary frequencies. As regards the latter point, it seems to have been assumed that the molecule as a whole absorbs one energy quantum at that subsidiary frequency. This assumption is very unsatisfactory, for the width of an absorption-band group is often very great ; and hence it becomes necessary at once to postulate the acceptance of a molecular quantum which may vary between very wide limits indeed on account of the great difference in frequency between the extreme subsidiary frequencies in a given absorption-band group. The variation necessary in the size of the molecular assumption is impossibly great. The conception of a molecular quantum given above defines it at once as a quantum measured at one of the exact multiples of the true molecular frequency, and on this conception it is impossible for a molecule as a whole to accept any quantity of energy which is greater or less than one molecular quantum.

These subsidiary frequencies have been attributed by Bjerrum to the rotation of the molecules and by Krüger [*] to their precessional motions ; but, as has been shown in the preceding paper of this series, both these theories break down. In the first place, neither theory takes account of the fact that the subsidiary frequencies are due to the atomic frequencies; and, in the second place, it is necessary for the purposes of these theories to postulate impossibly large variations in the values of the molecular rotation or molecular precession.

On the other hand, the conception now put forward of elementary atomic quanta of energy, whereby definite atomic frequencies are established, would seem capable of affording a very simple and straightforward explanation. Moreover, this conception leads to the establishment of exact frequencies without any possibility of variation. The case may again be considered of the molecule formed by the combination of the two elementary atoms for which the elementary quanta are $9 \times 6 \cdot 56 \times 10^{-17}$ and $1 \cdot 5 \times 6 \cdot 56 \times 10^{-16}$ erg, and which therefore exhibit the characteristic frequencies 9×10^{10} and $1 \cdot 5 \times 10^{11}$ respectively. *Ex hypothesi* the elementary quantum is associated with the shift of one stationary orbit to another, and, of course,

[*] *Ann. der Physik,* l. p. 346, li. p. 450 (1916).

there is no reason to assume that only one electron can be so shifted. There may be many such electrons which can be shifted, the amount of energy being the same for each; and consequently it will be possible for one atom to absorb 1, 2, 3, etc. elementary quanta in the same unit of time. The atom will therefore exhibit frequencies which are 1, 2, 3, etc. times its fundamental frequency. The two atoms specified above will in the free state exhibit frequencies of $n \times 9 \times 10^{10}$ and $n \times 1.5 \times 10^{11}$ respectively, where $n = 1, 2, 3$, etc. The molecule formed by the combination of these two atoms will also exhibit these frequencies, but now the upper limit of n will be fixed by the critical quantity previously defined. Since the least common multiple of the two atomic frequencies is 4.5×10^{11}, the upper limits of n for the two atomic frequency series shown by the molecule will be 4 and 2 respectively, since when $n = 5$ and 3, the two atomic frequency series will converge in the true molecular frequency. Perhaps, therefore, the true molecular frequency will be better understood as the convergence frequency of the atomic frequency series than as the least common multiple of the atomic frequencies.

We may now consider one of the true molecular frequencies. Since the molecule can absorb as a whole one quantum at that frequency, and since also each atom within the molecule can absorb one or more elementary quanta, there is no reason why the two processes should not be simultaneous. The molecule will then absorb in one unit of time an amount of energy equal to the sum of one true molecular quantum and one or more elementary quanta. This will result in the establishment of the subsidiary frequencies $M + nA$, where M is the true molecular frequency, A is the atomic frequency, and $n = 1, 2, 3$, etc., the upper limit of n being fixed by the critical value as already explained. The essential point is that, although one quantum is absorbed at a subsidiary frequency, the molecule itself as a whole only receives one molecular quantum. The amount of energy in excess of this is taken up by the atoms, and if this leads to the energy content of the atoms being greater than that associated with them when the molecule is in radiant equilibrium with its surroundings, the excess amount will be radiated as elementary quanta.

Similarly, there will be established the subsidiary frequencies $M - nA$, for the following reason. Let the molecule which is in radiant equilibrium with its surroundings absorb a quantum of energy at one of its atomic

frequencies. In order for it to gain a molecular quantum at one of its true molecular frequencies, it will now only be necessary for it to absorb the molecular quantum less the atomic quantum already absorbed. It has already been shown how on the present conception summation of atomic quanta can take place to form molecular quanta; so it would follow that, after the absorption of a given number of elementary quanta beyond that associated with the radiant equilibrium, the molecule will be able to absorb the balance necessary to form one molecular quantum. In other words, the molecules will be endowed with the frequencies $M - nA$.

Emphasis may be laid on the fact that under normal conditions when the molecule is in radiant equilibrium with its surroundings the subsidiary frequencies $M + nA$ are actually observed, and, further, that in these series of subsidiary frequencies the maximum observed value of n is one less than the critical value—that is to say, the subsidiary frequencies associated with two consecutive values of the molecular frequency do not overlap. Obviously, if the molecule is screened from all external radiation with frequency equal to its atomic frequencies—that is to say, it is cooled to low temperatures—the whole of the above deductions as to subsidiary frequencies fail, and the subsidiary frequencies must therefore vanish. This also has been observed, since at very low temperatures only the central molecular frequencies remain.

In the foregoing the simplest case only was dealt with of a binary molecule formed by the combination of atoms of two different elements. Exactly the same conditions will, of course, obtain in more complex molecules, but added to these will be new conditions resulting from the existence of groups of atoms within the molecule. For instance, even in the apparently simple case of the water molecule the conditions will be more complex, owing to the undoubted fact that in this molecule the hydroxyl (OH) group exists as an integral portion of the molecule. Whilst, of course, the true molecular frequency will be the convergence frequency of all the atomic frequencies, it is the subsidiary frequencies that will exhibit a greater complexity. This complexity, however, is only one of degree, and its explanation follows exactly the same principles as were laid down for the simplest possible binary molecule. The specific case of the water molecule may be discussed in which there are three atomic frequencies: $1 \cdot 0635 \times 10^{11}$, $2 \cdot 1159 \times 10^{11}$, and $2 \cdot 4531 \times 10^{11}$. Whilst the true molecular frequency of the

water molecule is the convergence frequency of these three, $6 \cdot 1326 \times 10^{12}$, we also have to take into account the intra-molecular frequency of the OH group. Now, in the molecule H–O–H there are two frequencies active for oxygen and one for hydrogen, and thus there are two possible intra-molecular frequencies for the OH group, depending on which oxygen frequency is concerned. In addition, therefore, to the three atomic frequency series the molecule will also show two intra-molecular or OH frequency series. Each of these intra-molecular frequencies is the convergence frequency of two atomic frequency series, and will be associated with subsidiary frequencies to form a band group. If I be the central intra-molecular frequency, the only subsidiary frequencies associated with I will be given by $I \pm nA_1$ and $I \pm A_2$, where A_1 and A_2 are the two atomic frequency series converging at I, and $n = 1, 2, 3$, etc., with an upper limit defined by the critical value. There will also exist two series of frequencies, I_1, $2I_1$, $3I_1$, etc., and I_2, $2I_2$, $3I_2$, etc., each associated with its subsidiary frequencies; and these intra-molecular frequency series will converge at the true molecular frequency.

In the case of the water molecule there are two intra-molecular frequency series—namely $7 \cdot 5 \times 10^{11}$, which is the convergence frequency of the atomic frequencies $1 \cdot 0635 \times 10^{11}$ and $2 \cdot 1159 \times 10^{11}$, and $1 \cdot 7301 \times 10^{12}$, which is the convergence frequency of the atomic frequencies $2 \cdot 1159 \times 10^{11}$ and $2 \cdot 4531 \times 10^{11}$. Since it is known that $2 \cdot 4531 \times 10^{11}$ is one of the atomic frequencies of oxygen, and since the two intra-molecular frequencies are the two possible combinations to form the OH group, it would follow that $1 \cdot 0635 \times 10^{11}$ is the second oxygen frequency and that $2 \cdot 1159 \times 10^{11}$ is the hydrogen frequency.

When the subsidiary frequencies associated with a given true molecular frequency are considered, instead of only the subsidiary frequencies $M \pm nA$, there will exist as subsidiary frequencies $M \pm nI \pm mA$, where n and $m = 0, 1, 2$, etc., each having its own critical limit : I is one or other of the intra-molecular frequencies, and A stands for the two atomic frequencies which have I as their convergence frequency. This will obviously result in the whole group of subsidiary frequencies associated with a given molecular frequency being divided into sub-groups. The central sub-group will be given by $n = 0$, and the central lines of the sub-groups will be given by $m = 0$. This is exactly the structure that has been observed in the case of water and

sulphur dioxide, both of which molecules have three atomic frequencies. Perhaps the most striking experimental confirmation is to be found in the fact that in any one sub-group the subsidiary frequencies are formed from only those atomic frequencies which have the intra-molecular frequency as their convergence frequency. None of the previous theories are able to account for this selective association of the atomic frequencies.

Fig. 1.

Although the system of subsidiary frequencies is more complex in such cases as the molecules of water and sulphur dioxide, yet it manifestly is exactly analogous in detail to

the simple case of the binary molecule. With still more complex molecules it becomes necessary to accept the existence of small atomic groupings within the principle atomic groupings. Without going into the resulting system in detail, it may be stated that this will result in the sub-division of the sub-groups into smaller sub-groups. The trace of the ultra-violet absorption-band of sulphur dioxide is shown in fig. 1, where each sub-group consists of absorption-lines associated in the manner explained with the central line of the sub-group. The next stage in complexity will give a trace similar to that shown in fig. 2. It is of considerable interest to note that the

Fig. 2.
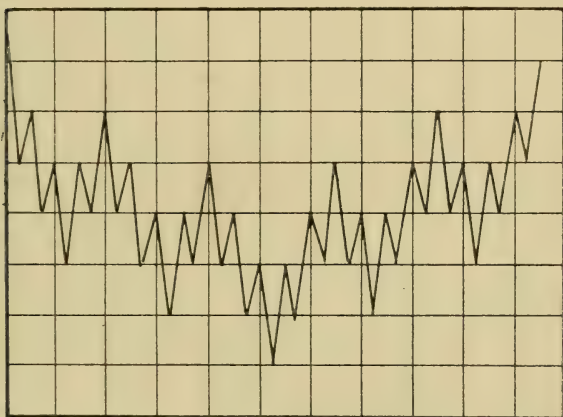
phosphorescence and absorption-bands shown by certain uranyl compounds exhibit a structure exactly analogous to that shown in fig. 2 *.

In the above I have only developed the conception of elementary and molecular quanta as far as the explanation of the establishment of that molecular frequency called the infra-red fundamental, and the association of atomic and intra-molecular frequencies with a true molecular frequency. There remains to be dealt with the origin of the combination of atoms to form molecules, and also the

* Nichols and Merritt, Physical Review, vi. p. 630 (1915) ; ix. p. 113 (1917).

establishment of those molecular frequencies which are multiples of the infra-red fundamental. Both of these are directly connected with problems of chemical reactivity, and are discussed in the following paper. One point only arising from the foregoing discussion of energy quanta may be mentioned here. It has been shown that in the water molecule the oxygen atom exhibits two characteristic frequencies and the hydrogen atom one, whilst in sulphur dioxide the oxygen atoms exhibit one and the sulphur atom two characteristic frequencies. It is difficult to avoid the conclusion that the characteristic atomic frequency is the basis of the valency of that atom. Thus a univalent atom may be one for which there is only one possible shift of its electrons, with a bivalent atom there may be two possible shifts, and so on. From this it would also follow that the numerical size of the elementary quantum associated with the atoms of an element determines the position of that element in the series of electropositivity. Obviously, the larger the elementary quantum associated with an atom, the greater will be the energy given out when that atom enters into combination. Further, when a multivalent atom enters into successive combination with atoms of a given univalent element, its largest elementary quantum will be concerned when it combines with the first atom. This will be followed by the next largest, and so on. This will mean that the "strength" of its different valencies will be different, and the individual bonds with the various atoms of the univalent element will require different amounts of energy to resolve them. This is, of course, well known. In spite of the interesting nature of these deductions, it is perhaps premature to write of them until the underlying phenomenon of chemical affinity has been dealt with.

In venturing to put forward the conclusions given in this paper, I gain some confidence from the fact that they lead at any rate to exact and rigid relationships as regards the energy changes suffered by a molecule. These would seem to be free from that vagueness which is so often associated with attempts to apply the energy quantum theory.

II. *Light Absorption and Fluorescence.*—VII. *Molecular Phases. By* E. C. C. BALY, *Grant Professor of Inorganic Chemistry, University of Liverpool* *.

IN the preceding paper the combination of atoms to form molecules was considered, and it was shown, on the assumption that every elementary atom is characterized by one or more elementary quanta of energy, that the resulting molecule when freshly synthesized is characterized by a molecular quantum of energy, and hence by a fundamental frequency in the infra-red. The affinity of the atoms for one another which causes the reaction to take place was not discussed, and in the present paper I propose to deal with this phenomenon, which, after all, is the fundamental principle of chemical reaction and reactivity.

In previous papers † I have suggested that chemical reactivity has its origin in the electromagnetic force fields of the atom, which, as will be shown below, condense to form atomic and molecular force fields. In the papers referred to it has been shown that these force fields are capable of explaining all the chemical properties of substances. Although this theory seemed to give a satisfactory explanation of chemical reactivity, and one that to a certain extent was quantitative, it lacked a complete quantitative basis. The conception, however, of atomic and molecular quanta brought forward in the preceding paper would appear capable of supplying the necessary quantitative foundation.

The electromagnetic force fields of atoms were first dealt with by Humphreys ‡, who showed that they are capable of giving a quantitative explanation of the Zeeman effect and also of the pressure-shift of spectrum lines. He deduced the fact that two atoms will attract one another when they approach in such a way that the direction of their electronic motions is the same, and will repel one another when their electronic motions are in opposite directions. Each atom therefore possesses two faces, and when one pair of faces comes together they attract one another, and when the other pair comes together they repel one another. In other words, an atom forms the centre of an electromagnetic field of force,

the opposite poles of which are localized in two opposite faces of the atoms.

Let it be supposed that two atoms of different elements are brought together in such a way that their mutually attracting faces come together. They will at once tend to form an addition complex, which can lose energy in the manner described in the preceding paper. The two atoms radiate equal amounts of energy as a whole number of elementary quanta whereby the resulting molecule becomes endowed with the frequency based on the least common multiple of the atomic frequencies. This molecule is now rendered a stable entity, and can only be resolved into its atoms by absorbing an amount of energy equal to that lost in its formation. This quantity of energy consists of a definite number of true molecular quanta.

As will be noticed, however, in this suggestion that the reactivity of atoms for one another is due to the attraction of their respective force fields and that their combination consists in their joint loss of equal amounts of energy, no account has been taken of the other faces of these combining atoms. Whereas the combination of the atoms produces a molecule characterized by a specific energy quantum, it is not possible to consider that the force fields due to external atomic faces can exist without influence on one another. These external force lines must condense to form an external molecular force field, and in this process energy must be evolved. It was not possible previously to determine the amount of energy lost by each molecule in this process, but the theory of elementary and molecular quanta put forward in the preceding paper now enables this to be done with accuracy. It was shown that a freshly-synthesized molecule is characterized by a definite molecular quantum, and hence by a specific frequency in the short-wave infra-red, which has been called the infra-red fundamental frequency. When a freshly-synthesized molecule loses energy as a whole, it must do so in quanta at the infra-red fundamental; and thus it would follow that, when the external force fields of the component atoms of a freshly-synthesized molecule condense together to form the molecular force field, the system loses energy in quanta at the infra-red fundamental of that molecule. Clearly the molecule itself will not suffer any loss of individuality as far as its characteristic frequencies are concerned. None of the deductions from the conception of elementary and molecular quanta made in the preceding paper will be contradicted, and the only change accompanying the formation of the molecular force field will be the

endowment of the system with an additional molecular frequency which is an exact multiple of the infra-red fundamental. Let it be supposed that in the formation of its molecular force field a given molecule loses one molecular quantum at the infra-red fundamental. If the freshly-synthesized molecule were allowed to absorb one quantum at the infra-red fundamental, it would become endowed with certain properties. If, now, it is required to bring the molecule with its molecular force field established by the loss of one quantum into this physical state, it will be necessary to supply it with energy equal to two energy quanta at the infra-red fundamental. There can be no reason against the molecule and its force field absorbing both these quanta simultaneously, and therefore it may be concluded that the system of molecule and force field becomes endowed with a new and additional frequency which is exactly twice the infra-red fundamental. Similarly, it follows that, if the force-field condensation proceeds to the extent defined by the loss of two molecular quanta at the infra-red fundamental, the molecule and its force field will be endowed with a new and additional frequency which is exactly three times the infra-red fundamental. Generally, if the infra-red fundamental of a freshly-synthesized molecule be denoted by M, and if in the formation of the force field x quanta are evolved at that frequency, the system will be characterized by two molecular frequencies—namely M and $M(x+1)$. Since the external atomic fields are bound to undergo a certain amount of condensation, it is evident that the molecule must exist in one of a number of possible phases, each molecular phase being defined by the number of molecular quanta lost in the force-field condensation and characterized by a specific frequency which is an exact multiple of the infra-red fundamental.

The initial assumption was made that the chemical reactivity of atoms is due to the attraction exerted by their electromagnetic fields. As the result of this attraction the atoms form an addition complex which constitutes the first stage in the reaction between them, the second stage being the joint loss of equal amounts of energy by all the atoms whereby the freshly-synthesized molecule is formed with its infra-red fundamental. Similarly, the reactivity of molecules will be a function of their force fields, and the first stage of any reaction between two or more molecules will be the formation of the addition complex due to the attraction between their respective force fields. It follows, therefore,

that the reactivity of a molecule will depend on the molecular phase in which it exists, and further, the greater the extent to which the condensation in the molecular force field has taken place the smaller will be the reactivity. The phase in which a molecule exists is governed by the nature of the external force fields of its atoms. The more equally balanced these are, the greater will be the condensation that takes place between them. The particular phase assumed by a molecule will depend on the external conditions such as temperature, nature of solvent, etc.

The experimental evidence in favour of the existence of these molecular phases is exceedingly strong. It is not possible to give here a detailed account of this evidence, but two or three of the most striking observations may be mentioned. For instance, it is common knowledge that substances which possess very small reactivity are characterized by molecular frequencies which are large multiples of their infra-red fundamentals and lie in the extreme ultraviolet. The converse of this is also true, that substances with measurable reactivity are characterized by frequencies which relatively are smaller multiples of the infra-red fundamental. Again, it is possible by changing the external conditions of temperature or solvent to change the molecular frequency exhibited by a given substance ; and in some cases as many as six different molecular frequencies have been brought into play, each of which is an exact multiple of the infra-red fundamental of that substance. This means that six different molecular phases of the same compound have been observed. Then, again, it has been proved that a particular frequency is associated with a specific chemical reactivity, or, in other words, a particular molecular phase is endowed with its own reactivity. It is manifestly impossible to discuss in detail all the applications of this molecular phase hypothesis within the limits of a few pages, and I propose in this paper to select a few instances, and, in particular, to deal with the energy changes which are involved in chemical reaction.

An interesting point arises at once when the force fields of free elementary atoms are considered. It has been assumed that in a molecular force field the force lines due to the external faces of its atoms undergo condensation to form a condensed molecular force field. It is manifest, if an atom consist of a central positive nucleus with a single plane ring of electrons, that the force lines at the two faces of that atom will be exactly equal and opposite, that condensation must occur to form an atomic field of force, and that this

condensation will be very great with the evolution of a large number of atomic quanta. Such an atom will under ordinary circumstances possess little or no power of attracting other atoms, and hence will have no measurable chemical reactivity. I suggest that the atoms of the inactive gases—helium, neon, etc.—are of this type. On the other hand, if there exist more than one plane orbit of electrons, a condition of asymmetry will be set up in the atomic force field, with the result that the complete condensation to form a non-reactive atomic field is no longer possible. It does not seem improbable that in the various types of asymmetry likely to exist the explanation is to be found of the various properties of elementary molecules which are familiar to the chemist. The extreme conditions resulting from this asymmetry would be (1) the non-reactive diatomic molecule such as H_2, N_2, etc., (2) the highly reactive monatomic molecule such as Na, K, etc., (3) the highly reactive diatomic molecule such as F_2, (4) the non-reactive polyatomic molecule such as that of carbon. Apart from this possibility, which need not now be discussed, it is necessary to take into account the fact that, at any rate in the case of elementary molecules containing more than two atoms, the different molecular phases may be capable of separate existence. Smits has put forward the theory that the different allotropic modifications of an element are equilibrium mixtures of different molecular species of that element. Thus the various allotropic modifications of sulphur are equilibrium mixtures of some or all of four molecular species of sulphur known as S_λ, S_μ, S_π, and S_ϕ. There seems little doubt that what Smits calls molecular species are in reality four different molecular phases of sulphur, which differ in their energy content by a definite number of quanta at the infra-red fundamental of sulphur. It is of considerable interest to note that each of the four varieties of the sulphur molecule exhibits a different molecular frequency in the visible or ultra-violet region, and that they therefore conform to the definition of molecular phases. An investigation of these frequencies is now being made in these laboratories.

The molecular phase hypothesis throws a considerable light on the mechanism of chemical reaction, and enables accurate calculations to be made of the complete energy changes which are involved in any reaction. In the first place, the calculation may be made of the total energy which is evolved during the combination of elementary atoms to form molecules which are in radiant equilibrium with their surroundings. Whereas in the preceding paper it was

shown to be possible to calculate the energy evolved in the actual combination to form the freshly-synthesized molecule, we are now in the position to evaluate the total energy evolved when atoms combine to give molecules as they exist under the ordinary conditions of experiment.

Let the case be considered of the combination of atoms of different elements, and, further, let the characteristic frequencies of these atoms be 9×10^{10}, 1.2×10^{11}, 1.5×10^{11}, and 2.1×10^{11}, respectively. The least common multiple of these four frequencies is 1.26×10^{13}, and this, therefore, will be the true molecular frequency of the resulting molecule. On the assumption made in the preceding paper that an equal amount of energy is contributed for each atomic frequency, the smallest equal amount evolved for each atomic frequency is $1.26 \times 6.56 \times 10^{-14}$ or 8.2656×10^{-14} erg. The total quantity of energy evolved, therefore, in the actual formation of each molecule will be $4 \times 8.2656 \times 10^{-14}$ or 3.30624×10^{-13} erg, which will result in the establishment of the infra-red fundamental 5.04×10^{13}. Since one quantum at this frequency equals the sum total of energy evolved, the absorption of one energy quantum at this frequency will result in the molecule just being resolved back again into its atoms.

The next stage in the process will be the formation of the molecular force field, and let this be accompanied by the loss of 20 quanta at the infra-red fundamental 5.04×10^{13}. As shown above, the molecular system will now be endowed with an additional characteristic frequency, $5.04 \times 21 \times 10^{13}$ or 1.0584×10^{15}, which lies in the ultra-violet region of the spectrum. The energy lost by each molecule during the condensation of its force field will be $5.04 \times 20 \times 6.56 \times 10^{-14}$ or 6.61248×10^{-12} erg. The total energy therefore evolved in the two processes is the sum of 3.30624×10^{-13} erg evolved in the combination of the atoms and 6.61248×10^{-12} erg evolved during the condensation to form the molecular force field, which amounts to 6.943104×10^{-12} erg. This amount of energy, however, is equal to one quantum at the frequency 1.0584×10^{15}, which is characteristic of the molecular phase. As this is obviously true whatever may have been the number of quanta at the infra-red fundamental lost during the formation of the molecular force field, the general conclusion is reached that one energy quantum measured at the largest frequency characteristic of the molecule is just sufficient to resolve that molecule into its atoms. This is a general conclusion which includes Einstein's photochemical law.

The values taken above of atomic frequencies *, infra-red fundamental, and molecular phase frequency closely approximate to those observed with many compounds. It will be seen that the amount of energy evolved in the complete process may be very large, and for a gram-molecule amounts in the above instance to about 102,320 calories. It must, of course, be remembered that in any reaction the observed heat evolved is less than the total amount evolved in the formation of the molecular systems of the products by the amount necessary to resolve the initial substance or substances into atoms.

An important deduction from this molecular phase theory may be made as regards the energy changes involved in chemical reaction. It is obvious that, in any reaction in which the first stage is the resolution of the molecule into its atoms, the energy necessary for this first stage can at once be found from the frequency of the phase in which that molecule exists. Unfortunately, there does not seem to be known at present a single instance of a simple reaction in which the molecular phase frequencies have been accurately measured both for the original substance and the products, and consequently it is not possible at the present time accurately to calculate the net change of energy observed in any reaction. On the other hand, in the vast majority of chemical reactions the reacting molecules are not resolved into their atoms in the first stage of the process. I have shown in a number of cases that it is only necessary to bring the molecules into a particular phase in order to enable them to enter into the desired reaction. A very typical example of the difference in reactivity shown by the different molecular phases of the same molecule is afforded by benzaldehyde. In alcoholic solution this substance exhibits two molecular frequencies in the ultra-violet, and therefore two molecular phases co-exist. It is well known that in alcoholic solution benzaldehyde is readily oxidized by gaseous

* In the example given simple numbers have been used for the atomic frequencies in order to avoid complexity in calculation. It is perhaps worth while to point out here that there are certain indications that the fundamental frequencies of the atoms of different elements are possibly connected by simple arithmetical relations. A sufficient number of these atomic frequencies has not yet been computed, owing to the dearth of accurate measurements of the subsidiary frequencies of simple molecules, to justify any conclusions being made. It is of some interest, however, to note that in sulphur dioxide the oxygen frequency $2 \cdot 4531 \times 10^{11}$ is almost exactly three times the sulphur frequency $8 \cdot 19 \times 10^{10}$, and that in the case of the water molecule the atomic frequency $2 \cdot 1159 \times 10^{11}$ is very nearly twice the atomic frequency $1 \cdot 0635 \times 10^{11}$.

oxygen to benzoic acid, and that it is not converted to benzaldehyde-sulphonic acid when sulphuric acid is added to the solution. The reaction with oxygen, therefore, is characteristic of one or both of the two molecular phases present in alcoholic solution. If benzaldehyde is dissolved in concentrated sulphuric acid, it exhibits two new molecular frequencies—one in the visible and the other in the ultra-violet region. Two further molecular phases therefore exist in solution in sulphuric acid. In this case the benzaldehyde is no longer oxidized by oxygen, but is readily converted into sulphonic acid.

Now, the question arises as to the amount of energy necessary to convert one molecular phase into another and the mechanism whereby this energy is supplied. The amount of energy required per molecule is readily calculated, and is equal to one or more quanta measured at the infra-red fundamental of that molecule. If the frequency characteristic of the first phase is x times the infra-red fundamental, and the required phase is characterized by a frequency which is y times the infra-red fundamental, then the energy required for each molecule is $x - y$ quanta at the infra-red fundamental. Obviously, the molecular system can absorb this energy when exposed to radiation of a frequency equal to its infra-red fundamental, or, as explained in the preceding paper, it may absorb it at any of the frequencies characteristic of its component atoms. Lastly, the molecule may absorb one quantum at its characteristic phase frequency, and under ordinary circumstances this energy will again be entirely radiated as quanta at a lower phase frequency, the infra-red fundamental, or the atomic frequencies. If there is present a substance capable of reacting with a less condensed phase, then the molecule is converted into that phase and reacts, the balance of energy being evolved as infra-red radiation. The essential point is that the necessary amount of energy to change the molecular phase is $x - y$ quanta at the infra-red fundamental, and that when one quantum is absorbed at the phase frequency the excess energy over and above that required is radiated. The change of molecules from one phase to another under the influence of light is readily enough shown experimentally, but it is necessary to stabilize the second phase in some way, since otherwise it returns instantaneously to the first phase. An interesting example is furnished by trinitrobenzene, an alcoholic solution of which contains a molecular phase characterized by a frequency in the ultra-violet. A piperidine solution contains a molecular phase of

trinitrobenzene which is characterized by a frequency in the blue, and the solution is deep red in colour. This second phase, therefore, is favoured by piperidine. If to an alcoholic solution of trinitrobenzene a small quantity of piperidine is added, not more than one molecule of piperidine to 10 molecules of trinitrobenzene, the solution remains perfectly colourless. On exposure to light of the frequency characteristic of the phase in alcohol, the solution turns red owing to the formation of the second molecular phase, and the solution slowly becomes colourless again when placed in the dark.

In order, therefore, to cause a molecule to react it is only necessary in the great majority of cases to bring it into one particular phase, and, in general, this will mean the supply to it of an amount of energy equal to a whole number of quanta at its infra-red fundamental. It is quite possible, of course, since the required reactivity is a function of a particular molecular phase, that it may be necessary to take energy from the molecule, if the phase in which the molecules exist initially happens to be less condensed than the required phase. For the present purpose it may be assumed that the initial phase is more condensed than the reactive phase, and that energy must be given to the molecule in order to enable it to react. Now, the Einstein photochemical law states that in a photochemical reaction a minimum amount of energy equal to one quantum at its absorbing frequency is required for every molecule which reacts. In view of the importance of this law and the very great divergencies that have been observed from it which have led to serious criticism of the theory of discontinuous absorption, it is of some importance to discuss the energy relations of chemical reaction, since the molecular phase hypothesis seems capable of giving a complete and quantitative basis to these relations. A chemical reaction may be divided for this purpose into two parts,—first, the supply of energy to the molecules to make them reactive, and, second, the reaction itself in which energy is evolved, the difference between the two being, of course, the observed heat of the reaction. We may deal first with the supply of energy to the molecules in order to initiate the reaction. If this first stage consists in the complete resolution of the molecule into its component atoms, then one quantum of energy must be absorbed by every molecule at its phase frequency, and therefore, as far as this initial stage is concerned, the Einstein law will hold for absorption at the phase frequency. In the more usual case, when the first stage is the change of the molecular

phase to a less condensed phase, an amount of energy is required for each molecule which is equal to a small whole number of quanta at the infra-red fundamental. If this energy is supplied at the phase frequency, then the one quantum is far larger than is required, and the excess beyond that necessary is radiated again at the infra-red fundamental. Since the molecules can absorb energy at the infra-red fundamental, part or whole of this radiated energy will be re-absorbed by fresh molecules, with the result that they are activated. A number of molecules, therefore, will react after the absorption of one single quantum of energy at the phase frequency, the number depending on the proportional amount of the radiated energy that is re-absorbed by the system. Unless, therefore, the conditions are such that the whole of the radiated energy escapes from the system, the Einstein law cannot hold for absorption at the phase frequency.

In the reaction proper energy is again evolved, since the reacting molecules are endowed with increased energy content as a result of the first stage. It is a matter of indifference whether this energy is radiated in frequencies characteristic of the reacting molecules or of the resulting molecules, since both are built up from the same atoms. The energy radiated during the reaction of the molecules can therefore be absorbed by fresh molecules which become activated. If any of this energy is re-absorbed by the system, then the divergence from the Einstein law, already established in the first stage, will still further be increased in the second stage.

A specific instance may be taken to illustrate the above, and that of the photochemical decomposition of hydrogen peroxide may be chosen. According to the observations of Henri and Wurmser[*], made with a dilute aqueous solution, 180 molecules were decomposed for every quantum of energy absorbed at the phase frequency, which is approximately $1 \cdot 3 \times 10^{15}$. As pointed out by these authors, this and other analogous results form as they stand a very damaging criticism of Einstein's law. Now, in all probability the infra-red fundamental of hydrogen peroxide is very near to that of water ($4 \cdot 9 \times 10^{13}$), and therefore the phase frequency may be taken as 26 times the infra-red fundamental. It may be assumed simply for purposes of calculation that the frequency of the reactive phase of hydrogen peroxide is 25 times the infra-red fundamental. If so, a molecule of hydrogen peroxide absorbs one quantum at the molecular

[*] *Compt. Rend.* clvi. p. 1012 (1913).

phase frequency and radiates 25 quanta at the infra-red fundamental, since only one quantum at this fundamental is required to activate it. If, now, these 25 quanta are completely radiated to their surroundings, then one quantum is absorbed at the phase frequency for every molecule of the hydrogen peroxide that reacts. Unless the conditions are especially suited this will not occur, and the radiated energy will be re-absorbed by fresh molecules of hydrogen peroxide. If none of this energy escapes, then altogether 26 molecules of hydrogen peroxide will be rendered reactive as the result of the absorption of one quantum at the phase frequency.

We may now consider the reaction itself, $2H_2O_2 = 2H_2O + O_2$. The total amount of energy evolved in this reaction will obviously be the sum of that absorbed in activating the molecules and the observed heat of reaction. As for the purposes of calculation we have assumed that 26 molecules of hydrogen peroxide have been activated and are therefore decomposed, the total energy evolved is 26 quanta at the fundamental infra-red frequency plus the observed heat of reaction for 26 molecules of hydrogen peroxide. The observed heat of decomposition for one gram-molecule of hydrogen peroxide is 23059 calories, which is 1.564×10^{-12} erg per molecule. The observed energy evolved for 26 molecules is therefore 4.0664×10^{-11} erg, which is almost exactly equal to 130 quanta at the infra-red fundamental. The total energy therefore evolved after the absorption of one quantum at the phase frequency of hydrogen peroxide (complete re-absorption being assumed) is equal to 156 quanta at the infra-red fundamental. If, again, this is completely re-absorbed, 156 fresh molecules will be rendered active, and so the reaction will proceed through the whole mass.

Two extreme conditions are possible—one in which the whole of the internally radiated energy escapes to the surroundings without re-absorption, and the other in which it is re-absorbed to the maximum possible extent by fresh molecules of hydrogen peroxide. In the first, the Einstein law will apparently hold—that is to say, whilst one quantum will be absorbed for every molecule reacting, this quantum is a multiple of the amount actually employed in making the molecule react. In the second, when one quantum at the phase frequency has been absorbed, an unlimited number of molecules will react; for it is obvious that the reaction velocity will rise to a critical limit, and in the extreme case will pass as an explosion wave through the substance.

In actual practice the most probable condition will be one lying between the two extremes—namely, the re-absorption of an aliquot part of the radiated energy. This will result in a large but definite number of molecules reacting for every quantum absorbed, and this doubtless gives an explanation of the observations by Henri and Wurmser. The number of molecules that react for every quantum of the energy absorbed at the phase frequency will vary directly with the proportion of the internally radiated energy that is re-absorbed by the system.

In this explanation of the divergence from Einstein's law use is made of two processes—first, when the quantum of energy at the phase frequency is larger than the amount required to activate one molecule, the molecule retains the amount it needs for its conversion into the active phase and radiates the excess; and, second, the re-absorption of this radiated energy by fresh molecules. Direct evidence has been obtained of the occurrence of both these processes. The conversion of one molecular phase into another phase of higher energy content by the absorption of energy at the frequency of the first phase—a process which involves the absorption of a quantum for each molecule far larger than required for the phase change—was instanced above in the case of trinitrobenzene. Many other instances are known, including the familiar phenomenon of fluorescence. In the latter case one molecule absorbs one quantum at its phase frequency, and is converted into a phase of greater energy content. The excess of energy beyond that necessary for the change of phase is radiated as one quantum at the frequency of the new phase, this radiation being recognized as fluorescence.

A characteristic instance of the re-absorption of the radiated excess energy beyond that required for the phase change is afforded by triphenyl-methane in alcoholic solution. The substance absorbs energy at its phase frequency, and is converted into a phase with higher energy content, the excess energy being radiated as one fluorescence quantum at the frequency of the new phase. This radiated energy is partly re-absorbed with the formation of a third phase, the excess again being radiated as one fluorescence quantum at the third phase frequency. Two fluorescence frequencies are therefore observed, the one at the smaller frequency being due to the partial re-absorption of the first.

It was also stated that the fact that the energy of the reaction proper may be radiated at frequencies characteristic of the products will make no difference as regards its

re-absorption, since these are based on the same atomic frequencies as those of the initial substance. It is obvious, as stated above, that the total energy evolved by the activated molecules when reacting will equal the sum of the energy absorbed and the known heat of the reaction. We have therefore

Known heat of the reaction

= total energy evolved, less total energy absorbed.

Now, the energy absorbed is equal to a whole number of quanta at the infra-red fundamental, and if the energy given up by the activated molecules when reacting is, as suggested, a whole number of quanta at the infra-red fundamental, then the known heat of the reaction must also be a whole number of quanta at the infra-red fundamental. Indeed, it would seem that considerable support would be obtained if the observed heat of the reaction for a single molecule is equal to a whole number of quanta at the infra-red fundamental of that molecule. Now, the observed heat of decomposition of hydrogen peroxide is 23059 calories, which is $1·564 \times 10^{-12}$ erg per molecule. The quantum at the infra-red fundamental of hydrogen peroxide (assumed equal to that of water) is $3·2184 \times 10^{-13}$, and therefore the heat of reaction per molecule is almost exactly 5 quanta at the infra-red fundamental.

There are relatively few substances for which accurate values are known of both the infra-red fundamental and heat of formation. But it is more than probable from the evidence which exists that this relation is a true one. Thus the heat of formation of the molecule of water is $2·312 \times 10^{-12}$ erg, which is very nearly equal to $2·2526 \times 10^{-12}$ erg, or 7 quanta at the infra-red fundamental. Again, the heat of formation of one molecule of sulphur dioxide from gaseous sulphur and oxygen is $4·737 \times 10^{-12}$ erg, which is very nearly equal to $4·782 \times 10^{-12}$ erg, or 18 quanta at the infra-red fundamental of sulphur dioxide. Since the infra-red fundamentals of these substances are known accurately, it is justifiable to calculate the heats of formation from these on the basis of the present relation. The heat of formation of a gram-molecule of water calculated on the basis of 7 quanta at the infra-red fundamental is 33,200 calories, and that of sulphur dioxide on the basis of 18 quanta is 70,360 calories, the observed values being 33,993 and 69,800 calories respectively.

Similar discrepancies to those in the case of photochemical reactions will also be found between the number of energy

quanta absorbed and the number of molecules which react in thermal reactions where the absorption of energy takes place at frequencies in the infra-red. In any exothermic reaction there will be a discrepancy in the sense that more molecules will react than are calculated on the basis of the quantum theory. Lewis * has drawn attention to the serious discrepancy which occurs in the thermal decomposition of phosphine, the velocity of the reaction being enormously greater than that calculated on the quantum theory. The decomposition of phosphine to give hydrogen and phosphorus is an exothermic reaction † : so that, if the energy radiated during the decomposition is re-absorbed by fresh molecules of phosphine the observed reaction velocity will be greater than that calculated on the basis of a direct relation between the energy absorbed from external sources and reaction velocity. The divergence will be enormous if the proportion of internally radiated energy that is re-absorbed is large. I venture to think that in this is to be found the explanation for which Lewis asks.

In general, it would seem probable that the proportion of internally radiated energy that is re-absorbed by the system will depend on the temperature and pressure. For example, it would be natural to expect that this proportion would be increased if the molecular concentration of the reacting system is increased. Without doubt this explains the much greater divergence from Einstein's law that is found in the case of a photographic plate than in the case of photochemical reactions in dilute solutions. Thus Henri and Wurmser found that with 0·037 normal solution of hydrogen peroxide 180 molecules were decomposed as the result of the absorption of one quantum at the phase frequency. With a normal solution of acetone 1360 molecules were decomposed for every phase quantum absorbed. On the other hand, these authors point out that Leimbach's measurements with a photographic plate lead to the conclusion that five million molecules of silver bromide are reduced to silver for every quantum absorbed at the phase frequency of silver bromide. These figures show clearly the increase in the divergence from the Einstein law that results from the increase of molecular concentration. This agrees with the view that the divergence is due to the re-absorption of the internally radiated energy.

There are obviously many directions in which this molecular phase hypothesis can be quantitatively applied, and

* Phil. Mag. xxxix. p. 26 (1920).
† P. Lemoult, *Comptes Rend.* cxlv. p. 374 (1907)

not the least interesting of these is the problem of the three states of matter and the difference in their energy contents. Following on the theory of allotropy, it is an obvious conclusion to draw that the three states are equilibrium mixtures of different molecular phases. Whilst it cannot be assumed that any change of state is due to a change of phase of every molecule present, yet it is not impossible that, at any rate, the latent heat of evaporation should approximate to the amount of energy associated with a change of phase—that is to say, one or more quanta at the infra-red fundamental for every molecule. The values of the infra-red fundamentals are at present known for very few substances, but it is possible to make use of the most important molecular frequency, in the infra-red, which, as I have shown, is the infra-red fundamental in the cases of water and sulphur dioxide. In Table I. are given the relations between the latent heat of evaporation per molecule and the quantum at the infra-red frequency. The agreement is so close that I have calculated the latent heat on the basis of it being equal to the number of infra-red quanta shown in the seventh column. The calculated values expressed as calories per gram-molecule are given in the last column.

In the cases of carbon tetrachloride and sulphur it may be noted that the infra-red measurements are not so trustworthy as those of the other compounds [*]. At the same time it must be noted that there are some compounds for which this relation does not appear to hold. Now, it is well known that water is associated in the liquid condition, and therefore the suggestion may be made that when the latent heat is equal to two or more infra-red quanta, this is due to the molecule of the liquid being more complex than the molecule of the vapour. The cases in which the relation does not hold would then be explicable on the ground that the molecular association is indefinite—that is to say, the liquid contains an equilibrium mixture of two molecular complexes. This application of the molecular phase hypothesis cannot, however, be further discussed here.

In conclusion, reference may be made to the deduction from the molecular phase hypothesis that, since a specific molecular phase is essential for a molecule to take part in a given reaction, a definite amount of energy must, in general, be supplied to the molecule before the reaction can take place. Whilst this is not new, the conception of the critical

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[*] Coblentz, Pub. Carnegie Inst. Washington, No. 35 (1905).

TABLE I.

Heat of Vaporization.

	Observed molecular latent heat.	Latent heat, in ergs per molecule.	Principal band in infra-red.	Infra-red frequency.	Quantum at infra-red frequency in ergs per molecule.	Number of quanta.	Calculated molecular latent heat.
Carbon disulphide............	6384	$4 \cdot 332 \times 10^{-13}$	$4 \cdot 6$ μ	$6 \cdot 522 \times 10^{13}$	$4 \cdot 278 \times 10^{-13}$	1	6305
Water.......................	9650	$6 \cdot 548 \times 10^{-13}$	$6 \cdot 115 \mu$	$4 \cdot 906 \times 10^{13}$	$3 \cdot 218 \times 10^{-13}$	2	9485
Ammonia	4950	$3 \cdot 259 \times 10^{-13}$	$12 \cdot 04$ μ	$2 \cdot 500 \times 10^{13}$	$1 \cdot 64 \times 10^{-13}$	2	4854
Acetic acid	5094	$3 \cdot 458 \times 10^{-13}$	$11 \cdot 5$ μ	$2 \cdot 609 \times 10^{13}$	$1 \cdot 711 \times 10^{-13}$	2	5044
Methyl acetate	8166	$5 \cdot 541 \times 10^{-13}$	$7 \cdot 1$ μ	$4 \cdot 225 \times 10^{13}$	$2 \cdot 772 \times 10^{-13}$	2	8170
Ether	6660	$4 \cdot 519 \times 10^{-13}$	$8 \cdot 75$ μ	$3 \cdot 429 \times 10^{13}$	$2 \cdot 249 \times 10^{-13}$	2	6629
Chloroform.................	6984	$4 \cdot 739 \times 10^{-13}$	$8 \cdot 3$ μ	$3 \cdot 614 \times 10^{13}$	$2 \cdot 371 \times 10^{-13}$	2	6988
Carbon tetrachloride.........	7190	$4 \cdot 879 \times 10^{-13}$	$12 \cdot 9$ μ	$2 \cdot 326 \times 10^{13}$	$1 \cdot 526 \times 10^{-13}$	3	6744
Sulphur	23160	$1 \cdot 572 \times 10^{-12}$	$11 \cdot 8$ μ	$2 \cdot 547 \times 10^{13}$	$1 \cdot 671 \times 10^{-13}$	9	22158

increment of energy being due to Marcelin and Rice [*], the present theory independently arrives at the same conclusion, and, moreover, shows that the critical increment is equal to a whole number of quanta at the infra-red fundamental. In a series of papers, Lewis [†] has made certain calculations of the critical increments necessary in certain reactions and the frequencies at which this energy is absorbed. He writes the expression given above in the form

$$\text{Observed heat of reaction} = E_0 - E_1,$$

where E_1 is the sum of the critical increments of the reactant molecules and E_0 that of the resultant molecules. When the energy is absorbed or evolved at the phase frequency, this expression will only be true if the reactant molecules are completely dissociated into atoms. It is evident from the present hypothesis that the critical increment is a whole number of quanta at the infra-red fundamental—an amount of energy which may be very much smaller than one quantum at the phase frequency. In such a case impossible results will be obtained if the frequencies are calculated from the critical increments derived from the heats of dissociation of the molecules into atoms.

III. *A New Reading of Relativity.*
By Prof. FREDERICK SLATE [‡].

A RECENT paper [§] has broken ground for a rectified comparison between Einstein's kinematics and Newton's methods by insisting first upon restoring the broader connexion of force with "Quantity of motion." New tribute is paid to the hypnotic power of a current view to evade challenge, in the delay of this conclusive step towards juster correlation, after the disadvantage within the range of electro-magnetics had been conceded against the narrowed form of Newton's equations. But an undeniable habit has inclined overmuch toward some particulars of rigid dynamics, however aware one is latently that the literal condition of variable mass is often directly natural, and that the devices lie close at hand which fit for parallel treatment the enlarged (or

* Rep. Brit. Assoc. p. 397 (1915).
† Trans. Chem. Soc. 1914 to 1919, *passim.*
‡ Communicated by the Author.
§ Slate, Phil. Mag., April 1920, p. 433.

more figurative) concept of inertia [*]. Else why Minkowski's words ? " Die Gleichungen der Newtonschen Mechanik zeigen eine zweifache Invarianz. Einmal bleibt ihre Form unverändert wenn man das zugrunde gelegte räumliche Koordinatensystem einer beliebigen Lagenveränderung unterwirft, zweitens, wenn man es in seinem Bewegungszustande verändert, nämlich ihm irgendeine gleichförmige Translation aufprägt " [†]. In the origins of relativity, the equivalent of equations (1, 2, 3) below seems nowhere drawn into consideration. Einstein and Lorentz do not break away radically from the former's equation :

" Massenzahl × Beschleunigungszahl = Kraftzahl " [‡].

This type of relation is in evidence unaltered, even where a variable " transverse mass " enters. For the Newtonian procedure, a force thus expressed implies an inertia held stationary at its epoch-value ; the derivative of momentum is partial. We shall meet an important instance presently [§].

The more thoroughgoing ascription of variable inertia to electrons, as a starting-point either for Newtonian dynamics or for relativity, carries with it then nothing forced, nor subtle, nor unique into the equations of motion, activity, and work. Grant freely how much a dense ignorance about detail in atomic and electronic systems compels us to leave vague, beyond the proof of inertia through observed partitions of energy. But neither Newton nor Einstein escapes that

[*] Careful elementary comment upon Newton's laws will not neglect this side. See Tait and Steele (1878), ' Dynamics of a Particle,' p. 330, etc. ; Slate (1900), ' Principles of Mechanics,' p. 220, etc. Passing over to moment of inertia, it may change with the rotation-axis. The idea of " effective inertia," expanded fruitfully by Sir J. J. Thomson, includes variableness of that quantity, especially where undetected (or ignored) forces are in play. This latter phase, in its application to electrons, I have indicated earlier: ' Science ' (1908), vol. xxviii. p. 180.

[†] Raum und Zeit. Conveniently accessible in the collection of foundation-laying papers (cited here as " Sammlung ") : Lorentz—Einstein—Minkowski; *Das Relativitätsprinzip*, Teubner (1913). See p. 56 ; and p. 72.

[‡] Sammlung, p. 51. See also (p. 28): " Die zu entwickelnde Theorie stützt sich . . . . auf die Kinematik des starren Körpers." The position taken by Lorentz shows on pp. 17, 78, etc. Expository writers like Silberstein conform : see his ' Theory of Relativity,' pp. 15, 17 ; Chapter VII, *passim*; etc. This is an eminently temperate summary. The terms of all such statements are at best misleading. It would be unfair to pin down to them every recent exponent of relativity ; shading of attitude there cannot fail to be. Yet they still muster heavy enough backing to call for definite abatement. The change of " rest-mass " with internal energy is set off as a distinct question.

[§] Equation (10), below.

indeterminateness now ; while the fullest employment of their united suggestions must mark the sanest course in adjudicating questions there, or in regard to gravitation. In that interest, this paper turns solely to detecting simple links of interrelation between the two methods. Whatever yokes standard dynamics and relativity for joint service based on complete reciprocal consistency—this the new line of approach seeks. Preferential choice may nevertheless remain open to individual opinion ; or indeed it may prove to shift with the class of problem in hand. Some resettlement of rating in this quarter is scarcely avoidable, because the extension to variable inertia certainly upsets at least one allegation. The fact looms up at once that the rigid dynamics (of Einstein's theory) becomes now a convergence-point of two more general forms, under approximations through $dm/dt = 0$; $c = \infty$; respectively. It is not tenable that broader Newtonian dynamics itself reduces directly from relativity by neglecting in the latter terms that contain powers of $(1/c)$ *.

Those expressions for tangential force, activity, and work laid down in the previous paper lie then at the heart of the matter. For convenience we quote them, with minor changes :—

$$T_o \equiv \frac{d}{dt}(Q_o) \equiv \frac{d}{dt}(mv_o) = m\frac{dv_o}{dt} + v_o\frac{dm}{dt} ; \quad . \quad . \quad (1)$$

$$A_o \equiv v_o T_o = \frac{d}{dt}\left(\frac{mv_o^2}{2}\right) + \tfrac{1}{2}v_o^2\frac{dm}{dt} ; \quad . \quad . \quad . \quad . \quad (2)$$

$$W_o \equiv \int_0^t v_o T_o dt = \left[\genfrac{}{}{0pt}{}{t=t}{E}{t=0}\right] + \tfrac{1}{2}\int_0^t v_o^2\frac{dm}{dt}dt. \quad . \quad . \quad (3)$$

The subscript letter (o) tags a quantity, here and elsewhere, as "observed," or as calculated without artifice from observations. The equations are written for one standard frame (F), always for standard signs and in C.G.S. measure. Plainly (Q_o) symbolizes momentum, and (E_o) kinetic energy. So long as the dynamical process mirrors quantitatively one of pure mechanics, nothing hinders a mixed reading for (m); it can cover narrow weight-mass and inclusive inertia, with (Q_o, E_o) read to correspond.

In equations (2, 3), the "Principle of *vis viva*" has gone by the board, along with an exclusive measurement of force

* *Cf.* Silberstein, p. 115; Laue, *Das Relativitätsprinzip*, p. 157 ; and others.

by a product of inertia and acceleration [*]. Equation (1) does not calculate the same value of (T_o) from the second member, when (v_o) alone is altered there. Neither are values of the acceleration equal for differing (v_o) but equal assigned (m, T_o). This equation of motion is not fully invariant thus in either aspect of its double function. But even under other conditions that do satisfy the " Newtonian transformation," the freedom due to its force-invariance should not be overrated. Not only do kinetic energy, momentum, activity, change with velocity-values, but since the relative path is affected, so also is the distribution of the same total acceleration into its tangential and normal parts. Therefore entire continuity across transfers among "legitimate frames" will require some composite scheme. The fuller scope of invariance for relatively fixed frames can be worked in here; at times with less than explicit credit for its help, as will be seen later.

Inquiry is still limited to progressive rectilinear motion of an electronic particle (m), in part because this case makes vital contacts and gives cues for less particular suppositions. To lay out its province for relativity gradually by induction runs truer to scientific form in any event; we are not declaring a creed.

Adopting the "deformable electron" brought forward by Lorentz and supported by experimental data, the rule is taken over:

$$\frac{dm}{dv_o} = \frac{mv_o}{c^2 - v_o^2}; \quad \frac{dm}{dt} = \frac{mv_o}{c^2 - v_o^2}; \quad m = m_0 \frac{c}{\sqrt{c^2 - v_o^2}}. \quad (4)$$

Retain:

$$\gamma(z) \equiv \left(1 - \frac{z^2}{c^2}\right)^{-\frac{1}{2}}; \quad m_0 \equiv [m]_{v_o=0}; \quad c \equiv \text{light-speed in (F)}.$$

Then all the work may go into field-structure, as we noted, and equations (1, 2, 3) become, if $v_o = (v)_0$ at $t = 0$,

$$T_o = m\left(1 + \frac{v_o^2}{c^2 - v_o^2}\right)\frac{dv_o}{dt} = m\gamma^2(v_o)\frac{dv_o}{dt} = m_0\gamma^3(v_o)\frac{dv_o}{dt}; \quad (5)$$

$$A_o = c^2\frac{dm}{dt}; \quad W_o = c^2 m_0(\gamma(v_o) - \gamma(v)_0). \quad \ldots \quad (6)$$

Whatever physical particulars record themselves through

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[*] Silberstein, p. 195; Laue, p. 5; illustrating the need of some such remark.

equation (4) are of necessity carried with it into all combinations that accept it. With its aid, standard dynamics and C.G.S. measure have led straight to these results for the frame (F). They are formally identical with what relativity would allow, for parallel conditions; though demanding for them also wider validity. Emphasize that (m_0) being a special value here, its identification with "Minkowski mass" requires constancy in the latter [*]. Modifications of equation (4) on this score or on others can be introduced, but they are not of immediate concern. It can remain plastically true, if held open to revision by further experimental success. The equivalence of consolidations in equation (5) through addition and through multiplication is a feature with notable consequences [†].

What proves to be one main thread of the subsequent analysis joins on to an elementary problem, whose results we quote in part. Consider a straight path, constant propelling force (P) and mass (m_1), and a resistance (R) proportional to (v^2). There is a terminal speed (v_1). With notation and detail

$$\frac{P}{m_1} \equiv a; \quad \frac{R}{m_1} \equiv kv^2; \quad v_1^2 = \frac{a}{k};$$

the equation of motion

$$P - R = m_1 \frac{dv}{dt}; \quad \frac{P - R}{m_1} = \frac{dv}{dt}; \quad . \quad . \quad . \quad (7)$$

by simple recasting yields the forms

$$P = \frac{m_1 v_1^2}{v_1^2 - v^2} \frac{dv}{dt}; \quad R = \frac{m_1 v^2}{v_1^2 - v^2} \frac{dv}{dt}; \quad . \quad . \quad (8)$$

$$P = m_1 \frac{dv}{dt} + \frac{m_1 v^2}{v_1^2 - v^2} \frac{dv}{dt}; \quad \frac{P}{m_1} = \frac{dv}{dt} + \frac{v^2}{v_1^2 - v^2} \frac{dv}{dt}. \quad . \quad (9)$$

But equations (7) apply legitimately to net field-action combining a constant propelling field (a), and an automatically excited resisting field (kv^2), the acceleration being then characteristically independent of the "body coefficient" (m_1). And any actual physical linkage of (a, k), when (k) changes

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[*] See note †, p. 32; and *cf.* Silberstein, p. 194.

[†] Among others this: it favours grafting forms due to variable inertia upon a root-idea of constant (m_0). Relativity's "complex" of force has the magnitude of (T_0): e. g., for the tensor of its quarternion; which the so-called "rest-system" then renders coincident with a "Newtonian" force. *Cf.* Silberstein, pp. 193-4. The same thought applies at equation (11) below.

with (a), that entails constancy of the ratio (a/k), would evidently fix also a common value of the terminal speed, whatever strength (a) has. Supposing this condition met, and with $(v_1 = c)$ given, equation (9) corresponds visibly to equation (5) save in one essential respect : the type of the original equation (7) makes (m_1) necessarily constant. It is true, the elimination of (m_1) would permit assigning any series of epoch-values to that quantity, without influencing the kinematics through the consequent readjustments of force. They might differ arbitrarily or in conformity with a rule laid down. They might follow, for example, the range of (m), as it varies under the rule of equation (4). Yet each such momentary value of (m_1) must be rated constant as a parameter, because equation (7) has required that.

The proposition is defensible that light-speed is also limiting speed for all electrons under any electromagnetic field-forces. It can borrow some confirmation from forms like equation (6), which somehow standardize in terms of (c), and it is plausibly consistent with an idea impressed upon relativity regarding (c) as an unexceeded value. That this critical speed should coincide with the wave-speed does not look unreasonable. Only one of these rôles for (c), then, would be common to light and gravitation, since the critical speed alone is known in the latter ; it separates the ellipse as an orbit from the two other conics. The analogies of these two field-actions might go astray on such an ambiguity. As affording a provisional background for some electronic dynamics, we shall write the above assumption about (c) into our expressions relative to (F).

Note next how the first of equations (8) in effect suppresses (R), which is *passive* in the sense of not contributing to the total energy-flux, but merely diverting part of it. It is clearly immaterial whether the diverted energy is reversible or not. Read the second member as a product of the true acceleration by an effective inertia [*]. Since that inertia-factor is here variable, the equation in the form

$$P = m_2 \frac{dv}{dt} = (m_1 \gamma^2(v)) \frac{dv}{dt} \quad . \quad . \quad . \quad (10)$$

must be incomplete, as judged by equation (1) which becomes

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[*] Effective inertia merits wider use perhaps ; it is so variously adaptable to bridge gaps in knowledge or to secure compacter statement. The pure translation that equation (5) supposes may thus replace a screw-motion of a rigid solid having constant mass and moment of inertia. The pitch of the screw would vary.

its obligatory type. The artificial infinity of (m_2) for $(v=c)$ is requisite to preserve the zero-acceleration at $(P=R)$ with finite (m_1). Within the freedom to utilize epoch-values for (m_1), choose a series that gives perpetual equality of (m, m_1). That device amounts to completing equation (10), and establishing an exact step-by-step agreement in force-magnitude with equation (5). Yet the two plans do not quite coalesce ; (dm) can never be primarily an increment of any constant (m_1), also residual divergence from equations (3, 6) must continue. The Principle of *vis viva* is differentially valid ; each constant (m_1) absorbs a work-element wholly into change of kinetic energy. Remark finally that assignment of permanent value (m_0) to (m_1) brings in a significant instantaneous relation

$$\mathrm{T}_o = \gamma(v)\mathrm{P} \quad [m_1 = m_0] \ . \ . \ . \ . \ . \ (11)$$

This line of possible connexion has been dwelt upon as preliminary at more length than its simple thought would justify, did it not strike centrally at the reasons—often left elusively subtle—which necessitate certain transitions peculiar to relativity. Its plain bearing will not be overlooked, it can be hoped, upon the duplicated forces of " Minkowski type" and of "Newton type"; nor upon the introduction of "proper time" as well as "local time." Both of which discriminations are given effect differentially, on the model of equation (11) *.

Associated with the standard frame (F) are a group (U) of comparison frames ("legitimate frames") having unaccelerated translations (u) relative to it, (u, v_o) being colinear, and for standard sign codirectional. Transfers between (F) and (U) disturb fundamental expressions ; but we shall test there what degree of approach can be disclosed nevertheless to that permanence of type which is relativity's victory. Velocity and tangential acceleration belonging to (F) will show in any (U) the magnitudes

$$v' \equiv v_o - u \ ; \quad \frac{dv'}{dt} = \frac{dv_o}{dt}. \quad [(u) \text{ is vector-constant.}]$$

* Relativity has invented manipulation of factors like $(\gamma(v))$, where it needs to add or to suppress them, with admirable success. But no more will be expected here than to indicate clues at important turns of the discussion, after which calculative detail is read with new meanings in mere routine. Moreover, the points made can appeal to those only who judge the argument with an interest due to knowledge of the subject.

Accordingly an "apparent" force (T_a') estimated in that (U) is given by

$$T_a' \equiv m\frac{dv_o}{dt} + (v_o - u)\frac{dm}{dt} = \frac{d}{dt}(mv') = T_o - u\frac{dm}{dt} \quad . \quad (12)$$

Add this explicit agreement: Effective inertia is inferred from physical relations in (F), and passes unchanged through such purely kinematical revisions. Direct combination of equations (4, 12) under their condition of equal accelerations shows

$$T_a' = \left(1 - \frac{uv_o}{c^2}\right)T_o. \quad . \quad . \quad . \quad . \quad (13)$$

The "reduction factor" ($1 - uv_o/c^2$) connects the forces manifest in (U, F) through using (m) with the respective kinematical data. Or equation (12) is evidently applicable to compare forces in (F), for the same inertia and acceleration, at differing speeds.

In particular at ($u = v_o$),

$$T_a' = m\frac{dv_o}{dt} \quad [u = v_o].. \quad . \quad . \quad . \quad . \quad (14)$$

This introduces the familiar "rest-system" of relativity. And since we may write

$$T_a' = \left[\left(1 - \frac{uv_o}{c^2}\right)m_0\gamma^3(v_o)\right]\frac{dv_o}{dt} \equiv m'\frac{dv_o}{dt},$$

under the suggestion of rigid dynamics, it would follow that

$$\frac{c^2 - v_o{}^2}{c^2 - uv_o}\,T_a' = \left(\frac{c^2 - v_o{}^2}{c^2 - uv_o}m'\right)\frac{dv_o}{dt} = m\frac{dv_o}{dt}. \quad . \quad . \quad (15)$$

Identification of "Fresnel's coefficient" (κ) in this second member fits the idea of its connexion with "inertia-drag" in (U) *.

Einstein's "Addition theorem for velocities" presents the same reduction factor as equation (13). But there it would reduce the velocity of (m) relative to (O') the origin of (U) to dependence upon specifying frames. Newton makes that a constant difference of any pair of corresponding values. The intrinsic meaning of the theorem must go deeper, since its characteristic factor offers itself unconstrainedly in a dynamic relation of the two frames. This must quicken the surmise that what underlies the "Lorentz transformation"

* *Cf.* Silberstein, pp. 172-3.

is not exhausted when redefining simultaneousness [Einstein] is added to the other avowed purpose of gaining in formal symmetry [Lorentz]. The same thought is continued, if we recall too how gravitation-force (G_1) is "apparent" in weight (W_1), with reduction factor that in the simplest case takes either form,

$$W_1 = G_1 \left(1 - \frac{\boldsymbol{\omega} v}{G}\right); \quad G_1 = W_1 \left(1 + \frac{\boldsymbol{\omega} v}{g}\right). \quad . \quad (16)$$

This essential parallelism of equations (13, 16) throws new light on reading (u) in terms of imaginary rotation *.

A second standard use of equations of motion adopts force as physically determinate (given) and predicts its kinematical effects by calculation. This would impose (T_o) invariantly upon (U, F): one stock instance is a convected compressed spring. Then we should pair with equation (12)

$$T_o = m \frac{dv'}{dt} + v' \frac{dm}{dt}, \quad . \quad . \quad . \quad . \quad (17)$$

where now the accelerations (dv'/dt, dv_o/dt) fall away from equality, when the given values accompanying the same (m) are

$$T_o \lesseqgtr T_a' \; ; \quad v' = v_o - u.$$

Evidently also, the last relation would not be a permanent adjustment. What devices may look towards reconciling the divergent plans of equations (13, 17) is the next natural question.

The answer will begin at considering the activity ($v'T_o$) developed by the force (T_o) of equation (17) at the working-speed (v'). In this aspect, both factors belong immediately to (U). In view of equation (13) that activity is equivalently

$$v' \, T_o = v' \frac{T_a'}{1 - \frac{uv_o}{c^2}} = \left(\frac{v'}{1 - \frac{uv_o}{c^2}}\right) T_a' \equiv v_c' \, T_a', . \quad . \quad (18)$$

(v_c') being a calculated (auxiliary) speed, but without departure from C.G.S. measure. Thus the activity within (U) of a force (T_o) implying unequal accelerations in (U, F) can be equalized with that of a force (T_a') implying equal accelerations, if at the same time the working-speed be

* Minkowski; Sommerfeld. It is arithmetic to adjust a "length-contraction" to producing numerical equality of the fields (G, g). The difference that these replace (c^2) is provably superficial.

modified from the observed value $(v_o' = v_o - u)$ as equation (18) denotes. Put into other words: Einstein's rule yields a distorted speed in (U) which compensates exactly the distortion of force into (T_a') from (T_o). What may well be called a process internal to (U) is made in so far indifferent about the supposition of equal accelerations. Plainly the same rule holds between (U) and any frame (F') fixed relatively to the original (F). But observe how our derivation locates that compensation within the experimentally verified scope of equation (4). As a matter of algebra, we obtain the four forms:

$$v_c' \equiv \frac{v_o - u}{1 - \dfrac{uv_o}{c^2}}; \quad v_o = \frac{v_c' + u}{1 + \dfrac{uv_c'}{c^2}}; \quad \gamma^2(u)(v_c' + u) = \frac{v_o}{1 - \dfrac{uv_o}{c^2}};$$

$$\frac{dv_o}{dt}\gamma^2(v_o) = \frac{dv_c'}{dt}\gamma^2(v_c'). \quad . . \quad (19)$$

They all connect some Newtonian velocity of (m) relative to (O, O') the origins of (F, U) with Einstein's specification of it. None of these alternative aspects is released, however, from its source in a strictly conventional expedient to the same end, which is here just nakedly announced, but which the Lorentz transformation has masked under the Einstein variables.

The completer activity $(v_o T_o)$ in (F), expressed also by means of (v_c', T_a') is

$$A_0 \equiv v_o T_o = \gamma^2(u) T_a'(v_c' + u). \quad . \quad . \quad . \quad (20)$$

Therefore

$$T_o = \gamma^2(u) T_a'\left(1 + \frac{uv_c'}{c^2}\right); \quad \gamma(u) T_a' = m_0 \frac{dv_c'}{dt}\gamma^3(v_c'). \quad (21)$$

Equations (13, 21) being demonstrated corollaries of equation (5), they are pivotal relations between the "observing-frame" (F), and the auxiliary quantities (appearances) in a comparison frame (U).

Continuing, we may undertake to render equation (13) more fully reciprocal between the frames (F, U). Instead of depending upon observations in (F), let them be primarily taken in (U), the distinctive notation being $(dv_o'/dt, v_o', T_o')$. Correlate the force denoted by (T_o') on the one hand with its associated kinematics and on the other with a supposititious partner (T_a) in (F). The plan of equation (18) gives

symmetrically, for equivalent activities now "internal" to
(F),

$$(v_o' + u)\, T_o' = v_c T_a; \quad \ldots \quad (22)$$

where the factors in the second member are first any pair
that satisfy the equality. Then equation (20) repeats in the
form

$$v_o'\, T_o' = \gamma^2(u)\, T_a(v_c - u). \quad \ldots \quad (23)$$

Since (T_a) is a force in (F) at the speed (v_c), equation (5)
holds; so

$$T_a = m_0 \gamma^3(v_c) \frac{dv_c}{dt}. \quad \ldots \quad (24)$$

Both equations (22, 23) are satisfied when (v_c) is determined
by the conversion rule that pursues the track of relativity:

$$v_c \equiv \frac{v_o' + u}{1 + \dfrac{uv_o'}{c^2}}; \quad v_o' = \frac{v_c - u}{1 - \dfrac{uv_c}{c^2}}; \quad \gamma^2(u)(v_c - u) = \frac{v_o'}{1 + \dfrac{uv_o'}{c^2}};$$

$$\frac{dv_o'}{dt}\gamma^2(v_o') = \frac{dv_c}{dt}\gamma^2(v_c) *. \quad . \quad (25)$$

And provable corollaries of this assumed value are

$$T_a = \left(1 + \frac{uv_o'}{c^2}\right) T_o'; \quad T_o' = \gamma^2(u) T_a \left(1 - \frac{uv_c}{c^2}\right);$$

$$T_o' = m_0 \gamma(u) \gamma^3(v_o') \frac{dv_o'}{dt}. \quad \ldots \quad (26)$$

The mathematics fixes upon equation (23) as committing us
already to the consequences in equation (26), by requiring
for consistency that (v_c) which equation (25) calculates.
The symmetry of (F, U) postulated by relativity is in fact
seen to lurk in equation (23). The logical sequence may be
reversed and begin by superposing the third of equations (26)
upon equation (5). Whatever is hypothetical in equation (23)
is reflected in equation (26), and *vice versa*.

It would not be overbold analogy, as the outcome thus
far shows, to anticipate through the second form of equation
(16) the factor that "reduces" from (U) to (F). In the
view of local action, (T_o, T_o', T_a, T_a') of an electromagnetic
statement would involve effective strengths of a "motionless
field" (F-space, medium), and of a "convected field" (U-
space, medium). But whereas physics has long labelled (W_1)
without hesitation "apparent." the notation here need not
be stressed hastily with similar decision. When *relations*
are ascertained clearly between mathematical sequences whose

* Connect equation (10) with this invariance, and one similar in
equations (19).

correspondence has been more obscure, and a way is opened to standardize in one frame by systematic reduction, the final issues in " true physics *versus* correct mathematics " are not prejudiced by some postponement. Indeed, the closer scrutiny is revealing multiplied chances for illusion and encouraging suspended judgment.

Certain critical values of the auxiliary velocities (v_c', v_c) deserve mention. We find

$$
\begin{aligned}
& v_o = 0, \ v_c' = -u \ ; \quad v_o' = 0, \ v_c = u \ ; \\
& v_o = c, \ v_c' = c \ ; \qquad v_o' = c, \ v_c = c \ ; \\
& \frac{v_c'}{v_o - u} = \frac{0}{0} = \gamma^2(u) \ \ [v_o = u]; \quad \frac{v_o'}{v_c - u} = \frac{0}{0} = \gamma^2(u) \ \ [v_c = u].
\end{aligned}
\qquad (27)
$$

These make plain first that the limiting speed (c), if affirmed for (v_o), applies also to (v_c'). The two series (v_o, v_c') in (F, U) respectively, and each within the range $(0, c)$, are so telescoped relatively that the initial overlap (u) is gradually annulled. Secondly, the relative translation $(\pm u)$ of (F, U) links all aspects of the combinations as an unchanged magnitude. There is just so much demand as can be read into these special ratios, for the " practical infinity of (c) ;" or for the " axiomatic necessity " that light-speed relatively to all frames (U) stands invariant at (c) *.

Equations (13, 21, 26) have connected force-values by four reduction factors ; with algebraically equal values shown by

$$
\begin{aligned}
& 1 - \frac{u v_o}{c^2} = \frac{v_o - u}{v_c'} = \frac{\gamma(v_c')}{\gamma(u)\gamma(v_o)} \ ; \\
& 1 + \frac{u v_c'}{c^2} = \frac{v_c' + u}{v_o} = \frac{\gamma(v_o)}{\gamma(u)\gamma(v_c')} \ ; \\
& 1 + \frac{u v_o'}{c^2} = \frac{v_o' + u}{v_c} = \frac{\gamma(v_c)}{\gamma(u)\gamma(v_o')} \ ; \\
& 1 - \frac{u v_c}{c^2} = \frac{v_c - u}{v_o'} = \frac{\gamma(v_o')}{\gamma(u)\gamma(v_c)} .
\end{aligned}
\qquad (28)
$$

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* The comment on equation (9) would lead to a finite activity of (P) expending work upon (R) during unlimited time of asymptotic approach to finite (c). Equation (6) also presents gross work (of (T_o)), with whose result relativity agrees. Finding $W_o = \infty$; $v_o = c$; constant (m_o) ; does not confirm the practical infinity of (c). Not even after redefining (W_o) as that " change of kinetic energy " whose disappearance from it we have traced. Attentive sifting of infinity-values is seldom misplaced in physics.

The second members appear as "telescoping ratios" for velocities. The third members may reduce effective inertia conveniently. For instance,

$$T_o = \frac{T_a'}{1 - \frac{uv_o}{c^2}} = \frac{m}{1 - \frac{uv_o}{c^2}} \frac{dv_o}{dt} + \frac{v_o - u}{1 - \frac{uv_o}{c^2}} \frac{dm}{dt}$$
$$= m_0 \gamma(u)\gamma(v_c') \frac{dv_c'}{dt} + v_c' \frac{dm}{dt}. \quad (28a)$$

The Fresnel coefficient (κ) of equation (15) is given also by

$$\kappa = \frac{\gamma(u)\gamma(v_c)}{\gamma(v_c')} \cdot \frac{1}{\gamma^2(v_o)} = \frac{\gamma(u)}{\gamma(v_c')\gamma(v_o)}$$
$$= \frac{\gamma(u)\gamma(v_c')}{\gamma(v_o)} \cdot \frac{1}{\gamma^2(v_c')} = \frac{c^2 - v_c'^2}{c^2 + uv_c'};$$

and by
$$\kappa = 1 - \frac{v_0 v_c'}{c^2}. \quad \ldots \ldots \quad (29)$$

Equations $(28a, 29)$ lead directly to the relation, significant like equation (15) of meaning for (κ),

$$[m_0\gamma(u)\gamma(v_c')]\frac{dv_c'}{dt} = T_0\left(1 - \frac{v_0 v_c'}{c^2}\right) = \kappa T_0. \quad (29a)$$

Because

$$\left(1 - \frac{uv_o}{c^2}\right)\left(1 + \frac{uv_c'}{c^2}\right) = \left(1 + \frac{uv_o'}{c^2}\right)\left(1 - \frac{uv_c}{c^2}\right) = \frac{1}{\gamma^2(u)},$$

the product of each factor by $\gamma(u)$ modifies the reductions so that the original magnitude is restored by a combination of direct and reverse reduction between (F, U). Therefore our results reproduce formally the transformations for Minkowski force (K). If we identify $T_o \equiv K_F$; $\gamma(u)T_a' \equiv K_u$;

$$K_u = \gamma(u)\left(1 - \frac{uv_o}{c^2}\right)K_F; \quad K_F = \gamma(u)\left(1 + \frac{uv_c'}{c^2}\right)K_u. \quad (30a)$$

Similarly, for $K_F' \equiv T_a$; $K_u' \equiv \frac{T_o'}{\gamma(u)}$;

$$K_u' = \gamma(u)\left(1 - \frac{uv_c}{c^2}\right)K_F'; \quad K_F' = \gamma(u)\left(1 + \frac{uv_o'}{c^2}\right)K_u'. \quad (30b)$$

On the line of this parallelism, the "Newton force" of relativity and its "local time" do not enter directly. Perhaps they are secondary in a larger sense, as more artificial alignment with Newtonian mechanics in part misread.

It is a striking feature about the forms referring to the frame (U) that $\gamma(u)$ recurs as a sort of "weighting factor" which also designates the particular frame that is associated with (F). Comparing the last forms in equations (21, 26), we may say that $\gamma(u)$ disturbs the symmetry or completes it; we may seek symmetry in the first member or in the second; and one additional step reaches either end. Consideration of the work-equations helps to analyse these connexions further. Direct integration of either extreme member in equation (18), referring to equations (5, 21), gives

$$\int_u^v T_o(v_o - u)dt = \int_o^{v_c'} T_a' v_c' dt = c^2 \frac{m_0}{\gamma(u)}(\gamma(v_c') - 1). \quad (31)$$

From equation (22) the work obtained is, remembering equations (24, 26),

$$\int_0^{v_o'} T_o'(v_o' + u)dt = \int_u^{v_c} T_a v_c dt = c^2 m_0 (\gamma(v_c) - \gamma(u)). \quad (32)$$

Complete the set ; adding in reliance upon equation (26)

$$\int_0^{v_o'} T_o' v_0' dt = c^2 m_0 \gamma(u)(\gamma(v_o') - 1). \quad \cdot \quad \cdot \quad (33)$$

Equations (6, 32) express work done in (F); equations (31, 33) work done in (U). The scheme of substituted velocities and new limits is symmetrical in all four. But transition from (F) to (U) divides by $\gamma(u)$ in one case and multiplies by it in the other. The deciding fact is patent : Equation (6) presents the original (or physical) quantity as belonging to (F), and makes allowance for its "appearance" as judged in (U); equation (33) takes its start in the physics of (U) and calculates what appears in (F). Substituting for equation (26) the form

$$T_o'' \equiv \left(1 - \frac{uv_c}{c^2}\right) T_a, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (34)$$

which would embody the reversed reduction with the same (T_a), gives immediate verification. Finally it is plain that the various reduction factors, in combination with original totals and with fractions of them, constitute a mode of projection *.

The above group of relations brings out the idea that they approach a treatment of motion from rest in (U) as though

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* This furnishes a strong hint about their affiliations with imaginary angles, and the natural adaptation of hyperbolic trigonometry to relativity.

the initial inertia were $(m_0' = \gamma(u)m_0)$, which continuity of value with our assumptions for the standard (F) would make it. The result that one vital difference hidden under identical kinematics in (F, U) is due to altered inertia affecting work provoked early comment. In one dynamical analysis of relativity, it was shrewdly proposed as a chief postulate *. The accompanying pairs of interchanges between $(v_o' + u, v_o, v_o')$ and $(v_c', v_o, v_c - u)$ must certainly not be ignored. Yet the commonsense reason for those is also one key to Einstein's redefined simultaneousness. The same value of fluxion time (t) as an argument in time functions defines Newtonian simultaneous values of them. In this meaning, the auxiliary (v_c') and the observed (v_o) are simultaneous; also (v_c, v_o'). In addition, simultaneous observations in (F, U) would of necessity be recorded as $(v_o, v_o - u)$, or as $(v_o' + u, v_o')$. It is clear that a pair of such observable data $(v_o' + u, v_o')$ would not realize, for instance, the simplicity of equations (26), if $(v_o' + u)$ were substituted for (v_o) there. But if time-slip (lag or lead) between straightforward C.G.S. observations in (F, U) be regulated under a known law of velocity-change, the paired values (v_c, v_o') requisite for simplicity are also attainable as observed. The same thought coordinates equation (13) [Newton] and equation (21) [Einstein]. Further, because this "propagated simultaneousness" and the Newtonian allowance for "apparent force" establish identical reduction factors; for Newtonian velocity and for Einstein's force-law respectively; it seems fairly proven that the two systems of procedure are effectively alternative—for the electronic case discussed.

The reciprocal relations between the dynamics of the standard frame (F) and that formulated for any one frame of the group (U) are to this extent conclusively settled. It remains to examine how much of such reciprocity persists, when neither of the compared frames is (F). This will confront the conditions where relativity can do best service through its simplifications. Choose then two comparison frames (U', U'') with origins (O', O'') and with translations (u', u'') relative to (F), still colinear with (v_o) of course. Denote observed velocities of (m) now by (v, v', v''), so that

$$v = v' + u' = v'' + u''; \quad v' - v'' = u'' - u'. \quad . \quad (35)$$

A reasonable notation for other quantities will also distinguish them by accents. Thus simultaneously for (m):

$$T_a' = T_o\left(1 - \frac{u'v}{c^2}\right); \quad T_a'' = T_o\left(1 - \frac{u''v}{c^2}\right). \quad . \quad . \quad (36)$$

* Frank, *Wied. Ann.* (1912) vol. xxxix. p. 693.

Observations in (F) would show the velocity of (m) relative to (O'')

$$v'' = v' - (u'' - u') \equiv v' - u_o. \quad . \quad . \quad . \quad (37)$$

Equation (19) applied correctly to each part of the third member gives for velocities in (U') auxiliary to (v', u_o),

$$v_c' \equiv \frac{v - u'}{1 - \dfrac{u'v}{c^2}}; \quad u_c' \equiv \frac{u'' - u'}{1 - \dfrac{u'u''}{c^2}}. \quad . \quad . \quad (38)$$

Then without complications the identity is verified :

$$\gamma(u'') \, T_a'' \equiv \gamma(u_c') \left(1 - \frac{u_c' v_c'}{c^2}\right) (\gamma(u') T_a'). \quad . \quad (39)$$

In verbal form : Direct transition (F, U'') and two successive transitions (F, U'), (U', U''), coincide upon the force finally apparent in (U''). But in terms made consistent with equation (18) as regards all entries under (v''); and only when each apparent force is properly "weighted." The previous developments furnish plain reasons for both conditions.

Begin with (U') as observation-frame, and under transferred guidance of equations (13, 26) construct the provable identity:

$$\gamma(u_o) \left(1 - \frac{u_o v'}{c^2}\right) T_o' \equiv \left[\gamma(u_c) \left(1 - \frac{u_c v_c}{c^2}\right)\right] \gamma(u') \left(1 + \frac{u'v'}{c^2}\right) T_o'. \quad . \quad . \quad (40)$$

Again results agree exactly for direct transition (U', U'') and for the two-step process, (U' F) followed by (F, U''). In this use, corresponding to equation (38) we must have in their relation to (v) and (U') :

$$v_c \equiv \frac{v' + u'}{1 + \dfrac{u'v'}{c^2}}; \quad u_c \equiv \frac{u_o + u'}{1 + \dfrac{u'u_o}{c^2}}. \quad . \quad . \quad (41)$$

Without repetitive detail, therefore, the conclusion can be put generally : When these discriminations about terms are upheld, the calculated net distortion (into apparent force) depends upon the terminal frames alone. Hence it vanishes if the series of transitions closes at the initial frame ; the remark under equation (29) becomes a wider truth [*]. As bearing upon our immediate purpose, it places all transitions within the group (U) in a comprehensive setting of partial reduction to the same standard (F).

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[*] A consequence that one might borrow from the familiar theorem on superposition of colinear Lorentz transformations, by assigning present meanings to its symbols.

Equation (14) records the special value of (T_a') for that rest-frame to which relativity concedes unique prominence through a coincidence in magnitude for the two force-types ("Minkowski" and "Newton") and a peculiar "rest-acceleration." Analysis of the transition from (F) to a rest-frame (R) in those aspects detects three stages :

(a) Changing Minskowski-force into Newton-type.

(b) Cancelling a factor $(\gamma^2(u))$; or $(\gamma^2(v))$ transiently undistinguished from it ; with some freedom among assignable reasons.

(c) Restoring the magnitude $(\gamma^3(v)\,dv/dt)$; now as acceleration in (R) under the sliding-scale of units for time and length.

A mathematically colourless regrouping of factors led to the important quantities $(v_c',\,v_c)$ of equations (18, 25); its convenience has wide range. But such fully interchangeable forms are often unequally accommodated to physics. Equation (5) presents in effect this same rest-acceleration as incidental to a (probably fictitious) fusion of force-items. Only an inflexible view about constant inertia can force upon relativity the result of (c) as an acceleration. In comparison, is the latter not artificial? What is worse, it is superficial as well, if it obscures that inclusion of rest-frames in the "shift process" common to many coordinate-systems and describable as a parameter-variation *. In that feature, it enforces the thought attached to equations (10, 11), and prompts a directer interpretation of rest-frame calculations, though the formal results stand uncorrected.

We build upon a more general relation for any frame (U) and specify a momentum (Q_1) determined from a velocity (v_1) and an inertia (m_1) through

$$Q_1 \equiv m_1\gamma(u)v_1 = (m_1\gamma(u))v_1 = m_1(\gamma(u)v_1). \quad . \quad . \quad (42)$$

This introduces the same weighting factor as equations (30, 31, 33) and it is written out to suggest a double possibility : associating $(\gamma(u))$ with either (m_1) or (v_1). Regarding (Q_1) as a function of $(u,\,v_1)$, its exact differential and its total

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* For the elaboration of this idea see Slate, 'Fundamental Equations of Dynamics' (1918); Index, under "Shift," Shift-rate." Nothing but unformed habit bars embracing in the same scheme continuous change in the unit-magnitudes. Other seed-thoughts of the present paper are to be found at pp. 38–43 ; p. 211 ; where the need of equations (1, 2, 3) is emphasized.

time-rate are, when (m_1) is constant,

$$dQ_1 = \frac{\partial Q_1}{\partial u} du + \frac{\partial Q_1}{\partial v_1} dv_1;$$

$$\frac{dQ_1}{dt} = m_1 v_1 \frac{cu}{(c^2-u^2)^{3/2}} \frac{du}{dt} + \frac{cm_1}{(c^2-u^2)^{1/2}} \frac{dv_1}{dt}. \quad (43)$$

Defining $m' \equiv m_1 \gamma(u)$, the last equation is mathematically presentable as a measure of tangential force,

$$\frac{dQ_1}{dt} \equiv T = v_1 \frac{dm'}{dt} + m' \frac{dv_1}{dt} = \frac{d}{dt}(m'v_1). \quad . \quad . \quad (44)$$

Yet the first term in the third member is spurious for the physics, so long as (m_1) is constant; it has its sole origin in a shift-rate among the frames (U).

In application to a finite interval, the name rest-system at equation (14) is a collective noun, comprising selected frames in the possible group (U); the earmark of a rest-frame is the transient equality of its permanent (u) and the velocity (v) of (m) at that one epoch. Identify (m_1, m_0) and (v_1, v); and let the shift-rate be so regulated that $(v=u)$ perpetually. If the spurious force were real (*i.e.*, physical), equation (44) would give (T_o) correctly, on making the substitutions

$$u = v; \quad \frac{du}{dt} = \frac{dv}{dt}; \quad m_1 = m_0. \quad . \quad . \quad (45)$$

Or it would repeat the essentials of equations (21, 24, 26), on exchanging $(v_c' \; v_c, \; v_o')$ for (v); while due use of the weighting factor harmonizes the forms completely. Thus an assumed constant inertia, plus illusory (imaginary, quaternionic) force due to a glossed-over shift, can replace with mathematical precision our assumed variable inertia*, through continuous use of the rest-frames for the several epochs.

Since the working-speed (v_c', v_o') becomes zero for a rest-frame, that cannot be self-sufficing for the expression of activity. The directest composite plan contains as well frames fixed relatively to (F) †; but more deviously, relativity reduces the quasi-force $(v_1 dm'/dt)$ by the factor (c/v_1), coins an unrealized velocity-term (c), attaches it loosely to (v_1), and arrives correctly at the activity (A_o) of equation (6) essentially thus:

$$A_o = c^2 \frac{dm}{dt} = c\left(c \frac{dm}{dt}\right) = c\left(\frac{c}{v}\right)\left(v \frac{dm}{dt}\right). \quad . \quad . \quad (46)$$

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* It is apposite to quote Sommerfeld's remark that the element $(d\tau)$ of proper time " Ist kein vollständiges Differential."

† Slate, 'Fundamental Equations,' pp. 147–54. That background of standard frame cannot be quite ignored. Lorentz remarks " Bei einer absoluten Genauigkeit wäre auch der Unterschied der 'Eigenzeit' der Erde von der Zeit des Sonnensystems zu berücksichtigen."

Ingenious device contrives a mathematical status for the last term in equation (2), whose recognition at first hand constancy of inertia excludes.

The natural inferences that equation (13) has forced upon attention by restating the situation of equation (16), offer more than a glimpse of a self-selected frame, basic for physical phenomena in this sense: Departures from it, either by rotation or by translation impress distortions of common type upon dynamical magnitudes. To render that deeply-seated symmetry convincing might crown our instinctive search better than inventing for physical laws a formal indifference among base-frames. If such ideal outlook has restricted appeal, there is practical service in coordinating at the same time elements of potential. That a potential is available which gives coherence to all phases of our electron's energy, the work equation indicates through its sole dependence upon terminals of the interval. Equations (39, 40) are another aspect of that thought. Moreover, the initial supposition of equation (5) and its probable connexions at equations (9, 10, 11) fit at sight the more standard form of the Lagrange function (L) as measuring appropriately a difference of energy-states. Write

$$\mathrm{L} \equiv -m_0 c^2 \left(\frac{\sqrt{c^2 - v^2}}{c} - 1 \right) = m_0 c^2 - m(c^2 - v^2). \quad . \quad (47)$$

Fixing the zero-phase as rest in the frame (F), the last member sets down an expectation then bounded by bringing (m_0) to the limiting speed (c). In the general phase, (m_0) has become (m) by gathered increment: so reading (mv^2) as a fact of realization the last term exhibits what other energy of (m) at that epoch is outstanding for final conversion into kinetic form; at the limit-value (c), whatever (m) may be attained by accretion. The form $(2\mathrm{E} - \mathrm{L})$ for total energy agrees with equation (6) for work done from rest.

Whatever cumulative pressure from these arguments is felt will carry us toward restoring to fuller proportions the shrunken claim that Lorentz urges for " Wahre Zeit " and for frames " Die im Äther ruhen; " a passage remarkable for its scientific candour [*]. The complications due to curvilinear path, to radiation, and to other causes do not weaken this primary correlation of Einstein with Newton. Both lines of thought alike must cope with the superposed difficulties.

University of California.

[*] *Sammlung,* p. 75.

IV. *The Relative Activity of Radium and the Uranium with which it is in Radioactive Equilibrium**. *By* J. H. L. JOHNSTONE *and* B. B. BOLTWOOD†.

ALTHOUGH the matter has been under consideration and discussion for a number of years, the genetic relationship between the earlier members of the uranium family of radio-elements is still a matter of considerable uncertainty. It is generally conceded that both ionium and actinium are products of the radioactive disintegration of uranium, but the exact point of origin of actinium and its immediate parentage have remained somewhat obscure and uncertain.

The work of Boltwood‡ on the relative α-ray activity of uranium minerals and the uranium which they contained demonstrated a constancy of relationship between the radio-active constituents of the older minerals and clearly indicated a close genetic relation between uranium and actinium. His determination of the activities of the more stable α-ray products relative to the activity of the associated uranium showed a simple and direct relation to exist between the products ionium, radium, and polonium, but showed an abnormally low value for the ratio in the case of the actinium series, which could only be explained on the assumption that actinium originates as a branch product and belongs to what may be termed a collateral branch of the ionium-radium-polonium family.

The values obtained by Boltwood in the course of his experiments showed that the activity of the uranium was about 2·2 times that of the radium with which it was in equilibrium, although at that time the range of the α-particle from uranium was supposed to be about 2·7 cm., which is less than that of the α-particle from radium. Since the ionizing power of an α-particle is nearly proportional to the range, and since, on the basis of the disintegration theory, an equal number of α-particles are emitted per second by each of two

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radioactive products in equilibrium with one another, it was necessary to assume that either the uranium atom emitted two α-particles simultaneously, which was improbable, or that two distinct α-ray changes existed in ordinary uranium. Neither of these assumptions, however, completely obviated the difficulty.

The fact that uranium actually did emit twice the number of α-particles to be expected on theoretical grounds was subsequently demonstrated by Geiger and Rutherford * and by Brown † who counted the number of α-particles emitted per second from a film of pure uranium oxide and a similar film of uraninite of known composition. Using the scintillation method, Marsden and Barratt ‡ made a careful examination of the α-radiation from uranium and concluded as a result of their experiments that ordinary uranium consists of a mixture of two successive α-ray products in equilibrium with one another. Attempts to measure the separate ranges of the α-particles emitted by these two products were made by Foch § and Friedmann‖. By the use of a better method of measurement, in which the Bragg ionization curves for a uranium film were compared with the corresponding curves obtained with polonium and ionium, Geiger and Nuttall calculated the ranges of the α-particles from uranium to be 2·5 cm. and 2·9 cm. (at 0° C.).

Numerous unsuccessful attempts have been made to reduce the specific α-ray activity of uranium. In one experiment conducted by the authors about two kilograms of pure uranium nitrate were subjected to fractional crystallization, and a least soluble "head" fraction weighing about twenty grams was obtained after about forty operations. The specific α-ray activity of the uranium in this material did not vary by as much as one per cent. from the specific activity of the uranium in the original nitrate. This shows that the two components are so closely allied chemically as to be inseparable, a conclusion which is supported by all the other known facts at our disposal.

We may outline, therefore, the progressive disintegration of the uranium atom, considering for the present only the products emitting α-rays, as taking place in the following manner: the parent element, uranium I., produces the product uranium II. This in turn produces ionium, which

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* Phil. Mag. xx. p. 691 (1910).
† Proc. Roy. Soc. A lxxxiv. p. 151 (1910).
‡ Phys. Soc. Proc. A xxiii. p. 367 (1911).
§ *Le Radium*, viii. p. 101 (1911).
‖ *Wien. Ber.* cxx. p. 1361 (1911).

disintegrates to form radium, followed successively by radium emanation, radium A, radium C, and polonium. When these are all present in equilibrium proportions, as is the case in a non-emanating, old, radioactive mineral, then certain comparatively simple relations will exist between the α-ray activities of the different constituents. It has been shown by Geiger* that the ionizing power of an α-particle is proportional to the two-thirds power of its range. The ionization produced by equal numbers of α-particles emitted by two different radio-elements will therefore be proportional to the two-thirds power of the ranges of these particles. In a series of successive products in equilibrium, each product emits the same number of α-particles in unit time. The relative ionization (and therefore the relative activities) due to each of these products should therefore be proportional to the two-thirds power of the range of the respective α-particles.

This relation has been shown† to hold quite closely in the case of radio-thorium and its α-ray products, and also in the actinium and the radium series of products. The chief object of the work described in the present paper was to apply the same methods to the case of the uranium-radium series with the expectation that the results would throw some light on the obscure relations of the earlier members of the series.

The Radioactive Measurements.

The determinations of the radioactivity of the different solids examined were carried out in an electroscope which has already been described‡. In the present experiments a telemicroscope was used for observing the position of the gold-leaf. The natural leak of the instrument was small and over a period of about six months varied from 0·4 to 0·7 scale division per minute. Before and after each series of measurements the sensibility of the electroscope was determined by measurements of the activity of a standard reference film of pure uranoso-uranic oxide. This film was carefully preserved throughout the entire period of the measurements here recorded, and all the results given in this paper are given in terms of this film as the standard.

The method of preparing the radioactive materials for measurement was essentially the same, with certain modifications, as that described by Boltwood. The material to be

* Proc. Roy. Soc. A lxxxiii. p. 505 (1910).

† McCoy and Viol, Phil. Mag. xxv. p. 333 (1913); McCoy and Leman, Phys. Rev. iv. p. 409 (1914); ibid. vi. p. 185 (1915).

‡ Boltwood, Am. Journ. Sci. xxv. p. 272 (1908).

examined was ground as finely as possible in the form of a thin paste with pure ethyl alcohol in a small agate mortar. A sheet of aluminium 7.5×9 cm. and 0.01 cm. thick was first carefully cleaned with liquid soap and distilled water, and was then placed in a drying oven at $65°$ C. for fifteen minutes. It was placed in a desiccator over sulphuric acid for half an hour, and then weighed on a sensitive chemical balance. The paste of material and alcohol was then thinly spread on the surface of the aluminium with a small camel's-hair brush*. The coated plate was placed in the oven, cooled in the desiccator and weighed as before. The weight of the films could be determined in this manner with an accuracy of one per cent. The solid material adhered quite strongly to the plate and showed no tendency to fall off even when the plate was inverted.

The measurements of radium emanation were made with a gold-leaf electroscope having an air-tight ionization chamber with a capacity of about three litres. The separation and collection of the radium emanation, its transfer to the electroscope, and the measurement of its radioactivity were carried out according to methods which have already been described†.

Ratio of the Activity of a Uranium Mineral to the Activity of the Contained Uranium.

The relation of the activity of the parent element, uranium, associated with equilibrium amounts of all of its disintegration products, to the activity of the parent element alone, is a fundamental quantity of great importance to any consideration of the relations existing between the individual products themselves. The actual progenitor of the series is uranium I., but this cannot be isolated from its invariable associate and isotopic product uranium II. The combined effect of these two elements when mixed in equilibrium proportions can be determined, however, and this can be compared with the activity of a similar mixture containing all the other disintegration products in equilibrium proportions.

Such a mixture is furnished by a pure, primary, unaltered uranite. A mineral containing a low proportion of thorium is preferable since a correction must be made for the activity

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* The brushes used were carefully cleaned in advance by long immersion in alcohol and subsequent washing in fresh quantities of the same liquid.

† Boltwood, Am. Journ. Sci. xviii. p. 378 (1904); Phil. Mag. ix. p. 599 (1905).

of the thorium products present. A specimen of uraninite from Spruce Pine in the possession of the authors was considered to fulfil all the necessary requirements. It consisted of essentially unaltered material selected with much care from a considerably larger quantity. It contained less than 0·2 per cent of silica and residue insoluble in dilute nitric acid. A determination of the uranium content was made by one of the authors and by Ledoux & Co., of New York City [*]. The mineral contained 1·9 per cent. of thorium oxide.

In determining the activity of uranium a very pure specimen of uranoso-uranic oxide was used. This had been prepared from a specimen of especially pure uranium nitrate

Fig. 1.
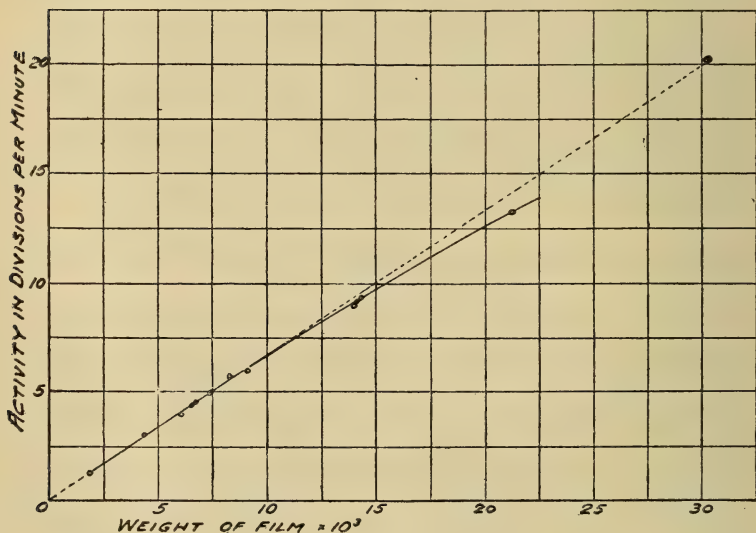
obtained by fractional recrystallization of a much larger quantity (see p. 52). The oxide was made from the nitrate with all the precautions which have been mentioned in an earlier paper[†]. It is very important to note that this oxide was used as a standard in the analytical determination of uranium (both volumetric and gravimetric) in the

[†] Boltwood, Am. Journ. Sci. xxv. p. 278 (1908).

mineral, so that the analytical determinations and radio-active measurements are in direct accord with one another, although it was assumed for purposes of calculation that the uranoso-uranic oxide contained 84·8 per cent. of uranium.

It has been found by McCoy[*] that considerable absorption of the radiation takes place in the film itself when its thickness is appreciable. In earlier work by one of us[†] it was shown that by the use of thin films any necessity for an absorption correction could be avoided. To further demonstrate this fact a series of films of uranoso-uranic oxide weighing from 0·0019 g. to 0·04 g. were prepared and their activities were measured. The results are given in Table I. and are shown graphically in fig. 1. In films weighing not more than 10 milligrams the absorption of the α-radiation was negligible. In all cases where values of importance were to be derived the weight of the films used was less than this maximum, so that no correction has to be made in the results for absorption of the radiations.

The average of the first eight values in the fourth column of Table 1. is 666, which denotes that the average activity of the eight lighter films was 666 divisions per minute per gram of uranium oxide. This corresponds to an activity of 785 (viz. 666/0·848) divisions per minute per gram of uranium.

TABLE I.

Film Number.	Weight of oxide in grams.	Activity Div./Min.	Activity Weight.
20	·00187	1·24	663
19	·00432	2·91	673
15	·00566	3·77	666
18	·00653	4·37	669
21	·00740	4·95	668
22	·00832	5·56	662
14	·00898	5·95	662
23	·00653	4·38	670
25A	·01405	8·89	633
8	·01380	8·94	648
25B	·01440	9·30	645
26	·02150	13·45	624
24	·04350	25·96	596

* Journ. Am. Chem. Soc. xxvii. p. 391 (1905); Phys. Rev. i. p. 393 (1913).

† Boltwood, Am. Journ. Sci. xxv. p. 176 (1908).

The specific activity of the uraninite was determined by the measurement of four films weighing from approximately 2 to 6 milligrams. The results are given in Table II.

<div align="center">TABLE II.</div>

Film Number.	Weight gram.	Activity in divisions per minute per gram.
27	0·00387	2627
28	0·00240	2655
29	0·00588	2627
30	0·00170	2600

These results give the mean value for the specific activity of the uraninite as 2624 divisions per minute per gram.

As already stated, the mineral contained 0·019 gram of thorium oxide (and other thorium products in equilibrium with this) per gram of mineral. The above value for the specific activity of the mineral includes the increment due to the thorium products which must be eliminated. To accomplish this measurements were made of a series of films prepared from a specimen of thorite containing 52 per cent. of thorium oxide and 0·37 per cent. of uranium. The results are tabulated in Table III.

<div align="center">TABLE III.</div>

Film Number.	Weight gram.	Activity per gram in divisions per minute.
39	0·0056	511
40	0·0076	515
42	0·00776	514
		——
		Av. 513

The activity of the uranium and its radioactive products contained in the thorite will closely equal

$$\frac{2624}{0\cdot73} \times 0\cdot0037 = 13\cdot3 \text{ divisions per minute.}$$

Correcting the specific activity of the thorite by this number and dividing the remainder by 0·52 (the weight of thorium oxide per gram) we obtain 960 divisions per minute as the activity of one gram of thorium in equilibrium with its products. We may now correct the value found for the activity of the uraninite by an amount equal to the activity of the thorium components (960 × 0·019), and obtain the value

2606 divisions per minute per gram of mineral for the uranium series of products which it contains and a value of 3570 divisions per minute per gram of uranium present (2606/·73).

The uraninite, however, contained less than the full equilibrium amounts of the uranium-radium products because of the fact that in the finely divided form in which it was used it spontaneously lost a small proportion of its radium emanation. The loss of this and the absence of the proportionate amounts of radium A and radium C would cause a deficiency which must be corrected for.

The relative proportion of radium emanation lost by the films of uraninite was determined by the method described by McCoy and Leman [*]. It was found to be 9·1 per cent. In applying the correction, the value for the ratio of the activity of the radium products (radium emanation, radium A and radium C) to the activity of the radium with which they are in equilibrium, as found by McCoy and Leman, namely 4·11, was made use of, as was also the ratio of the activity of radium to the activity of the uranium with which it is in equilibrium (0·49) which was derived in the course of the present investigation (see p. 60).

The correction has the following form,

$$3570 + (785 \times 4·11 \times 0·49 \times 0·091) = 3715,$$

which gives an activity of 3715 divisions per minute per gram of uranium as the activity of the mineral due to uranium and its products in a complete state of equilibrium.

From this final result we are able to calculate the value sought, namely, the ratio of the activity of the uranium with its equilibrium amounts of disintegration products to the activity of the uranium (uranium I. + uranium II.) alone.

This is 3715/785 = 4·73, which is in good agreement with the value 4·69 found earlier by Boltwood.

Ratio of the Activity of Radium to the Activity of the Uranium with which it is associated.

If the transformation of the atoms of uranium I. into atoms of uranium II. takes place directly without the production of any side products, and the transformations uranium II.—ionium—radium proceed in the same direct manner, then the relative activities of the three members— uranium I., uranium II., radium—should be proportional to

* Phys. Rev. vi. p. 185 (1915).

the two-thirds power of the ranges of the α-particles emitted by the respective elements, namely, the activities should be proportional to

$$(2 \cdot 37)^{\frac{2}{3}}, (2 \cdot 75)^{\frac{2}{3}}, (3 \cdot 13)^{\frac{2}{3}},$$

where the numbers in parentheses are the ranges at 0° C. of the α-particles from uranium I., uranium II., and radium, respectively. Any departure from this proportionality will indicate an irregularity in the mode of transformation and may serve to suggest the nature of the changes which are actually taking place. If the transformations are all simple the activity of the uranium (consisting of an equilibrium mixture of uranium I. and uranium II.) should be to the activity of the radium in the proportion

$$(1 \cdot 78 + 1 \cdot 96) : 2 \cdot 14 = 1 \cdot 00 : 0 \cdot 57.$$

An experimental determination of this ratio was carried out in the following manner :—

A quantity of radium was separated from Colorado carnotite and was carefully freed from other radioactive substances which can be separated by chemical operations. Since carnotite is free from thorium, the specimen of radium obtained did not contain any appreciable amounts of mesothorium or other products. A solution of this radium in dilute hydrochloric acid was then prepared and its approximate strength in radium was determined by the emanation method. Using this first solution as a basis, two other solutions (denoted hereafter as solutions B and C) were prepared, which contained about 0·025 g. of barium chloride and $2 \cdot 4 \times 10^{-8}$ g. of radium in 10 c.c. of solution. The quantities of radium were so chosen that the radium films ultimately obtained would have activities of the same order of magnitude as the activities of the uranium films with which they were to be compared.

An accurate determination was then made of the emanation in equilibrium with the radium in 10 c.c. of the radium-barium solutions. The results were recorded in terms of the leak produced in the emanation electroscope in divisions per minute.

The results were :—

    For 10 c.c. of Solution B............81·7 div. per min.
    For 10 c.c. of Solution C............71·0 div. per min.

The radium emanation in equilibrium with the radium contained in one gram of the uraninite was also determined and was found to correspond to 853·5 divisions per minute in the same electroscope. Since the uraninite contained

73·0 per cent. of uranium, the radium in equilibrium with 1 gram of uranium in the mineral was equivalent to a leak of 1170 divisions per minute. The quantity of radium in 10 c.c. of solution B, therefore, was the same as that in equilibrium with 0·0698 g. of uranium, and in 10 c.c. of solution C with 0·0607 g. of uranium.

The α-ray activity of the radium itself was determined in the following manner :—

Portions of solutions B and C 10 c.c. in volume were taken, and the barium and radium present were precipitated as sulphate under standard analytical conditions. The precipitates were removed and ignited as promptly as possible and the time at which the ignition was carried out was noted. The weight of the precipitate was determined and the material was quickly ground to a fine powder with ethyl alcohol.

Fig. 2.
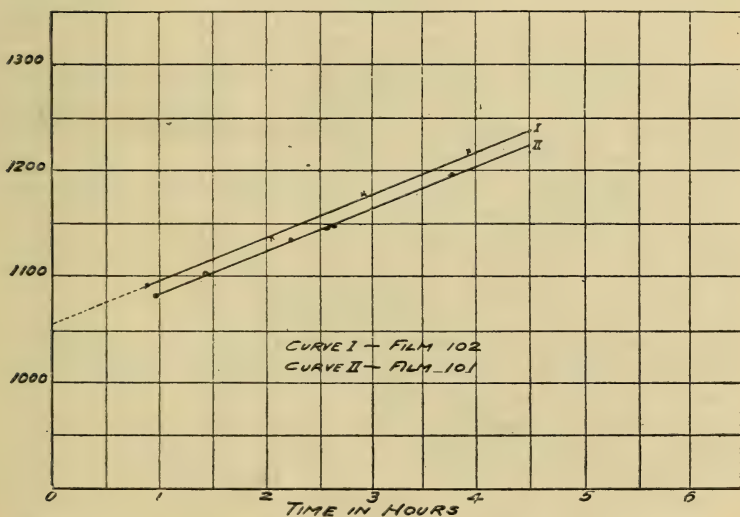
Films of this material were then prepared in the manner already described and the activity of these films was measured in the α-ray electroscope. Measurements of the activity were continued over a period of six to seven hours, and the increase with the time (due to the growth of the emanation and other active products) was noted at definite intervals.

Preparatory to the precipitation of the sulphates the radium-barium solutions were kept at a temperature slightly below the boiling-point for a period of four hours in order

to remove any emanation *as formed* and to permit the other products (radium A, radium C) to completely disintegrate. The activity of the material forming the films was therefore due to radium alone at the time of ignition, and this activity could be easily determined from the data available. The variation of the activity with the time for two typical films is shown in fig. 2, where the zero time is taken as the moment of ignition. By a simple extrapolation of the curve the initial activity could be obtained with accuracy.

The calculation of the ratio of the activity of the radium to the activity of the uranium was made by the use of the following equation, where

x = the required ratio.

Em_1 = the activity of the equilibrium amount of emanation from one gram of uraninite in div. per min. (in the emanation electroscope).

Em_2 = the activity of the equilibrium amount of emanation from 10 c.c. of radium-barium solution in div. per min. (in the emanation electroscope).

U = the activity of one gram of uranium oxide in div. per min. (in the α-ray electroscope).

R = the initial activity of one gram of radium-barium sulphate (in the α-ray electroscope).

W = the weight of sulphate precipitated from 10 c.c. of the radium-barium solution.

The value of x is given by

$$x = \frac{W \times Em_1 \times R \times 0.848}{0.73 \times Em_2 \times U.}$$

The advantage of this method of calculation lies in the fact that the question of either radium or uranium standards is not involved in the final value.

The results obtained from the measurement of the radium films are given in Table IV.

Table IV.

Solution.	Film Number.	Film. Weight.	U.	R.	W.	Em_1.	Em_2.	X.
B.........	101	0·00926	710*	1049	0·0278	853	81·8	0·493
B.........	102	0·00711	710*	1050	0·0278	853	81·7	0·497
B.........	103	0·00819	710*	1030	0·0277	853	81·7	0·487
B.........	104	0·00667	710*	1025	0·0274	853	81·8	0·480
C.........	110	0·00548	710*	1025	0·0237	853	71·0	0·478
C.........	113	0·00300	710*	1050	0·0237	853	70·0	0·495

Mean value of $x = 0.488$.

* The value here given is based on a different sensibility of the electroscope from that which it possessed in the case of the values given in Table 1.

The value obtained by Boltwood[*] for this ratio (0·45) is somewhat lower than that given above. When the experimental conditions are taken into consideration, however, the agreement is as good as might be expected. A determination has also been made by Meyer and Paneth[†], who compared the radiation from a known quantity of radium with the ionization produced by the α-particles from one gram of uranium. They obtained a value of 0·57 for the ratio. Aside from other objections to their method, the manner in which they obtained the uranium salt used as a standard is open to the most serious criticism. Comparatively crude uranyl nitrate was subjected to purely chemical methods of purification, methods which are generally recognized as unsuitable for obtaining a pure uranium product. Very little, if any, weight can therefore be attached to their determination of the value of the ratio.

Discussion of Results.

As already pointed out, if the entire series of transformations from uranium I., through uranium II. and ionium, to radium is a simple and direct one, the value to be expected for the uranium-radium ratio is approximately 0·57. The value found in this investigation is 0·49, which is lower by an amount far in excess of the probable experimental error. The result suggests that the number of radium atoms which disintegrate with the emission of α-particles in the unit time is less than the number of atoms of uranium I. or uranium II. which disintegrate in the same period. This indicates either (a) that a series of branch products is split off from the main series before the radium atom is produced, or (b) that radium itself disintegrates in a complex manner, a larger proportion (but not all) of the atoms being transformed with the emission of α-particles. Unless the accepted values for the ranges of the α-particles from uranium are greatly in error (which appears to be rather improbable) the progress of transformation from uranium I. to (and including) radium is at some point irregular and is accompanied by the production of a collateral series. This conclusion is supported by the occurrence of actinium and its products in association with radium in uranium minerals, and by the impossibility of tracing the origin of actinium to any point in the series subsequent to radium.

* Am. Journ. Sci. xxv. p. 269 (1908).
† *Wien. Ber.* cxxi. Abt. IIa (1912).

We will now proceed to a consideration of the two alternatives (*a*) and (*b*) mentioned in the preceding paragraph. As a preliminary to this the relative activities of the other members of the main-line series can be calculated from the ratio experimentally determined for the uranium and radium. Geiger's equation is employed

$$I = Nk\,R,$$

and the results obtained are given in Table V. The calculations are made on the assumption that the simplest (1 : 1) relation exists between all the products following and including ionium.

<div align="center">TABLE V.</div>

Element.	Range of α-particle in cm. (at 0° C.)	Relative Calc.	Activity Found.
Uranium I.	2·37		
Uranium II.....................	2·75	1·00	1·00
Ionium	2·95	0·46	
Radium..........................	3·13	0·49	0·49
Emanation	3·94	0·57	
Radium A	4·50	0·62	
Radium C.......................	6·57	0·80	
Radium F.......................	3·64	0·53	

<div align="right">Sum = 4·47</div>

Relative activity of actinium and actinium products as determined experimentally by Boltwood[*]   = 0·28

<div align="right">Total = 4·75</div>

Total activity as determined (p. 57)............   4·73

The *very* close agreement between the total activities as calculated and as found is purely accidental and merely indicates that the value given for the activity of the actinium products by difference (4·73 − 4·47 = 0·26) is practically the same as that suggested by Boltwood as a result of his experiments.

The ranges of the α-particles from uranium, radium, and each of the actinium products and also the value of the two-thirds power of the range are given in Table VI.

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[*] Am. Journ. Sci. xxv. p. 297 (1908).

TABLE VI.

Element.	Range at 20°.	$R^{\frac{2}{3}}$.
Uranium I.	$R_1 = 2\cdot54$	1·87
Uranium II.	$R_2 = 2\cdot95$	2·05
Radium	$R_3 = 3\cdot36$	2·24
Radioactinium	$R_4 = 4\cdot29$	2·64
Actinium X	$R_5 = 4\cdot34$	2·66
Actinium emanation	$R_6 = 5\cdot66$	3·18
Actinium A........	$R_7 = 6\cdot37$	3·44
Actinium C	$R_8 = 5\cdot24$	3·01

Applying the data available we may calculate what proportion of the total number of atoms of uranium II. would have to be assumed to disintegrate in a mode leading to the production of actinium in order that the ratio of the activity of the actinium products to the activity of the radium would have the value 0·28/0·49 indicated in Table V. There are five actinium products emitting α-rays as compared with a single α-ray change in the case of radium, and if equal numbers of atoms of each of the elements were disintegrating in unit time the ratio of the activities would be[*]

$$(2\cdot64 + 2\cdot66 + 3\cdot18 + 3\cdot44 + 3\cdot01) : 2\cdot24 = 6\cdot6 : 1.$$

The observed ratio is, however, 0·28 : 0·49. If 100 atoms of uranium II. are assumed to disintegrate in unit time of which x disintegrate to form actinium, we have the relation

$$\frac{14\cdot9 \; x}{(100 - x) \; 2\cdot24} = \frac{0\cdot28}{0\cdot49},$$

which gives a value for x of approximately 8. So that, if, out of every one hundred atoms of uranium II. disintegrating, a total of eight atoms changed into actinium and the remaining 92 changed into ionium (and ultimately radium), the observed relations would exist between the activity of the radium and the activity of the actinium products in a mineral.

Based on considerations of this character a number of attempts have been made to devise a scheme of transformation which will satisfactorily indicate the successive changes undergone by the uranium atoms. The most plausible of these have been proposed by Soddy and Cranston[†] and are given on the following page.

[*] Table VI.
[†] Proc. Roy. Soc. A xciv. p. 384 (1918).

(I) UI

$$UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} UII \xrightarrow{\alpha} Io \xrightarrow{\alpha} Ra \xrightarrow{\alpha}$$

IV   V   VI   IV   II

$\alpha\ 92\%$ VI

$\alpha\ 8\%$

$$UY \xrightarrow{\beta} UZ \xrightarrow{\alpha} Ac \xrightarrow{\circ}$$

IV   V   III

(II) $$UI \xrightarrow{\alpha} UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} UII$$

VI   IV   V   VI

$$Io \xrightarrow{\alpha} Ra \xrightarrow{\alpha}$$

IV — II

$\alpha\ 92\%$

$\alpha\ 8\%$

$$UY \xrightarrow{\beta} UZ \xrightarrow{\alpha} Ac \xrightarrow{\circ}$$

IV   V   III
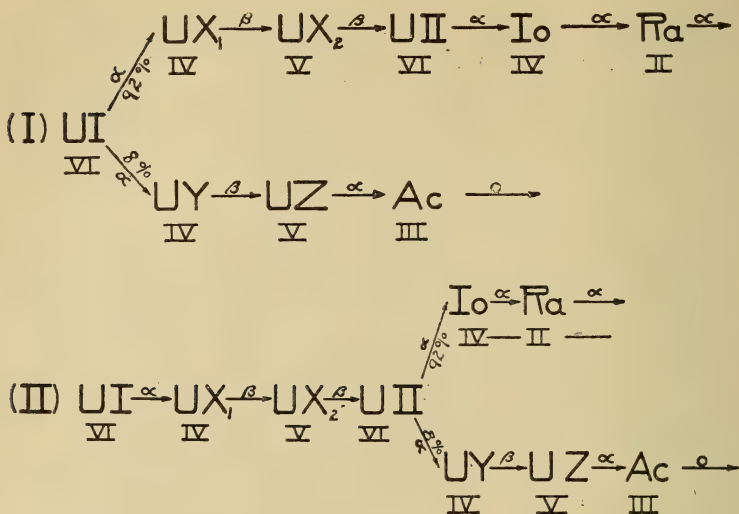
It is not proposed to discuss these schemes in detail or to consider at any length certain minor points involved to which exception might be taken. It is, however, difficult to understand just what is implied by the dual transformation with the expulsion of α-particles in both cases which is suggested for U I. in the first scheme and for U II. in the second. It would appear that the loss of an α-particle in each case should lead to the production of one and the same kind of matter, namely, to a single product and not to two different products to be designated as U X_1 and U Y in one example and as Io and U Y in the other. The main point under consideration is, however, whether either of these schemes gives us a clue to the explanation of the relative activities of uranium and radium as they have been found in our experiments, and it may be stated that they do not, since the first scheme would suggest a ratio of $1/{\cdot}55$ for the relative activities of the uranium and the radium, while the second scheme would imply a ratio of $1/{\cdot}53$ for the same quantities.

In order that Scheme I. might satisfactorily apply to the ratio as found by experiment it would be necessary to assume that about 26 out of every 100 atoms of U I. were transformed in the mode leading to the production of actinium. This in turn is contradicted by the relative activity of the actinium products in an equilibrium mixture.

In order to fulfil the conditions involved in Scheme II. it would be necessary for 14 out of every 100 atoms of

uranium to be transformed in the mode leading to the production of actinium. Nor is there any apparent advantage gained by assuming that the transformation of either U I. or U II. into the first member of the side series is accompanied by the expulsion of a β-particle instead of an α-particle.

It might, however, be assumed that the branching of the series takes place at some other point, as at radium, for example, and that 86 per cent. of the radium atoms disintegrate with the emission of α-rays to form the emanation, etc., while 14 per cent. disintegrate (emitting β-rays) to form actinium. Direct evidence of the emission of β-rays by a specimen of radium has been obtained by Hahn and Meitner[*]. Under these conditions the α-ray activity of ionium would be proportional to the uranium radiation and would equal 0·53. The activity of the actinium series would equal 0·56 and the activity of the radium + emanation + radium A, C, and F would be 3·01 (the sum of the values given in Table V.). The sum of all of these together with uranium is 5·10 for the total activity of the uranium series (as in uraninite). There are, however, serious objections to the assumption that the side branch arises at radium, aside from the fact that the values mentioned are widely different from those found in Boltwood's experiments and the value found in the present experiments for the total activity of the uranium products.

The most significant objection is presented by the agreement of the value found for the disintegration constant or radium by Rutherford and Geiger[†] and the value of this constant found by Miss Gleditsch[‡]. The Rutherford and Geiger estimate was based on the number of α-particles emitted per second by the radium C in equilibrium with one gram of radium. If only eighty-six out of every hundred of the radium atoms disintegrate to form radium C, then this estimate would be 14 per cent. too low. The method employed by Miss Gleditsch depended on the production of radium from the ionium in equilibrium with a known amount of radium, and was measured in terms of the fraction of the total equilibrium amount which was produced in a known period of time. This would have given the true value for the disintegration constant irrespective of the mode of

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[*] *Physik. Zeitschr.* x. p. 741 (1909).
[†] Rutherford, Phil. Mag. xxviii. p. 326 (1914).
[‡] Am. Journ. Sci. xli. p. 112 (1916).

disintegration. These two methods would therefore have given different and not similar values if the collateral series had originated at radium.

Among other objections may be mentioned the experiment made by Soddy[*], who examined a specimen of radium salt containing 13·2 mgs. of radium which had been sealed for a period of ten years. No evidence of the presence of actinium was obtained. Paneth and Fajans[†] examined a specimen containing 180 mgs. of radium which had been sealed for six years, but were unable to detect the presence of any actinium products. We may therefore dismiss the possibility of the side chain splitting off at radium as highly improbable in the light of our present knowledge.

The possibility that the collateral series originates at ionium may also be considered. The fact that the experimental evidence is all opposed to the emission of a β-radiation by ionium is in itself a decided objection to this view. Moreover, it would require (uranium taken as unity) an activity of 0·56 for the actinium products, an activity of 0·46 for ionium, and an activity of 3·01 for radium and its products, with a total activity of 5·02. Paneth and Fajans[‡] have directly attacked this problem by seeking for the presence of actinium in a strong preparation of ionium-thorium which had been undisturbed for four years. They were unable to discover the presence of any actinium products. Lacking any support, therefore, the supposition that the collateral series arises at ionium is untenable at present.

These circumstances compel a return to a consideration of the earlier members of the series, to U I. and U II., in the hope of being able to find there an explanation of the conditions indicated by our experiments. At first sight it might seem that the conditions would be satisfied by assuming that what we now call uranium consists of three radioelements, a parent element and two isotopic products in equilibrium, all emitting α-rays. But if these are present in relative amounts of the same approximate order of magnitude (*i. e.*, 100, 92, 92, etc.), then the α-rays emitted by at least one of them would have to be of exceedingly short range and small ionizing power and the rate of change of this substance would be excessively slow. It is not impossible, but it does not seem probable, that ordinary uranium may consist of what we know as U I. and U II., both radioelements in the main line of descent, and a third isotope

* 'Nature,' xci. p. 634 (1913).
† *Wien. Ber.* cxxiii. IIa, p. 1627 (1914).
‡ *Wien. Ber.* cxxiii. IIa, p. 1627 (1914).

which is a product in the collateral actinium series. But the difficulties here are not inconsiderable aside from the fact that the existence of such an isotope is somewhat difficult to imagine. If present in amounts proportional to the actinium this product would have to emit comparatively long range (7·2 cm.) α-particles and would therefore have a very short life period. Such a conclusion does not seem at all probable in the light of our present knowledge.

It is not impossible that the values accepted for the ranges of the α-particles from uranium are considerably in error and that this is the reason for the lack of agreement between theory and experiment. But until some more definite data have been obtained there seems to be little justification for abstruse speculation on the genetic relationship in the earlier stages of the uranium series.

Summary.

The relation of the activity of radium to the activity of the uranium with which it is in radioactive equilibrium has been redetermined. The results obtained indicate that if the activity of uranium is taken as unity the activity of the radium is equal to approximately 0·49.

The total activity of uranium mixed with equilibrium quantities of its disintegration products has been compared with the activity of the uranium alone, and the former has been found to be 4·73 times the latter.

A critical examination has been made of the various theories which have been proposed to explain the genesis of radium and actinium from uranium. None of these theories appears to satisfy the necessary requirements.

V. *The Bearing of Rotation on Relativity.*
By Prof. R. A. SAMPSON, *F.R.S.*[*]

CONSIDER two concentric spheres with a very small space between them so that we need not distinguish between their radii. An observer A is placed on the outer surface of the inner sphere and an observer B on the inner surface of the outer. All phenomena are supposed to pass in the space between the two spheres.

Regard this system and its changes first from a purely geometrical point of view. A and B will possess in common a natural unit of length, being the circumference of their

sphere. Let the arc AB as it exists at any moment be determined as a fraction of this unit. Let it be determined again in the same way at a later moment. If the two do not agree, we can say that a relative rotation of the two spheres must have occurred, through a definite angle, about an axis perpendicular to the plane of the great circle AB. Whether any relative rotation about an axis in the plane AB has taken place, or whether both spheres have executed in common any other rotation about any axis whatever, the observers at A and B will be unable to say. We may express this position by saying that A and B are under circumstances of complete geometrical relativity.

The whole description is, however, an abstraction. It is the abstraction which lies at the basis of geometry; it eliminates time from consideration and supposes figures to exist with definite distances between the points. But in reality any distance assigned requires time for its determination, and the standard case would be this : A and B each have hold of a graduated measure, allowing it to slip through their hands, and as they watch its successive readings they signal them to one another ; each will then only be aware of the other's reading, that is to say, of the other's distance at any moment, as complicated by the time of transmission of the signals. This aberrational allowance is an inevitable attendant upon actual physical measures. It is inseparable from motion. It would not be surprising if the ideas of motion required a complete surrender of the scheme of abstract geometrical relativity defined above.

How much the physical theory of motion affects our notions of absolute and relative is very well known. Let the sphere A be the Earth and the sphere B a complete opaque sheet of cloud rotating with it. A Foucault pendulum set up at the north pole would of itself change its plane of oscillation with respect to the meridians, pointing out an absolute direction in space, and an absolute rate of rotation, of which the observer would be unaware without this, or other similar, appeal to dynamics. A similar pendulum set up at the equator would show no change of azimuth at all. By no conceivable explanation can this familiar experiment be made consistent with complete geometrical relativity of the system, geometrically self-contained, within the bounds of which it occurs. Other cases could easily be mentioned. But my purpose at the moment is to pursue a little further the aberrational considerations introduced above.

In 1893 and 1897 Sir Oliver Lodge, considering the Michelson-Morley experiment, then not infrequently taken

as proving that the Earth swept with it the æther in its vicinity, spun two large heavy metal disks, parallel and close to one another, with high angular velocity, in order to test whether they exercised any viscous drag upon the æther between them. Light was transmitted to and fro across the intervening space, but the effect upon it was null. Now return to the two spheres A and B. Let their surfaces be perfect reflectors. Let light signals be emitted from A. Then according to Lodge's experiment, whatever rotations the spheres may have, the passage of this light will be unaffected by it. Let B be fixed and diametrically opposite to A at the moment of emission. The waves or rays will spread in a sheet over the sphere, converge upon B at the same moment and in the same phase, and issuing from B will return again to the point from which they were emitted. But if A has moved in the interval, this will permit the observer A to ascertain the point in space which he occupied at a given past moment, A_0 say. It is the point upon which the rays converge and are received all together and at once in the same phase—that is, the point diametrically opposite to B.

It may be said that when the globe A is in rotation, it must be supposed to undergo the FitzGerald contraction parallel to its equator, deforming it from a sphere; and therefore the geodesics which are the paths of rays will in general no longer converge upon a single point as they do for a sphere, but pass alongside it. This, however, is a second-order effect, and would not interfere with the determination of AA_0, which is of the first order; moreover, it would of itself demonstrate the rotation by the non-concurrence of the rays. We should therefore conclude that by the use of signals transmitted through the æther it is possible to determine the motion of A, imagined as a rotation. There is no sign of conflict here with results of experiments with matter alone, referred to earlier; but the conclusion bears awkwardly upon the Principle of Relativity for linear motions, and it is desirable to examine whether the division is apparent only or real.

Consider whether rotation is essentially connected with the discussion. Let A_0, A_1, A_2, A_3 be four points successively occupied by the observer. Describe a sphere through A_0, A_1, A_2, A_3, and let light pass round it as above, being emitted from A_0. Adjust the rotation of this sphere so that the time taken to carry the observer from the position A_0 to the position A_1 is equal to the time taken by light to girdle the sphere. Then the argument runs just as before, and the conclusion can be drawn that the previous position of A is

ascertainable in every case except when three of the points A_0, A_1, A_2, A_3 lie upon one straight line. The argument then has no bearing on the Principle of Relativity for linear motion, even if we include accelerated linear motion. The latter stands just where it did.

It is worth remarking that the Principle of Relativity, owing to its generality in asserting that no experiment can be derived that will falsify it, can never be established except upon trial. It suffers under the difficulty always found in proving a negative. Thus the Michelson-Morley experiment is, of course, consistent with it, but the experiment is explained without its aid by adopting the FitzGerald contraction, which there is otherwise strong reason to accept.

At each successive test of the principle there is the same possibility of escape. Thus, though the test imagined above fails as a criticism of its application to rectilinear motion, it is easy to imagine a test case which would exclude acceleration from its domain. The annual aberration of the stars is, in fact, just an observation of the variation of the motion of the Earth in direction ; and if we could observe with sufficient refinement, it would equally reveal a variation in its amount. The only field that remains is that of uniform linear motion ; and even here I cannot see that it is free from attack. The gradual transmission of light was first demonstrated by Roemer from the eclipses of Jupiter's first satellite. As the Earth approaches Jupiter, immersions alone are observed, and as it recedes only emersions, the changing distance is marked by an apparent reduction of the period of revolution in the former case, and a compensating increase in the latter. The quantities have been observed, and agree with dimensions of the orbits of the Earth and Jupiter found by Euclidean triangulation and a velocity of light found from terrestrial experiments. The comparisons take place in all directions in the ecliptic. The quantity directly determined is the time taken by light to travel a distance equal to that travelled by the Earth between two eclipses. There is here no question of contraction of the measuring rod, for the phenomenon is one involving the relative velocity of light in the first order. Hence we can conclude that if there is any undiscovered drift of the solar system through the æther, it must take place in a direction perpendicular to the plane of the ecliptic; this is reliable to such a degree of accuracy as these observations will bear, and that is by no means an inconsiderable one.

If we are unable to draw a conclusion one way or another with regard to relative drift of the æther perpendicular to the plane of the ecliptic, that is only because it happens that we

cannot find a system that supplies a natural test, and are unable to make one.

In the foregoing sentences it is, of course, adopted that when a phenomenon occurring on Jupiter is transmitted by light to the Earth, the velocity of its transmission through the intervening space is entirely independent of any drift that Jupiter may possess relative to the æther; this drift is shared, let us say, by the whole solar system, and it becomes an observable quantity at the receiving point—the Earth, because it may change the distance over which the transmission through pure æther must take place.

Returning to the imagined model of two concentric spheres, consider again this bearing upon relative time and its measurement, as these appear in the usual exposition of the Principle of Relativity.

Consider the two observers A and B, imagined at the beginning, and suppose for simplicity that A, B are both on the equator of the uniform relative motion of the spheres. If A, B compare their clocks by light signals, say, it may be shown, as in the works on Relativity, that their zeroes will differ by ux/c^2, where x is the arc AB, u the velocity of B relative to A, and c the velocity of light. If the relative motion of B is in the same direction as the transmission of the signal, B's time is slow. But in our imagined case, B will receive two signals, generally at different times and always in opposite directions, and might consequently set two clocks by them, one slow and the other fast. These clocks would keep permanently different rates, one losing and the other gaining $\tau u^2/c^2$ in each relative revolution or "day," where τ is the length of this "day." But this "day" would itself be an observable phenomenon, possessed in common by both A and B, and marked as the interval between two consecutive coincidences of B with A. In our case, then, B would be able to ascertain that the times kept by his two clocks rated by two light signals were both erroneous, nor would he require to adopt the same numerical measure of the velocity of light as A, in order to provide himself with a standard measure of time, as he is supposed to do, in the Theory of Relativity.

It is hardly necessary to point out that our imagined case of time-determination is not an artificial one, but is as close as an ideal construction permits to the actual practice by which the solar day and the sidereal day are found. We may go a little further. It has been the practice to observe at Greenwich the transit of the lunar crater Mösting A. Imagine an observer in the Moon, situated in Mösting A and taking the moment when Greenwich crossed the medial

line of the Earth's disk,—which would bring him into the meridian of Greenwich. If we suppose that there is a definite moment of occurrence of the geometric phenomenon, each observer would get it late by the same amount, about $1^s·3$, being the time of transmission of light; but on repeated observations each would have exactly the same time-intervals of what may be called a lunar day at his service for common standardization of time.

In conclusion, I would add a few sentences on the general bearing of these remarks. I take it there is no useful knowledge apart from repetition, including its opposite, contrast. An isolated event, with no indication of its history or relation, is meaningless—like an inscription without a clue. Consequently we find that in the field of mechanics, the cases that involve perpetual repetition are those reduced to the best order—as the rotation of the Earth, the revolution of the planets, and periodical mechanical motions of every kind. Therefore, in spite of the apparently greater simplicity of pure translational motion, I submit that it is in the simplest cases of circular motion that we should naturally look for light upon the question of how far we are able to perceive our own drift through the æther. It is not tolerable to erect a new theory, of completely general scope, and leave on one side these familiar natural events, the best analysed that we possess. Properly regarded, the paradoxes to which a theory leads are its most promising features, for they indicate points where something can be learnt by pressing the examination. Some of the numerous paradoxes to which the Theory of Relativity has given rise may prove to be merely verbal or otherwise unessential; those exposed above suggest, I submit, something more than this—namely, that the theory for rectilinear motion is a degenerate case, which leads to untrue results if we attempt to embrace circular motions; admirably compact as its mathematical form may be, it owes this coherence to a reduction that shuts off the best known fields of Nature.

Yet no one can doubt that we must have a theory of relativity, limiting, and probably limiting very much, what it is possible to know. It is the theory of the interdependence of our senses of intensity or measurement in their various fields—space, time, and if you like, others. It is the work of pure mathematicians to give us one. Owing to the difficulty of his task, the mathematician must be allowed to make any abstraction which he finds workable. The interest thereafter is to see how far his construction may be taken as depicting Nature, in the way that we know Nature to work.

VI. *Ionization and Resonance Potentials for Electrons in Vapours of Lead and Calcium.* By F. L. MOHLER, *Ph.D.*, PAUL D. FOOTE, *Ph.D.*, and H. F. STIMSON, *Ph.D.*[*]

PREVIOUS papers [†] have discussed measurements made in this laboratory of ionization and resonance potentials of a number of metals. A continuation of this work has led to satisfactory results for lead and calcium.

The method of measurement employed has been described in detail elsewhere. The metal is boiled at low pressure in a vacuum tube containing a Wehnelt cathode surrounded by a cylindrical grid and plate. Between the cathode and grid is placed a variable potential to accelerate the electron current from the cathode, while a small retarding field is fixed between the grid and plate. Measurement of the total current leaving the cathode as the accelerating potential is increased shows a sudden increase in the current when the ionization point is reached on account of the direct effect of ionization and the indirect effect of positive charges on the electric field. The " partial current " reaching the plate against a small retarding field decreases when the electrons near the grid lose nearly all their velocity by inelastic impact with vapour molecules. The curve of " partial current " versus accelerating potential shows a series of drops in the current at equal voltage intervals. This interval is equal to the resonance potential, and the distance of the first drop from the origin is the resonance potential minus the initial velocity in volts of electrons leaving the cathode. The initial velocity correction added to the applied potential at the ionization point gives the ionization potential.

This interpretation of the partial current curves is based on two assumptions :

1. That when the velocity of an electron is less than that corresponding to the resonance potential collisions are elastic.
2. That when equal to or greater than the resonance potential the velocity lost at collision is equal to the resonance potential.

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[*] Communicated by the Authors, being abstract of paper to appear in ' Bulletin Bureau of Standards.'

[†] Tate & Foote, Phil. Mag. xxxvi. p. 64 (1918) ; Bur. of Standards, S. P. 317. Foote & Mohler, Phil. Mag. xxxvii. p. 33 (1919). Jour. Wash. Acad. Sci. viii. p. 513 (1918). Foote, Rognley & Mohler, Phys. Rev. xiii. p. 59 (1919).

The first assumption is almost certainly justified, although no direct measurements of velocity lost by collision with metal molecules have been made. The second assumption seems to agree with all experimental results, but the evidence available does not exclude other hypotheses. Thus Akesson [*] has suggested that electrons with velocity several times the resonance potential may lose several "quanta" of energy at one collision. His conclusions are based on experiments with non-metallic gases, and the authors doubt whether he has conclusively proved this important point.

It has been found that the resonance and ionization potentials of metals are related to frequencies in their line spectra by the quantum equation $Ve = h\nu$, where V is the potential, e the electron charge, h Planck's constant of action, and ν the frequency.

The resonance potential is determined by the frequency of a prominent line in the spectrum, the first line in a principal or combination series in all cases so far observed. The ionization potential is determined by the limiting frequency of this series in all the metals studied except thallium. These spectral relations are similar among metals of the same group of the periodic table.

The metals were vaporized in porcelain tubes 3×35 cm., electrically heated.

A cylinder of iron gauze served as a grid, and with lead an outer cylinder of iron was used for the plate. With calcium the plate consisted of an iron tube closed at the bottom, thus protecting the porcelain from the hot metal. A temperature of $1050°$ C. was required for a sufficiently dense vapour of lead and $950°$ C. for calcium. At these high temperatures all parts of the apparatus emit electrons, and it is necessary to employ a cathode from which the thermionic emission is relatively high. A hot molybdenum wire coated with calcium oxide was satisfactory for calcium, but it was found necessary to use an equipotential source for lead. This consisted of a small steel tube coated with lime and heated by an inner coil of molybdenum wire. A low gas-pressure was maintained by means of mercury vapour pumps of the type designed by one of the writers [†].

Discussion of Results with Lead.

Fig. 1 gives some of the curves of partial and total current versus accelerating potential in lead vapour. Curves 4, 14

[*] *Lunds Universitets Arsskrift*, NF. Avd. 2, Bd. xii. Nr. 11.
[†] Wash. Acad. Sci. vii. p. 477 (1917).

20, and 26 are total current and curves 1, 3, 10, 19, and 23 partial current reaching the outer electrode. In all 19 partial current curves and 12 total current curves were obtained of which the curves illustrated are typical. The total current

Fig. 1.
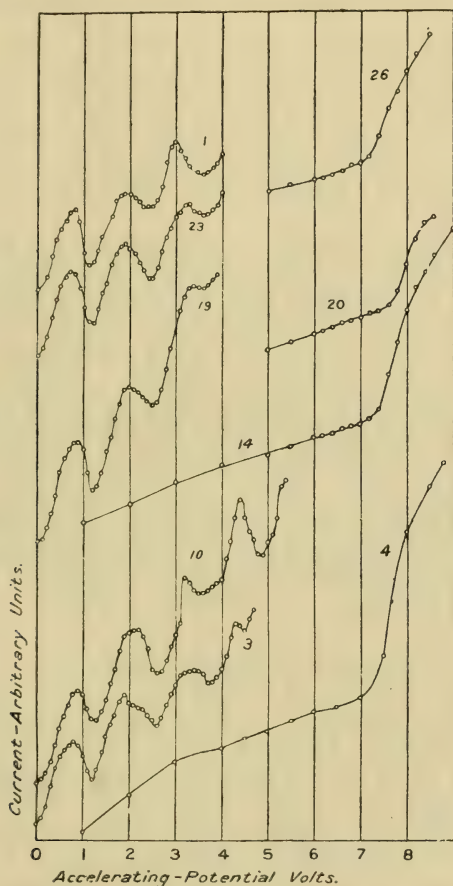
Electron Currents in lead vapour. Curves 4, 14, 20, and 26 " total current "; curves 1, 3, 10, 19, and 23 " partial current."

showed ionization when the temperature reached 900° C., but most of the data were obtained in the range 950° C. to 1050° C. Above the ionization point a blue arc was visible, due probably to the line λ = 4058 Å.

The data lead to a mean value for the resonance potential of 1·26 volts; for the ionization potential 7·93 volts.

No line series have been found in the lead spectrum, nor is there anything known of the lines appearing at low voltage. Applying the quantum relation $Ve = h\nu$; or $\lambda = \dfrac{12334}{V}$ where V represents volts and λ Ångström units; the resonance potential gives $\lambda = 9800$ Å. with a possible error of 800 Å. The single line spectrum of lead, if such exists, should be in this region. Thermopile measurements of the lead spectrum by Randall * show an isolated group of strong lines near this point, and the shortest wave-length line of the group $\lambda = 10291$ falls well within the limits of our prediction.

The ionization potential corresponds to $\lambda = 1550$. This may be the limit of a series of which $\lambda = 10291$ is the first line, but it is noticeable that the frequency ratio between the first line and limit of such a series is much greater than in the usual type. In nearly all known series the ratio of frequencies is between two and three, while this is nearly seven. In the case of thallium alone we found that ionization was not determined by the limit of a principal series, but our results have shown that there is little basis for reasoning by analogy when we are dealing with metals in different columns of the periodic table. If $\lambda = 10291$ is the single line spectrum we are able to compute an accurate value for the resonance potential. The above data thus give $V = 1·198$ volts.

Discussion of Results with Calcium.

Fig. 2 illustrates typical curves of total and partial currents in calcium vapour. Curves 8, 18, and 22 are total currents, and curves 1, 3, 9, 14, and 15 partial current. In all 11 total current curves and 11 partial current curves were obtained. The observations were made at temperatures between 800° C. and 900° C. The shape of the curves with steps of about 2 volts and intermediate inflexions which are less prominent can be explained on the assumption that there are two types of inelastic collision without ionization at approximately 1·9 volts and 2·9 volts, of which the first is the more probable. Thus in curve 14 the inflexions at a, c, and e are due to electrons undergoing one, two, and three

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* Astrophys. Journ. xxxiv. p. 1 (1911).

collisions of type 1. *b* is due to one collision of type 2. Two collisions of type 2 will fall very near the point *e*. *d* is due to one collision of type 1 followed by one of type 2 or

Fig. 2.
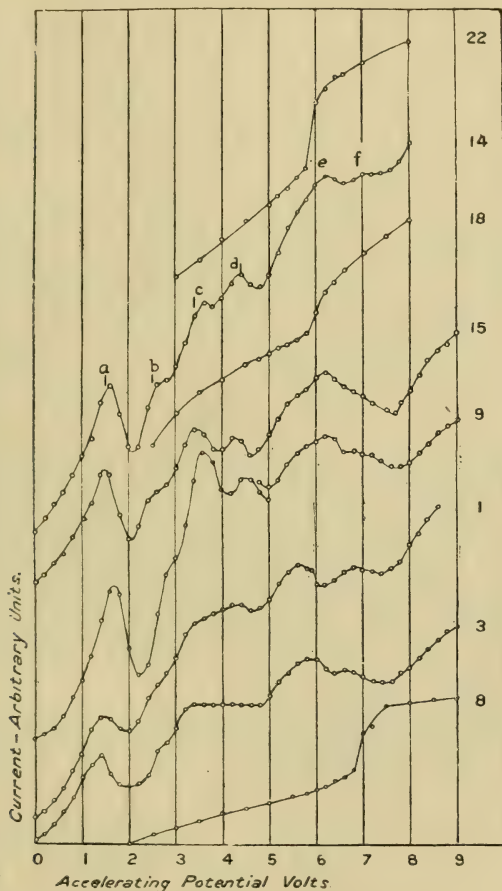
Electron currents in calcium vapour. Curves 8, 18, and 22 " total current "; curves 1, 3, 9, 14, and 15 " partial current."

vice versa, and *f* is due to two collisions of type 1 and one of type 2 in any of the three possible orders. The positions of *e* and *f* are above the ionization point, and for this reason somewhat variable. The point *b* is too faint for accurate

measurement, so the resonance potentials have been computed from the points a, c, and d. The mean value of $c-a$ gives for the first resonance potential 1·90 volts. The second resonance potential, $d-a$ is 2·85 volts. The observed ionization potential is 6·01 volts.

The occurrence of two resonance potentials has been suspected in the case of other metals, notably zinc and magnesium, but this is the first instance in which the phenomena were unmistakable. It suggests the possibility that in all metals there may be many potentials of inelastic impact, of which the observed resonance potential is the most probable.

For the metals of the second column of the periodic table previously studied, it has been found that the resonance potential is determined by the frequency of the combination series line $1·5 \text{ S} - 2\,p_2$, and the ionization potential by the limiting frequency $1·5 \text{ S}$. The first line of the principal series of single lines $1·5 \text{ S} - 2\text{ P}$ is, however, predominant in spectra of the alkali earths.

The frequency $1·5 \text{ S}$ for calcium is computed by F. A. Saunders [*] to be $\nu = 49304·8$, $\lambda = 2027·56$. This corresponds to $V = 6·081$ volts in close agreement with the observed value $V = 6·01$ volts. The line $1·5 \text{ S} - 2p_2$ has not been correctly identified in any published work, but is undoubtedly $\lambda = 6572·78$, as this agrees with the best values of series constants, and the physical properties of this line are characteristic. Accordingly we obtain for the theoretical value $V = 1·877$ volts, while the observed value is $V = 1·90$ volts. The line $1·5 \text{ S} - 2\text{P}$, $\lambda = 4226·73$ corresponds to $V = 2·918$ volts in good agreement with the observed value $V = 2·85$ volts.

The spectral relations of the second resonance potential are not surprising. McLennan [†] has found that the line $1·5 \text{ S} - 2\text{P}$ alone appears in the magnesium arc below the ionization potential, and that in zinc and cadmium arcs both $1·5 \text{ S} - \text{P}$ and $1·5 \text{ S} - 2p_2$ appear. Davis and Goucher [‡] by their photoelectric method of detecting different types of radiation found evidence that $1·5 \text{ S} - 2\text{P}$, as well as $1·5 \text{ S} - 2p_2$, appears in mercury at the voltage corresponding to its frequency. Interesting light on these fundamental frequencies in the spectra of the alkali earths is given by

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[*] Data furnished by Dr. Saunders.

[†] McLennan, Proc. Roy. Soc. xcii. p. 574 (1916). McLennan & Ireton, Phil. Mag. xxxvi. p. 461 (1918).

[‡] Phys. Rev. x. p. 101 (1917).

the work of A. S. King * with the tube furnace at different temperatures. In the calcium spectrum at high temperature the line $\lambda = 4227$ is predominant and $\lambda = 6573$ quite faint, while at low temperature $\lambda = 4227$, though still the brightest line, has lost considerably in relative intensity and $\lambda = 6573$ has increased until it is second only to $\lambda = 4227$. Magnesium shows the same phenomena, but in a more striking manner, for the line $1\cdot5\,\mathrm{S} - 2p_2$, $\lambda = 4571$ is the brightest line in the spectrum at low temperature though faint at high temperature, and in ordinary arc spectra.

That these two lines in calcium are related to the two observed resonance potentials is to be expected. However, the relative prominence of the 1st resonance potential due to $1\cdot5\,\mathrm{S} - 2p_2$ in calcium and magnesium is difficult to reconcile with the researches of McLennan on low-voltage arcs in magnesium where only the line $1\cdot5\,\mathrm{S} - 2\mathrm{P}$ was observed. The problem is evidently complicated. The tube furnace spectra show at least that the two emission centres are affected differently by a change in physical condition.

Summary.

The resonance and ionization potentials of lead are $1\cdot26$ and $7\cdot93$ volts respectively. The line $\lambda = 10291$ gives the probable theoretical value for the former as $1\cdot198$ volts.

Calcium has two resonance potentials, $1\cdot90$ volts and $2\cdot85$ volts, of which the first is more prominent. Ionization was observed at $6\cdot01$ volts.

The following spectral frequencies determine these potentials :—

First resonance.... $1\cdot5\,\mathrm{S} - 2p_2$, $\lambda = 6572\cdot78$ Å., $V = 1\cdot877$ volts.
Second resonance .. $1\cdot5\,\mathrm{S} - 2\mathrm{P}$, $\lambda = 4226\cdot73$ Å., $V = 2\cdot918$ volts.
Ionization .... $1\cdot5\,\mathrm{S}$, $\lambda = 2027\cdot56$ Å., $V = 6\cdot081$ volts.

Bureau of Standards,
    Washington, D.C.,
    October 20, 1919.

* Astrophys. Journ. xlviii. p. 13 (1918).

VII. *Atomic Theory and Low Voltage Arcs in Cæsium Vapour.*
By PAUL D. FOOTE, *Ph.D.*, *and* W. F. MEGGERS, *Ph.D.*[*]

[Plate I.]

I. THEORETICAL.

THE spectrum of cæsium is characterized by the principal doublet series $1.5s - mp_{\frac{3}{2}}$, where $m = 2$, 3, 4, etc.; the 1st subordinate series $2p_1 - md$ and $2p_2 - md'$, where $m = 3$, 4, 5, etc.; the 2nd subordinate series $2p_{\frac{1}{2}} - ms$, where $m = 2.5$, 3.5, 4.5, etc.; the Bergmann series $3d - m\Delta p$ and $3d' - m\Delta p$, where $m = 4$, 5, 6, etc.; satellites to the 1st subordinate series; and certain combination lines, those known lying in the far infra-red[†].

The spectroscopic data are sufficient to permit a schematic representation of the cæsium atom, as illustrated in fig. 1.

Fig. 1.

— Convergence — Prin. Series 1.5 S — 1st and 2nd Sub. Series $2p_1$ and $2p_2$ — Bergmann Series $3d$ —
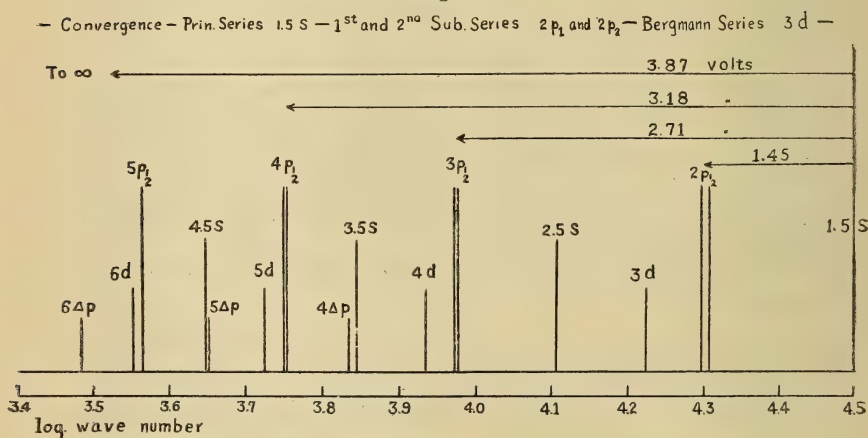
Schematic representation of cæsium atom.

This method was suggested to the writers by Dr. Raymond T. Birge; and, regardless of the theory of atomic structure, it affords a precise picture of the possible series lines in the spectrum of an element—a much clearer picture than may be

* Communicated by the Authors, and published by permission of the Director Bureau of Standards.
† The above notation is that employed by Dunz in his tables, except that for convenience we have written $p_{\frac{1}{2}}$ for p_1 and p_2 when both lines are referred to.

gained by one unfamiliar with series notation from an examination of the series formulæ. The first doublet of the principal series may be represented by electrons falling from the $2p_1$ and $2p_2$ rings into the $1·5s$ ring, thus emitting the lines $1·5s - 2p_{\frac{1}{2}}$. The second doublet of this series is represented by electrons falling from the $3p_1$ and $3p_2$ rings into the $1·5s$ ring, giving rise to $1·5s - 3p_{\frac{1}{2}}$, and so on. The lines of the 1st subordinate series are represented by electrons falling from the *md* rings into the $2p_1$ and $2p_2$ rings; the lines of the 2nd subordinate series by electrons falling from the *ms* rings into the $2p_1$ and $2p_2$ rings; the lines of the Bergmann series by electrons falling from the $m\Delta p$ rings into the *d* rings. Combination lines are represented in the same manner. Thus the line $2·5s - 3p_1$ arises from an electron falling from the $3p_1$ ring into the $2·5s$ ring. Few of the possible combination lines are probable enough to appear in spectroscopic measurements. For example, the line $2p_1 - 4p_1$, while possible, represents an extremely improbable type of transition, and has never been observed in the cæsium spectrum although it is known for sodium. There are other ways much more likely for an electron to leave the $4p_1$ ring.

On the basis of the Bohr theory, the lines shown in the diagram are really portions of the elliptical or ring orbits about the nucleus, which is located off the figure in the right. Surrounding the nucleus are the X-ray rings and many other orbits between the nucleus and the $1·5s$ ring in which electrons may be present.

In the unexcited cæsium atom no electrons exist outside of the $1·5s$ ring. This ring represents the outermost stable orbit and the innermost unstable orbit of the normal atom, and the diameter of this orbit should give the diameter of the *normal* cæsium atom. The evidence for this is fairly conclusive. That there are electrons in this ring is shown by the existence of the principal series, which converges at $1·5s$. That it represents the innermost unstable orbit for any ordinary method of excitation is shown by the fact that no spectroscopic series of cæsium converges at a higher frequency than $1·5s$, nor is any line of higher frequency known. That it represents the outermost stable orbit is evidenced by determination of the ionization potential for which Foote, Rognley, and Mohler [*] observed the value 3·9 volts. On the basis of the quantum relation, $h\nu = eV$, an electron falling through 3·877 volts possesses just sufficient energy to eject

[*] Phys. Rev. xiii. p. 59 (1919).

an electron from the $1·5s$ ring to infinity, in excellent agreement with the experimentally determined value of $3·9$ volts. Thus the ionization of the normal cæsium atom is produced by ejecting an electron from the $1·5s$ ring. If the outermost stable orbit were the $2p$ rings the ionization potential would be $2·4$ volts, unless we make the improbable (see later) assumption that electrons colliding with an atom could not displace an electron from the $2p$ ring.

Thus it is safe to conclude that any displacement of an electron from its orbit in the stable condition of the atom takes place from the $1·5s$ ring. The question arises as to what type of displacements may occur in electronic-atomic impact. Inelastic conditions take place when the impacting electron has the energy $e V$ where V is the ionization potential, this kinetic energy being just sufficient to account for the increase in total energy of the ionized atom. Another type of inelastic impact has been observed in which the colliding electron has the energy $e V$ where V is the resonance potential*, this kinetic energy being just sufficient to account for the increase in total energy of the atom arising from a displacement of an electron from the $1·5s$ ring to the $2p$ ring. The displaced electron being then in an unstable orbit falls to the $1·5s$ ring, giving up the quantum of energy $e V$ received from the collision as a quantum of energy $h\nu$ of radiation of frequency ν, as is shown by the experiments described later. Thus inelastic impacts are known when the colliding electron has sufficient energy to eject an electron from the $1·5s$ ring to infinity or to the $2p$ rings. In the former case the electron returning to the atom causes the emission of various lines, and with many electrons in different ionized atoms returning by various paths we obtain the complicated line-spectra in which the intensities of the lines represent to some degree the probabilities of each particular type of transition from orbit to orbit.

Suppose the colliding electron possessed just sufficient energy to eject an electron to some ring intermediate to ∞ and $2p$. Could the normal atom absorb the entire kinetic energy of the impacting electron? The only known series converging at $1·5s$ is the principal series $1·5s - mp_{\frac{1}{2}}$. Hence it is extremely probable that, if a displaced electron falls into the $1·5s$ orbit, it comes from one of the p rings. Accordingly it is reasonable to assume that in the original displacement from the $1·5s$ ring the electron is ejected to some p ring. Thus inelastic impacts might occur when the colliding electron had fallen through any of the following potential

* Foote, Rognley, and Mohler, *loc. cit.*

differences, the kinetic energy being in each case equal to the increase in total energy of the atom corresponding to displacements to the $2p$, $3p$, . . . to ∞ p rings.

Displacement from $1\cdot5s$ to mp_1.

m.		Volts.
2	. . . .	$1\cdot448$
3	. . . .	$2\cdot709$
4	. . . .	$3\cdot184$
5	. . . .	$3\cdot417$
6	. . . .	$3\cdot549$
.	. . . .	.
.	. . . .	.
∞	. . . .	$3\cdot877$

The first and last of these values are readily observable, as above mentioned. That the values corresponding to $m=3$, 4, etc., have not been observed may be due to the fact that such displacements are very much less probable than the displacement corresponding to $m=2$ and the method of detection accordingly insufficiently sensitive. This is supported by the fact that the probability of a transition from the mp ring to the $1\cdot5s$ ring decreases as m increases—evidence for which lies in the relative intensities of the lines of any series. The displacement to the ∞ ring may take place in an infinite number of ways, and hence is readily produced. The value $2\cdot709$ is nearly double the value $1\cdot448$, and accordingly might be mistaken for two successive collisions with different atoms, each resulting in a displacement to the $2p_1$ ring, the probability of which is quite high under ordinary experimental conditions.

Suppose that the inelastic impact resulted in a displacement to the $3p$ ring. The electron may return to the $1\cdot5s$ ring directly, resulting in an emission of the line $1\cdot5s-3p$, or it might fall to the $3d$ ring giving the line $3d-3p$, then to the $2p$ ring giving $2p-3d$, and finally to the $1\cdot5s$ ring giving $1\cdot5s-2p$, the total value of all the quanta being equal to the increase in total energy arising from the original displacement to the $3p$ orbit. Other modes of transition from ring to ring are possible. Hence, when a large number of atoms are considered, a certain group of spectral lines may result from a displacement of the type considered. The important point on the basis of Bohr's theory is that for the collision mentioned, lines resulting in displacement from rings beyond $3p$ could not exist although the size of the quantum involved might be

many times less. Thus an electronic impact of 2·7 volts could not excite the visually intense line λ 6973 ($2p_1 - 5d$) although the quantum involved requires but 1·8 volts. The energy ($4·3 \times 10^{-12}$ erg) is sufficient to produce this line ($2·9 \times 10^{-12}$ erg), but is not sufficient to displace the electron to the $5d$ ring ($5·1 \times 10^{-12}$ erg)—a condition necessary for its excitation.

The above conception is in agreement with fluorescence phenomena observed in sodium vapour. Thus D-light is absorbed by sodium vapour, and for each quantum absorbed an electron is displaced from the $1·5s$ to the $2p$ ring in an atom. The electron in falling back to the $1·5s$ ring emits the D-line ($1·5s - 2p$), which may be observed at right angles to the beam of incident radiation. Recently, Strutt[*] has found that the sodium line λ3303 ($1·5s - 3p_{\frac{1}{2}}$) similarly stimulates both $1·5s - 3p_{\frac{1}{2}}$ and $1·5s - 2p_{\frac{1}{2}}$. Thus, after absorbing a quantum of frequency $1·5s - 3p_{\frac{1}{2}}$, an electron is displaced to the $3p_{\frac{1}{2}}$ orbit. In returning to equilibrium it may fall directly to the $1·5s$ ring, in which case the line λ3303 is emitted, or it may fall to the $2p_{\frac{1}{2}}$ ring and then to the $1·5s$ ring, the second step involving an emission of the D-lines. This leaves a quantum of frequency $2p_{\frac{1}{2}} - 3p_{\frac{1}{2}}$ (λ7519) looked for but not observed by Strutt. However, this line represents a very improbable type of orbital transition, as is evidenced by the fact that the frequency is never observed in any sodium spectrum. A more probable method of falling from $3p_{\frac{1}{2}}$ to $2p_{\frac{1}{2}}$ is first to the $3d$ ring and then to the $2p$ ring, giving rise to the lines λ8196, 8184, 9048, and 9085, or from the $3p_{\frac{1}{2}}$ ring to the $2·5s$ ring and then to the $2p_{\frac{1}{2}}$ ring. In both cases the quantum relations are correct and the lines are well known, but, lying in the infra-red, they would not have been observed by Strutt.

The fact that an atom can absorb radiation of frequency $1·5s - mp$ (absorption has been observed[†] for $m = 2$ to 60 in the case of sodium), thus resulting in displacement of an electron to the mp ring, for each absorbing atom suggests that similar displacements may be produced by electronic collision. On the other hand, the failure to detect such displacements is not an argument against the Bohr theory. It is possible that the impacting electron must have the correct velocity as well as energy to produce any displacement at all. Thus, while the mass of an electron happens to be such that when its velocity is that obtained by falling through 1·45 or 3·88 volts, a collision with a cæsium atom is

* Proc. Roy. Soc. xcvi. p. 282 (1919).
† Wood and Fortrat, Astroph. Journ. xliii. p. 73 (1916).

inelastic, resulting in a displacement of a bound electron to the $2p_1$ and ∞p rings respectively: at other voltages, such as 3·18, the velocity condition is not fulfilled. This assumption, as far as displacement from the 1·5s ring is concerned, is, however, scarcely justifiable, since the range between 1·45 and 3·88 volts is small; and since it appears that when the electron possesses 3·18 volts velocity, 1·45 volts velocity *may* be absorbed at the impact, this going into increased total energy of the atom and the remainder into kinetic energy of the colliding electron. Also ionization is believed to occur from the $2p$ ring, since arcs may be operated below the ionization potential. At some stage, however, the mass of the colliding particle is effective, since the quantum relations do not appear to hold for low-speed positive or negative ions. Indeed, it is questionable whether a definite ionization potential for ions exists.

An electron of 1·45 volts velocity colliding with a cæsium atom ejects an electron from the 1·5s ring to the $2p_1$ ring. In returning to equilibrium the atom emits the frequency $1·5s - 2p_1$. This radiation, however, is capable of being absorbed by a neighbouring atom (resonance radiation effect) resulting in a displacement of an electron to the $2p_1$ ring. Hence, in an electron-tube there may be a building-up of the number of electrons in the $2p_1$ ring, and if all radiation emitted were absorbed, every atom might have electrons in this ring. Thus further collision with 1·45-volt electrons would result in an ejection of an electron to an extreme outer ring. A collision with a 2·4-volt electron would ionize the atom. Van der Bijl* has suggested as an explanation of low-voltage arcs operated below the ionization potential, a theory of successive impact. The atom collides with an electron, causing a displacement of a bound electron to the $2p_1$ ring. Before it is able to return to the 1·5s ring it collides again with a second electron, and the atom is ionized. The probability of a second collision under such conditions is, however, very small. The above suggestion of the absorption of radiation which was first proposed by Compton† is a much more plausible explanation of arcs below the ionization potential. In fact, one must consider how ionization could take place otherwise than from the $2p_1$ ring. It must be accordingly necessary that only a small proportion of the radiation emitted when electrons fall from the $2p_1$ to 1·5s ring is absorbed by the vapour. This is a reasonable

* Physical Review, x. p. 546 (1917).
† K. Compton, Chicago Meeting Am. Phys. Soc. 1919, Phys. Rev.

assumption, for a large amount of radiation escapes from the tube. Thus with sodium at 2·2 volts the D-lines are visibly intense, and with cæsium at 1·5 volts the infra-red lines λ8943 and 8521 may be readily photographed with properly sensitized plates. The ionization of a vapour below its ionization potential is observed when the vapour and electron densities are high. This fact substantiates the present hypothesis, for more collisions occur, more radiation is emitted, and more is absorbed when the electron current and the vapour pressure are increased. Thus, as pointed out by Compton, in the operation of the mercury arc at 5 volts and high-current density, electrons are maintained in the $2p_2$ ring, partly by electronic impact, but mainly by absorption of radiation of the frequency $1·5s - 2p_2$, and a 5-volt impact is sufficient to ionize from the $2p_2$ ring.

An extension of this hypothesis leads to interesting conclusions in the case of absorption of radiation. The lines of the principal series of the alkali metals are all absorption-lines, the energy absorbed increasing the total energy of the atom by a displacement of the electron from the $1·5s$ ring to some p ring. If, however, the vapour is excited by electronic impact (or radiation) corresponding to $Ve = h\nu$, where $\nu = 1·5s - 2p$, electrons normally in the $1·5s$ ring are driven to the $2p$ ring, and are no longer capable of absorbing $1·5s - mp$, but rather series lines which converge at $2p$. Hence, if the excitation is sufficient (*i.e.*, electron current very dense), the principal series should show less absorption, and the 1st and 2nd subordinate series should tend to become the prominent absorption-lines.

It appears from the above that the general impression of the existence of a single-line spectrum at a certain low voltage, and an abrupt transition to the many-line spectrum as the voltage is increased to the ionization potential is scarcely justified *a priori* on any theoretical basis. If a mechanical theory is accepted, it is quite conceivable, in spite of Stokes' law, that the lines of higher frequency may be excited by resonance when a fundamental line is produced. We have analogies to this effect in the relation between transverse and longitudinal vibrations of a rod, or in the "tripling" of the frequency of alternating current, etc. Thus, instead of a single line, a single series might appear— the fundamental frequency and its harmonics: a view held by certain spectroscopists.

On the basis of the Bohr theory various groups of lines may appear as the excitation is increased. There is no experimental evidence on this question. In all previous

work on single-line spectra the observations would not have shown the presence of other lines had they existed. Thus the observed single-line spectrum of mercury is $\lambda 2537$, but the second line of the series $\lambda 1436$ might be present, and, lying in the extreme ultra-violet, it could not have been detected by the methods employed *.

II. Experimental.

The present work was undertaken with the object of obtaining information as to the existence of single-line spectra, single-series spectra, and group spectra. Cæsium appeared to be a desirable material, since all of its spectral lines, except certain combination lines in the far infra-red, may be photographed by properly sensitized plates. The apparatus is shown in fig. 2. The ionization chamber consisted of a pyrex glass tube having an optically ground pyrex plate fused to one end, through which the arc was viewed. The anode was a nickel cylinder, and the cathode a lime-coated platinum cylinder about 5 mm. in diameter, heated by a small heating-coil inside. The cathode was thus made an equipotential surface, and because of its large area the current was high (150 milliamperes at six volts), even though the temperature was maintained at 500° C. It is quite desirable to operate the cathode considerably below a red heat, as otherwise, on long exposure, stray reflexion of the emitted light and heat may obscure the cæsium lines in the range $\lambda 6500$ to $\lambda 9000$. All lead-wire seals were tungsten in Corning G 702 P glass. The ionization tube was evacuated and maintained at about 0·0001 mm. of mercury gas pressure, and heated to 200° C., thus giving a considerable vapour-pressure. The radiation emitted near the anode where the electrons had gained their maximum velocity was photographed.

Fig. 2.

Cathode

Ionization tube.

* *Cf.* McLennan, Proc. Roy. Soc. Lond. xcii. p. 305 (1916); xci. p. 485 (1915).

The spectrum photographs were made on Seed 23 plates stained with dicyanin. A few of the plates were sensitized with Hoechst dicyanin, but most of them were prepared with dicyanin made by the Bureau of Chemistry, Department of Agriculture, since these American dyes appear to be equal or superior to the German ones in photo-sensitizing action. The process of staining has been described several times, and it has been used almost continuously in spectroscopic investigations at the Bureau of Standards for the past four years. This experience in staining has made it possible to reproduce sensitized plates which are remarkably similar, so that very nearly the same spectral sensitivity is shown by different plates. This uniformity is of importance in the comparison of spectroscopic data obtained from different plates.

The spectrograph was made by Carl Zeiss, and has a large flint prism of 10 cm. base length and 60° angle. The collimator and camera lenses have 5 cm. aperture and 26 cm. focal length. On account of the very low intensity of the low-voltage arc a spectograph with the highest attainable light efficiency is advantageous. About thirty lines with wave-lengths from 4555 A to 8943 A were recorded with an exposure of one minute to the 6-volt cæsium arc. An exposure of 5 minutes showed additional lines and extended the spectrum from 3878 A to 9208 A. The exposures were much longer when the arc was operated at 3 volts or less. Most of these averaged about 15 hours, although in some cases exposures of 40 to 60 hours were employed.

The length of the spectrum on the photographic plate was about 40 mm. between 3878 A and 9208 A, and the dispersion in this range was sufficient to separate all of the important doublets in the various spectral series, even when a relatively large slit width (0·2 mm.) was used.

Plate I. shows a photograph of several typical exposures at different voltages. Lower voltage exposures were made, but were not suitable for reproduction although the original negatives were measurable. It appears from visual observation that the first doublet of the principal series alone appears below the applied potential of 2·4 volts; but this fact, as has been heretofore, with other elements, assumed conclusive, should not be accepted as proof of the existence of a single-line spectrum. If the plates possessed a constant sensitivity to light of various wave-lengths, the line λ 8521 could be made to appear alone on very short exposure even in a high-voltage arc, because in absolute energy it is the most intense line of the spectrum. The sensitivity of the plate, however, varies with the wave-length, as shown by

fig. 3, so that on short exposure the line λ 6973 may appear alone. With ordinary blue sensitive plates the line λ 4555

Fig. 3.
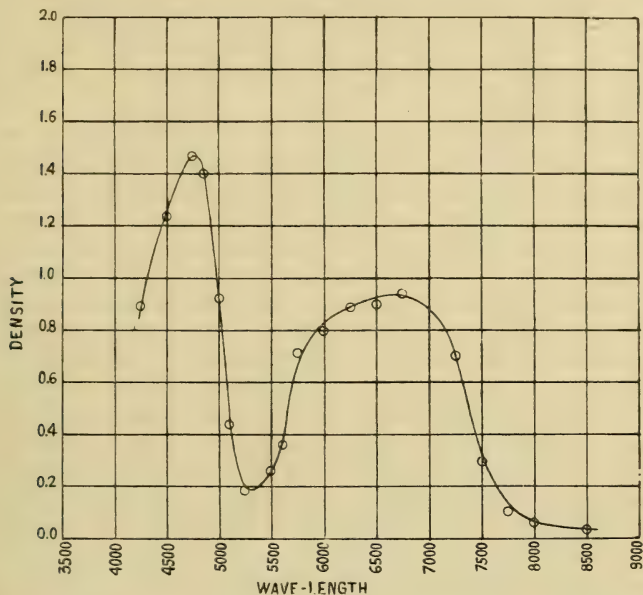
Sensitivity of dicyanin plates to equal energy spectrum.

is the most strongly reproduced. It is, however, possible to draw some conclusions by visually comparing various negatives. Thus, if the density of λ 8521 with a high-voltage arc is the same as that with a low-voltage arc, and in the latter case no other lines appear while in the former case the entire spectrum is shown, an argument is obtained for the single-line spectrum. However, it is desirable to eliminate the plate sensitivity from the data and reduce all measurements to the same scale of intensity of the lines in the arc. To do this the densities of all the lines photographed were carefully measured by a disappearing filament micro-photometer*. This instrument is essentially the micro-pyrometer described by Burgess†, except that a microscope of higher power is employed. The photographic plate was mounted immediately below the objective of the microscope on a horizontal bed movable with a graduated screw, and was illuminated

* This simple and effective instrument is described by the writers in a separate paper.
† Burgess, Bureau Standards Scientific Paper 198.

beneath by an intense beam of light from a tungsten-ribbon lamp. Light transmitted by the portion of the plate, the image of which was adjacent to that of the photometer-lamp filament, was matched against the filament brightness by adjusting the current through the lamp. The current readings are readily translated into measurements of photographic density, correcting, of course, for the " fog " of the gelatine films.

Several series of exposures from 2 to 200 seconds were made at different times on the 6-volt cæsium arc, and density measurements of the spectral lines showed that the dicyanin-stained plates have approximately the same development factor (gamma = 1·45) for all wave-lengths from 4555 A to 8521 A. To calibrate the plates in terms of absolute intensity of the source, series of exposures of different durations were made by sighting on a black body, the temperature of which was measured by an optical pyrometer. The D-lines of sodium were superposed on each spectrum as fiducial marks. The densities of the plates for various wave-lengths were measured with the micro-photometer, and from the " characteristic curves " of the plates and the computed distribution of energy in the spectrum of the black body, the photographic density as a function of wave-length was corrected for an equal energy distribution in the spectrum, a typical curve thus obtained being illustrated by fig. 3. With the general characteristics of dicyanin-stained plates thus determined, the relative absolute intensities of lines in the cæsium-arc spectra were obtained from their measured photographic densities and the durations of exposure. Since relatively long exposures were required to photograph the spectra of the low-intensity arcs, the reciprocity law of the photographic plate (density = function of intensity × time) was corrected* by giving the exposure time an exponent of 0·8.

III. Results.

Fig. 4 shows the logarithms of the actual intensities of various lines emitted in the cæsium arc plotted against applied accelerating potential. At slightly below 3 volts the entire line spectrum appears, only a few of the lines of which are shown in the figure. It is noted that the intensity of the lines λ8521 and λ8943 persists at voltages below which the intensity of all other lines vanishes. This is more clearly illustrated by the following table of ratio of intensity

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* Schwarzschild, *Photographische Correspondenz* 1899, p. 109.

of λ8521 to that of the prominent lines λ6973 and λ4555 for various voltages :—

Applied Voltage	J ÷ J 8521 6973	J ÷ J 8521 4555
6	105	350
5	(130)	(400)
4	(200)	(600)
3	560	2100
2·8	1100	8300
2·6	620	3400
2·4	3600	10500
2·2	>10000	>10000
1·8...	$\doteq \infty$	$\doteq \infty$
1·5	$\doteq \infty$	$\doteq \infty$

Fig. 4.
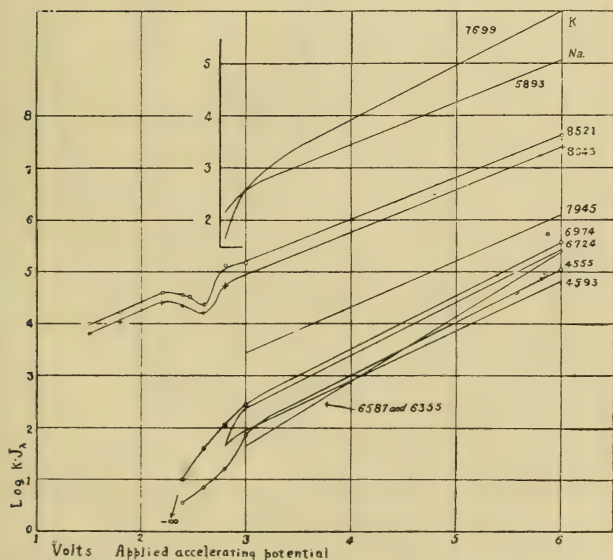
Logarithm of intensity of various cæsium lines as a function of the applied exciting voltage.

Thus, below 2·4 volts the intensity of λ8521 is thousands of times greater than λ6973, while above the ionization potential the ratio is approximately 100. The fact that the ratio of intensity of λ8521 (and λ8943) to that of any other line

rapidly approaches ∞ as the voltage is decreased, conclusively proves the existence of a single-line spectrum, in this case the doublet $1.5s - 2p_{\frac{1}{2}}$.

The results are somewhat complicated by the fact that most of the electrons have a velocity greater than that corresponding to the applied potential. The fact that all of the series lines begin to appear at the applied potential of about 2·5 volts, indicates the presence of ionization which should normally occur at 3·9 volts. This is again shown by fig. 5,

Fig. 5.

Current reaching anode as a function of the applied accelerating voltage.

which represents the current reaching the anode as a function of the applied accelerating potential. A marked break point, indicating ionization, occurs at 2·9 volts. This ionization might be explained on the assumption of ejection of electrons from the $2p$ rings, which requires but 2·4 volts velocity, but such is not the case. If a 3-electrode tube is employed, it

can be shown that most of the electrons possess an initial velocity of about 1 volt. Thus Foote, Rognley, and Mohler *, using a 3-electrode tube, found the initial potential to be 1·3 volts in rubidium, and 1·0 volts in cæsium, and Tate and Foote† observed similarly high initial potentials in sodium and potassium. These high-velocity electrons are not produced photo-electrically, because they appear at accelerating voltages below which any radiation is excited. Thus in cæsium the first resonance collision occurs at about 0·5 volt applied potential and the second at about 2·0 volts, instead of 1·5 volts and 3·0 volts. Neither can they be accounted for by velocity distribution due to temperature of the cathode. Thus the fractional number F of emitted electrons having a velocity greater by V_0 volts than the applied potential V, on the basis of the Maxwell distribution of velocities,

is $F = erf \chi + \dfrac{2}{\sqrt{\pi}} \times e^{-\chi^2}$, where $\chi^2 = 11600 V_0 / T$ and T = absolute temperature of the cathode. In the present case but 3 electrons per thousand could have a velocity 0·5 volt greater than the applied voltage and but 5 per 10,000,000 a velocity 1·0 volt greater. The intensities of the lines are thousands of times too great at the applied potential 2·9 volts to be explained by the presence of 5 electrons per 10,000,000 with velocities sufficient to ionize. The high-speed electrons are, however, present. Possibly their initial velocities are due to contact potentials occasioned by the presence of an alkali metal. Accordingly the curves of fig. 4 should be corrected by adding to each abscissa the initial potential 1·0 volt determined from the total current curve shown in fig. 5.

It is noted that the intensity of $\lambda 8521$ and $\lambda 8943$ begins to decrease at 3·3 volts true potential, reaching a minimum at 3·6 volts. This would follow directly from Bohr's theory. Thus, when the true accelerating voltage exceeds 1·45 volts the lines $1·5s - 2p_{\frac{1}{2}}$ are excited by electronic impact, and these lines continue to be produced until the ionization potential is reached. Above this latter voltage, however, electrons which at a slightly lower velocity would have given rise to $1·5s - 2p_{\frac{1}{2}}$ now produce ionization and the complete series spectrum. Any line of the principal series, for which $m > 2$, is excited at a sacrifice in intensity of $\lambda 8521$ and $\lambda 8943$, since each line of this series requires that electrons fall from the mp ring into the $1·5s$ ring. The subordinate

* *Loc. cit.*
† Phil. Mag. xxxvi. p. 64 (1918).

series lines, however, converge at $2p$, and hence do not affect the intensity of $1 \cdot 5s - 2p$, which may still be excited at the same collision.

In fig. 6 we have plotted the logarithm of the intensity for $\lambda 8521$, $\lambda 6973$, and $\lambda 4555$ per unit number of electrons reaching the outer cylinder as the accelerating voltage is

Fig. 6.
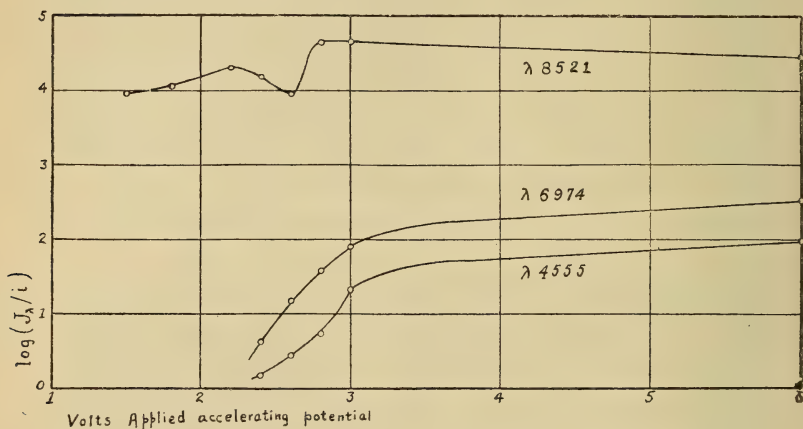
Logarithm of intensity per unit number of electrons reaching anode as a function of the applied accelerating voltage.

increased. At higher voltages this ratio becomes a constant for each line in agreement with the work of Jolly *, who observed that in discharge through hydrogen " the radiation is proportional to the current density both for the whole spectrum and for any portion of it." This follows (approximately) directly from the quantum theory. Above a certain minimum voltage the number of electronic atomic collisions, and hence the number of quanta of any particular frequency produced, is proportional to the number of electrons present. The existence of $1 \cdot 5s - 2p_{\frac{1}{2}}$ when the intensity of all other lines has dropped to zero is well illustrated in this plot. The above law is not rigorously applicable in the present case, since some of the electrons reaching the anode have been produced by ionization, and, in general, would not be able to accumulate sufficient velocity to cause radiation upon further collision.

An interesting phenomenon was observed in the operation of the cæsium arc at 120 volts. It was found that, after once

* Phil. Mag. xxvi. p. 801 (1913).

being started, the arc operated with either electrode as cathode, and that no rectification of alternating current was observable. This phenomenon is well known in certain types of mercury arc. With the outer cylinder as a cathode a quiet dazzling-glow discharge is obtained, while with the small hot cathode the arc forms streams of brilliant discharge which flicker back and forth along the tube.

A much discussed question as to the ratio of intensities of the components of a doublet when the exciting voltage is varied may be answered by referring to fig. 4. In absolute measure the ratio of intensities $\lambda 8521/\lambda 8943$ is constant and equal to 1·5 within the errors of observation. This value was further confirmed by observations on a 120-volt arc.

Although the cæsium employed was made from cæsium chloride of supposedly high purity, it contained traces of both sodium and potassium. All exposures above 2·2 volts applied potential show the presence of the first doublet of the principal series $1\cdot5s - 2p_{\frac{1}{2}}$ of both these metals, the ionization potentials of which are 5·1 volts and 4·3 volts respectively. Accordingly, in the light of the more extensive work described with cæsium, we may conclude that the doublets $1\cdot5s - 2p_{\frac{1}{2}}$ are the single-line spectra of sodium and potassium.

IV. Summary.

Theoretical.

On the basis of several possible theories of atomic structure, it is shown that the *normal* operation of an arc below ionization might result in the excitation of a single-line spectrum, a single-series spectrum, or a group spectrum consisting of certain lines of different series. This latter conclusion follows from an extension of Bohr's theory. Thus, if inelastic electronic-atomic impact occurred resulting in the ejection of an electron to the pth ring, the electron in returning to the nth ring or equilibrium may produce any combination of lines represented by inter-orbit transitions within this range, the single-line spectrum being a special case where $p = n + 1$.

A simple explanation is offered of fluorescence phenomena in vapours of the alkali metals.

A mechanism of absorption of radiation is described, and the theory proposed by K. Compton, that the ionization of an atom below the ionization potential may be explained by absorption of radiation arising in other atoms from electronic-atomic impact of insufficient energy to ionize, is further

discussed. This hypothesis suggests that vapours of the alkali metals may be so stimulated that the 1st and 2nd subordinate series lines, instead of the principal series, tend to become absorption-lines.

Experimental.

The cæsium spectrum was photographed for various accelerating voltages, from $\lambda 3878$ to $\lambda 9208$, by use of dicyanin-stained plates. The sensitivity of the plates was investigated by density measurements of the spectrum of a black body having a known energy distribution. The general characteristics of the plates were determined and all lines of the cæsium spectrum were reduced to an absolute scale of intensity by means of density measurements made with a micro-photometer and consideration of the plate sensitivity. No evidence of group or single-series spectra could be obtained. Thus the ratio of intensities of the first and second lines of the principal series, both of which should appear in a single-series spectrum or above 2·7 volts in a group spectrum, rapidly approaches infinity as the accelerating potential in the arc is decreased. This ratio is 350 in a 7-volt arc, 2100 at 4 volts, 10,500 at 3·4 volts, and as near infinity as can be measured at 2·8 volts. Similarly, the intensity ratio of either $1\cdot5s - 2p_1$ or $1\cdot5s - 2p_2$ to any other line approaches infinity at low voltage, proving for the first time the existence of a single-line spectrum rather than a single-series or group spectrum—in the case of cæsium the doublet $\lambda 8521$ and $\lambda 8943$.

The doublet $1\cdot5s - 2p_{\frac{3}{2}}$ is alone produced under excitation of 1·5 to 3·9 volts accelerating field. The intensity of both of these lines gradually increases approximately proportional to the total number of electrons reaching the anode until the ionization potential is reached. At this point a pronounced decrease in intensity of these two lines occurs, amounting to the factor one-third.

This decrease takes place at the voltage at which the complete line spectrum is produced, and is readily explainable on the basis of Bohr's theory—in fact, it affords a strong argument for this theory. Thus the lines $1\cdot5s - 2p_{\frac{1}{2}}$ are the result of inelastic collision with electrons having velocities between 1·45 and 3·9 volts, but as the latter voltage is exceeded, electrons, which at a slightly lower velocity would have given rise to $1\cdot5s - 2p_{\frac{1}{2}}$, now produce the complete-series spectrum;

and any line of the series $1 \cdot 5s - mp_{\frac{3}{2}}$, where $m > 2$, is necessarily excited at the sacrifice of $1 \cdot 5s - 2p_{\frac{3}{2}}$.

Above a certain voltage the intensity of any line per unit number of electrons reaching the anode attains a saturation value, in agreement with the quantum hypothesis, which requires that the number of quanta radiated be proportional to the number of collisions, and hence (approximately) to the number of electrons present.

Curves are given showing the relative intensities of the prominent cæsium lines at various voltages. The ratio of intensities of the components of the first doublet of the principal series $\lambda\, 8521 / \lambda\, 8943$ is constant and equal to $1 \cdot 5$ from $1 \cdot 5$ volts to 120 volts.

The cæsium arc of the type employed does not rectify alternating current of 120 volts.

Sodium and potassium occurring as an impurity of the cæsium similarly exhibited the single-line or doublet spectrum $1 \cdot 5s - 2p_{\frac{3}{2}}$ below their respective ionization potentials.

Only two types of inelastic impact between electrons and atoms of the alkali-metal vapours occur, at potentials known as the resonance and ionization potentials and given by the quantum relation $h\nu = eV$, where $\nu = 1 \cdot 5s - 2p_1$ and $\nu = 1 \cdot 5s$.

Bureau of Standards,
        Washington, D.C.,
    January 14, 1920.

VIII. *Stationary Waves in Water. By* A. R. RICHARDSON, *Imperial College of Science and Technology* *.

ALTHOUGH the subject is of very great practical importance, and has received much attention at the hands of engineers and experimentalists, very few exact solutions have been obtained of problems involving the flow of a liquid under gravity.

In this paper some exact solutions are obtained, and existing results are linked together through a differential equation which forms the subject of the first part. Amongst the problems discussed is that of the flow over a weir, and an approximate calculation is made of the constants which appear in the Francis formula.

Part I.

I. *Stream-line flow, under gravity, with a free surface.*

Adopt the usual notation :

$z = x + iy$, y being measured vertically upwards,
$w = \phi + i\psi$,
q, θ refer to the fluid velocity.

Consider the equation

$$-\frac{dz}{dw} = \frac{1}{\mu\{G(w)\}^{\frac{1}{3}}}\left[\{1 - G'^2(w)\}^{\frac{1}{2}} + iG'(w)\right] = \frac{1}{q}e^{i\theta}. \quad (1)$$

If along part of any stream-line, say $\psi = \psi_0$, $G(w)^{\frac{1}{3}}$, $G'(w)$, $\{1 - G'^2(w)\}^{\frac{1}{2}}$ are real, and finite, over that part

$$y = -\frac{3}{2\mu}\left\{C + \{G(w)\}^{\frac{2}{3}}\right\}, \quad \cdots \quad (2)$$

$$q^2 = \mu^2\{G(w)\}^{\frac{2}{3}}$$

$$= \mu^2\left[-C - \frac{2\mu y}{3}\right],$$

i. e. $\quad q^2 + 2gy = -\mu^2 C \quad \cdots \quad \cdots \quad (3)$

if $\quad\quad \mu^3 = 3g. \quad \cdots \quad \cdots \quad (4)$

Hence there will be a free surface, and (1) will give the solution of the problem provided $G(w)$ is chosen so as to satisfy the conditions over the rigid boundary. The presence of the term $\{G(w)\}^{\frac{1}{3}}$ makes this choice difficult, and in addition to singularities of $\frac{dz}{dw}$ which arise where a rigid boundary bends, or meets a free surface, others may occur at places such as the crest of a wave of maximum elevation.

If $w = 0$ is such a place, near $w = 0$

$$G(w) = \frac{w}{2}\left(1 + a_1 w + \cdots\right),$$

for $\quad -\dfrac{dz}{d\phi} = \dfrac{1}{\left(\dfrac{\phi}{2} + \cdots\right)^{\frac{1}{3}}}\left(\dfrac{\sqrt{3}}{2} + \dfrac{i}{2}\right)$ approximately,

i.e., if $\phi > 0 \quad \theta = \pi/6$

$\quad\quad \phi < 0 \quad \theta = -\pi/6$, and at the crest $q = 0$.

(a) It is not without interest to notice that $G(w) = \dfrac{w}{2}$ gives a complete free surface with straight boundaries inclined at $\pm 30^\circ$ to the horizontal.

(b) $G(w) = w^{\frac{3}{2}}$ gives flow in a deep tank having an inlet and outlet pipe in the bottom as in fig. 1.

Fig. 1.

Outlet   *Inlet*
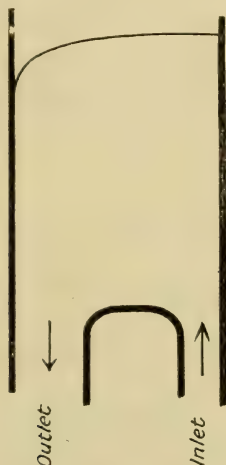
(c) Michell's examples in his paper on the Highest Wave (Phil. Mag. 1893, xxxvi. p. 437) are given by

$$G(w) = A(-i \sin w\, e^{iw})\{1 + c_1 e^{2iw} + c_2 e^{4iw} + \ldots\}^3.$$

There is, however, no simplification in the calculation of the constants by the use of (1).

It appears that the method used by Michell is the most direct when the form of the stream-bed is given.

Equation (1) is useful when the shape of the free surface is known approximately, and it is desired to obtain the general characteristics of the motion.

(d) *Flow in a stream with a finite drop.*

Consider $G(w) = B - \tanh \alpha w \quad B > 1, \ \alpha < 1.$

$$-\frac{dz}{dw} = \frac{1}{\mu\{B - \tanh \alpha w\}^{\frac{1}{3}}} \left[\{1 - \alpha^2 \operatorname{sech}^4 \alpha w\}^{\frac{1}{2}} - i\alpha \operatorname{sech}^2 \alpha w \right].$$

The singularities of $\dfrac{dz}{dw}$ are given by

$$B = \tanh \alpha w, \quad \text{and} \quad \cosh^2 \alpha w = \pm \alpha.$$

These limit the depth of the stream, and different cases arise according to the relative magnitude of the roots.

The stream-line $\psi = 0$ is a free surface over which

$$y = -\frac{3}{2\mu} \left\{ B - \tanh \alpha w \right\}^{\frac{2}{3}}.$$

Fig. 2 has been drawn for the special case $B=2$, $\alpha = \frac{1}{2}$, with $\mu = 1$, i. e $g = \frac{1}{3}$.

The extreme cases are given by $\alpha = 1$, when the free surface will be vertical at $\phi = 0$ and will tend to curl over

Fig. 2.
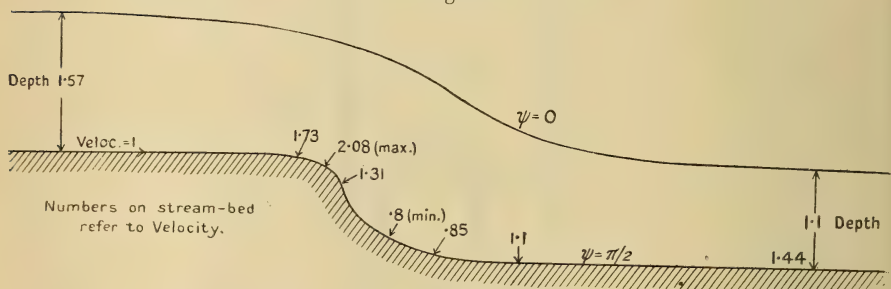
and break ; and $B = 1$ when the fluid is at rest at $\phi = \infty$ on the free surface. If $B < 1$ a rigid boundary is necessary over part of the stream-line $\psi = 0$ if this particular form of free surface is possible.

Referring to fig. 2, it is interesting to note how the velocity changes over the stream-bed, and how quickly a nearly uniform regime is established down stream *. The tendency for a more or less quiet pool to form at the bottom of the drop is apparent, as is also the tendency to erosion at the upper edge of the fall, and a short distance up-stream.

Evidently a form of $G(w)$ containing several factors of this type would give rise to cases of flow over more irregular shaped stream-beds.

(e) *Flow over a corrugated stream-bed.*

This problem has been solved approximately by Lord Kelvin ('Mathematical and Physical Papers,' vol. iv.) on the assumption that the irregularities are small compared with the depth of the stream.

* Searle's assumption is justified. Phil. Mag. May 1912.

Equation (1) with $G(w) = B - \cos \alpha w$ gives the exact solution of a case of flow illustrated in fig. 3, drawn for the values $B = 2$, $\alpha = \cdot 9$.

Fig. 3.

Numbers refer to Velocity.
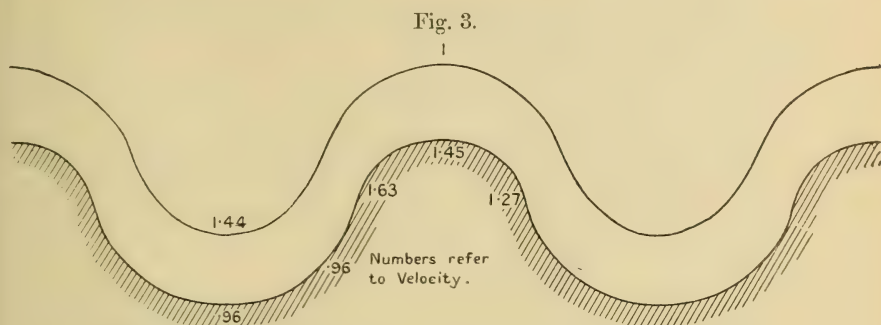
The singularities of $\dfrac{dz}{dw}$ are given by

$$B = \cos \alpha w, \quad \sin \alpha w = \pm \frac{1}{\alpha}.$$

$$-\frac{dz}{dw} = \frac{1}{\mu \{B - \cos \alpha w\}^{\frac{1}{3}}} \left[\{1 - \alpha^2 \sin^2 \alpha w\}^{\frac{1}{2}} + i\alpha \sin \alpha w \right] = \frac{1}{q} e^{i\theta},$$

if $\alpha < 1$ and $B > 1$ $\psi = 0$ gives a free surface. Now on the surface θ depends only on α, and not on B, so that an alteration in B will not alter the concavity or convexity of the free surface.
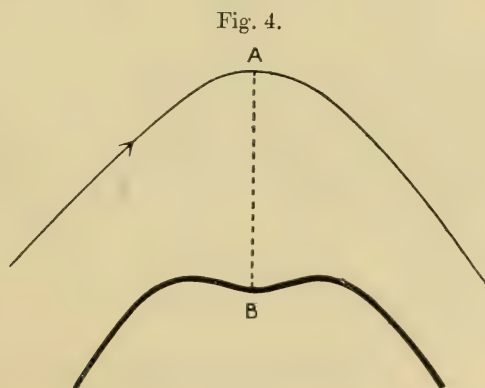
Fig. 4.

The shape of the stream-bed, however, alters as indicated in fig. 4, an elevation of the surface taking place over a depression of the stream-bed.

In such cases the velocity of the stream from surface to bed is not monotonic, but rises to a maximum at some point below the surface.

The following table has been calculated for the values $\alpha = \cdot 9$, $B = 1 \cdot 11$, $\phi = 0$, and represents the distribution of velocity across AB in fig. 4.

$\cdot 9 \psi$	0	$\cdot 05$	$\cdot 1$	$\cdot 15$	$\cdot 2$	$\cdot 25$	$\cdot 3$	$\cdot 35$	$\cdot 4$	$\cdot 45$
q	$\cdot 479$	$\cdot 499$	$\cdot 516$	$\cdot 529$	$\cdot 536$	$\cdot 536$	$\cdot 527$	$\cdot 499$	$\cdot 440$	$\cdot 288$

II. *Flow over a Weir.*

Take the origin at O, the sharp edge of the weir (fig. 5).

Fig. 5.
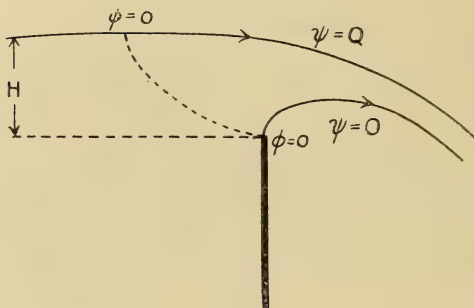
Let $\psi = 0$ be the stream-line from the edge,

$\quad \psi = Q$ be the upper stream-line ; Q being the quantity of fluid flowing over the notch in unit time.

Let v be the speed of the liquid at a place on the upper stream surface where $y = H$.

Then over $\psi = Q$

$$q^2 + 2gy = v^2 + 2g\,H,$$

and using equation (1)

$$q^2 = \mu^2 \{ G(\phi + iQ) \}^{\frac{2}{3}},$$

$$\therefore \quad G(\phi + iQ) = \left[\frac{2g\left(\dfrac{v^2}{2g} + H - y \right)}{\mu^2} \right]^{\frac{3}{2}} . \quad . \quad . \quad (4)$$

Similarly on the lower free surface close to the edge O

$$q^2 = \mu^2 \{\overline{G(O)}\}^{\frac{2}{3}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore \qquad G(O) = \left(\frac{r^2 + 2gH}{\mu^2}\right)^{\frac{3}{2}}, \quad . \quad . \quad . \quad . \quad (6)$$

where $\overline{G}$ is the value of G which will give the lower stream surface.

Hence, if y be measured at the point on the upper surface where $\phi = 0$,

$$G(iQ) - \overline{G(O)} = \tfrac{2}{3}\sqrt{2g}\left[\left(\frac{r^2}{2g} + H - y\right)^{\frac{3}{2}} - \left(\frac{r^2}{2g} + H\right)^{\frac{3}{2}}\right],$$
$$. \quad . \quad . \quad (7)$$

i.e. $\quad G(iQ) - \overline{G(O)} = K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$

where K is the right-hand side of (7).

Evidently Q depends on the form of the function $G(w)$, *i. e.* on the complete rigid boundary conditions both up and down stream, and not merely on the state of affairs at the edge and surface.

As a first approximation, however, it may be assumed that the function $G(w)$ is dominated by the terms giving its development near the point $w = 0$ corresponding to the edge of the weir.

Consider now

$$-\frac{dL}{dw} = \left[\{1 - G'^2(w)\}^{\frac{1}{2}} + iG'(w)\right]. \quad . \quad . \quad (9)$$

Under the conditions postulated as to $G'(w)$, this gives a flow with a free surface along which $q = 1$ and over which $y = G(w) + C$.

Moreover, $G(iQ) - G(O)$ is the y-component distance between the points $\phi = 0$ on the stream-lines $\psi = 0$, $\psi = Q$ in the associated flow (9).

For example, take $G(w) = e^{w\pi/Q}$,

$$G(iQ) - G(O) = \frac{\pi + 2}{\pi}Q = \cdot611\,Q,$$

or if $G(O)$ be assumed $= \overline{G(O)}$, (8) gives

$$Q = 3\cdot27\left[\left(H + \frac{r^2}{2g}\right)^{\frac{3}{2}} - \left(H + \frac{r^2}{2g} - y_0\right)^{\frac{3}{2}}\right] \quad . \quad (10)$$

for flow over such a weir.

The Francis empirical formula for such cases shows 3·33 as the coefficient.

(a) *Extension to the case of depressed nappes.*

If the pressures over the upper and lower surfaces are different,

$$G_2(\phi_0 + iQ) - \overline{G_2(\phi_0)} = \left[\frac{2g}{\mu^2}\left(\frac{v^2}{2g} + H - y\right)\right]^{\frac{3}{2}}$$
$$- \left[\frac{2g}{\mu^2}\left(\frac{v^2}{2g} + H\right) - \frac{2p_0}{\rho\mu^2}\right]^{\frac{3}{2}}. \quad (11)$$

In most cases $G_2(w)$ is not the same as G, for the nearest singularity to ϕ_0 on the down-stream side occurs where the nappe ceases to be a free stream-line, and this will be different in the two cases.

However, so long as this place is not close to the edge O c will not be altered very much, and the effect of a partial vacuum behind the nappe will be to increase the flow.

Experimental results show that the flow is approximately given by $Q = cK$.

Hence, if c' refers to a different shaped weir face and the nappe springs clear in both cases, c'/c should be nearly independent of the head. This agrees with Bazin's experiments [*].

(b) *Case* $G(w) = B - e^w$ (*approximation to flow over a weir*).

$$-\frac{dz}{dw} = \frac{1}{\mu\{B - e^w\}^{\frac{1}{3}}}\left[\{1 - e^{2w}\}^{\frac{1}{2}} - ie^w\right]. \quad |$$

Take $B > 1$.

The singularities of $\dfrac{dz}{dw}$ in the finite part of the w-plane are

$$w = in\pi,$$
$$w = \log B + i2n\pi.$$

Confine attention to the strip in the w-plane for which $0 \leqq \psi \leqq \pi$. The singularities are then

on $\psi = 0$, $\phi = \log B$ and $\phi = 0$,

on $\psi = \pi$, $\phi = 0$.

* Bovey, 'Hydraulics,' p. 101.

Over $\psi = 0$.

Start with those determinations which at $w = -\infty$ give $(B - e^w)^{\frac{1}{3}}$, $(1 - e^{2w})^{\frac{1}{2}}$ real and positive.

$-\infty < \phi < 0$ gives a free surface over which y goes from

$$-\frac{3}{2\mu} B^{\frac{2}{3}} \text{ to } y = -\frac{3}{2\mu}\left(B - 1\right)^{\frac{2}{3}}$$

and θ from π to $-\pi/2$.

$0 < \phi < \log B$: a rigid boundary parallel to y-axis ;
$$\theta = -\pi/2.$$

$\log B < \phi < +\infty$: a rigid boundary over which $\theta = 7\pi/6$.

Over $\psi = \pi$.

$-\infty < \phi < 0$: a free surface over which

$$y = -\frac{3}{2\mu}\left(B + e^\phi\right)^{\frac{2}{3}} - \frac{\pi}{\mu \sqrt[3]{B}}.$$

$0 < \phi < +\infty$: a rigid boundary parallel to the y-axis ;
$$\theta = \pi/2.$$

Fig. 6.
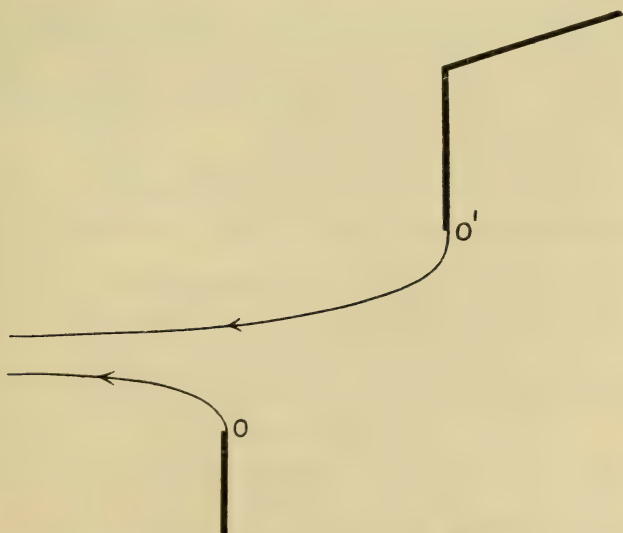
Fig. 6 shows that near O the solution approximates to that for a weir, near O' to that for a sluice.

Part II.

In this part a different form is given to equation (1). As in Part I., the solutions obtained are exact, and suffer from the same disadvantage, viz. that the rigid boundaries obtained are not straight.

I. *Discussion of the method.*

Evidently if both $F'(w)$ and $\{ \ \}^{\frac{1}{2}}$ are real over $\dot{\psi} = \psi_0$

$$\frac{dz}{dw} = \left\{ \frac{1}{c^2 + 2gh - 2g F(w) - P(w)} - F'^2(w) \right\}^{\frac{1}{2}} + i F'(w) = -\frac{1}{q} e^{i\theta} \quad (1)$$

will give flow, under gravity, with a free surface over which $y = y_0 + F(w)$, and pressure $P(w)$.

Exclude all the singularities of $\dfrac{dz}{dw}$ in the w-plane by small circles, and divide up the w-plane into strips so that these points lie on the boundaries of the strips. Then, so long as ψ is confined to a single strip, $\dfrac{dz}{dw}$ is uniform.

Different problems will be solved according to the particular strip or strips over which ψ is allowed to range.

For example, in the problem of the surface-wave due to a submerged body ψ would range over two adjacent strips[*]. The next example illustrates the sort of considerations which arise.

II. *Flow over a corrugated stream-bed.*

In (1) put $P(w) = 0$, $F(w) = \lambda \cos \mu w$, and $\beta^2 = c^2 + 2gh$.

$$\therefore \ \frac{dz}{dw} = \left\{ \frac{1}{\beta^2 - 2g\lambda \cos \mu w} - \lambda^2 \mu^2 \sin^2 \mu w \right\}^{\frac{1}{2}} - i \lambda \mu \sin \mu w.$$
$$. \ . \ . \ (2)$$

The singularities in the finite part of the w-plane are the roots of
$$\beta^2 - 2g\lambda \cos \mu w = 0 \quad . \quad . \quad . \quad . \quad (3)$$

and $\quad\quad 1 = \lambda^2 \mu^2 (1 - X^2)(\beta^2 - 2g\lambda X), \quad . \quad . \quad (4)$

where $X = \cos \mu w$.

There will be no real roots of (3) if $\beta^2 > 2g\lambda$.

---

[*] I have not succeeded in constructing a case of this kind.—A. R. R.

Suppose this is the case.

Put $\rho^2 = \dfrac{1}{\lambda^2 \mu^2}$: the roots of (4) are given by

$$(X^2 - 1)(2g\lambda X - \beta^2) - \rho^2 = 0.$$

There will always be one real root, say α_2, $> \dfrac{\beta^2}{2g\lambda}$. If there are three real roots the other two will lie between ± 1.

Now $\cos \mu w = \alpha_2$ gives $\mu w = 2n\pi \pm i \cosh^{-1} \alpha_2$,

$$\cos \mu w = \frac{\beta^2}{2g\lambda} = \alpha_1 \ \text{gives} \ \mu w = 2n\pi \pm i \cosh^{-1} \alpha_1,$$

and $\alpha_1 < \alpha_2$, *i. e.* $\cosh^{-1} \alpha_1 < \cosh^{-1} \alpha_2$.

Case (a). *Two imaginary roots* $\xi \pm i\eta$.

Let $\cos \mu(\phi_0 + i\psi_0) = \xi + i\eta$.

Hence the singularities all lie on the lines

$$\psi = \pm \cosh^{-1} \alpha_1, \ \pm \cosh^{-1} \alpha_2, \ \pm \psi_0,$$

and different problems will be solved according to the range of values taken for ψ and the relative magnitudes of ψ_0 and α_1.

Let $\psi_0 < \cosh^{-1} \alpha_1$ and take

$0 \leq \psi \leq \psi_0.$ $\psi = 0$ is a free surface over which $y = y_0 + \lambda \cos \mu\phi$. The stream-line $\psi = \psi_0$ is a rigid undulating boundary without sharp bends.

The extreme case arises when (4) has two equal roots ξ between ± 1.

In such a case the range $0 \leq \psi \leq \cosh^{-1} \alpha_1$ gives flow with a free surface $\psi = 0$, which is just on the point of breaking at places $\mu\phi = \pm \cos^{-1} \xi + 2n\pi$ where the tangent is vertical.

The stream-line $\psi = \cosh^{-1} \alpha_1$ is rigid, with periodic undulations, and sharp bends where $q = 0$, viz. at places $\mu\phi = 2n\pi$. The maximum elevation occurs over such places.

If $\cosh^{-1} \alpha_1 \leq \psi \leq \cosh^{-1} \alpha_2$ be taken the flow is between

two rigid corrugated boundaries,

and $\cosh^{-1} \alpha_2 \leq \psi \leq +\infty$: gives flow in a semi-infinite liquid with a corrugated surface.

Case (b).   *Two real roots between* ± 1.

$$\cos \mu w = \xi_2, \quad \cos \mu w = \xi_3, \quad \text{say},$$

i. e. $$\left. \begin{array}{l} \mu w = 2n\pi \pm \cos^{-1} \xi_2 \\ \mu w = 2n\pi \pm \cos^{-1} \xi_3 \end{array} \right\} \quad . \quad . \quad . \quad . \quad (5)$$

are the singularities additional to those in Case (a).

These lie on $\psi = 0$.

Hence, since $\sin \mu w$ changes sign on passage of μw through $n\pi$, over a range containing four consecutive values of (5), the stream-line must cut itself.

Two-dimensional irrotational motion is impossible, the explanation being that the wave-surface curls over when the tangent to it is vertical.

It is interesting to note that this occurs before the limiting height $\beta^2 = 2g\lambda$ is reached.

Hence the motion breaks up as soon as equation (4) has all its roots real.

To complete the discussion, suppose $\beta^2 < 2g\lambda$.

There are now zeros of $\beta^2 - 2g\lambda \cos \mu w$ on $\psi = 0$, viz. at

$$\mu w = 2n\pi \pm \cos^{-1} \alpha_1 \quad \text{where } \alpha_1 = \frac{\beta^2}{2g\lambda}.$$

In Case (a) these are the only singularities on $\psi = 0$, and passage through consecutive zeros will change the sign of $\dfrac{dx}{dw}$ and the surface will break as before.

A similar remark applies to Case (b) since $\alpha_3 < \alpha_4 < \alpha_1$, so that the above argument holds good.

It should be noticed that the limiting form when the bed of the stream is fixed in shape has not been discussed; the method is evidently unsuitable.

III. *Standing waves of Elevation.*

In view of the prominence given to the consideration of standing waves take in (1)

$$\mathrm{F}(w) = \frac{c^2}{g} (1 - a^2 \tanh^2 \mu a w) \quad \text{where } a^2 = 1 - \frac{gh}{c^2}, \quad (6)$$

$$\mathrm{F}'(w) = -\frac{2\mu c^2 a^3}{g} \frac{\sinh \mu a w}{\cosh^3 \mu a w}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and $$c^2 + 2gh - 2g\,\mathrm{F}(w) = c^2 (1 - 2a^2 \operatorname{sech}^2 \mu a w). \quad . \quad . \quad (8)$$

This will give a wave very closely resembling that of Lord Rayleigh (Lamb, 'Hydrodynamics,' art. 248).

The finite singularities of $\dfrac{dz}{dw}$ are given by

$$\cosh \mu a w = 0, \quad i.\,e. \ \ \mu a w = i(2n+1)\pi/2,$$

$$\cosh^2 \mu a w = 2a^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$X^4 = \rho^2(X-1)(X-2a^2), \quad . \quad . \quad . \quad . \quad (10)$$

where $X = \cosh^2 \mu a w,$

$$\rho^2 = \frac{4\mu^2 c^6 a^6}{g^2}.$$

Two main cases arise according as $2a^2 \gtrless 1$, $i.\,e.$ as $c^2 \gtrless 2gh$.

Case (a). $2a^2 < 1$, i. e. $c^2 < 2gh$.

The roots of (9) are

$$\mu a w = i(n\pi \pm \alpha_1) \quad \text{where } \cos \alpha_1 = a\sqrt{2}, \ 0 < \alpha_1 < \pi/2.$$

The roots of (10) are

one negative root $X = -\delta_5^2,$
one positive root between 0 and $2a^2$, say $\delta_2^2,$
and two imaginary roots $\xi \pm i\eta$.

The condition $2a^2 < 1$ prevents two other real roots > 1 occurring.

Hence the singularities are

$$\mu a w = i(2n+1)\pi/2 \pm \alpha_5 \quad \text{where } \sinh \alpha_5 = \delta_5,$$
$$\mu a w = i(n\pi \pm \alpha_2) \quad \text{where } \cos \alpha_2 = \delta_2, \ 0 \leqq \alpha_2 < \pi/2,$$
$$\mu a w = \alpha \pm i\beta.$$

No motion of this type is therefore possible in an unobstructed liquid of infinite depth.

There are no singularities on the real axis in the w-plane and the smallest zeros on the ϕ-axis are

$$\pm i\alpha_2, \ \pm i\alpha_1, \ \text{and on the stream-line } \psi = \beta \text{ at } \phi = \pm \alpha.$$

Different cases arise according as $\beta \gtrless \alpha_1$, and to the range of values taken for ψ.

The most interesting case is where $\beta < \alpha_1$, and $0 \leqq \psi \leqq \beta$.

Evidently $\psi = 0$ gives a free surface over which

$$y = \frac{c^2}{g} \left[1 - a^2 \tanh^2 \mu a \phi \right].$$

The stream-bed $\psi = \dfrac{\beta}{\mu a}$ has two singularities, viz. at $\phi = \pm \dfrac{\alpha}{\mu a}$, and a depression will occur under the highest part of the wave.

If $\alpha_1 < \beta$ a similar motion will ensue, but the stream-bed will have only one singularity and will be elevated under the highest point of the wave.

Case (b). If $2a^2 > 1$, i.e. $c^2 > 2gh$, the motion with a free surface of this form is impossible: the discussion follows the same lines as in the previous example.

IV. *Progressive waves in deep water.*

It is not without interest to obtain the expressions given by Stokes (Lamb, 'Hydrodynamics,' art. 230).

Interchange the variables w, z by writing $F(w) = H(z)$, (1) becomes

$$\frac{dw}{dz} = \{1 - 2iH'(z)\}^{\frac{1}{2}} \{c^2 + 2gh - 2g\,H(z)\}^{\frac{1}{3}}, \quad . \quad (11)$$

and will include cases of flow with a free surface.

There will be no singularities in the finite part of the w-plane if

$$1 - 2iH'(z) = \lambda \{c^2 + 2gh - 2g\,H(z)\},$$

i.e. if $\qquad H = C + B e^{-ig\lambda z}$,

i.e. if $\qquad \dfrac{dw}{dz} = \dfrac{1}{\sqrt{\lambda}}(1 - 2iH'(z))$,

i.e.
$$\left.\begin{array}{l} \phi = \sqrt{\dfrac{g}{k}}\,x + \beta e^{ky}\sin kx \\[2mm] \psi = \sqrt{\dfrac{g}{k}}\,y + \beta e^{ky}\cos kx \end{array}\right\} \quad . \quad . \quad (12)$$

where $g\lambda = k$.

V. *Conclusion.*

The above analysis shows that although the problem of the flow of liquid under gravity with a free surface, and given form of rigid boundary, is very difficult of solution, yet the main characteristics can be determined by noting the form of the free surface in such cases and using the methods of this paper.

IX. *On Radiation from a Cylindrical Wall.*
By A. C. Bartlett, *B.A.*[*]

ON page 359 and succeeding pages of the Phil. Mag.
of March 1920, in a paper under the above heading,
an expression is obtained for the amount of heat radiated
from the inner walls of a vertical cylinder on to a horizontal
coaxial disk.

The result is obtained from first principles by quadruple
integration over the surfaces of the disk and cylinder, and
the process is long and laborious. It is, however, possible to
deduce the result, by a method which is not only much simpler
but much more powerful.

It has been shown by Sumpner (Phys. Soc. 1892) that if
an element $d\mathrm{S}$ of the surface of a sphere is radiating according
to a cosine law, and ds is any other element of surface of the
sphere, then the radiated energy received by ds from $d\mathrm{S}$ is
independent of the position of ds on the sphere.

It can be shown that the amount of energy received by
ds is

$$\frac{\pi N a \mathrm{S} ds (\mathrm{T}_1{}^4 - \mathrm{T}_2{}^4)}{\mathrm{A}},$$

where N is the normal radiation from $d\mathrm{S}$; T_1 is the tempe-
rature of $d\mathrm{S}$ and T_2 of ds; A is the area of the sphere.

This result will obviously hold for finite portions of the
spherical surface; therefore, if S and s are two non-intersecting
curves lying on a sphere enclosing spherical areas S′ and s'
respectively, and maintained at constant temperatures T_1
and T_2 respectively, the energy received by s' from S′ is

$$\frac{\pi N \mathrm{S}' s'}{\mathrm{A}} (\mathrm{T}_1{}^4 - \mathrm{T}_2{}^4).$$

This result will still be true if the surfaces s' and S′ are
replaced by any two surfaces s'' and S″ provided that s'' and
S″ satisfy the following three conditions :—

(1) Their boundary curves s and S lie on a sphere.
(2) If V is any point in S″, then no portion of the surface
s'' visible from V lies outside the cone vertex V passing
through the curve s.
(3) If condition (2) is true when S and s and S″ and s''
are interchanged.

Provided these conditions are satisfied, the energy received by s'' from S'' will be

$$\frac{\pi N S' s'}{A}(T_1{}^4 - T_2{}^4).$$

From this result the problem can be readily solved. With the same figure as on page 360 and using the same notation, consider any point V on the disk. It is receiving radiation from a surface of temperature T_1 occupying the solid angle between the two cones having V as vertex and the circles M and K as bases. The disk therefore is receiving from the inner walls an amount of energy equal to that which it would receive from a circular disk K, less what it would receive from a circular disk M, both disks having the same temperature and emissivity as the walls of the cylinder.

Construct a sphere of which the circle K and the receiving disk O are small circles. The radius of this sphere is

$$\sqrt{b^2 + \frac{(a^2 - b^2 - x_1{}^2)^2}{4x_1{}^2}}.$$

By substitution of the spherical areas of the two disks in the formula, the result obtained after reduction is that the energy received by the disk O from a disk K is:

$$\frac{\pi\sigma}{2}\left[\sqrt{(x_1{}^2 + a^2 + b^2)^2 - 4a^2b^2} - (x_1{}^2 + a^2 + b^2)\right] \times (T_1{}^4 - T_2{}^4).$$

Similarly, the energy received by the disk O from a disk at M would be

$$\frac{\pi\sigma}{2}\left[\sqrt{(x_2{}^2 + a^2 + b^2)^2 - 4a^2b^2} - (x_2{}^2 + a^2 + b^2)\right](T_1{}^4 - T_2{}^4).$$

Therefore the energy received by the disk O from the walls of the cylinder is

$$\frac{\pi\sigma}{2}(T_1{}^4 - T_2{}^4)\left[\sqrt{(x_1{}^2 + a^2 + b^2)^2 - 4a^2b^2}\right.$$
$$\left. - \sqrt{(x_2{}^2 + a^2 + b^2)^2 - 4a^2b^2} - x_1{}^2 + x_2{}^2\right].$$

This is the result obtained on page 364.

In the same manner an expression can be obtained for the energy received by a circular disk from a surface bounded by any number of circles, provided that each of these circles is co-spherical with the disk and conditions (2) and (3) stated previously are satisfied.

This result can be generalized for the case where the radiating

surface is bounded by any curves and the receiving surface is bounded by a circle provided the same conditions are satisfied.

Any further attempt to generalize by allowing the bounding curves of the receiving surface to be non-planar reduces at once to the original theorem, since a non-planar curve cannot lie on more than one sphere.

Research Laboratories of the
General Electric Co., Ltd., London.

X. *On a Projective Theorem of Lippich's in Geometrical Optics.* (*With a Note on the Equations of the Projection of a Straight Line on a Plane.*) *By* ALICE EVERETT [*].

THE theorem referred to is the following :—If the corresponding incident and refracted portions of a ray, which is infinitely near to a chief ray lying in a principal section of a refracting surface, be projected upon either the tangential or sagittal sections of the chief ray, then the projections also correspond.

By near rays are meant rays which are nearly parallel and are incident at near points where the normals are nearly, parallel.

The tangential section is defined as that principal section of the surface, at the point of incidence of the chief ray, which contains the chief ray and normal ; it coincides with the plane of incidence. The sagittal plane is defined as a plane through the chief ray perpendicular to the plane of incidence. The sagittal sections for the incident and refracted chief rays are in general different, and not principal sections.

The theorem was proved by Lippich (1877) for the sphere only, in an essay on Refraction and Reflexion of Infinitely Thin Ray Systems by Spherical Surfaces (Vienna Academy, *Denkschriften*, Band 38, p. 176 (1878)). Culmann extends it to non-spherical surfaces in his chapter in von Rohr's ' Theorie der optischen Instrumente,' Band 1, pp. 183–185.

Its interest lies in the fact that it enables the path, after refraction at a non-spherical surface, of any oblique ray infinitely near to a ray in a principal section to be found by applying to its projections the ordinary method adopted for rays in an axial plane of a spherical refracting surface. We

have only to replace the radius of the sphere by the proper radius of curvature, find the refracted paths of the projections, and then the required refracted path of the oblique ray will be the ray of which these paths are the projections. The refracted ray is usually found in terms of its inclination

Fig. 1.
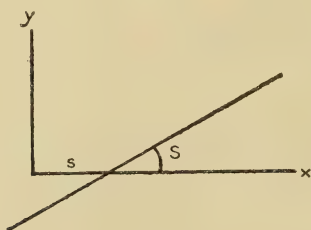
to the optic axis, and the "schnittweite" or distance from the last surface of the intersection of ray and axis. If these quantities be S, s for the sagittal projection, T, t for the tangential, and the planes of projection be taken as the xy and xz planes, then the required ray is given as the line of intersection of the planes

$$x - s = y \cot \mathrm{S}, \qquad x - t = z \cot \mathrm{T},$$

or as

$$x = \frac{y + s \tan \mathrm{S}}{\tan \mathrm{S}} = \frac{z + t \tan \mathrm{T}}{\tan \mathrm{T}}.$$

In general the theorem cannot be applied to tracing a ray through a series of surfaces, because the principal sections will vary from surface to surface. Culmann, however, applies it to a series of surfaces in two special cases :—
(I.) A series of non-spherical surfaces which are all normal to the chief ray, and have their principal sections coincident. (II.) Two infinitely thin non-spherical systems with principal sections not coincident. As an instance of (I.), Culmann mentions crossed cylinders. As another instance may be mentioned a coaxial series of tores having the centres of their generating circles all lying on a right circular cone with its axis on the axis of revolution (a tore being defined as the surface generated by a circle revolving about an axis in its plane). Thus in an axial section (fig. 2) the centres of the generating circles would lie on a pair of straight lines meeting on the axis, each line being a common normal to all

the tores. The cone may include a cylinder or plane as a
particular case. Suppose a telescope to sweep the horizon,

Fig. 2.
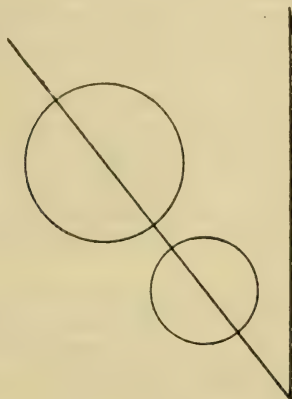
rotating about a vertical axis, then a vertical axial section of
its lens surfaces would trace a series of tores with the centres
of the generating circles in a plane, and a ray along the
optic axis of the telescope would be a common normal to
these tores.

Lippich's essay is based on the principle of collinear
correspondence. This simple geometric relationship is, of
course, far from being satisfied for rays making finite angles
with the axis, but he remarks :—" The following properties
(developed in the first place for a single refracting surface)
of an infinitely thin bundle of rays become very simple, and
approximate very closely to the properties of paraxial bundles,
when the axis of the incident, and consequently the axis of
the refracted, bundle lies in a plane through the optic axis."
He then proceeds to establish a series of theorems, of which
the first few are identical with Young's well-known properties
of the aplanatic spheres. Homocentric pencils are first dealt
with, and then theorem No. 12, the one here discussed, paves
the way for the treatment of non-homocentric pencils.

The proofs given by Lippich and Culmann involve the
assumption of certain properties of small pencils and Sturm's
focal lines. Owing to the elementary nature of the theorem,
the idea naturally suggests itself that it should be capable of
proof directly from first principles. Hence the following
attempt, in which no optical assumption is made except the

natural law of refraction   The question being really one of differential geometry, this method has been chosen as the most suitable to apply, though another very elementary proof by spherical projection is appended.

The analysis brings to light the following facts overlooked by Lippich. In the case of the tangential projection, the theorem has a wider application than he assigned to it, for here the variable ray need not be nearly parallel to the chief ray itself, but only to its plane of incidence. On the other hand, in the case of the sagittal projection, small quantities of the first order have to be neglected unless the angle of incidence is small, whereas in the tangential projection only small quantities of the second order need be neglected. Thus the theorem holds less accurately for the sagittal than the tangential projection.

When the chief ray is incident normally, the sagittal plane is a principal plane, and the two cases are interchangeable.

It seems improbable that a theorem of this nature should have been left undiscovered till Lippich's time. The writer, however, has so far been unable to find any mention of it by earlier investigators, and would be obliged for references.

Proof.

1. *Projection on the Tangential Section.*

Fig. 3.
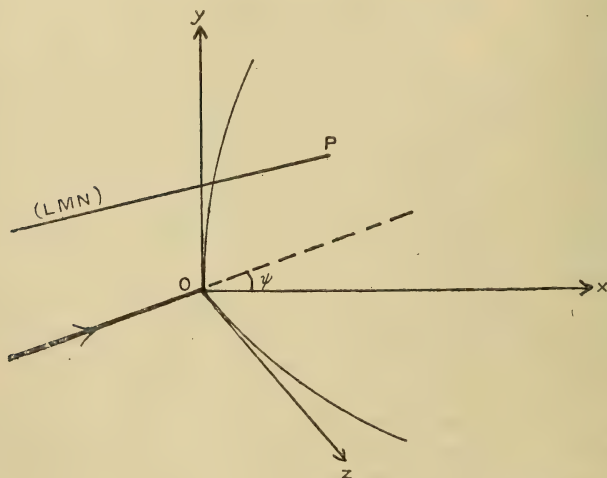
The condition that the plane of projection shall be a principal section is clearly necessary to ensure that the

normal to the surface shall remain in the plane of the section as the point of incidence moves along the curve of section. As will be seen later, the principal plane selected must be the one in which the chief ray lies. Suppose it to coincide with the plane of the paper, and take the principal sections as two co-ordinate planes.

Let O be the point of incidence of the chief ray, taken as origin,

P be the point of incidence of an infinitely near ray.

Take the axis of x along the normal at O,

the axis of y in the plane of the paper,

the axis of z perpendicular to the paper,

the co-ordinates of P as x', y', z'.

Then the equation of the refracting surface may be written

$$2x = by^2 + cz^2 + \text{higher terms in } y \text{ and } z,$$

b, c being the curvatures at O.

In the neighbourhood of the origin O we have

$$0 = -x + \frac{b}{2}y^2 + \frac{c}{2}z^2 \equiv \mathrm{F}(x, y, z), \text{ say,}$$

showing that x is a small quantity of the second order. In what follows small quantities of the second order are considered negligible, hence $x = 0$.

The direction cosines of the normal at a point x', y', z' near O are proportional to

$$\frac{d\mathrm{F}}{dx'} = -1, \quad \frac{d\mathrm{F}}{dy'} = by', \quad \frac{d\mathrm{F}}{dz'} = cz'.$$

Let the direction cosines of the chief ray at incidence be

$$[\cos\psi, \ \sin\psi, \ 0],$$

and the direction cosines of the incident ray at P be

$$[\mathrm{L}, \ \mathrm{M}, \ \mathrm{N}],$$

and use dashed letters to denote the same quantities after refraction.

The direction cosines of the normal at O are $[-1, \ 0, \ 0]$

and ,, ,, ,, ,, ,, P ,, $[-1, by', cz']$.

The general equations of refraction give, denoting the refractive indices by μ, μ',

$$\frac{\mu'\mathrm{L}' - \mu\mathrm{L}}{-1} = \frac{\mu'\mathrm{M}' - \mu\mathrm{M}}{by'} = \frac{\mu'\mathrm{N}' - \mu\mathrm{N}}{cz'}. \quad . \quad . \quad (1)$$

The equations of the ray incident at $P(0, y', z')$ are

$$\frac{x}{L} = \frac{y-y'}{M} = \frac{z-z'}{N} ;$$

the equations of the ray refracted at $P(0, y', z')$ are

$$\frac{x}{L'} = \frac{y-y'}{M'} = \frac{z-z'}{N'} ;$$

$$\left.\phantom{\begin{matrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \end{matrix}}\right\} \quad .. (2)$$

the equations of the normal at P are

$$\frac{x}{-1} = \frac{y-y'}{by'} = \frac{z-z'}{cz'}.$$

The projection of the incident ray on $z=0$ is

$$\frac{x}{L} = \frac{y-y'}{M} ;$$

the projection of the refracted ray on $z=0$ is

$$\frac{x}{L'} = \frac{y-y'}{M'} ;$$

$$\left.\phantom{\begin{matrix} a \\ b \\ c \\ d \\ e \end{matrix}}\right\} \quad . \quad . \quad . \quad (3)$$

the projection of the normal on $z=0$ is

$$\frac{x}{-1} = \frac{y-y'}{by'}.$$

The quantities in the denominators may be taken as actual direction cosines, since N is small by hypothesis, and therefore

$$L^2 + M^2 = L^2 + M^2 + N^2 = 1.$$

And by (1)

$$\mu'N' - \mu N = -cz'(\mu'L' - \mu L),$$

hence N' is of the first order of small quantities like N and z'. Also y' is small, therefore

$$1 + b^2 y'^2 = 1.$$

The projections (3) of the incident and refracted rays meet at the point $(0, y', 0)$, or Q say, which satisfies the equation of the surface, neglecting y'^2.

The equations of the normal at Q are

$$\frac{x}{-1} = \frac{y-y'}{by'} = \frac{z}{0},$$

which agree with the expression found for the projection of the normal at P. Hence the normal at P projects into the normal at the projection of P.

The condition that the projections (3) should be conjugate, or form part of the same ray of light, is

$$\frac{\mu' L' - \mu L}{-1} = \frac{\mu' M' - \mu M}{by'},$$

which is true by (1). Thus the theorem is proved for the tangential section, whatever the values of L and M may be.

If the projection had been upon the plane $y = 0$, the condition obtained for conjugacy of the projected paths would have been

$$\frac{\mu' L'}{\sqrt{L'^2 + N'^2}} - \frac{\mu L}{\sqrt{L^2 + N^2}} = \frac{\dfrac{\mu' N'}{\sqrt{L'^2 + N'^2}} - \dfrac{\mu N}{\sqrt{L^2 + N^2}}}{-cz'},$$

or neglecting N^2 and N'^2,

$$\pm(\mu' \pm \mu) = \frac{\dfrac{\mu' N'}{L'} \pm \dfrac{\mu N}{L}}{-cz'},$$

which does *not* agree with (1) generally. The expressions agree if $L' = L = \pm 1$, *i.e.* if the ray is parallel to the normal at O.

If the chief ray is normal, then evidently it is immaterial which of the two principal sections is regarded as the tangential section. The ray lies in both.

II. *Projection on the Sagittal Sections.*

The general equations (see Note at end of discussion) of the projection of a straight line

$$\frac{x - x'}{L} = \frac{y - y'}{M} = \frac{z - z'}{N}$$

on a plane $lx + my + nz = p$ (p being the perpendicular on the plane from the origin) are

$$\frac{x - x' + l(lx' + my' + nz' - p)}{L - l\cos\theta} = \frac{y - y' + m(lx' + my' + nz' - p)}{M - m\cos\theta}$$
$$= \frac{z - z' + n(lx' + my' + nz' - p)}{N - n\cos\theta},$$

θ being the angle between the straight line and the normal

to the plane, so that $\cos\theta = Ll + Mm + Nn$, and the sum of the squares of the denominators $= \sin^2\theta$.

In the present case the equation of the first sagittal plane is

$$x\sin\psi - y\cos\psi = 0,$$

thus $l = \sin\psi$, $m = -\cos\psi$, $n = 0$, $p = 0$, $x' = 0$, and $\cos\theta = L\sin\psi - M\cos\psi$. Substituting these values, we find for the projection of the ray (L, M, N) on the first sagittal plane

$$\frac{x - y' \cdot \sin\psi \cdot \cos\psi \cdot}{\cos\psi(L\cos\psi + M\sin\psi)} = \frac{y - y'\sin^2\psi}{\sin\psi(L\cos\psi + M\sin\psi)} = \frac{z - z'}{N},$$

or

$$\frac{x}{\cos\psi} = \frac{y}{\sin\psi} = \left(\frac{z - z'}{N}\right)(L\cos\psi + M\sin\psi) + y'\sin\psi. \ldots (4)$$

The projection cuts the axis of z at the point where

$$z = z' - \frac{Ny'\sin\psi}{(L\cos\psi + M\sin\psi)} = z' - \frac{Ny'\sin\psi}{\cos\alpha} = z' - Ny'\sin\psi,$$

α being the angle between the two incident rays, assumed small of first order.

Similarly, if α' be the angle between the two refracted rays, the projection of the refracted ray on the second sagittal plane cuts the axis of z where

$$z = z' - \frac{N'y'\sin\psi'}{\cos\alpha'}.$$

Hence, to the first order, the rays will meet in a point, N, N', y' being all small. If, in addition, ψ is small this will be true to the second order.

The point $(0, 0, z')$ satisfies the equation of the refracting surface $0 = -2x + by^2 + cz^2$, and the equations of the normal at this point are

$$\frac{x}{-1} = \frac{y}{0} = \frac{z - z'}{cz'},$$

thus it lies in the plane of zx, i.e. the plane through the normal at O perpendicular to the chief incidence plane.

The equations of refraction for the projections are, from (4)

$$\frac{\mu'\cos\psi' - \mu\cos\psi}{-1} = \frac{\mu'\sin\psi' - \mu\sin\psi}{0}$$

$$= \frac{\dfrac{\mu'N'}{L'\cos\psi' + M'\sin\psi'} - \dfrac{\mu N}{L\cos\psi + M\sin\psi}}{cz'}$$

$$= \mu'\cos\phi' - \mu\cos\phi,$$

ϕ, ϕ' being the angles made by the projections with the normal at their point of intersection. These are equivalent to two equations. The second expression is indeterminate since $\mu' \sin \psi' = \mu \sin \psi$, so the fourth is used instead. Two conditions are necessary in this case, because projection did not take place on a single plane as in the tangential case, so we have to show that the rays and normal are coplanar, besides satisfying the angular relation.

Now

$$\cos \phi = -\cos \psi + \frac{cz'N}{\cos \alpha} = -\cos \psi,$$

since N, z', and α are small. Similarly, $\cos \phi' = -\cos \psi'$.
Hence one condition holds, namely

$$\mu' \cos \psi' - \mu \cos \psi = -\mu' \cos \phi' + \mu \cos \phi.$$

The remaining condition is

$$\mu' \cos \psi' - \mu \cos \psi = \frac{\dfrac{\mu'N'}{\cos \alpha'} - \dfrac{\mu N}{\cos \alpha}}{-cz'}.$$

The equations of refraction of the original ray give

$$\mu'L' - \mu L = \frac{\mu'N' - \mu N}{-cz'}.$$

Eliminate z', since the result is to hold for all small values of z', and the required condition becomes

$$\frac{\mu'L' - \mu L}{\mu' \cos \psi' - \mu \cos \psi} = \frac{\mu'N' - \mu N}{\dfrac{\mu'N'}{\cos \alpha'} - \dfrac{\mu N}{\cos \alpha}}.$$

This evidently holds, since α, α' are small angles so that

$$\frac{\mu'N'}{\cos \alpha'} - \frac{\mu N}{\cos \alpha} = 1 \quad \text{approximately;}$$

and differentiation of the identity $\mu' \sin \psi' = \mu \sin \psi$ gives

$$\mu'L' - \mu L = \mu' \cos \psi' - \mu \cos \psi.$$

More exactly, differentiating $\mu' \sin \psi' = \mu \sin \psi$ we get

$$\mu' \cos \psi' \,.\, d\psi' = \mu \cos \psi \,.\, d\psi \,;$$

also $\qquad\qquad L = \cos(\psi + \alpha), \qquad L' = \cos(\psi' + \alpha'),$

hence

$$\frac{\mu' L' - \mu L}{\mu' \cos \psi' - \mu \cos \psi} = \frac{\mu'(\cos \psi' - \alpha' . \sin \psi') - \mu(\cos \psi - \alpha . \sin \psi)}{\mu' \cos \psi' - \mu \cos \psi}$$

$$= 1 + \frac{\mu' \sin \psi'(\alpha - \alpha')}{\mu' \cos \psi'(\alpha - \alpha')} \alpha = 1 + \alpha \tan \psi' = 1 + \alpha' \tan \psi.$$

Now if $\mu' > \mu$, $\tan \psi$ may become infinite, but $\tan \psi'$ cannot numerically exceed the tangent of the critical angle, a finite limit. The equality $\alpha \tan \psi' = \alpha' \tan \psi$, which may at first sight appear paradoxical when $\psi = 90°$, is explained by α' then becoming of the second order, as follows from $\mu' \cos \psi' . d\psi' = \mu \cos \psi . d\psi$, so that $\alpha' \tan \psi$ is not of order $0 \times \infty$, but $0^2 \times \infty$, *i. e.* of first order of smallness.

When $\tan \psi'$ is infinitely small, $\alpha \tan \psi'$ is of the second order; but for finite values of $\tan \psi'$, $\alpha \tan \psi'$ is of the same order as α, that is the first order by hypothesis. If $\mu' < \mu$, the same reasoning will apply by transferring the accents.

Thus Lippich's theorem applied to the sagittal projection requires neglect of small quantities of the first order, unless incidence is nearly normal; whereas in the tangential projection only small quantities of the second order have to be neglected.

In the following numerical examples $\alpha = d\psi$ is taken as $1''$, or $\cdot 00000484814$ in circular measure, so that millionths are regarded as first order quantities. Also $\mu' = 1 \cdot 5$, $\mu = 1$.

ψ.			ψ'.			$\alpha' = d\psi'$.	$\alpha \tan \psi = '\alpha' \tan \psi$.
°	′	″	°	′	″		
20			13	10	48·51	·00000312	·00000114
20	0	1	13	10	49·16		
30			19	28	16·39	·00000297	·00000172
30	0	1	19	28	17·01		
80			41	2	11·08	·00000074	·00000421
80	0	1	41	2	11·23		
88			41	46	44·776	·00000015	·00000432
88	0	1	41	46	44·807		
89	59	59	41	48	37·135	·00000000	·00000434
90	0	0					

Taking α as $1'$ or $\cdot 000291$, and $\psi = 45°$, would give

$$\alpha \tan \psi' = \alpha' \tan \psi = \cdot 0001555.$$

ELEMENTARY PROOF.

The following is an attempt at an Elementary Geometrical Proof of Lippich's Theorem.

In order that two rays may be conjugate :—

(1) They must meet in a point on the refracting surface.
(2) Their plane must contain the normal to the refracting surface at that point.
(3) The angles ϕ, ϕ' which they make with the normal must satisfy the relation $\mu' \sin \phi' = \mu \sin \phi$, where μ, μ' are the refractive indices.

Projection on the Tangential Section.

Let O be the point of incidence of the chief ray. If P' be the projection of P, the point of incidence of a neighbouring oblique ray, upon the plane of incidence of the chief ray, it is well known that the distance of P' from the tangent plane at O (the point of incidence of the chief ray) is of the second order of small quantities. Hence we may regard P' as lying on the surface, and the projections of rays and normal through P pass through P'. This disposes of condition (1). Condition (2) is satisfied if the plane of projection is in a principal section at O.

Fig. 4.
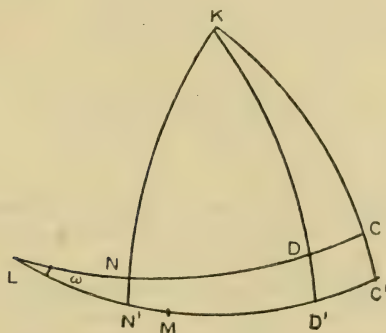
Suppose a sphere described about O as centre (figs. 4 and 6).

Let the (chief) ray incident at O cut the sphere at A,
  „   „   „   ray refracted at O   „   „   „   „ B,
  „   „ normal at O   „   „   „   „ M,
a radius parallel to the ray incident at P   „   „   „   „ C,
  „   „   „   „ ray refracted at P   „   „   „   „ D,
  „   „   „   „ normal at P   „   „   „   „ N.

Let K be the pole of the great circle ABM, L the point of intersection of the great circles ABM and CDN, and ω the angle between them. From K through N, C, D, draw great circles meeting AB at N', C', D' respectively.

Since the incident ray, refracted ray, and normal at a point are coplanar, the points A B M lie on a great circle, and so do C D N.

In the case of the tangential projection, the arcs AC and BD need not be assumed small, but the angles MN between the normals, and CC' between the second ray and the chief plane of incidence, are assumed small of first order. NN' will also be small,

since $\cos MN = \cos NN' \cdot \cos MN'$, $\therefore NN' < MN$.

DD' may be shown to be of the same order as CC' as follows. From N draw a great circle perpendicular to the great circle which bisects the angle CKD; let it cut KC at Y, and KD at Z, then the angles at Y and Z are equal, and C'Y = D'Z, hence $\sin CY : \sin DZ : : \sin CN : \sin DN : : \mu' : \mu$, hence CY and DZ are of the same order, and therefore the wholes CC', DD', are of the same order.

Now

$$\frac{\sin NC}{\sin NKC} = \frac{\sin KC}{\sin N}, \qquad \frac{\sin ND}{\sin NKD} = \frac{\sin KD}{\sin N},$$

$$\frac{\sin NC}{\sin ND} \cdot \frac{\sin NKD}{\sin NKC} = \frac{\sin KC}{\sin KD},$$

or $\qquad \dfrac{\mu'}{\mu} \cdot \dfrac{\sin N'D'}{\sin N'C'} = \dfrac{\cos CC'}{\cos DD'} = 1,$

$\therefore \qquad \mu' \sin N'D' = \mu \sin N'C',$

and thus the third condition is fulfilled. The projections are conjugate. The positions of A, B on the great circle LAB do not enter into the matter at all.

The result might also be deduced from the following considerations. If the angle of incidence CN is small, so is DN (by the law of sines); the sines of all the small arcs may be taken equal to the arcs, and CC', DD', NN' may be regarded as parallel straight lines dividing two other straight lines NC, N'C', proportionally.

If CN is finite, ω must be small. The equations

(i.) $\sin NN' = \sin LN \cdot \sin \omega$, (ii.) $\sin CC' = \sin LC \cdot \sin \omega$,

show that if LN is finite, ω must be of first order whatever

the incidence; while if LN is small and CN finite, LC must be finite, and therefore by (ii.) ω small of first order. Hence, if the second plane of incidence be brought into coincidence with the first by rotating about L the line of intersection, the points C, D, N will coincide with C', D', N' to the first order.

It may be noted that if ω is finite, the angle of incidence must be small, since by (i.) and (ii.) both LN and LC, and therefore CN, must be small. But the converse is not true. It is clear that if C coincides with N the planes of incidence may have any inclination without contravening the hypothesis.

Projection on the Sagittal Sections.

Let P'' be the projection of P on the first sagittal section, and t the line of intersection of the two sagittal sections. t is perpendicular to the tangential section, and is a tangent to the surface along a principal section.

To show that the projections meet in a point we may proceed similarly to Culmann :—

The projection of any ray through P must (1) pass through P'', and (2) intersect the line t. Let it intersect at R (see fig. 5, where the straight line QR or t is supposed at right angles to the chief plane of incidence).

Fig. 5.
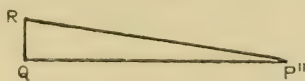
Let the plane through P parallel to the tangential section (chief plane of incidence) cut t at Q.

P''Q is parallel to the chief ray, since the sagittal plane cuts two parallel planes in parallel lines. By hypothesis the ray incident at P is nearly parallel to the chief ray, hence the angle QP''R is small. Also P''Q is given small. Therefore QR is small of the second order, and R may be taken as coinciding with Q. Similarly the projection of the refracted ray on the other sagittal plane passes through Q. Q being on the tangent plane at O, the point of incidence of the chief ray, and near O, may be regarded as a point on the surface. Hence the projections of the incident and refracted rays meet at a point of the surface.

Projecting on the sphere (fig. 6), and letting ABMNCDKL have the same meanings as before, the great circles KA, KB represent the sagittal sections, and KM represents the second principal section at O.

Fig. 6.
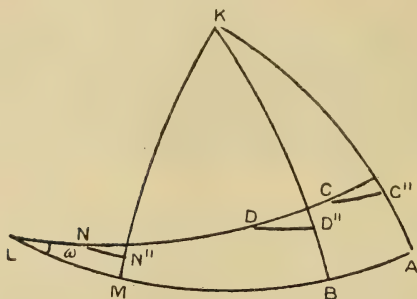
From N draw a great circle NN'' at right angles to KM,
,, C ,, ,, ,, CC'' ,, ,, ,, KA,
,, D ,, ,, ,, DD'' ,, ,, ,, KB.

In this case MN and AC are assumed small of first order. Hence MN'', AC'', are also small, being less than MN, AC.

MK is a principal section at M, and therefore at N'' near M, hence NN'' at right angles to MN''K is the other principal section at N'', and the line represented by N'', being the line of intersection of two principal sections, is a normal to the refracting surface.

If CN is small of first order, so is DN, and as before all the small arcs in the region NCC''AM may be taken as straight lines, and equal to their sines. Hence, since NC : ND : : MA : MB, it is easily seen that the points N'', C'', D'' lie in a straight line, and therefore the lines they represent are parallel to a plane, and having been shown to be concurrent, must be coplanar. Also N''C'' : N''D'' : : μ' : μ. Hence, if the angle of incidence is of the first order, the sagittal projections are conjugate, neglecting second order quantities, and obviously the smaller the angle of incidence the closer the approximation.

If the angle of incidence is not small, then by neglecting small quantities of the *first* order, N may be taken as coinciding with M, C with A, and therefore D with B. Hence the theorem holds with that proviso.

Angle ω between the planes of incidence.

Because two near incident rays are nearly parallel, and the normals also nearly parallel, it does not necessarily follow

that the planes of incidence are nearly parallel. Suppose one ray to be incident normally, and the other nearly so; then the plane of incidence of the nearly normal ray is fixed, while that of the normal ray may have any inclination to a given normal plane. If, however, both rays are incident at 90°, and the normals coincide, then $\omega =$ the angle between the rays, which is small by hypothesis. An idea of the connexion between ω and angle of incidence may be gained by supposing the great circles CN, AM, capable of rotating about fixed diameters through N, M, and CA to be a sliding bar with its ends moving on the circles. The remarks above on ω at the close of the discussion of the tangential projection apply in this case also, NN', CC' (fig. 4), being less than MN, AC, and therefore small. It is seen that for finite angle of incidence, ω must be small; but for small angle of incidence, ω may be either small or not.

Note on the equations of the Projection of the Straight Line.

$$\frac{x-x'}{L} = \frac{y-y}{M} = \frac{z-z'}{N} \quad \text{on the Plane } lx+my+nz+p=0.$$

The equations employed were originally obtained as follows :—

Let (x'', y'', z'') be a second point on the line, at distance r from (x', y', z').

Let p', p'' be the perpendiculars from these points on the plane; (ξ', η', ζ'), (ξ'', η'', ζ'') the co-ordinates of their feet, then

$$x'' - x' = Lr, \ \&c.$$
$$p' = p - lx' - my' - nz',$$
$$\xi' = x' + lp', \ \&c.$$
$$\xi'' = x'' + lp'', \ \&c.$$

The equations of the required projection are

$$\frac{x-\xi'}{\xi''-\xi'} = \frac{y-\eta'}{\eta''-\eta'} = \frac{z-\zeta'}{\zeta''-\zeta'},$$

and by substitution

$$\xi''-\xi' = x''-x'-lr(Ll+Mm+Nn) = r(L-l\cos\upsilon).$$

(If, as suggested below, x'', y'', z'' had been taken as the point where the line meets the plane, we should have had

$$\xi'' = x'', \quad p' = r\cos\theta,$$

and $\qquad \xi''-\xi' = x''-x'-lp' = Lr-lr\cos\theta.$)

The denominators were also derived by means of the relations

$$a\mathrm{L} + b\mathrm{M} + c\mathrm{N} = 0, \quad al + bm + cn = 0, \quad a\lambda + b\mu + c\nu = 0,$$
$$l\lambda + m\mu + n\nu = 0,$$

where λ, μ, ν are the direction cosines of the projection, and a, b, c of the normal to the projecting plane.

The result might also be obtained by changing the co-ordinate planes so as to make the plane of projection one of them, but it seems simpler to proceed directly.

For the following much neater method the writer is indebted to Mr. T. Smith.

Make use of the point in which the line meets the plane. (In the particular case where there is no intersection the projection result is obvious without investigation.) If the point of intersection is

$$x' + \mathrm{L}\rho, \quad y' + \mathrm{M}\rho, \quad z' + \mathrm{N}\rho,$$

then
$$lx' + my' + nz' + \rho \cos \theta = p.$$

The projection lies in the same plane as the line and the normal, and therefore its direction cosines are of the form

$$\alpha \mathrm{L} + \beta l, \quad \alpha \mathrm{M} + \beta m, \quad \alpha \mathrm{N} + \beta n.$$

Since it is perpendicular to the normal to the plane,

$$\alpha \cos \theta + \beta = 0,$$

$\therefore$ the direction cosines are

$$\alpha(\mathrm{L} - l \cos \theta), \quad \alpha(\mathrm{M} - m \cos \theta), \quad \alpha(\mathrm{N} - n \cos \theta),$$

from which it at once follows that $\alpha = 1/\sin \theta$.

The projection is then

$$\frac{x - x' + \dfrac{\mathrm{L}}{\cos \theta}(lx' + my' + nz' - p)}{\mathrm{L} - l \cos \theta} = \&\mathrm{c.} = \&\mathrm{c.},$$

or, adding to each fraction $-\dfrac{lx' + my' + nz' - p}{\cos \theta}$,

$$\frac{x - x' + l(lx' + my' + nz' - p)}{\mathrm{L} - l \cos \theta} = \text{two similar expressions.}$$

The writer desires sincerely to thank Mr. T. Smith for reading and criticizing the manuscript before publication, and suggesting (besides the matter just mentioned in the note) the clearer expression for the final analytical condition in the case of the sagittal projection, which led to the discovery that the theorem is less accurate for this case than for the tangential projection.

XI. *On the Theory of Ionization by Collision.*
By P. O. Pedersen [*].

1. IN an article in this journal Norman R. Campbell [†]
treats of the mathematical theory of ionization by
collision, making the simplest possible assumptions with
regard to the nature of this ionization. Only ionization
due to collisions between electrons and molecules is con-
sidered, and his assumptions may briefly be stated as
follows :—

(1) An electron will produce a fresh pair of ions
(electron + positive ion) when it collides with a
neutral molecule, if previously to that collision
its velocity v satisfies the following condition :

$$v \gtreqqless v_0 = \sqrt{\frac{2e}{m} V_0}, \quad \ldots \ldots \quad (1)$$

where m is the mass of the electron, $-e$ its charge,
and V_0 a certain constant voltage depending on
the nature of the molecule.

(2) Collisions between electrons and molecules take
place unelastically, so that after collision the electron
is free again but has the velocity zero.

(3) The electrons set free by ionization have also the
velocity zero.

(4) The velocities of the electrons due to the electric
field are so great that the thermal velocities of the
electrons and the molecules may be disregarded [‡].

2. Norman R. Campbell does not give the exact solution.
He says [§] : " Now it is possible to calculate accurately
according to the theory what should be the current between
electrodes a distance a apart (fig. 1) in a gas at pressure p,

* Communicated by the Author.
† Phil. Mag. (6) vol. xxiii. p. 400 (1912).
‡ With regard to the question of the validity of these assumptions,
see J. S. Townsend, 'Electricity in Gases' (Oxford, 1915), and the
discussion between Townsend and Norman R. Campbell, Phil. Mag. (6)
vol. xxiii. pp. 856 & 986 (1912).
§ *Loc. cit.* p. 404.

when (the electric field) X has a given value, but the
calculations are extremely complex, and the resulting

Fig. 1.
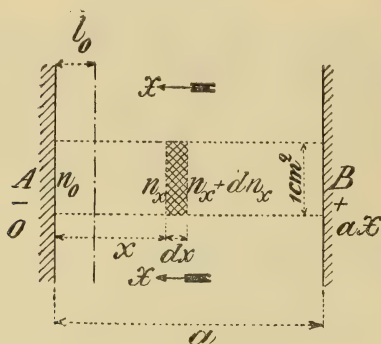
formula for the relation between i, a, p, X is not of a
form to which Townsend's measurements can be applied."
He therefore assumes that the number of electrons n_x
varies continuously with the distance x from the cathode
and thus obtains an approximate solution.

The exact solution is, however, quite simple and may be
given a form to which Townsend's measurements may
easily be applied. The deduction of this solution may
therefore, perhaps, be of sufficient interest to be given
here.

3. Let L be the mean free path of the electron; then
the probability s that a new collision results in ionization
is determined by

$$s = \epsilon^{-\frac{l_0}{L}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$l_0 = \frac{V_0}{X}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The electrons coming from A (see fig. 1) fall into two
groups 1 and 2. In the first we shall reckon the electrons
whose initial free path is greater than l_0 and which will
thus ionize at the first collision. The second group includes
the electrons whose initial free path is less than l_0: of these
the first collisions which occur between $x=0$ and $x=l_0$ will
not result in ionization.

The number of ionizations which take place in the space
element between the planes x and $x+dx$, and which is

due to the first group of electrons, we shall call $N_0(x) \cdot dx$, where the suffix 0 denotes that the electrons come directly from A without intermediate collisions.

Fig. 2.
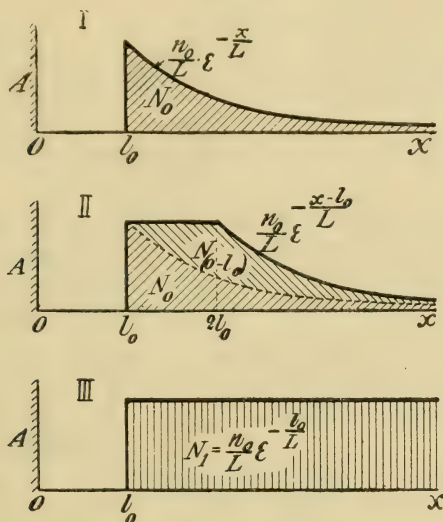
We have then

$$\text{for } x < l_0 : \quad N_0(x) = 0,$$
$$\text{and for } x \geqq l_0 : \quad N_0(x) = \frac{n_0}{L} \cdot \epsilon^{-\frac{x}{L}}. \quad \left. \right\} \text{(See fig. 2, I.).} \quad (5)$$

We shall then proceed to the determination of the first ionizations which are due to group 2.

In the element of space $(y, y + dy)$, where y in the same way as x signifies the distance from A and where $0 < y < l_0$, the number of collisions per second between electrons and molecules is $\frac{n_0}{L} \cdot dy$, but none of these collisions give rise to ionization. The next collision where these $\frac{n_0}{L} \cdot dy$ electrons take part will in the element of space $(x, x + dx)$ give $N_y(x) \cdot dx \, dy$ ionizations where

$$\text{for } x < y + l_0 : \quad N_y(x) = 0,$$
$$\text{and for } x \geqq y + l_0 : \quad N_y(x) = \frac{n_0}{L^2} \cdot \epsilon^{-\frac{x-y}{L}}. \quad \left. \right\} \quad . \quad (6)$$

K 2

The total number of ionizations $N_{(0-l_0)}(x) . dx$ in the element of space $(x, x+dx)$, which are due to electrons the direct collisions of which occurred between $x=0$ and $x=l_0$, is determined by :

$$
\begin{aligned}
&\text{for } x < l_0: \qquad N_{(0-l_0)}(x) = 0, \\
&\text{for } l_0 \leqq x \leqq 2l_0 : \ N_{(0-l_0)}(x) = \int_{y=0}^{y=x-l_0} N_y(x) . dy = \frac{n_0}{L}\left(\epsilon^{-\frac{l_0}{L}} - \epsilon^{-\frac{x}{L}}\right), \\
&\text{and for } x > 2l_0: \qquad N_{(0-l_0)}(x) = \int_{y=0}^{y=l_0} N_y(x) . dy = \frac{n_0}{L}\left(\epsilon^{-\frac{x-l_0}{L}} - \epsilon^{-\frac{x}{L}}\right).
\end{aligned}
\right\} (7)
$$

The total number of ionizations $N(x) . dx$ in the element of space $(x, x+dx)$, which are due to electrons which either come directly from A or the direct collisions of which took place within the distance l_0 from A, is thus determined by :

$$
\begin{aligned}
&\text{for } x < l_0: \qquad N(x) = 0, \\
&\text{for } l_0 \leqq x \leqq 2l_0 : \ N(x) = \frac{n_0}{L} . \epsilon^{-\frac{l_0}{L}}, \\
&\text{and for } x > 2l_0 : \qquad N(x) = \frac{n_0}{L} . \epsilon^{-\frac{x-l_0}{L}}.
\end{aligned}
\right\} \text{(See fig. 2, II.) . (8)}
$$

It is obvious that the number $N_1(x) dx$ in the element of space $(x, x+dx)$, which are due to collisions with electrons originally coming from A, is determined by :

$$
\begin{aligned}
&\text{for } x < l_0: \ N_1(x) = 0, \\
&\text{and for } x \geqq l_0: \ N_1(x) = \frac{n_0}{L} . \epsilon^{-\frac{l_0}{L}}.
\end{aligned}
\right\} \text{(Fig. 2, III.) . (9)}
$$

The total number of liberated electrons of that class which we called Class 1, of which the collisions are due to impacts between molecules and electrons originally coming from A, is therefore

$$
n_1 = (a - l_0) \frac{n_0}{L} \epsilon^{-\frac{l_0}{L}}. \qquad . \qquad . \qquad . \qquad (10)
$$

It is also possible to realize the correctness of this result directly, but the procedure followed above has the advantage that it gives some information about the " geometry " of ionization by collision.

These n_1 electrons cause directly by collision with molecules $N_2(x)\,dx$ ionizations in the element of space $(x, x+dx)$, where

$$\left.\begin{array}{ll} \text{for } x < 2l_0: & N_2(x) = 0, \\ \text{and for } x \geqq 2l_0: & N_2(x) = n_0(x-2l_0)\left(\dfrac{\epsilon^{-\frac{l_0}{L}}}{L}\right)^2. \end{array}\right\} \quad (11)$$

The total number of the liberated electrons of the class which we will denote by Class 2 is thus

$$n_2 = n_0 \frac{(a-2l_0)^2}{1.2}\cdot\left(\frac{\epsilon^{-\frac{l_0}{L}}}{L}\right)^2. \qquad (12)$$

Similarly, for Class ν,

$$\left.\begin{array}{ll} \text{for } x < \nu l_0: & N_\nu(x) = 0, \\ \text{and for } x \geqq \nu l: & N_\nu(x) = n_0 \dfrac{(x-\nu l_0)^{\nu-1}}{(\nu-1)!}\cdot\left(\dfrac{\epsilon^{-\frac{l_0}{L}}}{L}\right)^\nu. \end{array}\right\} \quad (13)$$

and the total number

$$n_\nu = n_0 \frac{(a-\nu l_0)^\nu}{\nu!}\left(\frac{\epsilon^{-\frac{l_0}{L}}}{L}\right). \qquad (14)$$

Fig. 3.
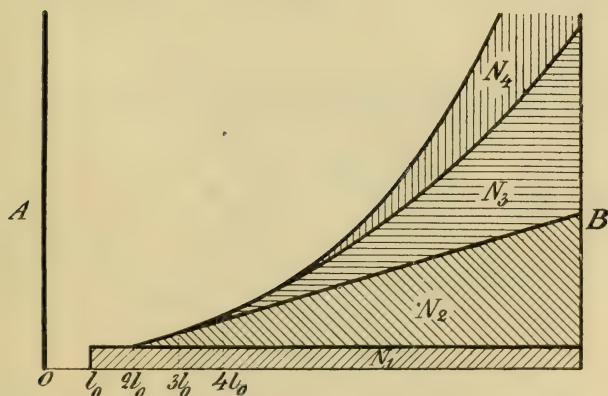
Fig. 3 shows an example of the distribution of the first four ionization classes.

The "centre of gravity" for the νth class—by which we

understand the centre of gravity for the area drawn in accordance with fig. 3 representing $N_\nu(x)$—lies at the distance r_ν from A given by

$$r_\nu + \frac{\nu}{\nu+1}\,(a+l_0). \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Fig. 4 shows for a definite case the position of the centre of gravity for the first ten classes and their relative magnitudes.

Fig. 4.
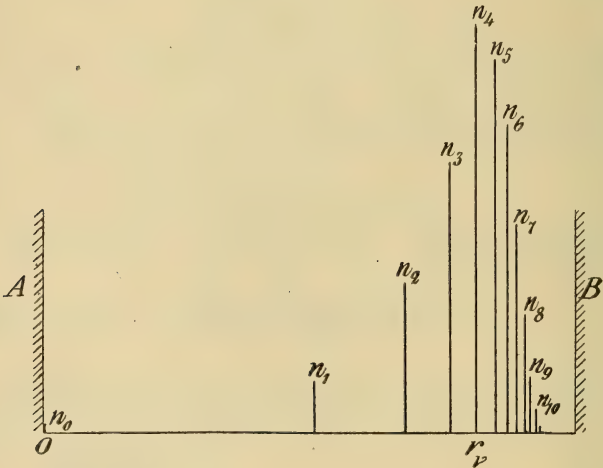
4. From the preceding it follows that the total number of electrons n_a which reaches the B electrode is

$$\left.\begin{aligned} n_a &= \sum_{\nu=0}^{\nu=\nu'} n_\nu = \sum_{\nu=0}^{\nu=\nu'} \frac{(a-\nu l_0)^\nu}{\nu!} \cdot \left(\frac{\epsilon^{-\frac{l_0}{L}}}{L}\right)^\nu \\ &= \sum_{\nu=0}^{\nu=\nu'} \frac{(h-\nu)^\nu}{\nu!} \cdot y^\nu = n_0 \sum_{\nu=0}^{\nu=\nu'} \frac{\left(1-\frac{\nu}{h}\right)^\nu}{\nu!}(\alpha a)^\nu, \end{aligned}\right\} \quad . \quad (16)$$

where $\quad h = \dfrac{a}{l_0}, \quad y = \dfrac{l_0}{L} \cdot \epsilon^{-\frac{l_0}{L}}, \quad$ and $\quad \alpha = \dfrac{1}{L}\epsilon^{-\frac{l_0}{L}}, \quad . \quad . \quad (16')$

while ν' is the greatest integer which is less than or equal to h.

In figs. 5 *a* and 5 *b* the curves I. and II. represent $\log \dfrac{n_a}{n_0}$ as function of h for respectively $y = 0.1$ and 0.2. It is

Fig. 5 *a*.
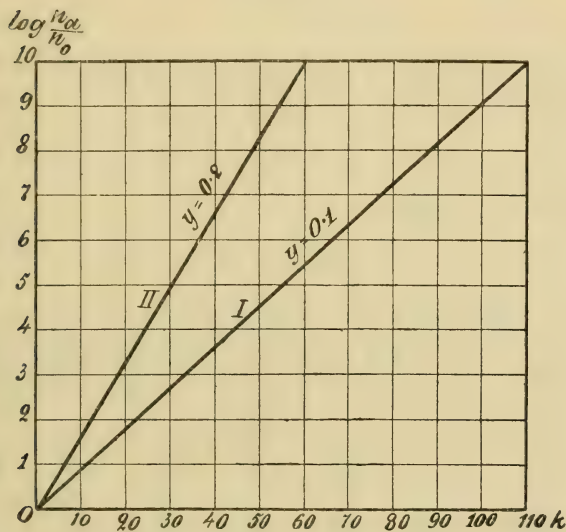
Fig. 5 *b*.
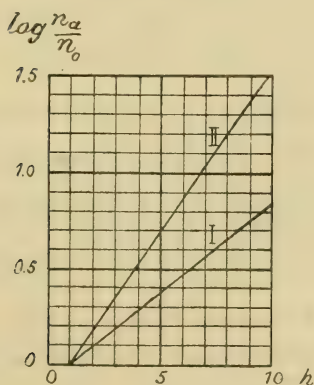
evident that I. and II. are very nearly straight lines, which intersect the abscissæ axis at the point $h = 1$.

The same holds also for other values of y; with sufficient approximation we can therefore put

$$\log \frac{n_a}{n_0} = \gamma y(h-1) \quad . \quad . \quad . \quad . \quad (17)$$

or

$$\frac{n_a}{n_0} = \epsilon^{\gamma y(h-1)}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where γ is a coefficient which only depends on y.

In place of Townsend's relation

$$\frac{n_a}{n_0} = \epsilon^{\alpha a},$$

we thus obtain the equation

$$\frac{n_a}{n_0} = \epsilon^{\gamma a(a-l_0)}. \quad . \quad . \quad . \quad (19)$$

In the table below are given approximate values of γ calculated on the basis of equations (16) and (17) for values of y between 0 and $0\cdot368 = \epsilon^{-1}$, which latter value is the highest y can obtain :—

$y.$	$\gamma.$	$y.$	$\gamma.$	$y.$	$\gamma.$	$y.$	$\gamma.$
0·00	1·00	0·10	0·92	0·20	0·85	0·30	0·79
·01	·98	·11	·91	·21	·84	·31	·79
·02	·98	·12	·90	·22	·84	·32	·79
·03	·97	·13	·89	·23	·83	·33	·78
·04	·96	·14	·89	·24	·83	·34	·78
·05	·96	·15	·88	·25	·82	·35	·77
·06	·95	·16	·87	·26	·82	·36	·77
·07	·95	·17	·87	·27	·81	·368	·76
·08	·93	·18	·86	·28	·81		
·09	·92	·19	·86	·29	·80		

5. The determinations of l_0, V_0, γ, and α are made on the basis of measurements of corresponding values of $\frac{n_a}{n_0}$ and a, and by use of equation (17) as well as the table above. As example, we will treat the following series of measurements by Townsend (*loc. cit.* p. 277; Phil. Mag. (6) vi. p. 598, 1903) :—

Atmospheric air ; Pressure 1 mm. Hg.

L$= 3\cdot2 \times 10^{-2}$ cm. ; X$= 350$ volt/cm.

$a = 0$	0·2	0·4	0·6	0·8	1·0	1·1 cm.
$\frac{n_a}{n_0} = 1$	2·86	8·3	24·2	81·0	373	2250
$\log \frac{n_a}{n_0} = 0$	1·05	2·12	3·19	4·39	5·92	7·72

The values of $\log \dfrac{n_a}{n_0}$ are drawn with a as abscissæ (fig. 6). One puts after a preliminary trial $l_0 = 0 \cdot 05$ cm., and draws through the point c on the abscissæ axis determined by $0c = l_0$ a straight line cb which for small values of a

Fig. 6.
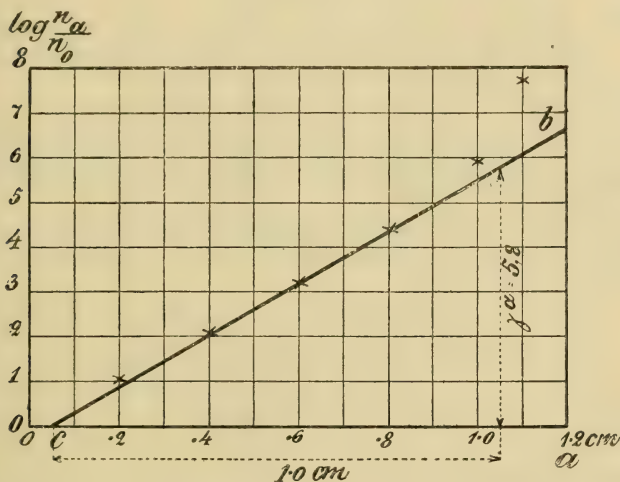
agrees as closely as possible with the found values of $\log \dfrac{n_a}{n_0}$. (For greater values of a, $\log \dfrac{n_a}{n_0}$ lies above the line cb on account of the ionization caused by the positive ions of which no account is taken.) From fig. 6 is obtained $\gamma a = 5 \cdot 8$. To $l_0 = 0 \cdot 05$ cm. corresponds $y = \dfrac{l_0}{L} \cdot \epsilon^{-\frac{l_0}{L}} = 0 \cdot 328$, to which again according to the preceding table corresponds $\gamma = 0 \cdot 78$. Consequently $\alpha = \dfrac{5 \cdot 8}{0 \cdot 78} = 7 \cdot 44$. From this is found by using equation (16′) $l_0 = 0 \cdot 046$ cm., and as this value is sufficiently near to the one previously assumed, namely $0 \cdot 05$ cm., there is no reason to make a new determination.

For the ionization voltage we now obtain,

$$V_0 = 0 \cdot 046 \times 350 = 16 \cdot 1 \text{ volt.}$$

A further discussion of this problem is to be found in a Danish paper *.

Copenhagen,
    November 1919.

* *Det Kgl. Danske Videnskabernes Selskab. Mathematisk-fysiske Meddelelser*, i. part 7 (1918).

XII. *On the Stability of two Rectilinear Vortices of Compressible Fluid moving in an Incompressible Liquid.* By BIBHUTIBHUSAN DATTA, *M.Sc., Lecturer in Applied Mathematics, University of Calcutta, India*[*].

THE stability of the circular form in two rectilinear vortices has been discussed by Sir J. J. Thomson [†] for incompressible fluid.

Dr. Chree [‡] attempted to extend his treatment to a compressible fluid but did not succeed except in some special cases. The object of the present paper is to complete the work begun by Dr. Chree.

When the vortex-lines are straight lines parallel to the axis of z, the velocity components u, v at any point (x, y) in the fluid are given by [§]

$$u = -\frac{\partial \phi}{\partial x} - \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \phi}{\partial y} + \frac{\partial \psi}{\partial x}; \quad . \quad . \quad (1)$$

hence

$$\nabla_1^2 \phi = -\theta, \quad \nabla_1^2 \psi = \zeta, \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\theta = \frac{du}{dx} + \frac{dv}{dy}, \quad \nabla_1^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}.$$

Then by the theory of attraction,

$$\left. \begin{array}{l} \phi = -\dfrac{1}{2\pi} \iint \theta' \log r \, dx' \, dy' + \phi_0, \\[2mm] \psi = \dfrac{1}{2\pi} \iint \zeta' \log r \, dx' \, dy' + \psi_0, \end{array} \right\} \quad . \quad . \quad (3)$$

θ', ζ' being respectively the value of θ and ζ at the point (x', y') and

$$r = \left\{ (x - x')^2 + (y - y')^2 \right\}^{\frac{1}{2}}, \quad \nabla_1^2 \phi_0 = 0, \quad \nabla_1^2 \psi_0 = 0.$$

If $\dfrac{d}{dt}$ denote partial differentiation, and $\dfrac{\mathrm{D}}{\mathrm{D}t}$ differentiation

---

following the fluid, the equation of continuity is

$$\frac{d\rho}{dt} + \frac{d\rho u}{dx} + \frac{d\rho v}{dy} = 0,$$

or

$$\frac{1}{\rho} \frac{D\rho}{Dt} + \theta = 0.$$

$$\therefore \quad \phi = \frac{1}{2\pi} \iint \frac{1}{\rho'} \frac{D\rho'}{Dt} \log r \, dx' \, dy' + \phi_0. \quad . \quad . \quad (4)$$

If ρ_0 be the mean value of the density of the fluid at the cross section σ of a circular vortex, defined by the relation

$$\iint \rho' \, dx' \, dy' = \rho_0 \sigma, \quad . \quad . \quad . \quad . \quad (5)$$

we get

$$\phi = \frac{1}{2\pi} \frac{\sigma}{\rho_0} \frac{D\rho_0}{Dt} \log r + \phi_0.$$

Again, the equation of continuity is

$$\frac{D \cdot \rho_0 \sigma}{Dt} = 0,$$

or

$$\frac{1}{\rho_0} \frac{D\rho_0}{Dt} + \frac{1}{\sigma} \frac{D\sigma}{Dt} = 0.$$

Hence

$$\phi = -\frac{1}{2\pi} \frac{D\sigma}{Dt} \log r + \phi_0. \quad . \quad . \quad . \quad (6)$$

Since σ always refers to a definite column of fluid, there is no difference between $\dfrac{D\sigma}{Dt}$ and $\dfrac{d\sigma}{dt}$.

Let us consider a truly circular cross section of radius a; if the vorticity be the same at any instant at all points of the section, we have, when $r > a$,

$$\left. \begin{array}{l} \phi = -\dfrac{1}{2\pi} \dfrac{d\sigma}{dt} \log r + \mathrm{C}, \\[2mm] \psi = \dfrac{\kappa}{2\pi} \log r + \mathrm{D} \, ; \end{array} \right\} \quad . \quad . \quad . \quad (7)$$

where κ is the strength of the vortex, C and D being

constants.   Also when $r < a$,

$$\left.\begin{aligned}
\phi &= -\frac{1}{4\pi a^2}\frac{d\sigma}{dt}r^2 + C', \\
\psi &= \frac{\kappa}{4\pi a^2}r^2 + D'.
\end{aligned}\right\} \quad \cdots \quad (8)$$

Let the equation of the boundary of the cross section at any instant be given by

$$r = a + \Sigma(\alpha_n \cos n\theta + \beta_n \sin n\theta), \quad \cdots \quad (9)$$

where α_n and β_n are functions of t, independent of θ, and very small compared with a.

Outside the vortex, $r > a$, let

$$\left.\begin{aligned}
\phi &= C - \frac{1}{2\pi}\frac{d\sigma}{dt}\log r + \Sigma(E_n \cos n\theta + F_n \sin n\theta)\left(\frac{a}{r}\right)^n, \\
\psi &= D + \frac{\kappa}{2\pi}\log r + \Sigma(A_n \cos n\theta + B_n \sin n\theta)\left(\frac{a}{r}\right)^n;
\end{aligned}\right\} \quad (10)$$

inside the vortex, $r < a$,

$$\left.\begin{aligned}
\phi' &= C' - \frac{1}{4\pi a^2}\frac{d\sigma}{dt}r^2 + \Sigma(E_n' \cos n\theta + F_n' \sin n\theta)\left(\frac{r}{a}\right)^n, \\
\psi' &= D' + \frac{\kappa}{4\pi a^2}r^2 + \Sigma(A_n' \cos n\theta + B_n' \sin n\theta)\left(\frac{r}{a}\right)^n.
\end{aligned}\right\} \quad (11)$$

Since ϕ and ψ must be continuous when crossing the boundary, we at once get, neglecting products of small quantities,

$$A_n' = A_n, \quad B_n' = B_n, \quad E_n' = E_n, \quad F_n' = F_n. \quad (12)$$

The radial and tangential velocities for points just inside and just outside the vortex must be the same.   Therefore when

$$r = a + \Sigma(\alpha_n \cos n\theta + \beta_n \sin n\theta)$$

$$\frac{1}{r}\frac{\partial \psi}{\partial \theta} + \frac{\partial \phi}{\partial r} = \frac{1}{r}\frac{\partial \psi'}{\partial \theta} + \frac{\partial \phi'}{\partial r}$$

and $\qquad -\frac{\partial \psi}{\partial r} + \frac{\partial \phi}{r \partial \theta} = -\frac{\partial \psi'}{\partial r} + \frac{\partial \phi'}{r \partial \theta}.$

Since products of small terms are neglected, these conditions become

$$\frac{\partial \psi}{\partial r} = \frac{\partial \psi'}{\partial r}, \quad \frac{\partial \phi}{\partial r} = \frac{\partial \phi'}{\partial r}.$$

Substituting the values of ψ, ψ', ϕ, ϕ' from (10), (11) and equating coefficients of $\cos n\theta$ and $\sin n\theta$, we get

$$A_n = -\frac{\kappa}{2\pi na}\alpha_n, \quad B_n = -\frac{\kappa}{2\pi na}\beta_n,$$

$$E_n = \frac{1}{2\pi na}\frac{d\sigma}{dt}\alpha_n, \quad F_n = \frac{1}{2\pi na}\frac{d\sigma}{dt}\beta_n. \quad . \quad . \quad (13)$$

Hence outside the vortex, we have

$$\left.\begin{array}{l} \phi = C - \dfrac{1}{2\pi}\dfrac{d\sigma}{dt}\log r + \Sigma\dfrac{\dfrac{d\sigma}{dt}}{2\pi na}(\alpha_n\cos n\theta + \beta_n\sin n\theta)\left(\dfrac{a}{r}\right)^n, \\[3mm] \psi = D + \dfrac{\kappa}{2\pi}\log r - \Sigma\dfrac{\kappa}{2\pi na}(\alpha_n\cos n\theta + \beta_n\sin n\theta)\left(\dfrac{a}{r}\right)^n. \end{array}\right\} (14)$$

Suppose there are two vortices of strengths κ, κ'; let their cross sections at time t be σ and σ' respectively, the distance between their centres being c. Let the radii of their cross sections be given by

$$\left.\begin{array}{l} R = a + \Sigma(\alpha_n\cos n\theta + \beta_n\sin n\theta), \\ R' = b + \Sigma(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta'). \end{array}\right\} \quad . \quad . \quad (15)$$

Let ϕ, ψ be the functions at an external point for the first and ϕ', ψ' for the second. If (r, θ) and (r', θ') be the coordinates of a point referred to the centres of the two vortices, ϕ and ψ will be given by (14), and

$$\left.\begin{array}{l} \phi' = C' - \dfrac{1}{2\pi}\dfrac{d\sigma'}{dt}\log r' + \Sigma\dfrac{\dfrac{d\sigma'}{dt}}{2\pi nb}(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta')\left(\dfrac{b}{r'}\right)^n, \\[3mm] \psi' = D' + \dfrac{\kappa'}{2\pi}\log r' - \Sigma\dfrac{\kappa'}{2\pi nb}(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta')\left(\dfrac{b}{r'}\right)^n. \end{array}\right\} (16)$$

We shall fix our attention on the second vortex. If $\mathfrak{R}$ be the radial velocity of a point on it and $b\Theta$ the velocity perpendicular to the radius vector, both relative to the centre

of the vortex, we have from (15)

$$\Re = \frac{db}{dt} + \Sigma\left(\frac{d\alpha_n'}{dt}\cos n\theta' + \frac{d\beta_n'}{dt}\sin n\theta'\right)$$
$$- \Sigma n\Theta(\alpha_n'\sin n\theta' - \beta_n'\cos n\theta'). \quad . \quad . \quad . \quad (17)$$

Since products and powers of α_n', β_n' are to be neglected, in (17) we may put

$$\Theta = \frac{\kappa'}{2\pi b^2}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Again

$$\Re = -\frac{\partial\psi'}{r'\partial\theta'} - \frac{\partial\phi'}{\partial r'} - \frac{\partial\psi}{r'\partial\theta'} - \frac{\partial\phi}{\partial r'} - \frac{\kappa}{2\pi c}\sin(\theta' - \epsilon)$$
$$- \frac{1}{2\pi c}\frac{d\sigma}{dt}\cos(\theta' - \epsilon), \quad . \quad . \quad (19)$$

where r' must be put equal to $b + \Sigma(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta')$ after differentiation, and ϵ is the angle made by the line joining the centres of the two vortices with its initial position. If b/c be small, ϕ and ψ can be expressed in terms of r', θ', and ϵ, such as

$$\phi = \mathrm{C} - \frac{1}{2\pi}\frac{d\sigma}{dt}\left[\log c + \sum_{s=1}^{\infty}\frac{(-1)^{s-1}}{s}\left(\frac{r'}{c}\right)^s\cos s(\theta' - \epsilon)\right]$$
$$+ \Sigma\frac{1}{2\pi n}\frac{d\sigma}{dt}\frac{a^{n-1}}{c^n}\left[(\alpha_n\cos n\epsilon + \beta_n\sin n\epsilon)\sum_{s=0}^{\infty}(-1)^s\right.$$
$$\times\frac{n(n+1)\ldots(n+s-1)}{s!}\left(\frac{r'}{c}\right)^s\cos s(\theta' - \epsilon)$$
$$+ (\beta_n\cos n\epsilon - \alpha_n\sin n\epsilon)\sum_{s=1}^{\infty}(-1)^{s-1}$$
$$\left.\times\frac{n(n+1)\ldots(n+s-1)}{s!}\left(\frac{r'}{c}\right)^s\sin s(\theta' - \epsilon)\right],$$

$$\psi = \mathrm{D} + \frac{\kappa}{2\pi}\left[\log c + \sum_{s=1}^{\infty}\frac{(-1)^{s-1}}{s}\left(\frac{r'}{c}\right)^s\cos s(\theta' - \epsilon)\right]$$
$$- \Sigma\frac{\kappa}{2\pi n}\cdot\frac{a^{n-1}}{c^n}\left[(\alpha_n\cos n\epsilon + \beta_n\sin n\epsilon)\sum_{s=0}^{\infty}(-1)^s\right.$$
$$\times\frac{n(n+1)\ldots(n+s-1)}{s!}\left(\frac{r'}{c}\right)^s\cos s(\theta' - \epsilon)$$
$$+ (\beta_n\cos n\epsilon - \alpha_n\sin n\epsilon)\sum_{s=1}^{\infty}(-1)^{s-1}$$
$$\left.\times\frac{n(n+1)\ldots(n+s-1)}{s!}\left(\frac{r'}{c}\right)^s\sin s(\theta' - \epsilon)\right].$$

Substituting in (19) we get

$$\mathfrak{R} = -\Sigma \frac{\kappa'}{2\pi b^2}(\alpha_n' \sin n\theta' - \beta_n' \cos n\theta') + \frac{1}{2\pi b}\frac{d\sigma'}{dt}$$
$$+ \frac{\kappa}{2\pi}\sum_{s=1}^{\infty}(-1)^{s-1}\sin s(\theta'-\epsilon)\frac{b^{s-1}}{c^s}$$
$$\times \left[1 + \frac{s-1}{b}\Sigma(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta')\right]$$
$$+ \Sigma \frac{\kappa}{2\pi n}\frac{a^{n-1}}{c^n}\left[(\alpha_n \cos n\epsilon + \beta_n \sin n\epsilon)\sum_{s=1}^{\infty}(-1)^{s-1}\right.$$
$$\times \frac{n(n+1)\ldots(n+s-1)}{(s-1)!}\frac{b^{s-1}}{c^s}\sin s(\theta'-\epsilon)$$
$$+ (\beta_n \cos n\epsilon - \alpha_n \sin n\epsilon)\sum_{s=1}^{\infty}(-1)^{s-1}$$
$$\left.\times \frac{n(n+1)\ldots(n+s-1)}{(s-1)!}\frac{b^{s-1}}{c^s}\cos s(\theta'-\epsilon)\right]$$
$$+ \frac{1}{2\pi}\frac{d\sigma}{dt}\sum_{s=1}^{\infty}(-1)^{s-1}\cos s(\theta'-\epsilon)\frac{b^{s-1}}{c^s}$$
$$\times \left[1 + \frac{s-1}{b}\Sigma(\alpha_n'\cos n\theta' + \beta_n'\sin n\theta')\right]$$
$$- \Sigma \frac{1}{2\pi n}\frac{d\sigma}{dt}\frac{a^{n-1}}{c^n}\left[(\alpha_n \cos n\epsilon + \beta_n \sin n\epsilon)\sum_{s=1}^{\infty}(-1)^s\right.$$
$$\times \frac{n(n+1)\ldots(n+s-1)}{(s-1)!}\frac{b^{s-1}}{c^s}\cos s(\theta'-\epsilon)$$
$$+ (\beta_n \cos n\epsilon - \alpha_n \sin n\epsilon)\sum_{s=1}^{\infty}(-1)^{s-1}$$
$$\left.\times \frac{n(n+1)\ldots(n+s-1)}{(s-1)!}\frac{b^{s-1}}{c^s}\sin s(\theta'-\epsilon)\right]$$
$$- \frac{\kappa}{2\pi c}\sin(\theta'-\epsilon) - \frac{1}{2\pi c}\frac{d\sigma}{dt}\cos(\theta'-\epsilon).$$
$$\qquad \qquad \cdots \quad (20)$$

The two values of $\mathfrak{R}$ as given by (17) and (20) must be the same; so that we can equate the terms independent of θ' in either expression as well as the coefficients of the sines and cosines of multiples of θ'. The terms independent of θ' simply verify the known result that $\dfrac{d\sigma'}{dt} = 2\pi b\dfrac{db}{dt}$. Equating the coefficients of $\cos\theta'$, we have

$$\frac{d\alpha_1'}{dt} = \frac{\kappa}{2\pi c^2}(\beta_1 \cos 2\epsilon - \alpha_1 \sin 2\epsilon) + \frac{1}{2\pi c^2}\frac{d\sigma}{dt}(\alpha_1 \cos 2\epsilon + \beta_1 \sin 2\epsilon):$$

so that to our degree of approximation $\dfrac{d\alpha_1{}'}{dt} = 0$; similarly we get $\dfrac{d\beta_1{}'}{dt} = 0$. Hence, so far as these terms are concerned, compressibility of fluid makes no change in the motion or shape of the vortices.

Equating the coefficients of $\cos 2\theta'$ and $\sin 2\theta'$, we get to the same degree of approximation

$$\frac{d\alpha_2{}'}{dt} + \frac{\kappa'}{2\pi b^2}\beta_2{}' = \frac{\kappa b}{2\pi c^2}\sin 2\epsilon - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\cos 2\epsilon, \quad . \quad (21)$$

$$\frac{d\beta_2{}'}{dt} - \frac{\kappa'}{2\pi b^2}\alpha_2{}' = -\frac{\kappa b}{2\pi c^2}\cos 2\epsilon - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\sin 2\epsilon . \quad (22)$$

About these equations Dr. Chree remarks : " It is scarcely likely that these equations admit of a complete solution." [*] But the solution of them is of essential importance, for on it depends the determination of the exact change in the form of the cross section. I shall presently show that they can be solved. The terms in α_3, β_3 will involve $\dfrac{a^3}{c^3}$, and thus will be relatively unimportant, so we shall not determine them here.

Let
$$u = \alpha_2{}' + i\beta_2{}', \text{ where } i = \sqrt{-1}. \Big\} \quad (23)$$
$$v = \alpha_2{}' - i\beta_2{}',$$

Multiply the equation (22) by i : the two equations (21), (22) become, by addition and subtraction,

$$\left. \begin{aligned}
\frac{du}{dt} - i\frac{\kappa'}{2\pi b^2}u &= -i\frac{\kappa b}{2\pi c^2}e^{2i\epsilon} - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}e^{2i\epsilon}, \\
\frac{dv}{dt} + i\frac{\kappa'}{2\pi b^2}v &= i\frac{\kappa b}{2\pi c^2}e^{-2i\epsilon} - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}e^{-2i\epsilon}.
\end{aligned} \right\} \quad (24)$$

These are linear differential equations. On integration we get

$$\left. \begin{aligned}
ue^{-i\kappa'\int\frac{dt}{2\pi b^2}} &= u_0 - \int_0^t e^{i\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)}\left\{i\frac{\kappa b}{2\pi c^2} + \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\right\}dt, \\
ve^{i\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}} &= v_0 + \int_0^t e^{-i\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)}\left\{i\frac{\kappa b}{2\pi c^2} - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\right\}dt;
\end{aligned} \right\} \quad (25)$$

where u_0 and v_0 are initial values of u and v. If $_0\alpha_2{}'$, $_0\beta_2{}'$ be the values of $\alpha_2{}'$, $\beta_2{}'$ respectively when $t = 0$, we must have

$$u_0 = {}_0\alpha_2{}' + i_0\beta_2{}', \quad v_0 = {}_0\alpha_2{}' - i_0\beta_2{}'. \quad . \quad . \quad (26)$$

[*] *L. c.* pp. 115, 118.

Now, substituting the values of u and v from (23) in (25), we get by addition and subtraction,

$$\alpha_2' \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) + \beta_2' \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)$$
$$= {}_0\alpha_2' + \int_0^t \left[\frac{\kappa b}{2\pi c^2}\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. - \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt,$$

$$\alpha_2' \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) - \beta_2' \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)$$
$$= -{}_0\beta_2' + \int_0^t \left[\frac{\kappa b}{2\pi c^2}\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. + \frac{b}{2\pi c^2}\frac{d\sigma}{dt}\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt.$$

Solving these equations for α_2' and β_2', we get

$$\alpha_2' = {}_0\alpha_2'\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) - {}_0\beta_2'\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)$$
$$+ \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. - \frac{d\sigma}{dt}\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt$$
$$+ \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. + \frac{d\sigma}{dt}\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt,$$
$$\cdots \quad (27)$$

$$\beta_2' = {}_0\alpha_2'\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) + {}_0\beta_2'\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)$$
$$+ \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. - \frac{d\sigma}{dt}\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt$$
$$- \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa\cos\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.$$
$$\left. + \frac{d\sigma}{dt}\sin\left(2\epsilon - \frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt.$$
$$\cdots \quad (28)$$

In our further investigations, we should remember that if $\epsilon = 0$ when $t = 0$, it can be proved that [*]

$$\epsilon = \frac{\kappa + \kappa'}{2\pi} \int_0^t \frac{dt}{c_0{}^2 + (\sigma + \sigma' - \sigma_0 - \sigma_0')/\pi}, \quad . \quad . \quad (29)$$

where c_0, σ_0, σ_0' are the values of c, σ, σ' respectively when $t = 0$.

The equations (27) and (28) show that there are two distinct types of vibrations of α_2' and β_2' of gradually varying periods given by

$$\frac{\kappa'}{2\pi} \int_0^t \frac{dt}{b^2} = 2n\pi, \quad . \quad . \quad . \quad . \quad (30)$$

$$\frac{\kappa + \kappa'}{\pi} \int_0^t \frac{dt}{c_0{}^2 + (\sigma + \sigma' - \sigma_0 - \sigma_0')/\pi} = 2n\pi, \quad . \quad (31)$$

where n is any integer. Evidently the period given by (30) is shorter than the period given by (31).

Suppose $_0\alpha_2' = {_0\beta_2'} = 0$; since $2\epsilon - \frac{\kappa'}{2\pi} \int \frac{dt}{b^2}$ is always negative, we get

$$\begin{aligned}
\alpha_2' = -\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) &\int_0^t \frac{b}{2\pi c^2}\left[\kappa \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} - 2\epsilon\right)\right. \\
&\left. + \frac{d\sigma}{dt}\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} - 2\epsilon\right)\right]dt \\
+ \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right) &\int_0^t \frac{b}{2\pi c^2}\left[\kappa \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} - 2\epsilon\right)\right. \\
&\left. - \frac{d\sigma}{dt}\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} - 2\epsilon\right)\right]dt, (32)
\end{aligned}$$

so that vibrations are becoming more and more prominent as the vortices are approaching one another; since

$$\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} - 2\epsilon\right)$$

is always real and b/c is also small, the value of α_2' cannot increase indefinitely so that the motion is stable [†].

We shall now proceed to consider some interesting particular cases.

[*] Chree, *l. c.* p. 109.

[†] This point will be clearer from equations (25) which are of the type

$$ue^{if_1(t)} = u_0 - \int_0^t e^{if_2(t)} \mathrm{F}\left(\frac{b}{c^2}\right)dt.$$

Since $\dfrac{dc^2}{dt} = 2\dfrac{d}{dt}b^2$ (Chree, p. 108), the function $\mathrm{F}\left(\dfrac{b}{c^2}\right)$ continually decreases as t increases so that in the limit the integral must be finite.

Case I.— *Two columns of fluids of varying density possessing no vorticity.*

In this case $\kappa = \kappa' = \epsilon = 0$,

so that the equations (27) and (28) become

$$\alpha_2' = {}_0\alpha_2' - \int_0^t \frac{b}{2\pi c^2} \frac{d\sigma}{dt} \, dt,$$
$$\beta_2' = {}_0\beta_2' ;$$

which agree with the result obtained by Dr. Chree. Since $\frac{d\sigma}{dt} = 2\pi a \frac{da}{dt}$, α_2' would increase or decrease according as a was decreasing or increasing. "Thus, if both columns were diminishing in cross section, and so approaching, there would be a decided tendency in both cross sections to assume an elliptical sort of outline, the major axes coinciding with the line joining their centres."

Case II.— *Two rectilinear vortices in an incompressible fluid.*

As previously mentioned, this case has been studied by Sir J. J. Thomson. We shall simply show that his results can be deduced from our more general results. Let ${}_0\alpha_2' = {}_0\beta_2' = 0$; also if n be the angular velocity of the central line, $\epsilon = nt$. Then putting $\frac{d\sigma}{dt} = 0$ in (27) we get, since $\kappa' = \zeta'\pi b^2$, $\kappa = \zeta\pi a^2$,

$$\alpha_2' = \cos\left(\frac{\zeta'}{2} t\right) \int_0^t \frac{\zeta a^2 b}{2c^2} \sin\left(2nt - \frac{\zeta'}{2} t\right) dt$$
$$+ \sin\left(\frac{\zeta'}{2} t\right) \int_0^t \frac{\zeta a^2 b}{2c^2} \cos\left(2n - \frac{\zeta'}{2}\right) t \, dt,$$

or $\quad \alpha_2' = \dfrac{\zeta' a^2 b}{2c^2\left(\dfrac{\zeta'}{2} - 2n\right)} \left\{ \cos 2nt - \cos\left(\dfrac{\zeta'}{2} t\right) \right\};$

similarly from (28),

$$\beta_2' = \frac{\zeta' a^2 b}{2c^2\left(\dfrac{\zeta'}{2} - 2n\right)} \left\{ \sin 2nt - \sin\left(\frac{\zeta'}{2} t\right) \right\}.$$

These will be found identical with the results obtained by Sir J. J. Thomson [*] when we remember that $\zeta = 2\omega$, and $\zeta' = 2\omega'$.

[*] 'Motion of Vortex Rings,' p. 77.

Case III.—A Vortex-pair.

A combination of two equal and opposite vortices is called a "vortex-pair." Put $\kappa = -\kappa'$, $a = b$; then $\epsilon = 0$: we have from (32)

$$
\alpha_2' = \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa'\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.
$$
$$
\left. - \frac{d\sigma'}{dt}\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt
$$
$$
- \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{2\pi c^2}\left[\kappa'\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.
$$
$$
\left. + \frac{d\sigma'}{dt}\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt ;
$$

so that in this case, the vortices have a single type of disturbance of period given by

$$
\frac{\kappa'}{2\pi}\int\frac{dt}{b^2} = 2\pi n.
$$

As a vortex-pair is the two-dimensional analogue of a circular vortex-ring some of the properties of the latter may be deduced from it.

Case IV.—A single vortex parallel to an infinite wall.

This is really a subcase of Case III. For the velocity of the fluid at all points of the plane of symmetry is wholly tangential, so that this plane may be supposed to form a rigid boundary of the fluid on either side of it; thus we obtain the case of a single rectilinear vortex in the neighbourhood of a fixed plane wall to which it is parallel. If h be the distance of the vortex from the wall we get

$$
\alpha_2' = \cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{8\pi h^2}\left[\kappa'\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.
$$
$$
\left. - \frac{d\sigma'}{dt}\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt
$$
$$
- \sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\int_0^t \frac{b}{8\pi h^2}\left[\kappa'\cos\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right.
$$
$$
\left. + \frac{d\sigma'}{dt}\sin\left(\frac{\kappa'}{2\pi}\int\frac{dt}{b^2}\right)\right]dt.
$$

Hence the diameter parallel to the wall is greater if b is increasing, *i. e.* the vortex is receding from the wall and *vice versa*.

University of Calcutta,
    1st September, 1919.

XIII. *On Electrical Disturbances due to Tides and Waves.*
By F. B. Young, *B.A.,* *D.Sc.,* H. Gerrard, *M.Sc., and*
W. Jevons, *M.Sc.**

[Plate II.]

Introduction.

IT was pointed out by Faraday † that when a stream of
water flows through the earth's magnetic field an E.M.F.
should be induced in the water. He carried out some ex-
periments at Waterloo Bridge, lowering metallic electrodes
from the parapet into the tide-way at various distances apart
up to a maximum of 960 feet. Deflexions were obtained
but were very irregular and were in succession referred to
other causes than that sought for, such as difference of con-
centration and of temperature, slight differences in the
plates, etc.

In the course of certain sea experiments which were
carried out during the year 1918, electrical disturbances
were encountered which were definitely traced to movements
of masses of sea-water in the earth's magnetic field. It was
found in fact that the sea is a region of considerable electro-
magnetic activity. The observations in question are com-
municated with the permission of the Admiralty.

I. Theoretical.

A. *E.M.F. induced in Stream of Water.*

A stream of water may be regarded as composed of a
collection of transverse filaments which in their motion cut
through the lines of the earth's vertical magnetic field. An
E.M.F. is therefore induced along each of these filaments
from right to left as one faces down-stream. Assume the
velocity to be uniform throughout the cross section of
the stream. If e is the E.M.F., v the velocity of the stream,
s the length of the filament, and V the earth's vertical field,
then

$$e = Vvs \text{ electromagnetic units or } Vvs \times 10^{-8} \text{ volt.}$$

If V is taken as $0\cdot43$, and v as 50 cm./sec. (*i. e.* about
1 knot), then $e = 2\cdot15 \times 10^{-7}$ volt per cm. per knot.

---

* Communicated by F. E. Smith, O.B.E., F.R.S.
† Bakerian Lecture, Roy. Soc. 12th January, 1832.

This is equivalent to about 2 millivolts per hundred yards per knot.

If the banks and bed of the channel are non-conducting no current will be produced. If the banks are conducting, an electric current will flow from right to left across the stream, returning through the earth. The current density C will reach a maximum when the resistance of the earth return circuit is negligible in comparison with that of the water ; in this case

$$C_{max.} = Vv/\rho \text{ E.M. units,}$$

where ρ is the specific resistance of the water.

B. *E.M.F. acting between Two Stationary Electrodes.*

Let two electrodes A and B be stationed on a line transverse to the stream at a distance s apart and let them be connected by stationary leads through a voltmeter G (Pl. II. fig. 1). Then the E.M.F. e_1 acting from A to B through the voltmeter will depend upon (*a*) the value of e ; (*b*) the current density C. Its value will be given by

$$e_1 = -e + C\rho s.$$

If the resistance of the earth return is infinite so that $C = 0$, then $e_1 = -e$ or Vvs.

If the resistance of the earth return is negligible so that $C = Vv/\rho$, then $e_1 = 0$.

Thus e_1 may have any value between 0 and $-Vvs$.

C. *E.M.F. acting between Two Drifting Electrodes.*

If the electrodes and their connexions are allowed to drift with the tide (as is the case if the former are suspended from a drifting vessel), then an E.M.F. equal to e is induced in the connecting cable in just the same manner as in the water filaments. Thus if e_2 is the E.M.F. measured by the voltmeter,

$$e_2 = e_1 + e = C\rho s.$$

e_1 and e_2 are opposite in sign and are together numerically equal to e. Thus as the resistance of the banks diminishes, the value of e_2 will rise to a maximum value of Vvs.

D. *Effects of non-uniform Velocity and Conducting Bed.*

The conditions assumed in B and C unfortunately never exist in nature, so that any precise verification of the theory

cannot be anticipated. It is not proposed to discuss the disturbing conditions exhaustively, but merely to indicate the general effect of some of them.

The velocity of a stream in general diminishes from the centre towards the banks. In this case

$$E = V v_0 S,$$

where v_0 is the mean velocity, S the total breadth of the stream, and E the E.M.F. acting across it.

Similarly $\qquad\qquad C_{max.} = V v_0 / \rho.$

In making observations in a broad channel, it would in general be necessary to moor the stationary electrodes near one shore. If the observed velocity in the experimental area is v_1, the relation

$$e_1 = -V v_1 s + C \rho s$$

still holds; but C may have a value as great as $V v_0 / \rho$, in which case

$$e_1 = -V v_1 s + V v_0 s.$$

The effect would be to reverse the sign of e_1 and give the impression that the observations disagreed even qualitatively with theory.

The corresponding effect with drifting electrodes would be to give an indicated E.M.F. above the theoretical maximum.

The tidal velocity diminishes not only toward the banks but also toward the bed. Hence v and consequently e has a different value for different strata. Near the centre of the channel the equipotential lines would probably still be vertical, C diminishing with the depth and possibly even reversing in sign in such a manner as to make $(V vs - C\rho s)$ constant. Near the banks C would probably have a vertical component. If the banks were non-conducting the result of the variation of v with depth would be the production of electrical "convection" currents in the water (Pl. II. fig. 2).

If the sea-bed is conducting it will operate in the same way as a stratum of water of zero velocity. Its general effect would be to increase C, thereby diminishing e_1, and increasing e_2. It would also probably tend to reduce the effects at a distance of non-uniform velocity.

Other disturbing factors are irregularities of the shores producing local variations in the direction of the tidal stream.

E. *Wave Motion.*

Electrical disturbances are produced by wave-motion similar to those due to tidal motion. If a series of regular undulations passes over a body of water, each water particle, according to the trochoidal theory, moves with uniform motion in a circular path whose diameter, for a particle at the surface, is equal to the height h of the wave from trough to crest. Hence water filaments parallel to the wave-crests will revolve in cylindrical paths passing to and fro across the lines of the earth's field. The effective strength F_1 of the earth's field will in this case vary from the total field F $(= 0.47)$ for waves propagated in a northerly or southerly direction to V $(= 0.43)$ for waves propagated in an easterly or westerly direction. The effect of the oscillations will be to produce oscillating E.M.F.'s in the water in a direction at right angles to the direction of propagation.

If W is the velocity of propagation and l the wave-length,

$$W = \sqrt{gl/2\pi}.$$

If t is the period of oscillation and v the speed of a water particle taken near the surface,

$$v = \pi h/t.$$

But $$t = l/W = \sqrt{2\pi l/g},$$

whence $$v = h \sqrt{\pi g/2l};$$

or if k is the ratio l/h,

$$v = \sqrt{\pi g h/2k}.$$

Hence if e is the amplitude of the E.M.F. induced in a water filament of length s,

$$e = F_1 s \sqrt{\pi g h/2k}.$$

According to the observations of Sir Wm. White [*] an average value for k is 20. Thus for a wave whose height has the very moderate value of 10 ft. $(= 305$ cm.$)$, $v = 153$ cm./sec. or about 3 knots; that is, the induced E.M.F. when at a maximum will be comparable with that due to a 3 knot tide. In the case taken,

$$e = 6 \text{ to } 6.5 \text{ millivolts per 100 yds.}$$

As in the case of the tidal disturbances, e is the upper limit both of the amplitude e_1 of the E.M.F. acting between two stationary electrodes and of the amplitude e_2 of the E.M.F. acting between two electrodes whose connecting leads are oscillating with the water.

[*] 'Manual of Naval Architecture.'

II. Experimental.

A. *Observations with Moored Electrodes.*

An opportunity occurred of making some observations with electrodes laid outside the entrance to Dartmouth Harbour. The electrodes found suitable for the purpose were of silver coated electrolytically with a film of silver chloride ; such electrodes were tolerably free from polarization effects. The positions of the electrodes are shown in Pl. II. fig. 3. Two selected electrodes were connected directly to a Paul recording galvanometer (" temperature recorder ") which acted as the voltmeter, and with this simple apparatus records were made continuously for prolonged periods. These records are reproduced in Pl. II. figs. 4–6. The recorder gives a dot about every two minutes on a paper roll, and the curves are obtained by joining these dots by hand. Owing to the intermittent character of the record the curves do not accurately represent the variations of short period such as those due to waves. The irregularities, however, which are introduced by such variations give a fair idea of the magnitude of those fluctuations.

Pl. II. fig. 4 shows a record made during the period 9.ix.18 to 14.ix.18, taken with electrodes M_1 and C_1 approximately 2000 yards apart. The record exhibits undoubtedly an E.M.F. varying periodically and having a period equal to that of the tide. The fact that the E.M.F. indicated does not reverse in sign has no significance, as a pair of electrodes generally exhibits a slight electrolytic E.M.F. which displaces the zero. The maximum change of E.M.F. between trough and crest is about 37 millivolts, so that the amplitude of the oscillation is 18·5 millivolts. It is impossible to make an accurate comparison between this figure and any calculated value, as there are so many unknown factors to take account of. For example, the flood tide runs practically parallel to the cable over most of its length and the ebb tide crosses it nearly at right angles. Again, the length of cable subject to tidal action is probably only about 1000 yards. It may be pointed out, however, that the observed E.M.F. is of the same order as the maximum E.M.F. to be expected from a 1 knot tide flowing between electrodes 1000 yards apart.

The record shows very markedly how the amplitude of the electromagnetic tide diminishes from spring tide to neap.

A remarkable feature of the record is the relation of the times of high and low water to the curve, these times

corresponding nearly with the maximum and minimum
E.M.F.'s.   Since these are times of slack water they should
correspond with the mean E.M.F. (*i. e.* zero E.M.F. if due
allowance is made for the displacement of the zero by the
intrinsic E.M.F. of the electrodes).   It appears therefore
that the "electromagnetic" tide is about 90° out of phase
with the sea tide.

During the period of observation a variety of weather was
experienced, and the corresponding variation in the nature
of the curve gives evidence of wave-action.   There are,
however, disturbances which are also mainly associated with
rough weather, but are obviously of too long a period to be
produced by wave-motion.   They are often of considerable
amplitude and may be due to local currents caused by the
wind.

Pl. II. fig. 5 represents a record obtained with electrodes
M_1 and M_2 which were about 200 yards apart.   This record
shows even more markedly than fig. 4 the progressive
diminution in amplitude of the electrical disturbance corre-
sponding with the diminution of the tidal amplitude.   The
records in this respect agree with the tide-tables which
indicate that the spring tide on 22.ix.18 was about 10 per
cent. higher than that occurring on 7.ix.18.   The maximum
amplitude of about 7 millivolts, or 3·5 millivolts per 100 yds.,
would correspond to the maximum E.M.F. $(-e)$ producible
by a tide of about 1·7 knots.   As in fig. 4 a phase lag is
exhibited between the electrical disturbance and the tide.

The first 12 hours of the record show very markedly
disturbances due to wave-motion.   The dotted part of the
curve is only an approximate representation of the record,
the dots being too irregularly scattered to be joined into a
curve.

Pl. II. fig. 6 represents a record taken with two electrodes
moored vertically one above the other.   The electrodes were
lashed on a rope which was held between a sinker on the
bottom and a canvas float on the top.   The record shows no
definite sign of a tidal variation, though faint suggestions of
such are perceptible.   It should be observed, however, that
with electrodes so close together any probable tidal variation,
even on the most favourable assumptions, would be small
compared with the short period disturbances.   These short
period disturbances are obviously, largely at least, due to
wave-motion.

The differences of phase mentioned in connexion with
Pl. II. figs. 4 & 5 strongly suggest that in the value of
$e_1 (= -e + C\rho s)$ the term $C\rho s$ plays a predominant part and

that C is determined less by the local tidal flow than by the general flow in that part of the English Channel. A difference of from 2 to 3 hours is known to exist between high or low water at Dartmouth and the turn of the tide at the Homestone Buoy (fig. 3), and the observed difference of phase may perhaps thus be accounted for.

B. *Experiments with Drifting Electrodes.*

Two electrodes were towed in tandem behind a vessel, the near electrode being about 60 yards and the distant electrode 160 yards astern. In this way the electrodes were conveniently extended along an approximately horizontal line at a distance of about 100 yards apart; and the orientation of this line could be readily altered by changing the course of the vessel. The vessel steered a course which may be termed a "tidal square." This simply means that she followed an approximately square course relatively to the water such that two sides of the square were parallel to the direction of tidal flow; owing to side drift the actual course would be as shown in fig. 7 B (Pl. II.). The electrode cables were connected to a Unipivot galvanometer, specially balanced for use at sea, which served as the voltmeter. Readings were taken at intervals of 5 seconds throughout the run and were plotted as shown in fig. 7 A, the deflexion being plotted as positive when it indicated the distant electrode to be at a higher potential than the near electrode. As a rule at least one side of the square was repeated as a test of the constancy of the electrodes.

The direction and strength of the tide were stated by the navigating officer, generally by observation of the wash past a buoy.

Examining the records reproduced in Pl. II. figs. 7, 8, & 9, we observe that though the reading is by no means constant even on a straight course, yet a distinct change of zero occurs as the vessel takes up a new course. The records were analysed as follows. Let the mean readings of the galvanometer (reduced to millivolts) be d_1 with the tide, d_2 across the tide from right to left, d_3 against the tide, d_4 across the tide from left to right. Then the transverse component of the apparent potential slope in the sea from right to left is $(d_2 - d_4)/2$ millivolts per 100 yards, whilst the component in the direction of flow is $(d_1 - d_3)/2$ millivolts per 100 yards. From these rectangular components the actual direction and magnitude of the apparent slope e_2 were obtained. The results thus obtained for 11 tidal squares are

given together with navigator's observations. e is the earth-induced E.M.F. calculated from the observed tidal velocity on the basis of 2 millivolts per 100 yards per knot. On some occasions simultaneous records were made with two independent pairs of electrodes towed side by side. In such cases both results are tabulated.

The experimental conditions were not sufficiently satisfactory to warrant any close analysis of the results. The two chief drawbacks were (a) the absence of any proper means of measuring tidal velocities; (b) the doubtful suitability of the Dartmouth waters for initial experiments owing to the uncertain nature of the tides. In some cases the navigator's observations were found to be at variance with the tide-tables, and the discrepancy may have been due to eddy effects or wind disturbances.

Some idea of the degree of consistency of the electrical measurements may be gained from the bracketed results under the heading "observed E.M.F." It will be seen in such cases that the directions agree to within a point (about $10°$) whilst the values of e_2 agree to within $0·7$ millivolt.

In regard to direction the table shows a tolerably good general agreement between "estimated" and "observed" directions, only 2 (Nos. 7 & 8) out of the 11 records giving the wrong sense of direction.

In regard to the values of e_2, it will be observed that they are of the same order as the corresponding values of e. According to the simple theory e_2 may be less than e, but should not be greater. On the average e_2 is rather less than e and only in one case (No. 3) is it definitely greater. No definite evidence of a constant ratio between e_2 and e is perceptible even for records made in the same locality. It must, however, be pointed out that the probable errors in e and e_2 would doubtless mask any such relation if it exists.

Further records of tidal squares are given in Pl. II. figs. 8 & 9.

Fig. 8 shows a much steadier zero line on each course than in fig. 7 A.

Fig. 9 is of interest as showing very clearly the electrical disturbances due to wave-motion. Theory would predict that the electrical oscillations would occur mainly in a direction transverse to the direction of propagation, so that they would be most effectively registered by the electrodes when the sea is abeam. On the occasion in question the tide and wind were opposed, creating a rather rough beam sea when the vessel was crossing the tide.

TABLE.

No.	Place	Date (1918).	Time (G.M.T.).	Observed tide. Direction (θ_1).	Strength. Knots	e. millivolts	e_2. millivolts	Observed E.M.F. Estimated direction of tide (θ_2).	Difference between θ_2 & θ_1.
1. (a)	Start Bay. Bell Buoy near Skerries.	25 July	9.14 A.M.	N.E. by E. (55°)	1	1 to 1·5	{ 0·7 / 0·8	{ E. by N. (80°) / E. by N. (80°) }	25°
(b)	,,								
2.	,,	,,	1.20 P.M.	S.W. by W. (235°)	1	2	3·4 / 1·6	W. by N. (280°) / S.W. by W. (235°)	0
3.	,,	,,	2.18 P.M.	S.W. by W. (235°)	1	2	3·4	W. by N. (280°)	45°
4. (a)	,,	27 July	10.54 A.M.	N.E. (45°)	1¾	3·5	{ 0·4 / 0·5	{ E. by N. (90°) / E. by N. (80°) }	40°
(b)	,,								
5. (a)	,,	,,	1.55 P.M.	S.W. by S. (215°)	1¾	3·5	{ 2·4 / 2·7	{ W. by N. (270°) / W. by N. (260°) }	50°
(b)	,,								
6.	,,	,,	3.5 P.M.	S.W. by S. (215°)	½	1	3·2	W. (270°)	55°
7. (a)	Start Bay, outside entrance of Dartmouth Harbour	29 July	3.7 P.M.	W. by S. (260°)	1 to 1½	2 to 3	{ 1·4 / 0·8	{ E. by N. (80°) / E. by N. (80°) }	180°
(b)	,,								
8.	Start Bay. Bell Buoy near Skerries.	28 Aug.	9.11 A.M.	N.E. (45°)	½	1	1·5	W.N.W. (295°)	120°
9.	,,	,,	1.14 P.M.	N.E. by E. (55°)	½ to 1½	1 to 1·5	0·4	N. by W. (350°)	55°
10.	Off Lulworth and St. Albans Head.	21 May	3.0 P.M.	E. (90°)	¼	0·5	2	E. (90°)	0
11. (a)	Off Portland (eastward)............	10 Oct.	3.33 P.M.	S.W. (225°)	1½	3	{ 3·5 / 2·8	{ S.W. by W. (235°) / S.W. by W. (225°) }	10°
(b)	,,								

A marked increase is observable in the roughness of the zero line under these conditions. The fluctuations in the E.M.F. are frequently from 1 to 1·5 millivolts indicating an oscillating E.M.F. e_2 with an amplitude of from 0·5 to 0·75 millivolts. It should be explained that the galvanometer was observed on open circuit for a short time in order to ensure that the recorded deflexions were electrical and not mechanical in origin.

C. *General Discussion of Experimental Results.*

In the experimental work recorded the examination of the electrical effects of waves and tides was only incidental to objects of more immediate practical importance. In a systematic observation certain obvious improvements in the methods are desirable.

(*a*) Two moored electrodes will indicate the direction of the E.M.F. recorded only to within 90° and will measure only the component of the E.M.F. parallel to the line between them. For complete measurements it is necessary to have electrodes stationed on lines at right angles to one another giving simultaneous records.

(*b*) It is desirable that the experiments with moored and towed electrodes should proceed simultaneously and in the same area in order that the results may be correlated.

(*c*) The experimental conditions would be simplified if an area were chosen near a coast-line comparatively free from indentations. Under such conditions refinements of the methods of measurement would probably prove profitable.

The results obtained clearly indicate the existence of periodic E.M.F.'s in the sea whose period and magnitude show them to be the result of earth-induction in tidal currents. The high values obtained with drifting electrodes indicate that the E.M.F.'s due to purely local induction which are measured by moored electrodes must be small, and that the E.M.F.'s actually measured by these electrodes are due principally to more remote tidal currents ; this view is supported by the phase differences observed. This merely means that the tidal " dynamo " is almost completely shorted by the earth return, a condition which might be expected. The failure of Faraday to detect any tidal E.M.F. in the Thames, in so far as it was not due to the disturbing conditions mentioned by him, may have been due to such an effect ; for assuming a nearly uniform velocity over the cross-section of the stream, an earth return of low resistance and an absence of currents generated at a distance, the potential would be sensibly uniform across the stream.

The observations at Dartmouth suggest that each locality may be subject to an "electromagnetic tide" approximating in regularity to the sea tides. Whether hydrographic observations of these would lead to any practical applications is doubtful; much would depend upon the degree of consistency of the data. It is, however, conceivable that a ship might utilize the phenomenon as a means of measuring her drift during thick weather.

XIV. *Note on the Secondary Spectrum of Hydrogen. By* Megh Nad Saha, *D.Sc., Lecturer on Physics, University College of Science, Calcutta*[*].

IN recent years the problem of the Secondary Spectrum [†] of hydrogen has again come to the forefront, on account of the interest which attaches to it with regard to Bohr's theory of quantum emission of spectral lines. Theoretical physicists are inclined to ascribe the Secondary Spectrum to the molecule of hydrogen, the Primary Spectrum being due to the atom. On the other hand, many experimental physicists are by no means satisfied by the explanation offered, but on the basis of the experiments of Fabry and Buisson [‡], the opinion is sometimes expressed that at least a part of the secondary spectrum may be due to the H-atom.

But a closer perusal of the above-mentioned works of Fabry and Buisson shows that probably proper interpretation has not been put on their experimental results. In their experiments the mass of the radiating centres was calculated from the limit of visibility of the line in question in the Fabry-Perot interferometer according to the formula

$$\frac{\Delta}{\lambda} = A \sqrt{\frac{\overline{M}}{\theta}},$$

where Δ = limit of visibility, M = weight of the radiating centre in terms of the H-atom as unity, θ = absolute temperature, A is a constant.

Fabry and Buisson found that for the red line $H_a = 6563$, $\frac{D}{\lambda} = 50,000$, while for a secondary line (not mentioned) $\frac{D}{\lambda} = 72,000$.

* Communicated by the Author.
† For example, Merton, Proc. Roy. Soc. Lond. vol. xcvi. p. 382. Lenz, *Ber. d. Ph. Gesellschaft*, pp. 632–643 (1919).
‡ Fabry and Buisson, *Journal de Physique*, pp. 435–445 (1912).

The value of A was taken from theoretical papers by Lord Rayleigh [*] and Schönrock [†]. Thus they obtained $M = 1$ for the secondary line (approximately), but a much smaller value—probably ($\cdot 5$)—for the H_α-line.

Since the second value is impossible, they concluded that in both cases $M = 1$, the value of Δ for H_α being considered unreliable, because H_α is a double line, and it is rather difficult to determine its limit of interference.

But it has been shown in a paper published in the Physical Review [‡] that the value of A is subject to fluctuations depending upon the silvering of the mirrors, the definition of visibility, and other causes. In the papers of Lord Rayleigh and Schönrock the value of A is calculated from two interfering beams only, while in the Fabry-Perot apparatus we have to do with an infinite number of interfering beams. Hence no absolute reliance can be placed upon a theoretically deduced value of A.

Since for a certain particular apparatus A has a definite value, the best interpretation of Fabry and Buisson's results seems to be the relative estimation of the masses of the radiating centres in the two cases. We thus have

$$\sqrt{\frac{M_2}{M_1}} = \frac{72,000}{50,000} = 1\cdot4, \quad \text{or} \quad M_2 = 2M_1 \text{ (approximately)};$$

i. e., the mass of the radiating centre responsible for the emission of a secondary line is twice the mass of the radiating centres emitting H_α. In other words, according to the interpretation given here, the experiments prove the contrary of what is generally deduced from them—viz., if the H_α-line is emitted by an H atom, the secondary lines are emitted by the H molecule.

It is to be hoped that the problem may be again experimentally attacked.

On the theoretical side the difficulty is not only mathematical, but also physical. We have not as yet any mechanical model before us visualizing in a satisfactory manner the coupling of two Bohr atoms into an H-molecule. In the Bohr-Debije model the individuality of the component atoms is entirely lost [§]. This is a serious theoretical objection which has not yet been overcome.

Nicholson [‖] has already calculated, on the basis of Bohr's

[*] Lord Rayleigh, Phil. Mag. vol. xxvii. (1889).

[†] Schönrock, *Ann. d. Physik,* vols. xx. & xxii. (1906).

[‡] Saha, Phys. Rev., Dec. 1917.

[§] Lenz, *Ber. der Deutsche Physikalische Gesellschaft,* pp. 632–643 (1919).

[‖] Nicholson, Month. Not. Roy. A. S. vol. lxxix. (1919).

theory, the radiation from a Bohr model, consisting of a single nucleus and two electrons. But none of the calculated lines agree with any of the observed secondary lines.

I tried to calculate the radiation from a system consisting of two fixed positive centres*, and one electron, on the lines of Sommerfeld's generalization of Bohr's theory. It would give, it was expected, the radiation from a positively charged H-atom. The complete mathematical solution of this problem has already been given by Jacobi †. The quanta-integrals come out in terms of elliptic integrals of the first, second, and third kind, but it has not yet been found possible to extricate the energy out of these functions, and express it in terms of the quanta-numbers.

XV. *On the Measurement of Time and other Magnitudes.*

To the Editors of the Philosophical Magazine.

SIRS,—

OWING to illness I have only just seen Dr. Silberstein's criticisms of my remarks (Phil. Mag. xxxix. p. 366, March 1920). Since my statements were very much condensed. perhaps you will allow me a few words in reply.

(1) I do not deny that many instruments for measuring time employ the assumption that some motion is uniform. But it should be remembered that such instruments do not include the pendulum-clock and the tuning-fork; the introduction of the former, replacing methods involving an assumption of uniform motion, is probably the most important advance that has ever been made in the measurement of time.

(2) What I deny is that there is any *experimental* ground for the assumption made, except that the results of making it are in accordance with measurements of time as a fundamental magnitude, in the manner sketched in my paper.

There may be theoretical grounds for the assumption ; that

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* This incomplete paper was communicated to the Indian Science Congress held at Bombay in January 1919. I find in the January No. of the Phil. Mag. that Dr. Silberstein has traversed the same ground and arrived at identical mathematical results, but this paper likewise contains no reduction of the energy-expression to quanta numbers.

† Jacobi, *Vorlesungen über Mathematik*, Article 28-30. Appel, *Traité de Mécanique Rationelle*, Tome ii. p. 407 *et seq.*

is to say, it may happen that unless the assumption is true, some generally accepted theory must be false. But why is the theory generally accepted? Surely because it predicts true laws. But these laws will involve measured magnitudes: how are we to know that the laws are true unless we can measure the magnitudes independently of any assumption that they, or the theory from which they are deduced, are true? An attempt to found upon theory the measurement of so basic a magnitude as time leads to a circular argument. Of course, scientific truth is so different from mathematical truth and capable of so many degrees that an argument formally circular may not be really valueless. But if it can be avoided, so much the better. I maintain that measurement of all fundamental magnitudes can be stated as a purely experimental process without any appeal to theory.

(3) In reply to Dr. Silberstein's question, distance is not a fundamental magnitude; but it is very closely connected with the length of a straight rod, which is a fundamental magnitude and measured by a process precisely similar to that which I sketched for weight and period of time.

(4) Temperature is certainly not a fundamental magnitude; it cannot be added. From two bodies at temperature 1, there cannot be produced by any physical means a body at temperature 2. The international hydrogen scale is purely arbitrary—as arbitrary as that of the mercury-in-glass thermometer; it does not express any physical laws. But if hydrogen were a perfect gas, temperature on that scale would be a pure derived magnitude, like density or viscosity. That is to say, it would be a constant in a numerical law relating fundamentally measured magnitudes.

(5) Lastly, when I said that my observations were " elementary," I used the word in its proper sense to mean that only the elements of the matter, and not the complexities, were considered. If Cayley has really asserted anything contrary to my contentions—I do not think he has,— I would reply that even the giants are liable to error, especially if, being mathematicians, they discourse upon experimental physics.

<div style="text-align:right">

Yours faithfully,
NORMAN R. CAMPBELL.

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XVI. *On the Propagation of Electromagnetic Waves round the Earth.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper under the above title which appeared in the issue of the Phil. Mag. for Sept. 1919, p. 365, I derived an expression [(15) page 377] for the current, generated in a receiving antenna for wireless telegraphy, as a function of the constants of a transmitting station and of the angular distance between transmitter and receiver. This theoretical formula is based on the assumption of a perfectly insulating atmosphere ($\sigma = 0$, $\epsilon = 1$), and, as an instance, it was compared with Dr. Austin's measurements of the received current at Darien due to the waves sent out by the Nauen station. Unfortunately in this application of Dr. Austin's data to our formula (15), a numerical oversight crept in which Dr. G. Vallauri (Livorno) was kind enough to point out to me in a private letter.

The correct value yielded by (15) for the received current is $I_2 = 1.9 \cdot 10^{-10}$ amp. instead of $0.6 \cdot 10^{-12}$ amp. The value obtained experimentally was $1.3 \cdot 10^{-6}$ amp., hence, in this instance, the theoretical value for the received current is about *seven thousand* times too small.

If, as another instance, we apply (15) to Dr. Austin's measurements of the Eilvese-Darien transmission, we find the theoretical value for the received current to be *twelve thousand* times too small.

Hence, notwithstanding this numerical oversight, the conclusion arrived at in my paper, that, assuming the atmosphere to be a perfect insulator ($\sigma = 0$, $\epsilon = 1$), one obtains values for the wave-amplitude at a big distance from a transmitting station in flagrant contrast with the experiments, remains valid.

Yours faithfully,

BALTH. VAN DER POL, jun.

Physical Laboratory,
Teyler's Institute,
Haarlem (Holland).
12. 4. 20.

XVII. *Notices respecting New Books.*

Applied Aerodynamics. By LEONARD BAIRSTOW, F.R.S., C.B.E.; expert adviser on Aerodynamics to the Air Ministry, &c. Longmans, Green & Co. 1920. 560 pages.

THE engineer and mechanical constructor will appreciate this book highly for the numerical information provided by the author, in official contact with the collection of confidential data; this information is given clearly to the eye in the plentiful supply of diagrams and tables, result of experiment in the wind channel, and up in the laboratory of the air.

And the practical engineer will not be able to take up the usual ungrateful attitude, and disparage the theory preliminary to an ascent from the ground; but he will learn to realise the importance of calculation required to ensure the stability, and the possibility of descent without a crash.

In the early days the enthusiast was prepared to take this risk of his neck and life, if only he could fly for once; and the difficulty he dreaded most was in the preliminary run required before leaving the ground in taking off. This difficulty was soon overcome with the extra power provided, and a flying start comparatively short is found to suffice.

But when he flies a swift powerful large heavy machine, the landing speed mounts up to a dangerous extent; and one of the chief problems of Flight awaiting solution is how to diminish this landing speed as much as possible, by the artificial aid of aileron and air break.

Flight is hardly over ten years old, and may be said to date from Blériot's Channel crossing. A preliminary chapter of historical interest could give us in a score of pages the chief events leading up to success and Victory.

The first essential was an engine of small weight per horse-power, and here the motor car came in, and made the flying machine a present ready made of the petrol motor, internal combustion.

Maxim could not succeed, with all his mechanical skill in the reduction of the weight of engine to about half a pound per horse-power, as he was obliged to take a steam-boiler up in the air as well, and here he was beaten.

Gyroscopic and heeling effect were bugbears feared in the early days, to be corrected by a brace of screws, right and left handed. But the Vickers-Vimy Atlantic machine to be seen today in the Science Museum has both screws left-handed; the advantage of interchangeability outweighs any of these imaginary complaints. Colonel Cody might easily have left the ground at Farnborough if he had not been obsessed with these ideas, and had coupled up his engine into the direct drive of a single screw.

In an instructional treatise a short initial chapter would be

acceptable, to give the elementary theory of Flight on the simplest assumptions, of flat plane wings, and the simple sine law for lift, based on the quadratic law for normal incidence. The accompanying corresponding lines of lift and drag could find a place on the diagrams here of actual experiment, to show the extent of divergence, and how slight this may prove.

The standard law assumed in the treatise for normal air resistance at a speed of V, f/s, is taken at $0 \cdot 00237 \, V^2$, lb/ft^2, and then this is multiplied by a coefficient, K_L or K_D, to obtain the lift and drag. This law would appeal better if written $23 \cdot 7 \left(\dfrac{V}{100} \right)^2$, lb/ft^2, meaning that the resistance is $23 \cdot 7$ lb/ft^2 at a normal velocity of 100, f/s; either as measured directly in a wind channel, or inferred on the quadratic law from measurement at any other velocity.

There would be no need then for any mention of air density, or explanation of the dreadful confusion of poundal and slug: send them both to oblivion, to join spouds, celoes, boles, and all such dynamical Esperanto-Volapuk, superseded today by the rational Hospitalier system, keeping the units and dimensions always in sight.

Weighing the Air was a favourite experiment in the early days of the Royal Society, in which Charles II took a great interest.

But no measurement of air density is ever made in an aeronautical workshop, but the air thrust is measured directly, and the speed of the air current. The solecism of lbs should not be allowed to appear under official sanction as abbreviation of pounds ; lb is short for the Latin word *libra*, plural *libræ*.

Applied Aerodynamics is a book indispensable to the constructor and lecturer instructor, prepared by an authority with access to all official information known on the subject, and a pioneer himself in theoretical development.

But not a book for the pilot to take up into the air, to consult for the reason of every step ; as counselled by a well-known authority on the teaching of Arithmetic. Intrepid on his bicycle it is not the advice he would give a novice, but rather to let himself go by pure instinct, and inconsiderately by reflex action.

The Theory of Determinants in the historical order of development. By Sir Thomas Muir. Vol. III. The period 1861–1880. Macmillan & Co. 1920. 500 pages.

In the two previous volumes, vol. I carries the theory of general and special determinants up to 1841 ; and vol. II covers the period 1841 to 1860.

The work is an obvious labour of love, and to be completed in a fourth volume. It will prove a handbook indispensable to the mathematician who has occasion to pursue this branch of Pure Analysis.

The subject was cultivated by C. L. Dodgson, who called the Determinant a Block, and published a work with this title, which did not reveal his identity with the author of 'Alice in Wonderland.' Another standard work on Determinants is by R. F. Scott, Master of Saint John's College, Cambridge.

In these days of the Ramification of Research all over the world, a book of this kind is invaluable to the worker in putting him immediately in the fore front of the progress achieved already ; to prevent him from overlapping, and losing time over repetition of what has been done before.

The Physiology of Vision, with special reference to Colour-Blindness. By F. W. Edridge-Green. G. Bell & Sons. 12s. net.

Card Test for Colour-Blindness. By F. W. Edridge-Green. G. Bell & Sons. 25s. net.

The subject of colour-vision, though largely a branch of physiology, is of peculiar interest to the physicist. Having followed the rays of light from an object as far as the retina, he cannot abandon them there without curiosity as to the machinery by which they are perceived. In the text-books of physics, however, treatment is usually restricted to a brief exposition of the Young-Helmholtz theory of colour-vision ; and it speaks much for the respect inspired by these great names that, inadequate as the theory is, it is scarcely ever criticised. Outside the circle of text-book writers it is becoming generally known that the three-colour theory has failed to represent the facts accumulated during the past thirty years, mainly by the efforts of Dr. Edridge-Green, whose name is inseparably connected with the subject. Owing, however, to the fact that his work is mostly contained in short papers scattered over many years in a large number of publications, the points established by him in his experiments, observations, and criticisms are not familiar to many who would like to study them. The book under notice, which will be welcomed by all interested in the problems of vision, should remedy this state of affairs, for it presents concisely, in a very well produced volume, the views developed by the author on the physiology of vision in general.

The artificiality of the three-colour theory is so obvious that we venture to suggest that nothing but the eminence of its founders and supporters has kept it alive so long. From the anatomical point of view it has nothing to commend it, for all attempts to demonstrate three kinds of nerve elements, or retinal elements, have failed signally. From the physical and physiological point of view Dr. Edridge-Green has brought forward a series of criticisms which we have never seen successfully refuted. In his chapter on the simple character of the yellow sensation—a sensation which on the Young-Helmholtz theory should, of course, be resolvable into red and green—he adduces sixteen pieces of evidence which, whatever interpretation they may receive, seem

to us conclusively against any three-colour theory. The cases of colour-blindness which he records provide what will be to many the most convincing refutation of the theory so long accepted. The shortening of the red—or violet—end of the spectrum without defective hue perception ; the great variety of defects of colour-vision, which on the Young-Helmholtz theory should fall into three definite classes ; the peculiar and characteristic mistakes of hue perception made by the colour-blind, detailed at length in the book—all are irreconcilable with the three-colour theory of vision. Of course, by letting the form of curve chosen to represent each of the three sensations vary from case to case, and by making the nature of the curve complicated enough, the theory might be adapted to meet some of these objections, but in the process of adaptation it would lose all its force. Dr. Edridge-Green's own theory of vision falls into two main parts—one dealing with the machinery of reception, and the other with the machinery of perception. As regards the retina, he believes that the cones alone receive and transmit the message, but they are sensitized by the visual purple secreted by the rods, and liberated into the retinal fluid in response to light stimulation. Unless so sensitized the cones are irresponsive. This very simple hypothesis explains admirably all the peculiarities of foveal vision, and a whole series of observations, including remarkable entoptic phenomena, for which we must refer the reader to the book. As regards perception, the author holds that the power of distinguishing colours is one that has evolved from the power of distinguishing light alone up to our present recognition of seven colours. He has shown that a person of acute vision maps out twenty-seven patches in the spectrum, each of which appears to him to be monochromatic, and he regards this number as expressive of the efficiency of the colour-perceiving centres of the brain. The less developed these centres the smaller the number of " perceptively " monochromatic patches, and the more colour-blind the person. Some of these patches will, of course, in all cases be named as of the same colour as their neighbours, though differing in hue. Dr. Edridge-Green in his classification of the colour-blind distinguishes the heptachromic, whose colour perception is acute and who sees seven colours in the normal spectrum ; the hexachromic, who sees six colours ; pentachromic, who sees five ; and so on down to the dichromic, the worst class of colour-blindness usually met with, one variety of whom see the spectrum as blue one end and red the other, with a grey band in the middle. He does not attempt to explain the precise mechanism of differentiation. Dr. Houstoun, however, has recently put forward an interesting mathematical theory which has led him to results in harmony with Dr. Edridge-Green's view.

Dr. Edridge-Green's theories seem to us to accord better than any so far put forward with the present knowledge of the subject. Whatever may be the ultimate judgment on this point, there can be no question as to the value of his experiments and observations.

Many of these, detailed in the book, can be repeated with the simplest means. A variety of experiments of the greatest interest on simultaneous and successive contrast, positive and negative after-images, flooding, and similar effects demand nothing but a few pieces of white and coloured paper and the like. The conditions necessary for observing the various entoptic phenomena are also carefully recorded, so that for the experimenter in vision the book is invaluable. There is an excellent discussion of binocular vision.

On the practically very important subject of testing for colour-blindness our author has naturally much to say, having devoted many years to devising tests for the Board of Trade and other bodies. He has shown that the old wool test passes fifty per cent. of the colour-blind! His colour perception lantern, now the official test at the Admiralty and elsewhere, is probably the best device of the kind, but it is expensive and bulky. The new card test just devised by him, and issued by the publishers of the book, is extremely handy and simple to use, while at the same time it is reliable. The ingenious design renders it impossible for the examinee to rely on anything but colour discrimination for reading the cards, which are faithfully reproduced by lithography. We have used the test, and judge that it will be universally adopted where a quick, reliable, and portable test is required.

Mesures Pratiques en Radioactivité. Par W. MAKOWER et H. GEIGER. Traduit de l'anglais par E. PHILIPPI. Gautier-Villars.

THIS is a translation of the well-known little book of Makower and Geiger, published in this country in 1912 by Longmans. Judging by the places in which we have checked it, the work of rendering it into French has been done carefully and adequately. No alterations or additions seem to have been made.

Elements of Vector Algebra. By L. SILBERSTEIN.
Longmans, Green & Co. Price 5s. net.

THIS little book is an account of the elements of vector algebra up to and including the meaning and use of the linear vector operator. The convenience of vectors in connexion with the mathematics of physical problems is becoming more widely realized every day; and we think that there is a real need for a booklet of this character, giving in a few pages just what is necessary as preliminary information for reading any book in which the method is employed. Dr. Silberstein's work is too well known to readers of this magazine for there to be any need for us to speak of the soundness or elegance of the exposition.
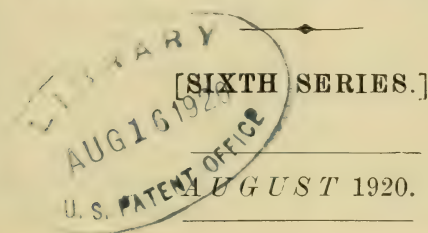
XVIII. *The Arrangement of Atoms in Crystals. By* W. Lawrence Bragg, *M.A., Langworthy Professor of Physics, The University of Manchester*[*].

[Plate III.]

1. IN many simple crystalline structures the atoms are so arranged that their exact positions are determined by the symmetry of the crystal. In the diamond, for example, each carbon atom is at the centre of four other carbon atoms arranged at the corners of a regular tetrahedron. In the crystal of sodium chloride, the sodium atoms may be regarded as arranged at the corners and face-centres of the unit cube, the chlorine atoms being situated at the centres of the cube-edges and at the centre of the cube. Every sodium atom is surrounded symmetrically by six chlorine atoms, every chlorine atom by six sodium atoms. The atoms cannot be displaced from these positions without destroying the symmetry of the structure, and therefore their exact positions are defined by this symmetry.

In the case of a crystal such as iron pyrites, FeS_2, the positions of the sulphur atoms are not defined in this manner. The atoms of iron are at centres of symmetry of the structure, and so must be regarded as fixed in position. The sulphur atoms lie on axes of threefold symmetry, but they,

[*] Communicated by the Author.

on the other hand, may be anywhere along these axes, provided they all occupy similar positions, and yet be in accordance with the symmetry. The determination of their positions must be made by a quantitative examination of the diffraction of the X rays by the structure, since the parameter which fixes their positions may have any value between certain limits. The oxygen atom in the series of carbonates isomorphous with calcite has similarly an indeterminate position depending on the value of a certain parameter. In the case of the ruby, Al_2O_3, two parameters are necessary to define the crystal structure; in quartz, SiO_2, four parameters must be determined. The difficulty of analysing a crystal structure by the X rays is greatly increased by the necessity for defining these parameters, and it is this which has limited the types of crystals which have so far been fully worked out to the simpler forms where these parameters are few in number.

The first part of this paper deals with certain empirical relations, which hold between the distances separating atoms from their nearest neighbours in the simpler crystalline structures, and which the author has found to be of service in the analysis of complex crystal forms. In the latter part of the paper the physical significance of these relations will be discussed, particularly in relation to the theories of atomic structure proposed by Lewis[*] and Langmuir[†].

2. These relations may be expressed in a simple manner by regarding the atoms in a crystal as an assemblage of spheres packed tightly together, the centres of the spheres coinciding with those of the atoms. Each sphere is held in place by touching several neighbours. It will be shown that, within certain limits, it is possible to assign to the sphere representing an atom of any element a constant diameter characteristic of that element. The distance between the centres of two neighbouring atoms may be expressed as the sum of two constants, represented by the radii of the corresponding spheres. The molecular volume of a compound is in general very far from being equal to the sum of the molecular volumes of the elements composing it. On the other hand, if the distances between the atoms are considered, it will be shown that an additive law holds with considerable accuracy. The apparent variations in the contribution of any particular element to the molecular volume of compounds of which it forms a constituent are to be explained by differences

[*] G. N. Lewis, Journ. Amer. Chem. Soc. xxxviii. p. 762 (1916).

[†] I. Langmuir, Journ. Amer. Chem. Soc. xli. p. 868 (1919).

in crystalline structure, and not by variations in the space occupied by the atoms.

This additive law is only intended to be regarded as a working approximation, an aid to the analysis of complex structures. In analysing such a structure, various arrangements of the atoms have to be tried to explain the intensities of the reflected spectra. It will be shown that, when marshalling the atoms together, each atom must be given a certain space in the structure, so that two atoms may not be placed closer together than a distance equal to the sum of the radii of the spheres representing them. This greatly facilitates the determination of the parameters, which are confined to a much more limited range.

The diameter of the sphere representing an atom is, for the sake of brevity, called the diameter of the atom, and is expressed in Ångström units ($\mathring{A} = 10^{-8}$ cm.).

Fig. 1 *a*.

Unit of Iron Pyrites Structure.
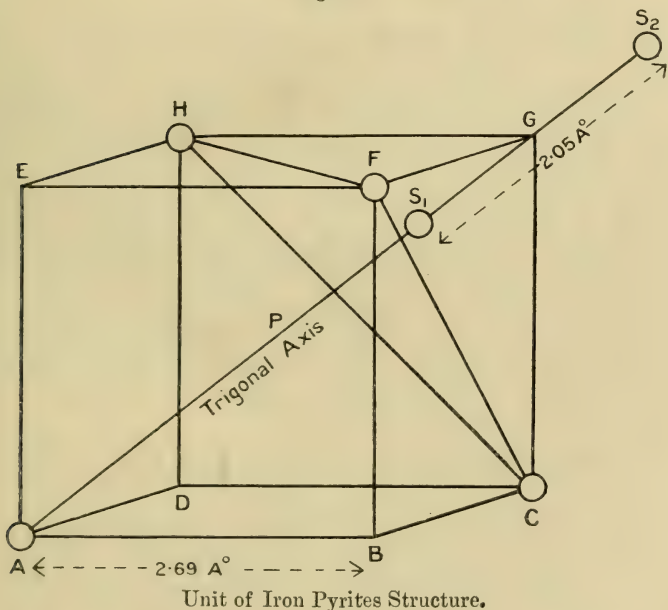
3. In the Iron Pyrites structure[*], the iron atoms are situated on a face-centred cubic lattice. If the unit cube of this lattice is divided into eight smaller cubes, each of these latter will have an iron atom situated at four of its eight corners. Figure 1 *a* represents such a unit of the structure

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[*] W. L. Bragg, Proc. Roy. Soc. lxxxix. (Nov. 1913).

of iron pyrites, the iron atoms being at the corners A, C, H, and F. One diagonal of the cube, the diagonal AG in the figure, is an axis of threefold symmetry, and the sulphur atom lies at some position along this axis. Each corner of the cube is a centre of symmetry. If a sulphur atom is centred at the point S_1, there will be a corresponding atom at the point S_2 where $S_1G = S_2G$. A pair of sulphur atoms is thus associated with each corner of the cube not occupied by an iron atom, since one threefold axis passes through every corner. On the conception of the atoms as a set of spheres packed together, it will be seen that there are two possible positions for the sulphur atom. It may lie at the centre of the cube, where it is symmetrically surrounded by four iron atoms at A, C, H, and F. Alternatively, it may move along the diagonal until it is at G, on the other side of the plane HFC, where it will be packed between the three atoms of iron at H, C, and F and the corresponding sulphur atom at S_2.

The structure of metallic iron has been determined by Hull *. The iron atoms are situated on a cube-centred lattice, the side of the cube having a length of 2·86 Å, and the distance between the centres of neighbouring iron atoms is 2·47 Å. If this length is taken as a first approximation to the diameter of the sphere representing the iron atom, and spheres of corresponding radius are described with their centres at H, C, and F, the centre of the sulphur atom is thereby fixed. The atom must touch the three iron atoms and also the other sulphur atom at the point G, as shown in fig. 1 *b*. The ratio S_1G/AG which determines the position of S_1 can be calculated to be 0·22/1. This ratio was originally determined by the author as 0·20/1. A more exact determination by Ewald†, based on the Laue-photograph of Pyrites, gave the value of the parameter as 0·226/1.

The exact correspondence of the position of the sulphur atom calculated in this way with that found by experiment is not to be expected, the diameters of the spheres representing the atoms cannot be regarded as absolutely fixed. It will be seen, however, that the conception of the atoms as spheres packed together does lead in this case to an approximate value for the parameter not far from the true one. The diameter of the sulphur atom is given by the distance S_1S_2, which is equal to 2·05 Å. Each sulphur atom is surrounded by three iron atoms and a sulphur atom, each iron atom by six sulphur atoms.

* Hull, Phys. Rev., 10 Dec. 1917.
† Ewald, *Phys. Zeit.* April 15, 1914.

4. In Zinc sulphide (Zinc-blende) the zinc atoms lie on a face-centred cubic lattice. The sulphur atoms lie on a similar lattice in such a way that every sulphur atom is surrounded by four zinc atoms arranged at the corners of a regular

Fig. 1 *b*.

Section through A C G E. The broken circle is the projection of the iron atoms centered at F and H.

tetrahedron, every zinc atom by four sulphur atoms similarly arranged. The distance between the centres of the zinc and sulphur atoms is 2·35 Å. Taking the diameter of the sulphur atom as 2·05 Å., this gives the diameter of the zinc atom as 2·65 Å.

In zinc oxide * the zinc atoms have an arrangement which is that of hexagonal close-packing, The oxygen atoms have a similar arrangement, each oxygen atom being surrounded by four zinc atoms at the corners of a tetrahedron and each zinc atom by four oxygen atoms. The distance between

* W. L. Bragg, Phil. Mag. vol. xxxix. p. 647, June 1920.

zinc and oxygen centres is 1·97 Å. The oxygen atom appears to occupy a smaller space than the sulphur atom, and the diameter 1·30 Å. must be assigned to the sphere representing it.

5. In comparing zinc oxide and zinc sulphide, the substitution of oxygen for sulphur decreases the distance between atomic centres by 0·38 Å. This holds true for a number of compounds, as will be seen by the following comparison. It is assumed that the compounds MgO, CaO, SrO, BaO and MgS, CaS, SrS, BaS, have the same structure as NaCl. This is known to be the case for MgO*, and all these compounds fall into two isomorphous series of cubic crystals with cleavage parallel to the cube faces.

The distances given in the table are those between neighbouring atomic centres.

			Difference.
MgO	....	2·11	
MgS	....	2·54	0·43 Å.
CaO	....	2·40	
CaS	....	2·77	0·37 Å.
SlO	....	2·63	
SlS	....	2·99	0·36 Å.
BaO	....	2·81	
BaS	....	3·20	0·39 Å.
ZnO	....	1·97	
ZnS	....	2·35	0·38 Å.

6. Similar relationships are shown by the alkaline halides† the molecular volumes of which form a regular series. All these salts crystallize in the same form as NaCl. The following table gives the distances between atomic centres expressed in Ångström Units.

NaF ...	2·39	KF......	2·73				
Diff.............	·41		·40				
NaCl ...	2·80	KCl ...	3·13	RbCl...	3·28	CsCl ..	3·26
Diff.............	·17		·15		·16		·14
NaBr ...	2·97	KBr ...	3·28	RbBr...	3·44	CsBr .	3·40
Diff.............	·26		·24		·22		·21
NaI ...	3·23	KI ...	3·52	RbI ...	3·66	CsI ...	3·61

The replacement of Fluorine by Chlorine, Chlorine by Bromine, and Bromine by Iodine, increases the dimensions of the structure by an approximately constant amount.

This series is peculiar in that the replacement of Rubidium by Cæsium appears to diminish the dimensions of the

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* Hull, Journ. Amer. Chem. Soc. August, 1919.
† The figures from which these results have been worked out are taken from Groth's *Chemische Krystallographie*.

structure. In most compounds the reverse is the case, as is illustrated by the following comparison of molecular volumes :—

K_2SO_4...	64·91	K_2SeO_4...	71·67	$KClO_4$...	54·91	$KMnO_4$...	58·53
Rb_2SO_4.	73·34	Rb_2SeO_4.	79·94	$RbClO_4$.	61·33	$RbMnO_4$.	63·23
Cs_2SO_4.	84·58	Cs_2SO_4.	91·09	$CsClO_4$.	69·84	$CsMnO_4$.	70·01

7. The structure of the isomorphous series of rhombo-hedral carbonates typified by Calcite, $CaCO_3$, is illustrated by fig. 2. In Calcite the calcium atoms lie on a face-centred

Fig. 2.
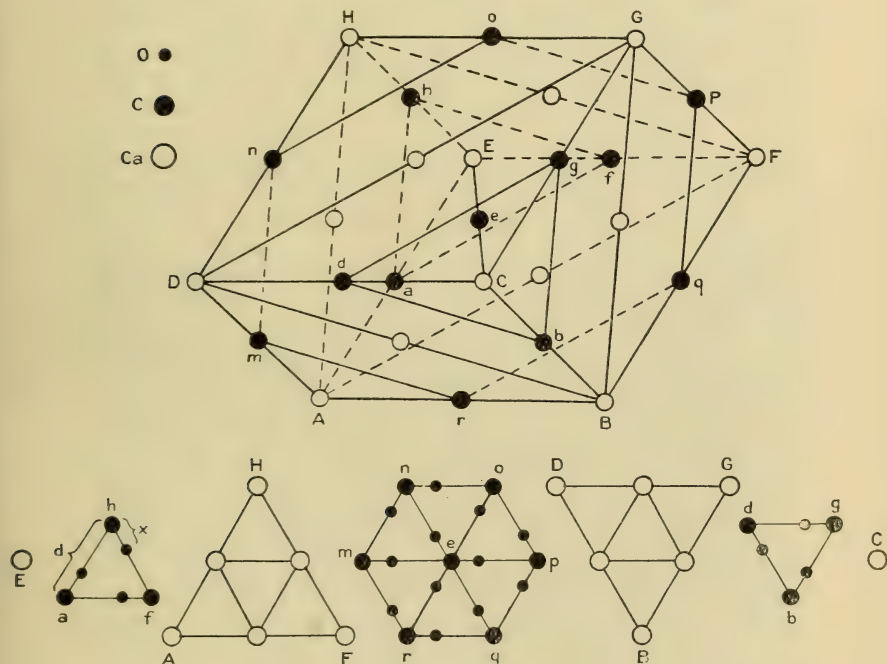
rhombohedral lattice, corresponding to a face-centred cubic lattice compressed parallel to a trigonal axis so that the angle of 90° between the edges of the cube becomes an angle of 101° 55′. The carbon atoms occupy the intermediate posi-tions. Each carbon atom is surrounded by three oxygen atoms, as shown in the figure. The precise position of the oxygen atoms is not determined by the symmetry of the structure, they lie at some point along the line joining neigh-bouring carbon atoms in the planes parallel to the face (111) of the crystal. The ratio x/d in the figure, which fixes their

position, was found by the author to be approximately 0·30/1, corresponding to a distance between oxygen and carbon centres of 1·47 Å. This distance is the same for all compounds of the series.

In the diamond the distance between the centres of the carbon atoms is 1·54 Å. Taking the diameter of the carbon atom as 1·54 Å., and that of the oxygen atom as 1·30 Å., the distance between oxygen and carbon centres should be 1·42 Å. This is in agreement with the distance of 1·47 Å. deduced from the X-ray measurements.

The distance between the centres of the metallic atom and the oxygen atom may be compared with the distance in the metallic oxide. In the carbonates the atom of the metal is surrounded by six oxygen atoms. In zinc carbonate the distance between zinc and oxygen centres is 1·99 Å, in zinc oxide it is 1·97 Å. The agreement is not so good in other cases. The distance between calcium and oxygen centres is 2·40 Å. in CaO, 2·30 Å. in $CaCO_3$. The corresponding figures for MgO and $MgCO_3$ are 2·10 and 2·00 Å. In $FeCO_3$ the distance between the iron and oxygen centres is 2·04 Å., in Fe_3O_4,[*] (magnetite) it is 2·00 Å. This leads to a value 2·74 Å for the diameter of iron, greater than the value 2·47 Å calculated from pyrites and metallic iron. Although this is the case, it will be seen that the conception of the crystal as a number of spheres packed tightly together leads to a determination of the parameter which is near the true one.

8. Two other examples will be taken as affording a cross-check on these measurements. In fluorspar, CaF_2, the distance between calcium and fluorine centres is 2·34 Å. In sodium nitrate, $NaNO_3$, the arrangement of the sodium and nitrogen atoms is that of the calcium and carbon atoms in calcite. The ratio x/d determining the position of the oxygen atoms is approximately 0·25. This gives the distance between oxygen and nitrogen centres as 1·30 Å., between oxygen and sodium centres as 2·33 Å. We thus have the relations—

Na—O ...	2·33 Å. ($NaNO_3$)	Ca—O......	2·30 Å. ($CaCO_3$).
Na—F ...	2·39 Å. (NaF).	Ca—F	2·34 Å. (CaF_2).

The space occupied by calcium in a crystal is much the same as that occupied by sodium; that occupied by oxygen is much the same as that occupied by fluorine.

9. These examples will indicate the manner in which the results shown in fig. 3 have been calculated. For instance, the diameter of oxygen has been taken to be 1·30 Å., and that

[*] W. H. Bragg, Phil. Mag. vol xxx. (Aug. 1915).

of fluorine to be slightly greater, 1·35 A. From a comparison of the alkaline halides, the diameters of the halogens are found to be :

Fluorine	1·35 Å.
Chlorine	2·10 Å.
Bromine	2·38 Å.
Iodine	2·80 Å.

Sulphur has been taken to have a diameter of 2·05 Å. The structure of Galena (PbS) corresponds to that of NaCl. The substitution of Selenium and Tellurium for Sulphur in the compounds PbSe and PbTe increases the distance between atomic centres by 0·15 Å. and 0·31 Å. respectively. We therefore get the values for the diameters :—

Oxygen	1·30 Å.
Sulphur	2·05 Å.
Selenium	2·35 Å.
Tellurium	2·66 Å.

The diameter of nitrogen is taken to be 1·30 Å. So far as the author is aware, no compounds containing phosphorus, arsenic, or antimony have yet been fully worked out, and the diameters of arsenic and antimony in the figure are the distances between atoms in crystals of the element.

The diameters of carbon and silicon* are taken to be those separating the atoms of the element, 1·54 Å. and 2·35 Å. Gray tin† has a similar structure, with an inter-atomic distance of 2·80 Å.

Aluminium in its compounds occupies a volume slightly less than trivalent iron.

The divalent metals Nickel, Zinc, Magnesium, Copper, Cobalt, Iron, Manganese, Cadmium, and Calcium form several series of isomorphous compounds, which have been studied in detail by Tutton. The metals are arranged in the order of the molecular volumes of their compounds, those containing nickel having the least volume and those containing calcium the greatest.

The diameters of the spheres representing the monovalent alkali metals are calculated from the dimensions of the alkaline halides, diameters having been already fixed for fluorine, chlorine, bromine, and iodine.

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* Debye and Scherrer, *Phys. Zeit.* xvii. (1916).
† A. J. Bijl and N. H. Holkmeyer, Proc. Roy. Soc. Ac. Amsterdam, June–Sept. (1918).

These data have been used in calculating the diameters
of fig. 3.
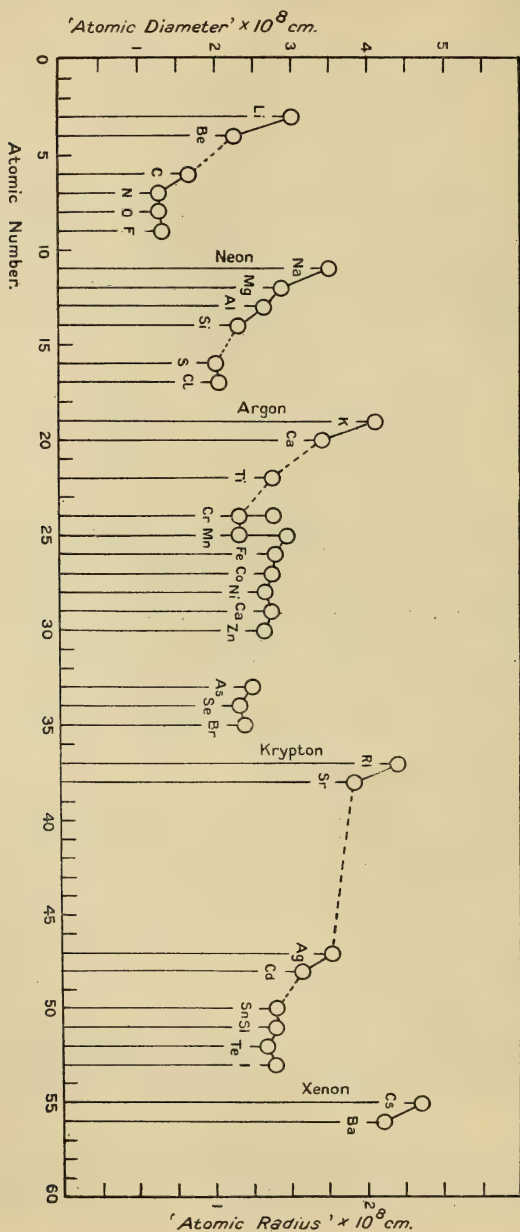
Fig. 3.

10. In fig. 3 the elements are arranged in the order of their Atomic Numbers. The ordinates represent the diameters of the "Atomic Domain" measured in Ångström Units. The figure summarizes the empirical relation which has been found to hold, namely, that the distance between neighbouring atomic centres in a crystal is the sum of two constants characteristic of the atoms. The crystal may be imagined as an assemblage of spheres packed together, the constants then representing the radii of the spheres.

The atomic diameters lie on a curve resembling Lothar Meyer's curve of atomic volumes. The alkali metals head each period with the greatest diameter, followed by the alkaline earths. The diameter diminishes steadily as the atomic weight is increased, reaching a minimum for the electronegative elements at the end of the period. In other words, when the atomic arrangement of compounds is taken into account, the periodic relation between the atomic volumes shown by Lothar Meyer's curve can be extended to the compounds of the atoms.

A list is given below of the "atomic diameters" assigned to the elements, and for convenience the "atomic radii" are added. The second table is a comparison of the observed distance between atoms in crystals with those obtained by adding together the radii of the two atoms concerned. It will be seen that the difference between observed and calculated values is never large, the average difference being 0.06×10^{-8} cm.

It is not intended to assign any physical significance to these "diameters" other than that discussed below. Sodium, for instance, has been given a diameter much larger than that of chlorine, yet it will be seen that there is every reason for supposing that the group of electrons surrounding the sodium nucleus in sodium chloride has smaller dimensions than that surrounding the chlorine nucleus in the same crystal.

The way of regarding the atoms as spheres packed tightly together is useful in constructing models of crystalline structures. Such models are illustrated in Plate III., the crystalline structures being those of sodium chloride, calcium carbonate, and zinc-blende.

Atomic Number.	Element.	Atomic Diameter, in Å.	Atomic Radius, in Å.
3.	Lithium	3·00	1·50
4.	Beryllium	2·30	1·15
6.	Carbon	1·54	0·77
7.	Nitrogen	1·30	0·65
8.	Oxygen	1·30	0·65
9.	Fluorine	1·35	0·67
11.	Sodium	3·55	1·77
12.	Magnesium	2·85	1·42
13.	Aluminium	2·70	1·35
14.	Silicon	2·35	1·17
16.	Sulphur	2·05	1·02
17.	Chlorine	2·10	1·05
19.	Potassium	4·15	2·07
20.	Calcium	3·40	1·70
22.	Titanium	2·80	1·40
24.	Chromium	2·80	1·40
	("electronegative")	2·35	1·17
25.	Manganese	2·95	1·47
	("electronegative")	2·35	1·17
26.	Iron	2·80	1·40
27.	Cobalt	2·75	1·37
28.	Nickel	2·70	1·35
29.	Copper.........................	2·75	1·37
30.	Zinc	2·65	1·32
33.	Arsenic	2·52	1·26
34.	Selenium......................	2·35	1·17
35.	Bromine	2·38	1·19
37.	Rubidium	4·50	2·25
38.	Strontium	3·90	1·95
47.	Silver	3·55	1·77
48.	Cadmium......................	3·20	1·60
50.	Tin	2·80	1·40
51.	Antimony	2·80	1·40
52.	Tellurium	2·65	1·33
53.	Iodine	2·80	1·40
55.	Cæsium	4·75	2·37
56.	Barium	4·20	2·10
81.	Thallium	4·50	2·25
82.	Lead	3·80	1·90
83.	Bismuth	2·96	1·48

Compound.	Atomic centres.	Sum of radii, in Å.	Observed Distance, in Å.	Difference, in Å.
Element Li.		3·00	3·03	+0·03
LiF.	Li,F.	1·50+0·67=2·17	2·05	−0·12
LiCl.	Li,Cl.	1·50+1·05=2·55	2·57	+0·02
LiBr.	Li,Br.	1·50+1·19=2·69	2·79	+0·10
LiI.	Li,I.	1·50+1·40=2·90	3·15	+0·25
Element Be.		2·30	2·52	+0·22
BeO.	Be,O.	1·15+0·65=1·80	1·78	−0·02†

* Assuming close packing.

† Assuming ZnO structure.

Compound.	Atomic centres.	Sums of radii, in Å.	Observed Distance, in Å.	Difference, in Å.
Element Na.		3·55	3·72	+0·17
NaF.	Na,F.	1·77+0·67=2·44	2·39	−0·05
NaCl.	Na,Cl.	1·77+1·05=2·82	2·80	+0·02
NaBr.	Na,Br.	1·77+1·19=2·96	2·97	+0·01
NaI.	Na,I.	1·77+1·40=3·37	3·23	−0·14
NaNO₃.	Na,O.	1·77+0·65=2·42	2·33	−0·09
Element Mg.		2·85	3·22	+0·37
MgO.	Mg,O.	1·42+0·65=2·07	2·10	+0·03
MgCO₃.	Mg,O.	1·42+0·65=2·07	2·00	−0·07
MgS.	Mg,S.	1·42+1·02=2·44	2·54	+0·10
Element Al.		2·70	2·87	+0·17
Al₂O₃.	Al,O.	1·35+0·65=2·00	2·02	+0·02
KF.	K,F.	2·07+0·67=2·74	2·78	+0·04
KCl.	K,Cl.	2·07+1·05=3·12	3·13	+0·01
KBr.	K,Br.	2·07+1·19=3·26	3·28	+0·02
KI.	K,I.	2·07+1·40=3·47	3·52	+0·05
CaO.	Ca,O.	1·70+0·65=2·35	2·40	+0·05
CaCO₃.	Ca,O.	1·70+0·65=2·35	2·30	−0·05
CaS.	Ca,S.	1·70+1·02=2·72	2·77	+0·05
CaF₂.	Ca,F.	1·70+0·65=2·35	2·34	−0·01
MnCO₃.	Mn,O.	1·47+0·65=2·11	2·10	−0·01
MnS₂.	Mn,S.	1·47+1·02=2·49	2·59	+0·10
Element Fe.		2·80	2·47	−0·33
FeCO₃.	Fe,O.	1·40+0·65=2·05	2·04	−0·01
Fe₂O₃.	Fe,O.	1·40+0·65=2·05	2·10 app.	+0·05
Fe₃O₄.	Fe,O.	1·40+0·65=2·05	2·00	−0·05
FeS₂.	Fe,S.	1·40+1·02=2·42	2·28	−0·14
Element Cu.		2·75	2·55	−0·20
Cu₂O.	Cu,O.	1·37+0·65=2·02	1·87	−0·15
ZnO.	Zn,O.	1·32+0·65=1·97	1·97	0·00
ZnCO₃.	Zn,O.	1·32+0·65=1·97	1·99	+0·02
ZnS.	Zn,S.	1·32+1·02=2·32	2·35	+0·03
RbCl.	Rb,Cl.	2·25+1·05=3·30	3·28	−0·02
RbBr.	Rb,Br.	2·25+1·19=3·44	3·44	0·00
RbI.	Rb,I.	2·25+1·40=3·65	3·66	+0·01
SrO.	Sr,O.	1·95+0·65=2·60	2·63	+0·03
SrS.	Sr,S.	1·95+1·02=2·97	2·99	+0·02
CdCO₃.	Cd,O.	1·60+0·65=2·25	2·21	−0·04
CdS.	Cd,S.	1·60+1·02=2·62	2·67	+0·05
CsCl.	Cs,Cl.	2·37+1·05=3·42	3·26	−0·14
CsBr.	Cs,Br.	2·37+1·19=3·56	3·40	−0·16
CsI.	Cs,I.	2·37+1·40=3·77	3·61	−0·16
BaO.	Ba,O.	2·15+0·65=2·80	2·81	+0·01
BaS.	Ba,S.	2·15+1·02=3·17	3·20	+0·03

11. These empirical relations will now be considered with reference to the theory of atomic structure proposed by Lewis[*], which has been greatly extended by Langmuir[†]. Briefly stated, some of the principal features of the theory in the form in which Langmuir presents it are the following :—

(a) The electrons surrounding the positively charged nucleus of an atom are either stationary, or oscillate about certain fixed positions.

(b) The electrons are distributed in a series of approximately spherical shells surrounding the nucleus.

(c) Certain arrangements of electrons around a nucleus, those of the atoms of the inert gases, are very stable. These arrangements are :—Helium, where a nucleus with two unit positive charges is surrounded by a shell containing two electrons. Neon, nuclear charge 10, surrounded by an inner shell containing two electrons and an outer shell containing eight electrons. Argon, nuclear charge 18, surrounded by three shells containing two, eight, and eight electrons. Krypton, nuclear charge 36, shells containing two, eight, eight, and eighteen electrons. Xenon, nuclear charge 54, shells containing two, eight, eight, eighteen, and eighteen electrons. Niton, nuclear charge 86, shells containing two, eight, eight, eighteen, eighteen, and thirty-two electrons.

(d) The chemical properties of the elements depend primarily on the tendency of the atom to surround itself with a more stable arrangement of electrons. The most simple chemical properties are exhibited by those atoms which revert most easily to the inert gas form, *i. e.*, the atoms nearest the inert gases in the periodic table. An electropositive element is one which tends to give up electrons in doing this, an electronegative element one which tends to take up electrons.

12. Broadly speaking, the theory distinguishes between two different types of combination in chemical compounds. The first type is represented by a compound such as KCl. The potassium atom has a nuclear charge of 19 units, and is surrounded by 18 electrons arranged in the same way as those of the argon atom, with in addition an electron which finds

* G. N. Lewis, *loc. cit.*
† I. Langmuir, *loc. cit.*

no place in the stable argon arrangement. Chlorine has a nuclear charge of 17, and is surrounded by 17 electrons, one less than the number required to form the stable argon arrangement. When an atom of potassium combines with one of chlorine, the chlorine atom absorbs into its system the additional electron from the potassium atom. Both atoms are now surrounded by the argon shells, but as the nuclear charges are 19 and 17, and each atom is surrounded by 18 electrons, there will be a resultant positive charge of one unit on the potassium atom and a negative charge of one unit on the chlorine atom. The electrostatic attraction of these charges holds the molecule together. The nuclei, surrounded by the stable argon shells, compose the monovalent kations and anions of potassium and chlorine.

The other type of combination is represented by a compound of two electronegative elements. In this case both atoms have fewer electrons than correspond to a stable system. They complete the required number of electrons in their outer shells by holding one or more pairs of electrons in common. In such compounds as SO_2, CO_2, the atoms complete their outer shells of eight electrons by sharing them with their neighbours.

The crystalline structure of a compound such as KCl is very simply explained by this theory. As has been pointed out by Langmuir, the crystal is to be regarded as an assemblage of potassium and chlorine ions arranged on a cubic lattice *. The ions consist of the stable argon shells, but as the nuclear charges are 19 and 17 the ions have resultant unit positive and negative charges. Each ion tends to surround itself with as many ions of the opposite sign as possible. This is realised in the KCl structure, where each ion is surrounded by six ions of the opposite sign. There are no individual molecules in the crystal structure, the potassium ion has exactly the same relation to the six chlorine ions surrounding it, and *vice versa*. Some repulsive force must exist between the outer shells, which holds the atoms apart against the electrostatic attraction.

In the structure of calcium sulphide, the calcium atom loses two electrons, and the sulphur atom gains two, in reverting to the argon form. The resultant charges on the ions are twice as great as those in the KCl structure, and as a result of the increased attraction between the ions the structure, while being similar to that of KCl, has all its dimensions reduced.

* Cp. Debye and Scherrer, *Phys. Zeit.* xix. (1918), where evidence is given that an electron has passed from the Li atom to the F atom in LiF.

In the diamond, each carbon has a nuclear charge of six units. The atom has two electrons in its inner shell and four in the outer shell. In order to complete the number of electrons, eight, which would make its outer shell correspond to the stable neon form, it shares its electrons with the four carbon atoms surrounding it in the diamond structure. Each pair of atoms holds two electrons in common. The forces binding the atoms together are of a different type, the atoms are united because they share electrons, not as a result of opposite charges on ions as in KCl.

A crystal of an electropositive element, such as sodium, consists of an assemblage of the stable "inert gas" shells with an additional electron associated with each in order to neutralize completely the nuclear charge. These electrons have no fixed positions in the structure, they move under the action of an electromotive force and convey a current of electricity through the metal. On the other hand, a crystal in which the atoms are bound together by sharing electrons, so that there are no free electrons, is a non-conductor. This is the case for the typical electronegative element.

13. The empirical relations of fig. 3 are readily explained by this theory. In each period, the alkali metal which follows one of the inert gases has been assigned a large "diameter." This expresses the fact that it appears to occupy a large space in any crystal structure; the centre of the atom is separated by a considerable distance from the centres of the neighbouring atoms. Successive elements are assigned smaller diameters, and at the end of the period the electronegative elements immediately preceding the next inert gas have diameters which approximate closely to a limiting minimum value for that period.

The small diameters have been assigned to the electronegative elements on account of their proximity in a crystal structure. In sodium nitrate, for example, the distance between the oxygen and nitrogen centres is 1·30 Å., that between the oxygen and sodium centres 2·38 Å. In all these atoms the nuclei are surrounded by the stable neon arrangement of electrons, and presumably these electrons are approximately the same distance from the nucleus in sodium, nitrogen, and oxygen. The oxygen and nitrogen atoms have realized the stable arrangement, however, by sharing electrons, and their centres are correspondingly close together. The sodium atom is already surrounded by a stable shell and is isolated in the structure. In sodium nitrate there is the same arrangement of positive and negative ions as in sodium chloride, except that the negative ion in this case is the

complex NO_3 group. In order to complete a stable arrange-
ment around the four nuclei, the NO_3 group has borrowed
an electron from the sodium atom, leaving it a positively
charged ion. These ions are arranged in the same way in
$NaNO_3$ and $NaCl$, each ion being surrounded by six of the
opposite sign. The form of the NO_3 group has, however,
distorted the structure so that the crystal is rhombohedral
instead of cubic.

In $MgCO_3$ the arrangement of the atoms is the same
as in $NaNO_3$. The magnesium ion has a double positive
charge, the CO_3 ion a double negative charge. As a result
of the greater electrostatic forces, the dimensions of the
structure are reduced, the distance between magnesium and
oxygen centres being $2 \cdot 00$ Å., as compared with $2 \cdot 38$ Å. in
the case of sodium nitrate. This will make it clear why the
divalent element appears to occupy a smaller space in a
crystalline structure than the monovalent element preceding
it in the periodic series.

The large diameters assigned to the electropositive elements
as compared with the electronegative elements do not imply
a corresponding difference in the dimensions of the atomic
structure. They are an expression of the fact that the
electropositive element does not share electrons with neigh-
bouring atoms, it is always surrounded by a complete stable
shell. The repulsion between this outer shell and the shells
of neighbouring atoms keeps the atom at a distance from its
neighbours, so that it appears to occupy a large space in the
crystal structure.

It is interesting to compare the structure of graphite with
that of diamond from this point of view. The graphite
crystal has been analysed by Debye and Scherrer[*]. It
corresponds to a diamond structure in which, firstly, the
dimensions of the whole structures parallel to a trigonal axis
have been lengthened in the ratio $0 \cdot 598 : 1$, and, secondly,
the carbon atoms in the pairs of (111) planes of the diamond
have been so displaced that they lie very nearly in the same
plane. The atoms in a (111) plane are therefore very much
closer to each other than they are to the atoms in the next
planes. This may be explained by supposing that they are
sharing electrons with their neighbours in the (111) planes
but not with the other atoms, the very ready cleavage
parallel to (111) lending support to this view (cp. Debye's
paper). In such a case as this, the analogy of the crystal
structure to a set of spheres packed together obviously

[*] Debye and Scherrer, *Phys. Zeit.* xviii. (June 1917).

Phil. Mag. Ser. 6. Vol. 40. No. 236. *Aug.* 1920.   O

breaks down. The distance between neighbouring carbon atoms in graphite is 1·45 Å.

14. It has been seen that in each period the diameters of the electronegative atoms appear to approach a lower limit. If it is true that these atoms share electrons when combined together in the crystal, the diameters which have been assigned to them should give an estimate of the diameters of the outer shells in which the electrons are situated.

In the first short period the diameters assigned to the atoms of carbon, nitrogen, oxygen, and fluorine are 1·54 Å., 1·30 Å., 1·30 Å., 1·35 Å. The first three of these have been calculated from compounds in which the atoms share electrons, the nitrates, carbonates, and diamond. No compound in which fluorine shares electrons has been analysed, but evidence has been given that it occupies the same volume as oxygen. The outer electron shell which these atoms tend to complete is that of Neon. We may therefore estimate the diameter of the outer neon shell as being 1·30 A. Since two electrons at least are held in common by the elements this estimate may be somewhat too large.

In the second short period the diameters of silicon, sulphur, and chlorine are 2·35 Å., 2·05 Å., 2·10 Å. The structure of phosphorus has not yet been analysed. The diameter of the outer Argon shell appears to be 2·05 Å.

In the first long period, the lower limit to which the diameters tend is 2·35 Å. The structure of arsenic has not been analysed, but it crystallizes in a form isomorphous with antimony, the structure of which has been recently determined by James and Tunstall. If its structure is that of antimony, the distance between the nearest atoms is 2·52 Å. Selenium has been assigned a diameter of 2·35 Å., bromine a diameter of 2·38 Å. Other elements in the same period tend to approach this limit. When manganese and chromium act as acid-forming elements and so share electrons with other atoms, they enter into compounds isomorphous with the sulphates and selenates, and the molecular volumes of the compounds are very nearly those of the selenates, so that the atoms appear to have dimensions identical with those of selenium. The distances between atomic centres in iron, nickel, and copper are 2·47 Å., 2·39 Å., 2·55 Å. These figures confirm the estimate of 2·35 Å. as the lower limit to which the diameter tends.

In the second long period, the distance between atomic centres in gray tin is 2·80 Å., in antimony 2·80 Å. Tellurium

and iodine have been assigned diameters of 2·66 Å. and 2·80 Å. The evidence for the lower limit is imperfect, but it may be estimated as 2·70 Å.

The diameters of the outer electron shells of the inert gases therefore appear to be—

Neon	....	1·30 Å.
Argon	....	2 05 Å.
Krypton	....	2·35 Å.
Xenon	....	2·70 Å.

On Langmuir's theory, the crystal of an electropositive element consists of an assemblage of positively charged ions held together by electrons which are free to move in the structure. The empirical relation between inter-atomic distances in compounds is less accurate when applied to the metals, perhaps as a result of the different nature of the forces in this latter case. For instance, in a number of isomorphous series the substitution of magnesium for iron decreases the molecular volume, yet the distances between atomic centres in metallic magnesium and iron are 3·22 Å.* and 2·47 Å, respectively. Silver and sodium form many isomorphous salts of nearly identical molecular volume. The distances between atomic centres in crystalline silver and sodium are 2·87 Å. and 3·72 Å. Isomorphous salts of the same molecular volume are formed by rubidium and thallium, by strontium and lead, substances whose atomic volumes differ widely. The relations shown in fig. 3 hold most accurately for compounds and for the electronegative elements.

The electropositive elements crystallize in the cubic or hexagonal systems. This was pointed out by Barlow and Pope, and used as a basis for the theory of close-packing in crystalline structures, since an assemblage of equal spheres packed together in the closest manner has either cubic or hexagonal symmetry. It is now known that the atoms of some metals are not arranged in a close-packed manner. Nevertheless, the idea of a metal as an assemblage of positive ions held together by electrons indicates a reason for the simple crystalline structure. Each atom has the same relation to its neighbours, it is not bound in any way to one rather than another of them, and the assemblages will take a form like the arrangement of a set of equal spheres. The crystal of an electronegative element, on the other hand, where atoms are linked by holding electrons in common, will have a more complicated structure, as is the

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* A. W. Hull, Phys. Rev., July 1917.

case for sulphur, selenium, tellurium, iodine, arsenic, antimony, bismuth.

15. In order to obtain a more complete knowledge of the distances between atoms which hold electrons in common, the examination of salts such as the nitrates, chlorates, bromates, sulphates, and selenates would be desirable. The investigation of these salts presents some difficulty, since their crystalline forms are complex. The symmetry of the crystal is of less assistance in determining the arrangement of the atoms than it is for the simple crystals, as it is of a much lower type. It is hoped that the empirical relations formulated in this paper will help in this investigation. The conception of the atoms as a set of spheres of appropriate diameters packed tightly together limits the number of possible arrangements and aids in deciding the correct disposition of the atoms. The scheme may be of assistance in analysing the structure of crystals such as quartz[*], sulphur[*], and the alkaline sulphates[†], crystals for which the dimensions of the lattice are known, but which have so far proved too complicated for complete analysis.

Summary.

1. An examination of the distances between neighbouring atoms in a crystal leads to an empirical relation determining these distances. The distance between the centres of two atoms may be expressed as the sum of two constants characteristic of the atoms. The arrangement of the atoms in a crystalline structure may therefore be pictured as that of an assemblage of spheres of appropriate diameters, each sphere being held in place by contact with its neighbours.

2. This empirical law is summarized by the curve of fig. 3, where the constants for a number of elements, arranged in the order of their atomic numbers, are plotted. The curve is periodic and resembles Lothar Meyer's curve of Atomic Volumes. Each atom occupies a constant space in any crystalline structure of which it forms part. The space occupied by the alkaline metals and alkaline earths is greatest, that occupied by the electronegative elements least.

3. The accuracy of the relation is discussed. Variations of the order of 10 per cent. between the calculated and observed distances occur, so that the law is only approximately true. Nevertheless, it is of considerable assistance

[*] W. H. Bragg, Proc. Roy. Soc. A. vol. lxxxix. (Jan. 1914).
[†] Ogg and Hopwood, Phil. Mag. [6] xxxii. p. 518 (1916).

in the analysis of the more complex crystal structures, since the conception of the atoms as an assemblage of spheres of known diameters packed tightly together limits the number of possible arrangements which have to be tried in interpreting the diffraction of X rays by the crystal.

4. The physical significance of the relation is examined with reference to Langmuir's theory of atomic structure. From this point of view, it follows that two electronegative atoms are situated close together in a crystalline structure because they share electrons, and the spheres representing them are therefore assigned small diameters. On the other hand, an electropositive element does not share the electrons in its outer shell with the neighbouring atoms, and is therefore situated at a distance from other atoms so that it appears to occupy a greater space in the structure.

5. It is shown that the relation is less accurate when applied to the crystals of metals, which, on Langmuir's theory, consist of an assemblage of positive ions held together by electrons which have no fixed positions in the structure.

6. From the distance between electronegative atoms holding electrons in common, an estimate is made of the diameter of the outer electron shell in the inert gases.

Manchester University,
    April 1920.

XIX. *The Dissociation of Iodine Vapour and its Fluorescence. By* St. Landau, *B.Sc., Lecturer in Physics at the Governmental Technical School, Warsaw, and* Ed. Stenz [*].

I. *The aim of this work.*

THE researches of R. W. Wood on the fluorescence of the vapours of sodium, mercury, and iodine are generally known; he discovered the remarkable phenomenon of optical resonance in these vapours. The most complicated relations were found by Wood [†] in the case of iodine vapour; the number of lines in the absorption spectrum of iodine is estimated by Wood to be 40,000–50,000. Different " resonance spectra " may be obtained, when the exciting line covers different absorption lines.

We put the following question : Is the complicated vibrating system, which corresponds to these various resonance

spectra, inherent to the atom or to the molecule ?   In this last case we should suppose that the vibrating mechanism lies in the bond of the atoms.   The experiments described below show that the atom of iodine is incapable of fluorescence, at least in the visible part of the spectrum.   It seems interesting to notice that the result obtained is in accordance with the work of Dunoyer [*] on the fluorescence of sodium vapour.   This author showed that the fluorescence of *pure* sodium vapour is reduced to the D-lines ; he admits that the complicated fluorescence spectrum hitherto observed with sodium vapour is due to the aggregates of molecules of sodium with the molecules of the impurities, perhaps hydrocarbons.   Thus in the case of iodine and sodium, as well as in the case of mercury, one would think that the structure of the atom is not of an excessive complication.

It was impossible to foresee the results obtained, as the absorption spectrum of the monatomic iodine is yet unknown. Konen [†], who did the most complete work on the spectra of iodine, states that he only observed that the absorption spectrum of iodine becomes less marked with increasing temperature, but he never remarked its complete vanishing ; he also never observed a separate absorption spectrum belonging to the dissociated iodine vapour (*l. c.* p. 259).

The plan of our work was very simple.   We raised the temperature of iodine vapour at a known low pressure and observed its fluorescence, the degree of dissociation being calculated.   Three factors come then into account : temperature, pressure, and dissociation.   The pressure remained at a constant value in the majority of our experiments.   It was important to study separately the effect of the temperature and the effect of the dissociation.   The separation of the two factors can be only partially done, as will be seen in the following.

II. *The effect of the temperature ; observations below* 400° C.

R. W. Wood and W. P. Speas [‡] have made a photometrical study on the fluorescence of saturated iodine vapour between $-30°$ and $+75°$ C.   In that research it was found that the maximum of the fluorescence corresponds to 20°–25° C. With higher temperatures the fluorescence decays rapidly ; at 75° C. the fluorescence is quite invisible.   It is clear that in these experiments it was vapour density that played

* D. Dunoyer, *Le Radium*, 1912, p. 177.
† *Annalen der Physik*, vol. lxv. p. 257 (1898).
‡ Phil. Mag. vol. xxvii. p. 531 (1914).

the most prominent role. The light cannot penetrate dense layers of vapour; the light of the fluorescence is also absorbed on its way to the eye of the observer.

When our experiments were terminated, we learned that W. H. Westphal [*] had also observed below 400° C. the effect of the temperature on the fluorescence of iodine vapour, kept at constant pressure. But as that author has accomplished only few and rough measurements (he attributes a certain sense only to the mean value), we give here a short description of our experiments, which seem to us more complete and more conclusive.

In all our experiments we used iodine carefully purified by distillation *in vacuo*. The apparatus joined to the pump is shown at fig. 1. Purified iodine crystals were put in part C;

Fig. 1.
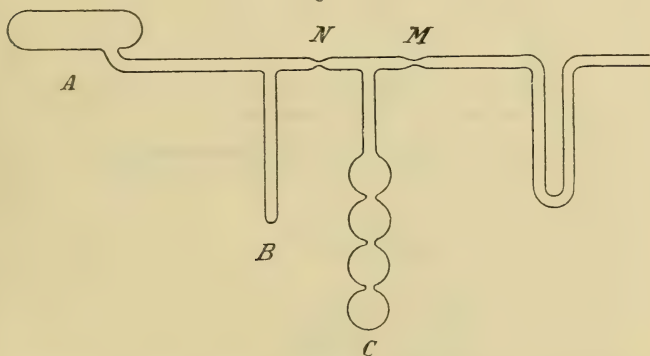
the Gaede mercury pump working, the whole apparatus was strongly heated during 1–2 hours, excepting the lower part of C, containing iodine crystals; the U-tube immersed in solid CO_2 served to exclude mercury vapour from the apparatus and iodine vapour from the pump; the apparatus was then sealed at M. During 24 hours some of the iodine sublimated from A to B; then the apparatus was closed at N. The bulb A, which served for observations, was from Jena glass (called "durobax"—with red stripe), as ordinary glass was found to be attacked by iodine vapour at high temperatures.

The photometer we used was the same as is described by Wood and Speas (*l. c.*) with little improvements. Through

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[*] *Verhandlungen d. Deutschen Physik. Ges.* 1914, p. 829.
During the war (and even now) it was impossible to receive regularly scientific journals at Warsaw; the authors excuse themselves for having perhaps omitted some papers concerning the question treated.

the nicols the eye looked at a surface of paper, which was painted with a colour resembling closely the hue of fluorescence (*p*, fig. 2). This screen was illuminated by light,

Fig. 2.
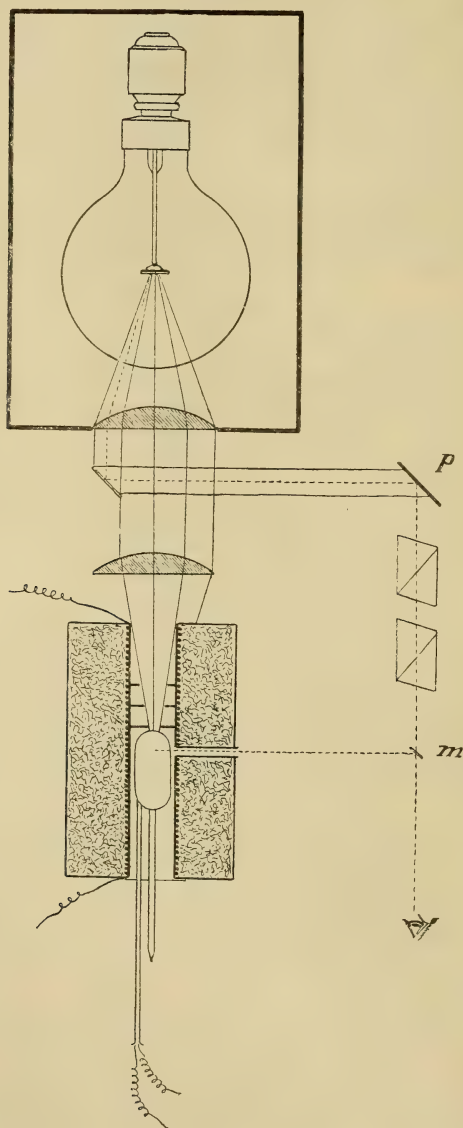
reflected by a glass mirror, coming from the source, which was a 500 watts incandescent lamp. A little fragment of

galvanometer-mirror *m* occupied the centre of the field of vision. Thus we realized something like the Lummer-Brodhun photometer.

The experiments were also performed using a mercury-quartz lamp (Westinghouse, Cooper-Hewitt); in this case the screen, painted in orange-red, was illuminated separately by a little incandescent lamp.

The oven for the heating was an electrical one; in the case of the mercury lamp the observations were made "end" on, and a gas-furnace supplied with suitable cuttings for the passage of light was adapted.

The pressure of the iodine vapour was kept constant by placing the tube B (fig. 1) in a water-bath of the temperature of 20° C.

The results obtained were generally the same, whether we used the incandescent or the mercury-lamp, and whether the vapour was saturated or unsaturated. A typical curve is shown in fig. 3: in this case, which corresponds to the mercury light excitation, saturated iodine vapour at a pressure of 0·25 mm. was used. In this figure the observations taken with rising temperature are marked by points; the observations obtained when lowering the temperature by crosses.

Fig. 3.
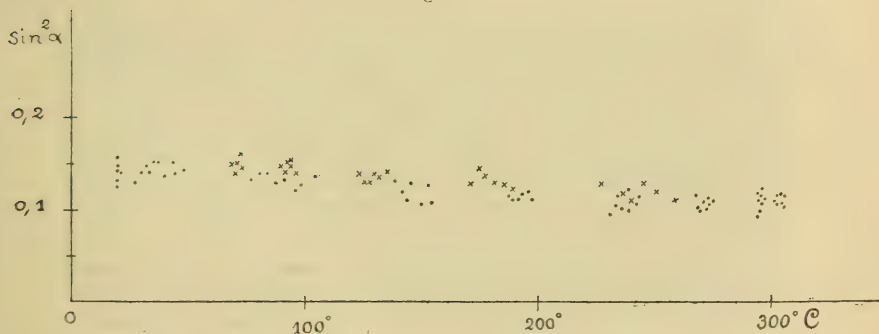
It will be seen that the intensity of the fluorescence diminishes with rising temperature, but the diminution is not as great as might be supposed. At 360° C. the fluorescence is still very intense[*].

[*] We find in the *Fortschritte d. Physik,* ii. p. 385 (1915) an abstract from a paper of McLennan (Proc. Royal Society of London, A. xci. pp. 23–26 (1919)). It is said there that the author has found a disappearance of the resonance radiation at the temperature of 326° C. It will be seen that our observations are opposite to that, as we did observe the resonance radiation very clearly even above 700° C. It was impossible for us to obtain the original paper of McLennan (see footnote p. 191).

III. *Observations above* 400° C.; *influence of dissociation.*

The dissociation of iodine vapour was the subject of a very thorough research of Bodenstein and Starck[*]. Denoting by K a constant, by p_I and p_{I_2} the pressures of the mono- and diatomic iodine, by T the absolute temperature, they obtained

$$\frac{p_I{}^2}{p_{I_2}} = K \text{ and } \log K = -\frac{7762}{T} + 1.75 \log T - 0.000416\,T + 0.422.$$

That formula, based on the thermodynamical theorem of Nernst, is in good accord with the experiments. We applied that formula in our calculations of the degree of dissociation of the iodine vapour.

The vapour we had to do with was kept at a pressure of 0·25 mm. mercury. The formula above permits us to calculate K for different temperatures, and then to find the ratio x of the number of dissociated molecules to the total number of molecules which would be present were there not any dissociation.

Temperature ... $t = 500°$ C.;   600°;   700°;   800°;   900°.
Ratio x of the dissoc. mol. $\Big\}$ $x = 0.1$;   0·36;   0·76;   0·95;   0·99.

The main difficulty of such observations is due to the fact that every furnace heated above 500° C. emits so much light that the weak light of fluorescence vanishes. We remarked that a gas flame, when sufficiently supplied with air, is pale enough to permit observations to be made, the bulb with the vapour being in the flame. A great Méker furnace was fed with the gas exhausted from the gas pipes by a Gaede rotatory oil-pump; the gas passed through a vessel of 20–30 litres capacity to reduce oscillations of pressure. The lower part of the burner was supplied with a ring to regulate the quantity of air drawn into the burner. The flame had a length of 25 cm. and a diameter of 4 cm., although the gas pressure in the pipes was very low. It may be mentioned that such a flame was found to be useful in many cases for the glass-work; it is longer and hotter than the blowpipe-flame.

The quartz apparatus we employed was similar to that shown in fig. 1; the part corresponding to A was a sphere of $3\frac{1}{2}$ cm. in diameter, the part B was likewise of quartz, the

[*] *Zeitschrift f. Elektrochemie*, vol. xvi. p. 961 (1910).

other parts were of glass. Glass and quartz were joined together by chalk sealing-wax; a compact layer of clean asbestos interposed between the quartz and glass tubes prevented the iodine vapour from coming in contact with the sealing-wax. The iodine was introduced in the apparatus in the way described above.

In an experiment the tube with iodine crystals was held in a water- or air-bath of suitable temperature. An intense light-beam was directed on the bulb, and then the bulb heated in the flame of the Méker burner. The fluorescence disappears gradually; the bulb seems optically empty. After removing the flame, the fluorescence reappears. The phenomenon was observed as well with carbon-arc as with mercury-arc light, and employing iodine vapour of different density. The temperature of the flame exceeds 1000° C.: using iodine vapour of the pressure of $\frac{1}{4}$ mm., we had complete dissociation.

It seemed to us to be of interest to determine the temperature of extinction of the fluorescence. For that purpose we employed a large iron pipe of 70 cm. length and 8 cm. diameter. That pipe was vertically set; the large flame of the Méker burner was introduced into the lower part of the pipe. The pipe was covered by a piece of asbestos provided with an opening, the size of which could be changed. In that manner the draught and also the temperature in the different parts of the iron pipe were regulated. The walls of the pipe scarcely emitted any light, although the temperature near the axis in the middle part of the pipe reached 800–900° C. The middle part of the pipe was protected externally by a thick layer of asbestos. Four openings were made, two of a diameter of 9 mm. for the passage of the light; a large window of a diameter of 36 mm. served for the observation of the fluorescence, it was placed somewhat above the openings mentioned; a fourth little opening permitted the introduction of a thermocouple platinum–platino-rhodium. The three larger windows were covered with thin mica sheets. The joint of the thermocouple was placed very near to that place on the quartz bulb where the light came out. The lateral tube containing iodine crystals was kept at a constant temperature of 20° C. by a stream of water.

Using the light emitted by a little carbon arc-lamp we were able to state, that the fluorescence is very distinct still at a temperature of 700° C.; at 780° C., when the fraction of dissociated molecules was equal to about 0·9, we were able to distinguish a faint glimmer of fluorescence.

Thus dissociation and disappearance of the fluorescence are parallel to each other.

One more experiment may be mentioned, which seems to confirm our idea. The unsaturated iodine vapour, heated while the volume remains constant, is less dissociated at a given temperature than the saturated vapour kept at a constant pressure. This is obvious without any calculation, as the raising of the pressure causes a diminution of the dissociation. We isolated the quartz bulb containing iodine vapour from the tube with the crystals. A quartz rod was sealed to the bulb and the last placed in the iron pipe. In that case we observed the fluorescence at 825° C.

To be quite conclusive the experiment should be arranged as a differential one. We were impeded by material difficulties from accomplishing this, but we intend to do it next time. The calculation shows that the experiment is a hopeful one, as is shown in the table below containing the fractions of dissociated molecules in the case of a vapour kept at a constant pressure of $\frac{1}{4}$ mm. mercury, and in the case of vapour kept at constant volume (quartz vessel), having originally (20°) a pressure of $\frac{1}{4}$ mm. mercury.

Temperature.....	500° C.	600°	700°	800°	900°
Fraction x of diss. mol. at const. press.	0·1	0·36	0·76	0·95	0·99
,, ,, ,, ,, volume	0·06	0·20	0·47	0·76	0·90

IV. *Conclusions.*

A. The raising of temperature does not produce as much effect on the fluorescence of the iodine vapour as has hitherto been thought. We have observed the fluorescence even above 800° C.

B. Dissociation destroys the fluorescence and the resonance spectra.

Thus the complicated vibrating system, corresponding to the thousands of absorption lines in the visible part of the spectrum, is not inherent in the atom, but in the molecule. *The structure of the atom should be relatively simple.* That idea based on our observations is perfectly in accord with other facts from the domain of the fluorescence of vapours. The monatomic mercury vapour gives a simple resonance; the complicated fluorescence spectrum of the sodium vapour, as shown by Dunoyer, is due to impurities; pure sodium gives D-lines only.

It seems also nearly certain that the absorption lines, which are so characteristic for the diatomic iodine and so sensitive

to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine.

XX. *On the Equation of State.* By M. P. APPLEBEY, *M.A.*, *Fellow of St. John's College, Oxford*, and D. L. CHAPMAN, *M.A., F.R.S., Fellow of Jesus College, Oxford* [*].

I T has long been known that Clerk Maxwell's law of the equipartition of energy between the degrees of freedom cannot hold for the molecules of gases. The specific heats of solids at low temperatures prove that the translational kinetic energy of the atoms is not subject to the law, and even the energy of free translation of the atoms of helium has been shown to fall below the theoretical value $3/2R$ at high pressures and low temperatures [†]. We are therefore no longer justified in assuming that the mean kinetic energy of translation of a molecule is proportional to the temperature. Apparently the dynamical definition of temperature must be abandoned.

The best known equation of state is that of Van der Waals. It does not accurately represent the behaviour of gases; but this was scarcely to be expected, since in its deduction it was assumed that the volume occupied by the molecules is small in comparison with the volume of the gas, and the quantities "a" and "b" were taken as constant, whereas it is probable that these magnitudes vary with the temperature and density of the gas. On theoretical grounds, however, it seems to us that fewer objections can be urged against Van der Waals' equation than might be raised against other equations of state which are in much closer accord with the facts.

Van der Waals in deriving his equation assumed that the

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[*] Communicated by the Authors.
[†] Eucken, *Ber. Deutsch phys. Ges.* xviii. p. 4 (1916).

mean kinetic energy of translation of a molecule was proportional to the temperature. Strictly this is not true. We are only justified in concluding that

$$\left(p + \frac{a}{v^2}\right)(v - b) = \tfrac{2}{3} nm \overline{V}^2, \quad . \quad . \quad . \quad (1)$$

where the letters have their usual significance. In other words, the equation relates the pressure and volume of the gas with the total kinetic energy of translation of the molecules, but not with the temperature. If any relation is to be established between the pressure, volume, and thermodynamic temperature of a gas, some assumption will have to be made in order to replace that which is no longer strictly valid.

We assume that in a closed space which contains a large number of like molecules the ratio of the number of molecules per unit volume whose potential energy is A *to the number of molecules per unit volume whose potential energy is zero is given by the expression* $e^{-\frac{A}{kt}}$, k *being the gas constant for a single molecule, and* t *the thermodynamic temperature.*

It will be observed that the distinction between this assumption and the corresponding proposition deduced from Maxwell's laws of the partition and distribution of energy, is that t is substituted in the assumption for $\tfrac{2}{3}$ of the mean kinetic energy of translation in the corresponding proposition.

Starting from this assumption, a modified form of Van der Waals' equation can be deduced in the following way. Consider a column of gas in a field of force—let us say gravity. Take the axis of x in the direction of the force. The density of the gas will increase in the direction of increasing x. The increasing density of the gas will set up a field of cohesive force acting in the same direction as gravity and equal in magnitude to $\alpha \dfrac{d\rho}{dx}$, where ρ is the density of the gas and α a constant. Let m be the mass of a molecule of the gas. The sum of the forces due to gravity and cohesion, acting in the direction of x, on this molecule will be $m\left(g + \alpha \dfrac{d\rho}{dx}\right)$, g being the acceleration of gravity. From this must be subtracted the upthrust due to the fluid displaced by the molecule. Let the volume of fluid displaced be represented by b'. Then the total downward force acting on the molecule becomes : $(m - b'\rho)\left(g + \alpha \dfrac{d\rho}{dx}\right)$. If the molecule is displaced

through a distance dx the increase of potential energy is $-(m-b'\rho)\left(g+\alpha\dfrac{d\rho}{dx}\right)dx$ or $-(m-b'\rho)(g\,dx+\alpha\,d\rho)$. Whence, introducing the assumption which relates the temperature, the potential energy, and concentration of the molecules, we obtain

$$\frac{\rho+d\rho}{\rho}=e^{\frac{(m-b'\rho)(g\,dx+\alpha\,d\rho)}{kt}};$$

$$\therefore\quad \frac{d\rho}{\rho}=\frac{(m-b'\rho)(g\,dx+\alpha\,d\rho)}{kt}.$$

Substituting dp for $\rho g\,dx$ and solving the equation, we find

$$p=-\frac{kt}{b'}\log\frac{m-b'\rho}{m}-\frac{\alpha}{2}\rho^2.$$

If in this equation we put $\rho=\dfrac{m}{v}$, v being the volume occupied by a molecule, the equation reduces to

$$p=-\frac{kt}{b'}\log\frac{v-b'}{v}-\frac{a}{v^2}^{*}, \quad \cdot \quad \cdot \quad \vdots \quad \cdot \quad (2)$$

where $a=\dfrac{\alpha m^2}{2}$.

If in the above equation (2) P is substituted for $p+\dfrac{a}{v^2}$, the total internal pressure, the relation expressed by the equation

$$kt\frac{\dfrac{\mathrm{P}b'}{kt}}{e^{\frac{\mathrm{P}b'}{kt}}-1}=\mathrm{P}(v-b') \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

can easily be shown to hold.

The similarity between the left-hand side of equation (3) and the expression deduced by Planck for the mean energy of a resonator at temperature t will be immediately recognized, and the similarity suggests that there may be a close relation between the product $\mathrm{P}b'$ and the quantum $h\nu$.

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* If a and b are assumed to be constant the above equation has the defects of Van der Waals' equation. For example, it leads to the relation $\dfrac{\mathrm{R}t_c}{p_c v_c}\backsimeq 2\cdot 6$.

In this connexion it may be pointed out that when v is large in comparison with b', b' is the volume of the sphere whose radius is the mean minimum distance between the centres of two molecules during a collision. Bearing this in mind and comparing equations (3) and (1), it will be seen that $P\left(v - \dfrac{b'}{2}\right)$ is two-thirds of the mean kinetic energy of a molecule, and therefore

$$kt \frac{\dfrac{Pb'}{kt}}{e^{\frac{Pb'}{kt}} - 1} + \frac{Pb'}{2} = \frac{2}{3} \frac{m\bar{V}^2}{2}. \quad . \quad . \quad . \quad (4)$$

The left-hand side of (4) with $h\nu$ substituted for Pb' is Planck's modified expression for the mean energy of a resonator of period ν.

The distinction which is drawn above between thermo-dynamic temperature and the kinetic energy of a degree of freedom we regard as a provisional hypothesis which needs to be more carefully examined.

Note.—The above communication is a portion of a paper written in January 1919. It has been kept with a view to testing its practical applicability. However, in the correspondence of the April number of this Journal, M. N. Shaha and S. N. Basu refer to a paper on the Equation of State published by them in 1918 which had escaped our notice. In this communication the authors deduce from the well-known Boltzmann's entropy theory the equation

$$p = -\frac{Rt}{2b} \log \frac{v - 2b}{v},$$

which (since $2b = b'$) is identical with the characteristic equation deduced by us from apparently entirely different considerations. This agreement in the final results of two different modes of attacking the problem makes it desirable that the publication of our method of obtaining the above equation should not be further delayed.

Jesus College and St. John's College,
Oxford.

XXI. *Static Friction.*—II. *By* W. B. HARDY [*].

A. CHEMICAL CONSTITUTION AND THE LUBRICATION OF BISMUTH.

THESE experiments are a continuation of earlier work on the static friction of glass faces (Phil. Mag. ser. 6, vol. xxxviii. p. 32 (1919)). A slider having a curved surface was applied to a plane surface, both slider and plate being of bismuth [†]. This metal was chosen because it is highly crystalline and at the same time takes a high degree of polish. It therefore offered unusual facilities for comparing the friction of the amorphous state of the metal found on a burnished face [‡] with that of the crystalline state.

One of the faces being curved, contact was over an area defined by the weight and the elasticity of the material. The extent of this area is unknown, and the normal pressure over it not uniform. There are therefore unknown quantities which make it impossible to express the static friction in terms of a normal pressure. The observations of Burgess [§] show that nothing would be gained in this respect by employing two plane surfaces. The best obtainable surfaces touch only at points, and if of glass, show Newtonian colours.

The tractive force was applied slowly, and in such a way as to make the slider rock forwards. The static friction therefore is that between freshly applied faces. The method is apt to give undue importance to viscosity, and care is needed to distinguish between transitory effects due to viscosity and true lubrication (see the earlier paper).

Passing from glass to bismuth faces, one enters another world. Meticulous care perfected by practice is needed to secure clean glass faces, and, once secured, they readily contaminate by the spreading of a film of matter from solids with which they are in contact or by condensation from the air. The edges of a plate oppose the spreading of most if not all fluids, and it is this interesting property of edges which renders exact work with glass possible.

Bismuth, on the other hand, can be cleaned by simply rubbing the face with wash-leather, and the clean plate

[*] Communicated by the Author.
[†] I am indebted to my friend Mr. Heycock for a specimen.
[‡] Beilby, Proc. Roy. Soc. lxxii., p. 218 (1993).
[§] Proc. Roy. Soc. A. lxxxvi., p. 25 (1911).

may be handled freely if actual contact with the burnished face is avoided. To clean the faces the plate and slider were washed in ethyl alcohol 98 per cent., drained, and burnished with wash-leather. Wash-leather clings to a clean face of bismuth. When the surface is rubbed with it, there is a characteristic harsh feel and characteristic notes of high pitch are given out *if the surface be clean*. Rarely a lubricant is found which will not be displaced from the surfaces in this simple way: it is then necessary to clean them with rouge.

What is the test of cleanliness? There is no criterion other than static friction itself. When static friction is maximal it is assumed that the surfaces are clean, or, to put it more exactly, " clean " faces are defined as those whose static friction reaches a certain level such that a force of 34,300 dynes just fails to produce movement in the slider used throughout, whose weight was 70·5 grammes and radius of curvature 25·5 millimetres. This assumption is justified by the fact that every substance tried was found to reduce this datum value when applied to the surface. In this bismuth differs from glass. Many substances are neutral to glass in that they do not alter the static friction. No substance neutral to bismuth was found.

This section, with the limitations noticed in paragraph 2, is confined to a study of one variable—namely, the chemical constitution of the lubricant. One point should, however, be mentioned and reserved for future discussion. A few lubricants appear to abolish the static friction of bismuth altogether (*e. g.* ricinolic acid). In these cases the value given is that at which the tractive force produced sliding so slow as to be just detectable by unaided vision.

In testing a fluid the surfaces were flooded so that the slider moved in a pool. The thickness of the film of lubricant then was that determined naturally by capillarity acting in opposition to the normal pressure. Solid lubricants were deposited in a layer, thick enough to dull the burnished surfaces, from dilute solutions in ethyl alcohol, benzene, or ether. There is a danger lest the friction of bismuth against the solid in mass be mistaken for what is sought for, namely, the friction of bismuth against bismuth lubricated by the solid. The former obviously is an important limiting value when the lubricant is a solid. Whether it is the only value and identical with the latter will be considered on some future occasion. In the meantime it may be noted here that the value of the friction of bismuth lubricated with

cholesterol was the same for an obvious smear of the solid and for the invisible film left when the smear had been wiped away by cotton-wool moistened with alcohol. On the other hand, the value of the coefficient for a visible layer of stearic acid deposited from benzene or ether was ·20 and for an invisible film ·15. I incline to the view that the difference is due to the difficulty of getting rid of the last traces of the solvent from some substances.

The force which just fails to move the slider *immediately it is applied* is taken as the measure of the friction. Precision in this matter is needed, because static friction is sometimes a function of the time during which the external force has acted. The significance of this time factor is not yet clear.

Solid Bismuth.—Surface burnished : some of the fluids used, however, etched the surface so as to expose the crystals : such are the acids formic, acetic, propionic, and valeric, and the sulphur compounds thiophenol and benzyl-hydrosulphide. Temperature 11–14° C. Measurements made in a current of dry air. Weight of slider 70·5 grammes ; radius of curvature 25·5 millimetres.

The results given in the column headed Static Friction are the values of the ratio applied force in grammes divided by the weight in grammes of the slider.

Static friction is a function of the molecular weight of the lubricant ; and in a simple chemical series of chain compounds such as fatty acids and alcohols or paraffins a good lubricant will be found if one goes high enough in the series. But it is not a simple function, as inspection of the charts and curves shows. The friction, for instance, rises sharply in moving from $CHCl_3$ to CCl_4 and from phenol to catechol and quinol. The influence of molecular weight is overshadowed by the influence of chemical constitution.

In some simple chemical series the relation appears to be a linear one. Examples are paraffins ; the series benzene, naphthalene, anthracene ; and, making allowance for the fact that the ammonia was a solution in water, the series ending with propylamine.

In the aliphatic alcohols and acids the chain is weighted at one end with the ·OH or ·COOH group, and the simple linear relation to molecular weight is disturbed thereby.

The relation of lubricating qualities to viscosity broadly resembles that to molecular weight. In a simple chemical series lubrication and viscosity change in much the same

P 2

way with molecular weight, but that there is no fundamental relation between viscosity and lubrication is shown by the following figures :—

	Viscosity at 20°.	Static friction.
Carbon tetrachloride	·0096	·43
Chloroform	·0056	·30
Acetic acid	·0122	·40
Octyllic acid	·0575	·19
Benzene	·0065	·39
Toluene	·0058	·28
Benzyl alcohol...............	·0558	·31

Fig. 1.

Fig. 2.

Fluidity of the lubricant has no constant significance, as indeed might be expected on the surface-energy theory of lubrication. The curves for acids, alcohols, and paraffins show no break where with increasing molecular weight the lubricant becomes a solid at the temperature of observation. Compare also benzene, naphthalene, and anthracene ; menthone and menthol ; thymol and carvacrol,

The upward trend of the first part of the curve for the aliphatic alcohols is in agreement with the fact that methyl alcohol is abnormal in some of its physical properties such as specific gravity.

In their qualities as lubricants of bismuth, ring compounds are the converse of chain compounds : thus the effect of a double-bonded atom is to decrease the lubricating value of the former and to increase that of the latter. As examples, compare naphthoic acid with double-bonded oxygen, with naphthalene, menthone with menthol, cyclohexanone with cyclohexane, benzoic acid with benzene. As examples of double-bonded carbon compare cinnamic ester with hydrocinnamic ester, dipentene, having two unsaturated carbon atoms, with menthol and cyclohexane. On the other hand, the presence of unsaturated atoms increases the lubricating qualities of chain compounds, whether it be the double-bonded oxygen of ketones or acids, or carbon of olefines and alcohols ; but this rule is departed from (in the case of acids) when the chain becomes much elongated.

Whatever view be taken of the structure of the benzene ring, it must be admitted to be less saturated than cyclohexane, and we find consistently that the more saturated cyclohexane and its derivative are the better lubricants.

When ring and chain are joined as in butylxylene, the result is a better lubricant than either.

When the atoms are disposed with complete symmetry about a carbon atom the result is a very bad lubricant, as we see in carbon tetrachloride and the alcohol penterythritol $C(CH_2OH)_4$.

In the ring compounds the replacement of hydrogen decreases lubricating power in the case of N, : O, or $\cdot COOH$, and increases it in the case of other groups in the order $C_2H_5 < CH_3 < OH$.

The effect of a second group of the same or of a different kind is to decrease the effect of the first. Compare for instance toluene with xylene ; catechol, quinol, and cresol with phenol ; and methyl cyclohexanol with cyclohexanol. The simpler the group the more effective it is. Compare cymene with toluene or xylene ; and benzyl alcohol with phenol.

The esters occupy a quite unexpected position. The simple aliphatic esters are much worse lubricants than their related acids or alcohols. On the contrary, the ring esters are better lubricants than are their related acids (*e. g.*, ethyl benzoate and benzoic acid).

Perhaps the most interesting substances are the hydroxy

acids with OH and COOH groups. This conjunction pro-
duces a remarkable increase in the lubricating power of
a chain compound (α. lactic acid and ricinolic acid), and
almost destroys lubricating action in the case of the ring
compounds (salicylic and benzylic acids).

It will be noticed that no ring compound is a good
lubricant. Even cholesterol with the molecular weight 366
is no exception.

The group SH acts much as OH, thiophenol C_6H_5OH
and benzylhydrosulphide $C_6H_5 . CH_2SH$ resembling phenol
and benzyl alcohol respectively.

It need hardly be stated that these conclusions are pre-
sented not as generalizations, but as a summary of the
relations which actually obtain amongst the limited number
of compounds studied. The fact that the influence of
chemical constitution differs widely in degree if not in kind
when glass is lubricated would alone enforce caution.

Mixtures of lubricants were not specially studied, but
it is certain that they will reveal complex relations of
great practical importance. In the experiments solids were
deposited in thin layers on the plate from very weak
solutions in ether, ethyl alcohol, or benzene. In most cases
the change in friction was followed whilst the solutions were
drying and nothing abnormal noted, the friction changing
rapidly to the value for the solid in the last stage of drying,
and in such a way as to suggest that the combined effect of
the two substances was merely additive. In some cases,
however, *e. g.* phenol and cetyl alcohol, abnormal values
were noted. Just before drying was complete the friction fell
to a comparatively low level (·07 cetyl alcohol, ·15 phenol).

The values for paraffins can be considered only as
approximate. Octane was the purest specimen employed.
The solid paraffins were identified by their melting-points
and were not wholly free from unsaturated substances, but
the displacement of the observed frictions due to this may
be considered as being small.

The lower members of the fatty acid series etched the
surfaces so as to expose the crystals, the action being slow
and slight in the case of valeric acid. Capryllic acid did
not etch the surface. This action no doubt contributed to
the bending downwards of the first part of the curve.

I am indebted to Professor Lapworth for examples of
cyclic compounds, to Sir George Beilby, Mr. Dootson, and
Dr. Ida Maclean for various specimens, and especially to
Sir William Pope for permission to raid his large collection
of substances.

Faces clean. Static friction ·5.

CHAIN COMPOUNDS.

Alcohols.

	Static friction.		Static friction.
Methyl	·29	Isopropyl	·32
Ethyl	·32	Isobutyl	·30
Propyl	·34	Allyl	·29
Butyl	·30	Glycol	·30
Amyl	·27	Glycerol	·22
Octyl	·25	Penterythritol	·40
Cetyl	·17		

Acids.

Formic	·45	Stearic	·15
Acetic	·40	Oleic	·10
Propionic	·31	Ricinolic	·02
Valeric	·28	α Lactic	·20
Capryllic, fluid	·19	Glyceric	·22
,, frozen on plate	·05		
Acetone	·32	Ethyl ether	·33
Methyl ethyl ketone	·29		
Ethyl acetate	·36	B.P. " paraffin "	·20
,, valerianate	·35	Solid paraffin, m.p. 30·5	·09
Tristearin	·24	" ,, m.p. 46	·07
Triolein	·14	Carbon tetrachloride	·43
Acetone di carboxylic di		Chloroform	·30
ethyl ester	·29		
		Amylene	·26
n. Hexane	·37	Octylene	·28
n. Heptane	·346		
n. Octane	·32	Butyl xylene	·27

RING COMPOUNDS.

	Static friction.		Static friction.
Benzene	·34		
Ethyl benzene	·32		
Iodo benzene	·30	Thiophenol	·22
Toluene	·28	Benzylhydrosulphide	·23
Xylene	·30		
p-Cymene	·31	Pyridine	·33
		Piperidine	·32
Phenol	·25		
Catechol	·39	Naphthalene	·29
Quinol	·40	Anthracene	·26
m-Cresol	·26	β Naphthol	·33
Benzyl alcohol	·31	Naphthoic acid	·39
Benzoic acid	·38	Carvacrol	·23
Phthalic acid	·37	Thymol	·24
Cinnamic acid	·27	Menthol	·26
Benzilic acid	·45	di Pentene	·31
Salicylic acid	·41	Camphor	·24
Ethyl benzoate	·33	Active ethyl ester of	
o-Phthalic ester	·27	Camphor oxime	·33
Ethyl hydrocinnamate	·28	Iso-Cholesterol	·27
Ethyl cinnamate	·32		

CYCLIC COMPOUNDS.

Cyclohexane	·31			
Methyl cyclohexane ...	·30			
1.3. di Methyl cyclohexane	·29	Cyclohexanone	·35
		1.2. Methyl cyclohexanone	·32
Cyclohexanol	·20	1.3. ,, ,,	·35
1.2. Methyl cyclohexanol	·28	1·4. ,, ,,	·33
1.3. ,, ,,	·25		
Ammonia fortiss.	·34	Castor oil	·03
Triethylamine............	·30		
Tripropylamine	·26	Water	·33

B. INFLUENCE OF THE BEILBY FILM.

In 1903 Beilby described how, in the process of burnishing, or polishing, the substance of the solid actually flows so as to cover the surface with a film of amorphous material. The formation of the Beilby film can be readily followed on bismuth, and in order to test its influence some measurements of friction were made after it had been etched off by dilute acid so as thoroughly to expose the coarse crystalline structure of the metal. The following values were obtained :—

	Burnished.	Etched.	Ratio.
Benzene	·34	·39	·87
Pyridene	·33	·4	·83
Ethyl alcohol	·32	·39	·82
Butyl xylene	·27	37	·72
Octyl alcohol...	·25	·36	·7
Cyclohexanol	·20	·33	·6

The substances are arranged in the order of the value for static friction of burnished faces. The values for etched faces do not follow this order, whilst the ratios do. This may be merely coincidence, but it raises questions which must be reserved for discussion until more facts are available.

C. ADSORPTION OF LUBRICANTS.

The theory outlined in the first paper (this journal, ser. 6. vol. xxxviii. p. 32 (1919)) embodies two propositions : the first, that resistance to slipping is due to cohesion even when a lubricant is present, and that a lubricant decreases friction by partially or wholly masking the cohesive forces of the solids ; the second, that a lubricant maintains its position against the normal pressure because its surface energy is a function of the thickness of the layer.

The capacity for decreasing friction, then, is a function of the potential of the attractive forces between lubricant and

solid integrated through the depth of the layer, whilst the stability of a layer of a given thickness is a function of the differential coefficients of the interfacial energy taken with reference to the thickness.

The integral is the work done by the cohesive forces acting between lubricant and solid when the layer of the former is interposed between the faces of the latter. This may be expressed in terms of a tension, and thereby become measurable, if one solid face alone is considered. Let t be the work in ergs done per unit area in removing a layer from the surface of a mass of fluid, the layer being so thin that the fluid composing it is not in mass; t will then also be the tension of the free layer. Now apply the layer to the solid face. The forces of attraction between the two will do work. Let this be t' per unit area. The tension T of the composite surface so formed will then be

$$\mathrm{T} = t + \mathrm{T}_s - t',$$

where T_s is the tension of the solid.

For the difference between the tension of two composite surfaces formed on the same solid but with different fluids a and b we have

$$\mathrm{T}_a - \mathrm{T}_b = (t_a - t_b) + (t_b' - t_a').$$

If we assume that t_a bears the same ratio to t_b as do the tensions of the fluids in mass and choose for the purpose of experiment two fluids whose surface tensions are equal, the term $(t_a - t_b)$ will vanish, and the left-hand side of the equation be positive or negative according as the term $(t_a' - t_b')$ is positive or negative.

In an earlier paper (this journal, ser. 6, vol. xxxviii. p. 49 (1919)) I described how films of insensible thickness form on a plate of glass about drops of certain fluids, and how the drops are moved over the surface of the plate by the contractility of the films. This property may be utilized to measure the sign of the term $(t_a' - t_b')$. Let one drop of each of two fluids a and b be placed on the plate: there will form about each a composite surface of tensions T_a and T respectively. If T_a is greater than T_b the drop a will move away from drop b and the latter will pursue it and, if the surface tensions of the fluids are equal, such movement will show that the adhesion of the film of b to the surface is greater than that of a.

Benzene and propionic acid are a pair of fluids whose surface tensions are practically equal, while the former

does not and the latter does lubricate the surface of glass. A drop of each was placed on a clean glass plate a few millimetres apart with striking results. The drop of acid chased the drop of benzene to the edge of the plate where, owing to the characteristic edge repulsion, the latter was split into two. We have, I think, in this observation direct evidence that the forces of attraction operate more strongly between a solid face and a good lubricant than between it and a bad lubricant.

The better lubricant is more strongly adsorbed by the solid face. Olefines are better lubricants than paraffins, and one of the methods in use for freeing the latter from the former is by taking advantage of the fact that olefines are more strongly adsorbed by a solid. The impure paraffin, in commercial practice, is filtered through a dry powder to clear it of unsaturated subtances.

Of the pair of fluids acetic acid–water, a drop of the latter pursues strongly a drop of the former on a plate. The surface tension of water is much higher than that of acetic acid, and, since water does not and acetic acid does lubricate glass, the decrement due to interaction with the solid face is, according to theory, less for water. Therefore, in respect of both terms of the right-hand member of the equation the advantage lies with the insensible film of water.

In both of these pairs the result was the same whichever one of a pair was placed first on the plate. Another pair, benzene and acetic acid, gave uncertain results. According to theory benzene should move away and the acid follow, and this usually happened. Sometimes, however, when a drop of acid was placed on a plate on which a drop of benzene already stood, the latter darted away, as though the vapour of acetic acid had lowered the tension of the insensible film of benzene between the drops ; sometimes the drops simply moved away from each other. These complications are to be expected, for we have the tensions of three films to consider—those of the relatively pure films outside each drop, and that of the film of mixed origin between them. If the vapours condense in the last in such proportions as to produce a film of tension less than that of either pure film, the drops will be pulled apart.

Reasons are given in the earlier paper for believing that an insensible film about a drop is formed always by condensation of vapour and not by direct spreading.

XXII. *On the Specific Heat of Saturated Vapours and Entropy-Temperature Diagrams of Fluids.* By ALFRED W. PORTER, *D.Sc., F.R.S.*[*]

IN a paper with the above title in the June number of the Philosophical Magazine (p. 633) Sir J. A. Ewing extends our detailed knowledge of the specific heats of saturated vapours, and at the same time corrects certain loose statements which have appeared at various times.

I desire to point out that the question (as might be expected) is very thoroughly discussed by Duhem in his *Traité Elémentaire de Méchanique Chimique*, t. ii. p. 211, &c. Duhem shows that if the specific heat of the saturated vapour is plotted against temperature, its form is that of an inverted, unsymmetrical U ; that sometimes this lies wholly in the negative region ; but that it may lie higher up so as to cross into the positive region, and that if it does this it crosses twice.

These are the two possibilities of which Sir J. A. Ewing gives detailed examples.

He asserts, however, that positive values do not occur for sulphurous acid. This statement itself appears to be in error. The case of sulphurous acid (SO_2) has been directly studied by Mathias (*Comptes Rendus*, t. cxix. p. 849 ; *Ann. de la Faculté des Sciences de Toulouse*, t. x. (1896), quoted by Duhem, *loc. cit.*). The importance of this substance in connexion with mechanical refrigeration warrants one in quoting his results in the following table :—

t° C.	$K_s.$	t° C.	$K_s.$
0	$-0\cdot410$	100	$+0\cdot027$
10	$\cdot390$	110	$+0\,062$
20	$\cdot357$	120	$-0\cdot078$
30	$\cdot330$	125	$\cdot176$
40	$\cdot300$	130	$\cdot306$
50	$\cdot270$	135	452
60	$\cdot235$	140	$\cdot620$
70	$\cdot205$	145	$\cdot848$
80	$\cdot165$	150	$1\cdot253$
90	$-0\cdot095$	155	$-3\cdot850$

The temperatures of inversion are 97°·5 C. and 114° C.

In order to free the subject from all possible misunderstanding, I wish to add that the entropy of the liquid is not

$$\int_0^t \frac{C_p dT}{T},$$

where C_p is the specific heat at constant pressure, even with

the proviso that the value of C_p taken must be that at saturation. The value C_p must be replaced by K_w, the specific heat of saturated liquid. The difference between C_p and K_w is certainly negligible at temperatures sufficiently remote from the critical temperature, but it tends towards $+$ infinity as the critical temperature is approached. The relation between the two quantities is

$$K_w = C_p - T\left(\frac{\partial v}{\partial T}\right)_p \frac{dp}{dT},$$

or K_w may be given conveniently in terms of C_v, the specific heat of the liquid at constant volume ;

$$K_w = C_v - \frac{T\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T} \frac{ds}{dT},$$

where s is the specific volume of the liquid at saturation.

The values of K_w obtained by Mathias for SO_2 are given herewith :—

$t°$ C.	K_w.	$\Delta \times 10^4$.	$t°$ C.	K_w.	$\Delta \times 10^4$.
−20 ...	+0·315				20
		1	110 ...	+0·442	
−10 ...	·316				32
		1	120 ...	·470	
0 ...	·317				40
		2·5	130 ...	·510	
10 ...	·3195				110
		4·5	140 ...	·620	
20 ...	·324				252
		6	150 ...	·872	
30 ...	·330				480
		8	151 ...	·920	
40 ...	·338				600
		9	152 ...	·980	
50 ...	·347				900
		12	153 ...	1·070	
60 ...	·359				2850
		13	154 ...	1·355	
70 ...	·372				4450
		15	155 ...	1·800	
80 ...	·387				10500
		16	155·5...	2 85	
90 ...	·403				
		19			
100 ...	·422				

I have added the increase per degree, Δ, in order to show that K_w for SO_2 is not a linear function of the temperature even in a region remote from the critical region.

XXIII. *On Cohesion*. *By* Herbert Chatley, *D.Sc.* (*Lond.*), *Harbour Investigation Office, Huangpu Conservancy Board, Shanghai, China* *.

THE objects of this note are as follow :—

    (1) To disprove the Kelvin theory of Newtonian cohesion.

    (2) To indicate dimensional relations of cohesion to gravitation and electric chemical affinity.

    (3) To suggest an empirical gravitation-cohesion formula.

    (4) To indicate cohesion values in certain hydrogels.

(1) Kelvin's theory of Newtonian cohesion † states that " Cohesion will be a necessary consequence of gravitational attraction provided only that the space occupied by the atoms of a material body is sufficiently small in comparison with its bulk " (de Tunzelman).

If two cubes in " perfect contact " be considered, each can be imagined to consist of three sets of n straight bars, each set mutually perpendicular. The bars perpendicular to the interface each have a mass $\frac{1}{3n}$ of the original mass of either cube, and " however small may be the masses of two such bars, the attraction between them, per unit of sectional area, *may be increased without limit* by diminishing the sectional area of the two bars while keeping their masses constant. Now, the total attraction between the two groups (of bars) is greater than the sum of the attractions between the pairs, that is to say, greater than n times the attraction between any pair of conterminous bars. The whole attraction between the two cubes may therefore be made to *attain any value, however great*, by sufficiently diminishing the sectional area of the bars while keeping their number and the mass of each constant " (author's italics).

As far as the writer is aware, this reasoning has not been definitely challenged, and has certainly been accepted by many physicists. Nevertheless, it appears not only unconvincing but incorrect. The area for which the attraction between two of the postulated conterminous bar elements is

* Communicated by the Author.

† Trans. Roy. Soc. Edin. Apr. 21, vol. iv. (1862); Pop. Lect. vol. i.; Dewar, *Encyclopædia Britannica*, 11th ed. Article, " Liquid Gases "; de Tunzelman, 'Electrical Theory and the Problem of the Universe.'

effective is the whole section of the bar, and the actual size of the atoms, independent of the space they occupy, has nothing whatever to do with it.

One can scarcely conceive how Kelvin overlooked the fact that the mass of the atom is a function of the spacing, so that in the molecular realm the gravitational stresses still remain minute. If we consider two 1-centimetre cubes of a substance of density *three* and an atomic interval of one Ångström unit, the mass of a bar of atoms of the type postulated is 10^{-16} gram.

The mutual attraction of two collinear bars of unit length end to end is

$$f = M_1 . M_2 . \log_\epsilon \left[\frac{(1+\delta)^2}{\delta(2+\delta)} \right],$$

where M_1, M_2 are the masses per unit length and δ the distance between the ends (Earnshaw, 'Dynamics,' p. 327). In this case, when $M_1 = M_2$ and $1/\delta$ is very large, we can write

$$f = 2 \cdot 3026 \, M^2 . \log_{10} \left(\frac{1}{2\delta} \right).$$

If $\delta = 10^{-8}$ and $M = 10^{-16}$,

$$f = \text{about } 2 \times 10^{-31} \text{ dyne.}$$

If the number of bars, "n," is $(10^8)^2$, then

$$F_1 = nf = 2 \times 10^{-15} \text{ dyne on a square centimetre.}$$

The additive effect of the various bars on those other than their own partners must also be considered. *Even* if we assume that each bar of the cube acts on all those of the second cube other than its own mate with the same force as on its own mate, then the total attraction, due to the longitudinal bars only, is but

$$F_2 < n^2 f = 20 \text{ dynes per sq. cm.}$$

[*Note.*—Taking the cubes as wholes, we have for the *whole* attraction (of all the masses across the interface) about 20 dynes.]

In actual fact, most solids have a tensile strength of more than 1 kilogram per sq. cm. or 10^6 dynes per sq. cm., and certain steels (with atomic intervals certainly larger than 10^{-8} cm.) have tensile strengths as great as 25 tonnes per sq. cm. or $2 \cdot 5 \times 10^{10}$ dynes per cm.^{2} It is to be presumed that Kelvin had in mind the fact that $\log_{10} \left(\frac{1}{2\delta} \right)$ becomes

infinity when $\delta = 0$, and alludes to this in the words "perfect contact"; but it is quite certain that δ cannot be less than the distance between the centres of the atoms (because it may be taken anywhere when considering a solid piece). This consideration appears to the writer a clear disproof of Kelvin's hypothesis, and shows that cohesion immensely exceeds Newtonian gravitation.

(2) Van der Waals's gas formula indicates that the "molecular pressure" per molecule pair varies inversely as the inverse fourth power of the distance between the molecules [*]. The mere existence of the fluid phase at almost the same temperature as the solid phase of the same substance with only very slight expansion also seems to show that the rate of diminution of the cohesive forces is higher than the inverse square.

If the space variation is higher than the inverse square, then the additive effect of distant atoms in the solid is much less important and even negligible, so that the forces per atom pair may be considered as indicating roughly the actual bonds between the atoms. In the case of the special steels referred to above, if the number of atoms per sq. cm. is 10^{15}, the ultimate tension at rupture (with less than 5 per cent. *mean* separation of the atoms) is over 10^{-5} dyne per atom pair.

As Sutherland has pointed out, pairs of electron doublets at atomic distances may have differential attractions of this order at close proximity. The electrostatic bond of a doublet is of the order .

$$2 \times 10^{-19} \div (10^{-8})^2 = 10^{-3} \text{ dyne,}$$

and differential effects may easily exceed 10^{-5} dyne at small distances. There does not, on the other hand, seem to be a complete basis in the Sutherland theory for the chemically indifferent character of cohesion (as distinguished from adhesion). Van der Waals's gas formula also implies that "molecular pressure" is to some extent a function of mass.

The writer suggests that, as far as the fragmentary information goes, it may be stated that cohesive forces are less, but not greatly less, than the electrostatic tractations of chemically active atoms, and that in homogeneous substances they are functions of the mass and positions of the individual atom or atom-group (molecule).

Crystallization shows that cohesive forces are vectorized.

[*] Chatley, Proc. Phys. Soc. Lond. vol. xxx. pt. iii. April 15, 1918.

It would appear that in "amorphous" solids crystalline grains are cemented together by "solid" films of the mother liquor from which the crystals have formed (Desch, Institute of Metals, Sept. 11th, 1919), and in such thin films presumably the principal crystal axes are perpendicular to the faces of the films.

(3) Cohesion being vectorized, no "central-force" formula can correctly express it, but the writer suggests an empiric rule for *mean* cohesions of hypothetical atom spheres

$$t_2 = Gm^2/d^{2+\frac{n}{k}},$$

where n is between 4 and 5 ; t_2 is the cohesion bond ;
             k is ratio (>1) of mean atomic interval to that at absolute zero ;
             G, m, and d as in the Newtonian formula.

This formula has three possible advantages :—

(a) It is continuous with the Newtonian formula, *i. e.* when $k = \infty$, $t = Gm^2/d^2$.
(b) It is dimensionally fairly correct for many cases of cohesion.
(c) At absolute zero (*i. e.* atomic "contact") it practically agrees with chemical affinity.
(d) Its space rate of decrease is not inconsistent with known strengths of materials. Near absolute zero the index of the distance is the inverse sixth.
(e) It is polarized (possibly not correctly), since for all powers other than the inverse square the force is not centralized.

[*Note.*—The inter-atomic repulsion appears to be of the order

$$t_1 = \frac{RT}{Nd_0} \cdot \frac{1}{3(k-1)},$$

where $d_0 =$ atomic spacing at absolute zero ; R, T, and N as in kinetic theory of gases.]

(4) The writer is especially interested in this subject in connexion with problems of accretion, erosion, and stability of river-mud, and has obtained certain indications of interest from conditions in the Huangpu River :—

(a) Fine mud resists erosion until the hydrodynamic tangential drag on a surface particle equals about 10^{-6} dyne, *i. e.* each particle, containing some millions of molecules, is retained by at least one inter-molecular "cohesion" bond.

As a result of this, fine mud beds are not easily eroded, whereas coarser sand is easily moved.

(*b*) Colloidal suspension and plasticity in gels becomes of importance when the weight of the particles is about equal to one inter-molecular cohesion bond (*e. g.* with cubic particles, s. g. 2·5, each has a diameter

$$d = \sqrt[3]{\frac{10^{-6}}{(2{\cdot}5 - 1)981}} = 9 \times 10^{-4}\,\text{cm.}).$$

This agrees with the dimension usually assigned as a maximum to colloidal particles.

XXIV. *The Adjustment of Observations.*
By R. Meldrum Stewart [*].

IN a recent article[†] on this subject, Dr. Norman Campbell describes a method of reduction of observations which is proposed to replace the " method of least squares." Among other statements of a similar tenor, it is claimed that the latter is " an intolerably cumbrous method for obtaining quite misleading results," and that the method proposed " is incomparably simpler and gives results which are not misleading " ; and the intention is expressed of attempting to entirely subvert the method of least squares. In the interests of mathematical accuracy, and to prevent the acceptance without due examination of misleading theory, it does not seem right that such statements as these, and such reasoning as occurs in parts of the above article, should be allowed to pass unchallenged.

The " method of least squares " is based on two fundamental postulates, neither of which appears to be questioned by Dr. Campbell: (1) that the probability of the occurrence of an error of any given magnitude is a function of that magnitude ; (2) that in the case of several observations to determine a single quantity, made under the same conditions, the arithmetic mean is the most probable value of the quantity sought : these postulates are the mathematical equivalent of the Gaussian law of errors. Whether or not this law of errors, and therefore these two assumptions, be strictly true or not, is a question which it is not proposed to argue at present ; the result of experience, however, shows the law to be at least a close approximation to the

* Communicated by the Author.
† Phil. Mag. February 1920, p. 177.

truth.   The point which it is desired to emphasize is that, if
these two postulates be granted, the whole method of least
squares, as properly stated and applied, follows inevitably
by rigorous mathematical reasoning.

It is quite true that in most, if not all, of the present-day
text-books on the subject, the reasoning which purports to
establish the principles of the method is anything but
rigorous; and the method itself is at least in some in-
stances grossly misapplied.   There is perhaps no subject in
the realm of mathematics where clear and careful thinking
and rigorous reasoning are more necessary than in the theory
of probability and its application to the theory of errors ;
and yet it would be difficult to find a subject where con-
fusion of thought and loose reasoning are more prevalent :
among the most obvious examples of this might perhaps be
mentioned the common confusion of the terms " true value "
and " most probable value," "error" and "residual," with the
loose reasoning that inevitably arises from such confusion.

But from the fact that loose reasoning is frequently used
in attempts to deduce the principles of the method, it by no
means follows that these principles have not been, or cannot
be, established by rigorous reasoning.   Most, if not all, of
the fundamental principles, and many of the details, of the
theory have been correctly developed by the classic authors
on the subject, as may be readily verified by reference to the
original memoirs.   It seems worth while to emphasize this
fact because, by most of those who have occasion to adjust
observations, these classic authors are seldom read, and the
prevalent ideas on the method of least squares are those
garnered from the more or less faulty text-books of the
present day.

It remains to consider briefly the three types of problems
mentioned by Dr. Campbell.

The first type is the ordinary case of the arithmetic mean.
It may be remarked in passing that the problem before us
is not the determination of the " true value," even with the
limitation * imposed by Dr. Campbell.   The true value must
for ever remain unknown ; all that we can hope to attain is
the " most probable value," and this is all that is, or can be,
claimed for the arithmetic mean.   Further—and here we
arrive at the crux of the whole theory of errors—the adoption
of the arithmetic mean as the most probable value is a *pure
assumption* ; in fact, if the law of errors is any other than
the Gaussian law, the arithmetic mean is *not* the most

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* *Loc. cit.* p. 178, footnote.

probable value. It is therefore (as also on practical grounds) absurd to speak of the possibility of establishing it directly by experiment.

The second type of problem is the familiar one of direct conditioned observations. Dr. Campbell makes the indefinite statement * that in one type of this problem the method of least squares is not applicable : the statement is supported by no reasoning, and his objections are not clear ; the point will not be discussed here, but it will appear from the discussion of the general case below that the allegation is incorrect.

It is, however, to the problem of what he calls the third type that he pays more particular attention. As enunciated †, this is the perfectly general case of indirect observations ; as such, it includes not only the case of the arithmetic mean, but also those of both direct and indirect conditioned observations : in fact, the first and second types are merely particular cases of the third ; the solution given ‡, however, and stated to be that of the method of least squares, is entirely incorrect. It may be worth while to consider this general problem in some detail, and to indicate the correct method of solution, more especially since the treatment in the text-books is less general, and does not appear to cover all cases §.

It is assumed that measurements have been made on quantities whose true values are $x_1, y_1, z_1 \ldots x_2, y_2, z_2 \ldots x_3, y_3, z_3 \ldots x_N, y_N, z_N \ldots$, and that these quantities are known to be related by the equations

$$\left. \begin{array}{l} f_1(x_1, y_1, z_1 \ldots a, b, c \ldots) = 0, \\ f_2(x_2, y_2, z_2 \ldots a, b, c \ldots) = 0, \\ \quad \vdots \qquad \vdots \qquad \qquad \vdots \\ f_N(x_N, y_N, z_N \ldots a, b, c \ldots) = 0, \end{array} \right\} \quad . \quad . \quad (1)$$

the forms of the functions $f_1, f_2 \ldots f_N$ being known, but not the values of the constants $a, b, c \ldots$. It is required to determine the most probable values of $a, b, c \ldots$, the number of which we shall suppose to be q $(q < N)$. If the number of the observed quantities in each of the equations (1) be n, there are in all evidently Nn observed

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* *Loc. cit.* pp. 182 and 191.
† *Loc. cit.* p. 179.
‡ *Loc. cit.* p. 180.
§ See, for example, the two specific problems solved below.

quantities, and therefore Nn observation equations[*]; the equations (1) are condition equations[†], expressing conditions which are exactly fulfilled by the true values of all the quantities involved, and must therefore also be exactly fulfilled by the most probable values to be deduced.

If we denote the actual results of the observations on the quantities x_1, y_1, z_1, etc. by x_1', y_1', z_1', etc., the Nn observation equations will be

$$\left.\begin{array}{cccc}
x_1 = x_1' & y_1 = y_1' & z_1 = z_1' & \text{etc.} \\
x_2 = x_2' & y_2 = y_2' & z_2 = z_2' & ,, \\
\cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot \\
x_N = x_N' & y_N = y_N' & z_N = z_N' & ,,
\end{array}\right\} \quad . \quad . \quad (2)$$

There are then in all (including the observed quantities and the unknown constants $a, b, c \ldots$) $Nn + q$ unknown quantities whose most probable values are to be deduced from the Nn observation equations (2) in conjunction with the N condition equations (1).

Since, however, the equations (1) are non-linear, they must first be reduced to the linear form. To effect this, we deduce by some approximate method quantities $A, B, C \ldots X_1, Y_1, Z_1 \ldots X_2, Y_2, Z_2 \ldots$ etc., which are reasonable approximations to $a, b, c \ldots x_1, y_1, z_1 \ldots x_2, y_2, z_2 \ldots$ etc., and put

$$\begin{array}{cccc}
a = A + \triangle a & x_1 = X_1 + \triangle x_1 & y_1 = Y_1 + \triangle y_1 & \text{etc.} \\
b = B + \triangle b & x_2 = X_2 + \triangle x_2 & y_2 = Y_2 + \triangle y_2 & ,, \\
\cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot
\end{array}$$

where $\triangle a, \triangle b, \triangle c \ldots \triangle x_1, \triangle x_2, \triangle x_3 \ldots$ etc. are corrections to the approximate values $A, B, C \ldots X_1, X_2, X_3 \ldots$ etc., and are so small that for a first approximation their squares

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[*] An observation equation is a statement of equality between an observed value and an expression which in its simplest form may be merely the true value of the observed quantity, or on the other hand may be a function of one or more quantities whose values are required. Thus to every observation there corresponds one observation equation, and *vice versa*; and further, an observed value can enter an observation equation only as a linear quantity with coefficient unity. It seems desirable to stress these points, since they are sometimes overlooked; in fact it appears to be a certain confusion on this subject which has led Dr. Campbell astray in his solution.

[†] For a very sensible remark on the distinction which should be observed between the terms "observation equation" and "condition equation" (terms which are often confused), see Merriman's 'Theory of Least Squares' (original edition), footnote to Art. 56, p. 60.

may be neglected; these corrections are now the quantities whose most probable values we require. Substituting the above values in equations (1) and expanding by Taylor's Theorem we obtain

$$f_1(X_1, Y_1 \ldots A, B \ldots) + \frac{\partial f_1}{\partial X_1} \Delta x_1 + \ldots + \frac{\partial f_1}{\partial A} \Delta a + \ldots = 0,$$

$$f_2(X_2, Y_2 \ldots A, B \ldots) + \frac{\partial f_2}{\partial X_2} \Delta x_2 + \ldots + \frac{\partial f_2}{\partial A} \Delta a + \ldots = 0,$$

etc.,

or putting

$$f_1(X_1, Y_1 \ldots A, B \ldots) = -\phi_1 \text{ etc.,}$$

$$\frac{\partial f_1}{\partial X_1} = \xi_1, \quad \frac{\partial f_2}{\partial X_2} = \xi_2 \text{ etc.,}$$

$$\frac{\partial f_1}{\partial Y_1} = \eta_1, \quad \frac{\partial f_2}{\partial Y_2} = \eta_2 \quad ,,$$

$$\frac{\partial f_1}{\partial A} = \alpha_1, \quad \frac{\partial f_2}{\partial A} = \alpha_2 \quad ,,$$

$$\frac{\partial f_1}{\partial B} = \beta_1, \quad \frac{\partial f_2}{\partial B} = \beta_2 \quad ,,$$

the equations become

$$\left. \begin{aligned} \xi_1 \Delta x_1 + \eta_1 \Delta y_1 + \ldots + \alpha_1 \Delta a + \beta_1 \Delta b + \ldots &= \phi_1, \\ \xi_2 \Delta x_2 + \eta_2 \Delta y_2 + \ldots + \alpha_2 \Delta a + \beta_2 \Delta b + \ldots &= \phi_2, \\ \xi_N \Delta x_N + \eta_N \Delta y_N + \ldots + \alpha_N \Delta a + \beta_N \Delta b + \ldots &= \phi_N. \end{aligned} \right\} \quad (3)$$

Substituting the same values of x_1, y_1, z_1, etc. in equations (2) they become

$$\left. \begin{aligned} \Delta x_1 &= x_1' - X_1 & \Delta y_1 &= y_1' - Y_1 & \text{etc.,} \\ \Delta x_2 &= x_2' - X_2 & \Delta y_2 &= y_2' - Y_2 & ,, \\ \Delta x_N &= x_N' - X_N & \Delta y_N &= y_N' - Y_N & ,, \end{aligned} \right\} \quad (4)$$

The equations (3) and (4), $Nn + N$ in number, and involving $Nn + q$ unknown quantities, are all linear, and the coefficients and absolute terms are all known numerical

quantities.   From the N exact condition equations (3) we now proceed to determine the values of any N of the unknown quantities in terms of the $Nn + q - N$ remaining ones; and substituting these values in the equations (4) there result Nn observation equations for the determination of the most probable values of $Nn + q - N$ unknown quantities.   Having formed the normal equations in the usual way and derived the solutions, we then find the most probable values of the remaining N unknowns from the exact equations (3).

If the corrections so obtained to the assumed approximate values A, B, C ... X_1, Y_1, Z_1 ... etc. are sufficiently small, this may be accepted as the definitive solution; if not, we assume as new approximate values the quantities $A + \Delta a$, $B + \Delta b$ ... $X_1 + \Delta x_1$, $Y_1 + \Delta y_1$ ... etc. and proceed exactly as before to a further approximation.

The solution of this general problem is thus perfectly straightforward and unambiguous, but is entirely different from the erroneous solution given by Dr. Campbell.

It may of course be claimed that when either q or n is large (and indeed even when they are small) the rigorous solution of the general case as described above is cumbersome and tedious, and that in many cases more approximate results are quite sufficiently accurate for all practical purposes.   This may readily be granted; and Dr. Campbell's paper may serve a very useful purpose in drawing attention to a fact which is undoubtedly true, that when the number of observations is large compared with that of the unknown quantities required it is comparatively easy, by the application of common sense, to devise approximate methods which will lead to very nearly the same results as the more rigorous method of least squares, and with much less labour.   It is necessary, however, to exercise considerable caution in the choice and application of such methods; and the fact remains that (provided we accept the principle of the arithmetic mean) it is more than an even chance that the results obtained by least squares are nearer the truth than any other results from the same data, however obtained.   And it may be worth emphasizing that the statement (see pp. 191, 192, 193) that there are certain classes of problems in which the method of least squares is not applicable, or gives ambiguous results, is quite untrue.   It will also do no harm to insist once again on the fact that the method of least squares makes no claim to deduce the *true values* of the quantities sought, but only their *most probable values.*

Though all cases are covered by the solution of the general

problem as given above, it may be interesting in conclusion to apply it to one or two specific cases.

The first is an example taken from Merriman*, and has been chosen partly as illustrating the occasional misapplication of the method of least squares mentioned earlier in this article. In introducing the example Merriman says :—" In the last article the quantities y and x were both observed; but the latter was regarded free from error, because .... The following example gives an outline of a method that may be used when both observed quantities are affected by accidental errors.— In order to determine the most probable equation of a certain straight line, the abscissæ and ordinates of four of its points were measured with equal precision. The observed co-ordinates are

$$y = 0\cdot5,\ 0\cdot8,\ 1\cdot0,\ \text{and}\ 1\cdot2,$$
$$x = 0\cdot4,\ 0\cdot6,\ 0\cdot8,\ \text{and}\ 0\cdot9.$$

And the most probable straight line for the four points is expressed by the equation

$$y = Sx + T$$

in which S and T are constants whose most probable values are to be found."

Then, notwithstanding his preamble, he proceeds to a solution which is the exact equivalent of the assumption that the measured values of x are free from error. That is, he forms normal equations which are the equivalent of

$$\Sigma xy = S\Sigma x^2 + T\Sigma x,$$
$$\Sigma y\ = S\Sigma x\ + 4T,$$

obtaining the solution

$$S = 1\cdot339,$$
$$T = -\cdot029.$$

Had the equation of the line been written in the equivalent form

$$x = \frac{1}{S} \cdot y - \frac{T}{S}$$

and a similar solution made, the results would have been

$$S = 1\cdot354,$$
$$T = -\cdot039.$$

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* 'Theory of Least Squares' (original edition), Art. 107.

He would thus have been confronted with exactly the same difficulty as experienced by Dr. Campbell in the problem of the determination of density *. The first solution corresponds to the suppositious case in which the abscissæ have been measured with absolute precision, while the measures of the ordinates are subject to accidental error ; the second to the converse case. When both the co-ordinates are subject to errors of measurement neither solution is correct.

Denoting, for the moment, the numerical measured values of the co-ordinates by $x_1', x_2' \ldots y_1', y_2' \ldots$ we have the eight observation equations

$$\begin{aligned}
x_1 &= x_1' & y_1 &= y_1', \\
x_2 &= x_2' & y_2 &= y_2', \\
x_3 &= x_3' & y_3 &= y_3', \\
x_4 &= x_4' & y_4 &= y_4',
\end{aligned}$$

and the four condition equations

$$\begin{aligned}
y_1 &= Sx_1 + T, \\
y_2 &= Sx_2 + T, \\
y_3 &= Sx_3 + T, \\
y_4 &= Sx_4 + T,
\end{aligned}$$

from which to determine the most probable values of ten quantities, the eight observed co-ordinates and the two constants S and T.

To reduce the condition equations to the linear form we put

$$\begin{aligned}
S &= S_0 + \Delta S, \\
x_1 &= X_1 + \Delta x_1, \\
x_2 &= X_2 + \Delta x_2, \\
x_3 &= X_3 + \Delta x_3, \\
x_4 &= X_4 + \Delta x_4,
\end{aligned}$$

where $S_0, X_1, X_2 \ldots$ are approximate values and $\Delta S, \Delta x_1,$ $\Delta x_2 \ldots$ the most probable corrections to these. Neglecting products of the latter, the condition equations become

$$\begin{aligned}
y_1 &= S_0 x_1 + X_1 \Delta S + T, \\
y_2 &= S_0 x_2 + X_2 \Delta S + T, \\
&\quad \text{etc. ;}
\end{aligned}$$

and substituting in the observation equations these take

* Phil. Mag. *loc. cit.* pp. 192, 193.

the form

$$x_1 = x_1',$$
$$x_2 = x_2',$$
$$x_3 = x_3',$$
$$x_4 = x_4',$$
$$S_0 x_1 + X_1 \Delta S + T = y_1',$$
$$S_0 x_2 + X_2 \Delta S + T = y_2',$$
$$S_0 x_3 + X_3 \Delta S + T = y_3',$$
$$S_0 x_4 + X_4 \Delta S + T = y_4',$$

from which the following normal equations are obtained:

$$(S_0^2 + 1)x_1 + S_0 X_1 \Delta S + S_0 T = S_0 y_1' + x_1',$$
$$(S_0^2 + 1)x_2 + S_0 X_2 \Delta S + S_0 T = S_0 y_2' + x_2',$$
$$(S_0^2 + 1)x_3 + S_0 X_3 \Delta S + S_0 T = S_0 y_3' + x_3',$$
$$(S_0^2 + 1)x_4 + S_0 X_4 \Delta S + S_0 T = S_0 y_4' + x_4',$$
$$S_0 . \Sigma X x + \Sigma X^2 . \Delta S + \Sigma X . T = \Sigma X y',$$
$$S_0 . \Sigma x + \Sigma X . \Delta S + 4T = \Sigma y';$$

or eliminating x_1, x_2, x_3, x_4,

$$\Sigma X^2 . \Delta S + \Sigma X . T = \Sigma X y' - S_0 \Sigma X x',$$
$$\Sigma X . \Delta S + 4T = \Sigma y' - S_0 \Sigma x'.$$

As a first approximation we assume $X_1 = x_1'$, $X_2 = x_2'$, etc., and obtain the values

$$S = 1 \cdot 339,$$
$$T = - \cdot 029,$$
$$x_1 = \cdot 397,$$
$$x_2 = \cdot 612,$$
$$x_3 = \cdot 780,$$
$$x_4 = \cdot 911.$$

Using these in turn as approximate values and re-solving, we obtain

$$\Delta S = \cdot 010,$$
$$S = 1 \cdot 349,$$
$$T = - \cdot 035,$$

which are correct to within one unit in the last place *.

* The same result would of course have been arrived at by the methods of analytical geometry, assuming $y = Sx + T$ as the equation of the line required, and imposing the condition that the sums of the squares of the perpendicular distances from it of the points $(x_1' y_1')$, $(x_2' y_2')$, $(x_3' y_3')$, $(x_4' y_4')$ should be a minimum; the solution by this method would have been direct.

We now proceed to the solution of the problem of determination of density from measurements of a mass and a volume, in which case Dr. Campbell states [*] that the method of least squares is clearly inapplicable. The mass (x) and the volume (y) of a number of different samples of a substance are supposed to have been measured. Then if b be the density, the general condition equation connecting the measured quantities is $x = by$. It is required to find the most probable value of b.

Eliminating x_1, x_2, x_3 ... by substituting their values from the condition equations, and putting

$$b = B + \Delta b,$$
$$y_1 = Y_1 + \Delta y_1,$$
$$y_2 = Y_2 + \Delta y_2,$$
$$\text{etc.,}$$

the observation equations become

$$y_1 = y_1' \qquad B y_1 + Y_1 \Delta b = x_1',$$
$$y_2 = y_2' \qquad B y_2 + Y_2 \Delta b = x_2',$$
$$\cdots \qquad \cdots \qquad \cdots$$

Assume that x_1', x_2' ... are measured with weight unity, and y_1', y_2' ... with weight p; then the normal equations are

$$(B^2 + p) y_1 + B Y_1 \Delta b = B x_1' + p y_1'$$
$$(B^2 + p) y_2 + B Y_2 \Delta b = B x_2' + p y_2'$$
$$\cdots \qquad \cdots \qquad \cdots$$
$$B \Sigma Y y + \Sigma Y^2 . \Delta b = \Sigma x' Y.$$

We may now make use of a simple device to obviate the necessity of successive approximations. Assume that the approximate values B, Y_1, Y_2 ... have been chosen exactly correctly: then necessarily $\Delta b = 0$, $B = b$, $Y_1 = y_1$, $Y_2 = y_2$, etc., and the normal equations become

$$(b^2 + p) y_1 = b x_1' + p y_1'$$
$$(b^2 + p) y_2 = b x_2' + p y_2'$$
$$\cdots \qquad \cdots \qquad \cdots$$
$$b . \Sigma y^2 = \Sigma x' y.$$

[*] *Loc. cit.* p. 192.

Eliminating $y_1,\ y_2,\ y_3\ \ldots$ we obtain easily

$$(b^2-p)\,\Sigma\,x'y' = b(\Sigma\,x'^2-p\,\Sigma\,y'^2),$$

or putting $\Sigma\,x'^2-p\,\Sigma\,y'^2=2m\,\Sigma\,x'y'$,

$$b^2-2mb-p = 0\ ;$$

whence

$$b = m+\sqrt{m^2+p},$$

the negative value being obviously inadmissible.

Had the relation between x and y been written $ax=y$, a being the specific volume, we should have obtained by an exactly similar process $a=\dfrac{1}{p}(-m+\sqrt{m^2+p})$, which is equal to $\dfrac{1}{b}$. Thus the two methods of attack give identical results, as should be the case.

It follows from the form of the result (as is indeed evident *a priori*) that to obtain an intelligent solution we must know the value of p, that is, the relative accuracies of the measurements of mass and volume. If p is infinite (measurements of volume exact) $b=\dfrac{\Sigma\,x'y'}{\Sigma\,y'^2}$, while if p is zero, or rather $\dfrac{1}{p}$ infinite (measurements of mass exact) $b=\dfrac{\Sigma\,x'^2}{\Sigma\,x'y'}$. These are the two results given by Dr. Campbell, and are of course in general, as is to be expected, different; when p has a finite value, that is, when both sets of measurements are fallible, the value of b lies between these two extremes.

Summary.

Dr. Campbell's article serves a useful purpose in drawing attention to the fact that a rigorous least squares solution is sometimes laborious, and that more approximate methods will often yield results sufficiently accurate for most purposes. On the other hand, many of his statements in regard to the principles of the method of least squares are erroneous, and his application of them to several classes of problems which he considers is incorrect. The method of solution for the general case, including as particular cases all the problems treated by him, is indicated, and is applied to two specific examples.

Dominion Observatory, Ottawa,
    March 4th, 1920.

XXV. *A Method of finding the Scalar and Vector Potentials due to the Motion of Electric Charges.* By Prof. A. ANDERSON[*].

LET the coordinates of a moving electron be $x = \phi(t)$, $y = \psi(t)$, $z = \chi(t)$. Let AQ be its path, and Q its position at time t: also let Q' be its position at time $t - \dfrac{r}{c}$,

Fig. 1.
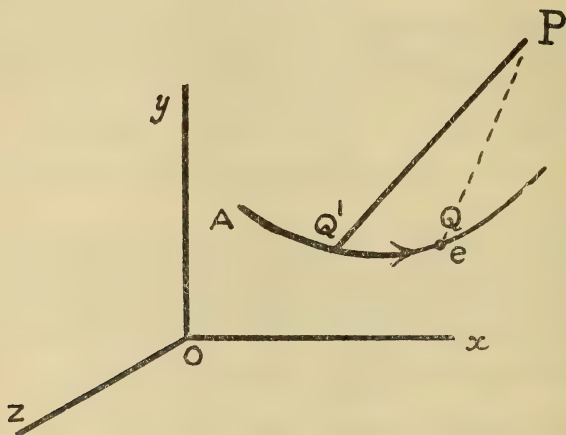
where $r = $ Q'P, and c is the velocity of light; then the coordinates of Q' are $x = \phi\left(t - \dfrac{r}{c}\right)$, $y = \psi\left(t - \dfrac{r}{c}\right)$, $z = \chi\left(t - \dfrac{r}{c}\right)$. In what follows, we shall use the symbols ϕ, ψ, χ to denote these functions of $t - \dfrac{r}{c}$. Thus the component velocities of Q' are ϕ', ψ', χ'.

Let $\xi = [\phi'(x - \phi) + \psi'(y - \psi) + \chi'(z - \chi)]/c$: we want to show that if $A = \dfrac{1}{r - \xi}$, A satisfies the equation of wave-propagation,

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0.$$

Since $r^2 = (x - \phi)^2 + (y - \psi)^2 + (z - \chi)^2$, we have

$$\frac{\partial r}{\partial t} = -\frac{c\xi}{r - \xi}, \quad \text{and} \quad \frac{\partial \xi}{\partial t} = \frac{\lambda r}{r - \xi},$$

where λ denotes the quantity

$$[\phi''(x - \phi) + \psi''(y - \psi) + \chi''(z - \chi)]/c.$$

* Communicated by the Author.

Thus
$$\frac{\partial A}{\partial t} = \frac{1}{(r-\xi)^3}(c\xi + \lambda r),$$

and
$$\frac{\partial^2 A}{\partial t^2} = \frac{3(c\xi + \lambda r)^2}{(r-\xi)^5} + \frac{1}{(r-\xi)^3}\left(\lambda c + r\frac{\partial\lambda}{\partial t}\right)$$
$$= \frac{\lambda(3\lambda + c)r^2 + 4\lambda c\xi r + c(3c+\lambda)\xi^2}{(r-\xi)^5} + \frac{\mu r^2}{(r-\xi)^4},$$

where
$$\mu = [\phi'''(x-\phi) + \psi'''(y-\psi) + \chi'''(z-\chi)$$
$$-3(\phi'\phi'' + \psi'\psi'' + \chi'\chi'')]/c.$$

Also
$$\frac{\partial r}{\partial x} = \frac{x-\phi}{r-\xi}, \qquad \frac{\partial r}{\partial y} = \frac{y-\psi}{r-\xi}, \qquad \frac{\partial r}{\partial z} = \frac{z-\chi}{r-\xi},$$

$$\frac{\partial \xi}{\partial x} = \frac{\phi'}{c} - \frac{\lambda}{c}\cdot\frac{x-\phi}{r-\xi}, \quad \frac{\partial \xi}{\partial y} = \frac{\psi'}{c} - \frac{\lambda}{c}\cdot\frac{y-\psi}{r-\xi}, \quad \frac{\partial \xi}{\partial z} = \frac{\chi'}{c} - \frac{\lambda}{c}\cdot\frac{z-\chi}{r-\xi},$$

$$\frac{\partial \lambda}{\partial x} = \frac{\phi''}{c} - \frac{\mu}{c}\cdot\frac{x-\phi}{r-\xi}, \quad \frac{\partial \lambda}{\partial y} = \frac{\psi''}{c} - \frac{\mu}{c}\cdot\frac{y-\psi}{r-\xi}, \quad \frac{\partial \lambda}{\partial z} = \frac{\chi''}{c} - \frac{\mu}{c}\cdot\frac{z-\chi}{r-\xi}.$$

Hence
$$c\frac{\partial A}{\partial x} = \frac{1}{(r-\xi)^3}[\phi'(r-\xi) - (c+\lambda)(x-\phi)],$$

and
$$c^2\frac{\partial^2 A}{\partial x^2} = \frac{3}{(r-\xi)^5}[\phi'(r-\xi) - (c+\lambda)(x-\phi)]^2$$
$$+ \frac{1}{(r-\xi)^3}\left[-2\phi''(x-\phi) - \phi'^2 + \mu\cdot\frac{(x-\phi)^2}{r-\xi} - c(c+\lambda)\right],$$

with similar expressions for $c^2\dfrac{\partial^2 A}{\partial y^2}$ and $c^2\dfrac{\partial^2 A}{\partial z^2}$. Adding these three expressions, we easily find that

$$c^2\left(\frac{\partial^2 A}{\partial x^2} + \frac{\partial^2 A}{\partial y^2} + \frac{\partial^2 A}{\partial z^2}\right)$$
$$= -\frac{2c\lambda}{(r-\xi)^3} - \frac{6c\xi(c+\lambda)}{(r-\xi)^4} - \frac{3c(c+\lambda)}{(r-\xi)^3} - \frac{3(c+\lambda)^2 r^2}{(r-\xi)^5} + \frac{\mu r^2}{(r-\xi)^4}$$
$$= \frac{3c^2\xi^2 + 3\lambda^2 r^2 + c\lambda r^2 + c\lambda\xi^2 + 4c\lambda r\xi}{(r-\xi)^5} + \frac{\mu r^2}{(r-\xi)^4}$$
$$= \frac{\lambda(3\lambda + c)r^2 + 4\lambda c\xi r + c(3c+\lambda)\xi^2}{(r-\xi)^5} + \frac{\mu r^2}{(r-\xi)^4};$$

and, therefore,
$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = 0.$$

Thus $\dfrac{1}{r-\xi}$ satisfies the equation of wave-propagation.

If A be any function of x, y, z, t that satisfies this equation and F be any other function of x, y, z, t, then AF will also satisfy the equation if

$$\frac{1}{c^2}\left(A\frac{\partial^2 F}{\partial t^2} + 2\frac{\partial A}{\partial t}\cdot\frac{\partial F}{\partial t}\right)$$
$$= A\nabla^2 F + 2\left(\frac{\partial A}{\partial x}\cdot\frac{\partial F}{\partial x} + \frac{\partial A}{\partial y}\cdot\frac{\partial F}{\partial y} + \frac{\partial A}{\partial z}\cdot\frac{\partial F}{\partial z}\right).$$

Let A be $\dfrac{1}{r-\xi}$ and F any function of $t-\dfrac{r}{c}$. We have

$$\frac{\partial A}{\partial x}\frac{\partial F}{\partial x} + \frac{\partial A}{\partial y}\cdot\frac{\partial F}{\partial y} + \frac{\partial A}{\partial z}\cdot\frac{\partial F}{\partial z} = \frac{F'}{c^2(r-\xi)^4}\left[(c+\lambda)r^2 - c\xi(r-\xi)\right],$$

and

$$\nabla^2 F = \frac{F''}{c^2}\cdot\frac{r^2}{(r-\xi)^2} + \frac{F'}{c(r-\xi)^2}\left[\left(1+\frac{\lambda}{c}\right)\frac{r^2}{r-\xi} - 2\xi\right] - \frac{3F'}{c(r-\xi)}.$$

and thus

$$A\nabla^2 F + 2\left(\frac{\partial A}{\partial x}\frac{\partial F}{\partial x} + \frac{\partial A}{\partial y}\cdot\frac{\partial F}{\partial y} + \frac{\partial A}{\partial z}\cdot\frac{\partial F}{\partial z}\right)$$
$$= \frac{{}_tF''r^2}{c^2(r-\xi)^3} + \frac{F'}{c^2(r-\xi)^4}(3\lambda r^2 + 2c\xi r + c\xi^2).$$

Also

$$\frac{\partial A}{\partial t}\cdot\frac{\partial F}{\partial t} = \frac{F'r}{(r-\xi)^4}\cdot(c\xi + \lambda r),$$

and

$$\frac{\partial^2 F}{\partial t^2} = \frac{F''r^2}{(r-\xi)^2} + \frac{F'}{(r-\xi)^3}(\lambda r^2 + c\xi^2).$$

Therefore

$$A\frac{\partial^2 F}{\partial t^2} + 2\frac{\partial A}{\partial t}\cdot\frac{\partial F}{\partial t} = \frac{F''r^2}{(r-\xi)^3} + \frac{F'}{(r-\xi)^4}(3\lambda r^2 + 2c\xi r + c\xi^2).$$

Hence $\dfrac{F\left(t-\dfrac{r}{c}\right)}{r-\xi}$ satisfies the equation of wave-propagation.

The co-ordinates, velocities, and accelerations of Q' are all functions of $t - \dfrac{r}{c}$, and, therefore, we have a number of expressions satisfying the equation. Thus, if the co-ordinates of Q' are x', y', z', its velocities u_x, u_y, u_z, and its accelerations f_x, f_y, f_z,

$$\frac{x'}{r\left(1 - \dfrac{u_r}{c}\right)}, \quad \frac{u_x}{r\left(1 - \dfrac{u_r}{c}\right)}, \quad \frac{f_x}{r\left(1 - \dfrac{u_r}{c}\right)}, \quad \&c. \ldots$$

all satisfy the equation of wave-propagation at any point P at a distance r from the position Q' of the moving electron, u_r being the velocity of Q' resolved along $Q'P$, and c the velocity of light.

Suppose, now, we have a distribution of moving electricity, and we wish to find solutions of the equations of wave-propagation that will hold at any point P.

If $A = \iiint \dfrac{\rho \, dx' \, dy' \, dz'}{r\left[1 - \dfrac{u_r}{c}\right]}$, then $\nabla^2 A - \dfrac{1}{c^2} \cdot \dfrac{\partial^2 A}{\partial t^2}$ will vanish

at any point P where there is no electricity. If there is electricity at P moving with velocity u, we draw a small sphere round P as centre. As this sphere diminishes it is clear that A and $\dfrac{\partial^2 A}{\partial t^2}$ contributed by the charges inside the sphere tend to zero, but $\nabla^2 A$ tends to the value

$$-\frac{2\pi\rho c}{u} \log \frac{c+u}{c-u}.$$

Hence $A = \iiint \dfrac{\rho \, dx' \, dy' \, dz'}{2\pi r \left[1 - \dfrac{u_r}{c}\right]}$ is the solution of the equation

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = -\rho \frac{c}{u} \log \frac{c+u}{c-u}.$$

But, since u is a function of $t - \dfrac{r}{c}$, it follows that

$$A = \iiint \frac{\rho u \, dx' \, dy' \, dz'}{2\pi c \log \dfrac{c+u}{c-u} \left[r\left(1 - \dfrac{u_r}{c}\right) \right]}$$

is the solution of the equation

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho \quad \text{or} \quad \square A = -\rho,$$

and the solution of $\square A = -\rho\,\dfrac{u_x}{c}$ is

$$A = \iiint \frac{\rho u\, u_x\, dx'\, dy'\, dz'}{2\pi c^2 \log\dfrac{c+u}{c-u} \cdot \left[r\left(1 - \dfrac{u_r}{c}\right)\right]},$$

with similar expressions for the solutions of the equations

$$\square A = -\rho\,\frac{u_y}{c} \quad \text{and} \quad \square A = -\rho\,\frac{u_z}{c}.$$

These are the scalar potential and the components of the vector potential at P.

It would seem from the above, if correct, that for a single charge e at Q moving in any manner the scalar potential at any point P is

$$\frac{eu}{2\pi c \log\dfrac{c+u}{c-u}\left[r\left(1 - \dfrac{u_r}{c}\right)\right]},$$

where $r = $ Q'P, and u is the velocity of Q', and the components of vector potential at P are

$$\frac{eu\, u_x}{2\pi c^2 \log\dfrac{c+u}{c-u}\left[r\left(1 - \dfrac{u_r}{c}\right)\right]}, \quad \frac{eu\, u_y}{2\pi c^2 \log\dfrac{c+u}{c-u}\left[r\left(1 - \dfrac{u_r}{c}\right)\right]},$$

$$\frac{eu\, u_z}{2\pi c^2 \log\dfrac{c+u}{c-u}\left[r\left(1 - \dfrac{u_r}{c}\right)\right]}.$$

If the square of $\dfrac{u}{c}$ is neglected, we get the expressions given by Liénard and Wiechert.

XXVI. *The Crystalline Structure of Antimony.* By R. W.
James, *M.A.,* B.Sc., *and* Norman Tunstall, *B.Sc., Lec-
turers in Physics in the University of Manchester* *.

ANTIMONY crystallises in the dihexagonal-alternating
class of the hexagonal system. As in the case of
calcite, the crystalline symmetry is that of a rhombohedron,
the three edges of the rhombohedron which meet in the
trigonal axis being taken as the axes of the crystal. The
angle between any two of these edges is 86° 58′, and the
angle between the rhombohedral faces 100 : 010 is 92° 53′,
so that the antimony rhomb is a slightly distorted cube.
The crystals have a very perfect cleavage at right angles to
the trigonal axis and parallel to the (111) planes, and a
somewhat less perfect one parallel to {110}.

From some observations made in 1914, Sir W. H. Bragg
and Prof. W. L. Bragg† concluded that the arrangement of
the atoms in Antimony was similar to that in diamond, except
that the whole structure was distorted along the trigonal
axis. As the observations on which this conclusion was based
were incomplete, it was suggested by Prof. W. L. Bragg
that it would be worth while to repeat them more carefully.
This has now been done, and it has been found that a struc-
ture similar to that of diamond will not explain the spectra
observed from the various faces.

The observations were made with the X-ray spectrometer,
a bulb with a palladium anticathode being used, and five
faces in all were examined. The (111) and (110) faces
were obtained by cleavage from a large mass of crystals, and
surfaces parallel to the (100), (1$\bar{1}$0), and (11$\bar{1}$) planes were
ground on slices of the crystal, the angles which they made
with the cleavage planes having been calculated. Antimony
is very brittle, and no distorted surface layer appears to be
formed by grinding, for the ground faces were found to
reflect X-rays nearly as well as the natural ones.

The positions and relative intensities of the spectra
observed from the various faces are shown diagrammatically
in fig. 1. The glancing angles for the first-order spectra
were as follows :—

(100)	(110)	(1$\bar{1}$0)	(111)	(11$\bar{1}$)
5° 27′	7° 24′	7° 50′	4° 26′	19° 14′.

The sines of these angles are in the ratio

$$1 : 1\cdot36 : 1\cdot44 : 0\cdot815 : 1\cdot760.$$

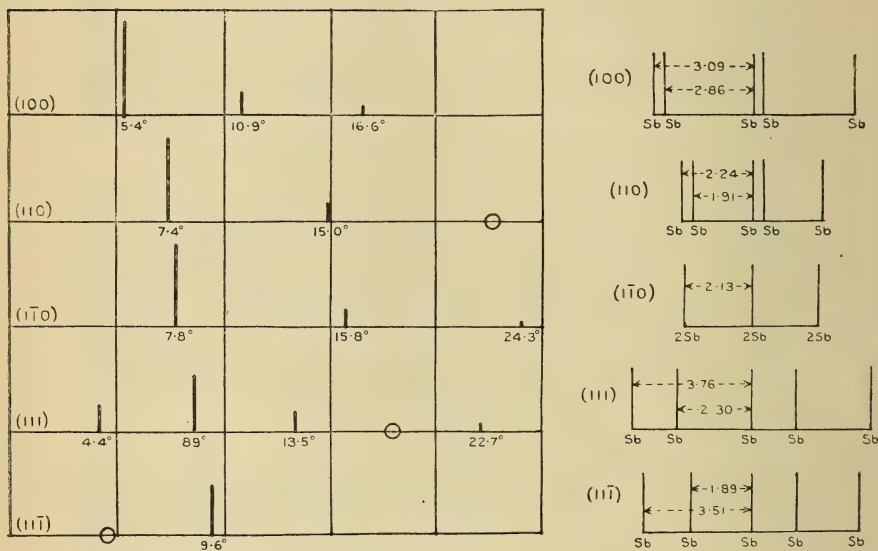* Communicated by Prof. W. L. Bragg.
† 'X-rays and Crystal Structure,' p. 227.

Now, for a face-centred rhombohedral lattice, as calculated from the geometry of the rhombohedron, the corresponding ratios should be

$$1 : 1\cdot377 : 1\cdot450 : 0\cdot820 : 0\cdot880,$$

while for a simple rhombohedral lattice they would be

$$1 : 1\cdot377 : 1\cdot450 : 1\cdot651 : 1\cdot761.$$

Fig. 1.

Glancing angles and intensities for wave-length 0·584 A.U.

Spacings of planes.
Distances in Ångström Units.

The small glancing-angle for the first-order spectrum from the (111) face indicates that the underlying structure is the face-centred lattice. Assuming this to be the case, we find from the glancing angle for the (100) face, that the edge of each unit rhomb of the face-centred lattice has a length of 6·20 A.U.

Taking the density of antimony as 6·70, and calculating the number of atoms in such a unit rhomb, we find the number to be eight. (The number actually found was 7·96.) Now, if one atom is associated with each corner and face centre of the unit lattice, the number would be four only. Thus it appears that the structure, as in the case of diamond *, consists of two interpenetrating face-centred lattices. The

* W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. A, vol. lxxxix. p. 277.

arrangement of these lattices is, however, different, as may be seen from a consideration of the intensities of the spectra from the different faces.

The following structure will be found to account completely for the observed angles and intensities of the spectra. The antimony atoms lie in two interpenetrating face-centred lattices. Suppose for one of the lattices, diagonals are drawn parallel to the trigonal axis for each of the eight equal rhombohedral cells into which the unit lattice may be divided.

Fig. 2.
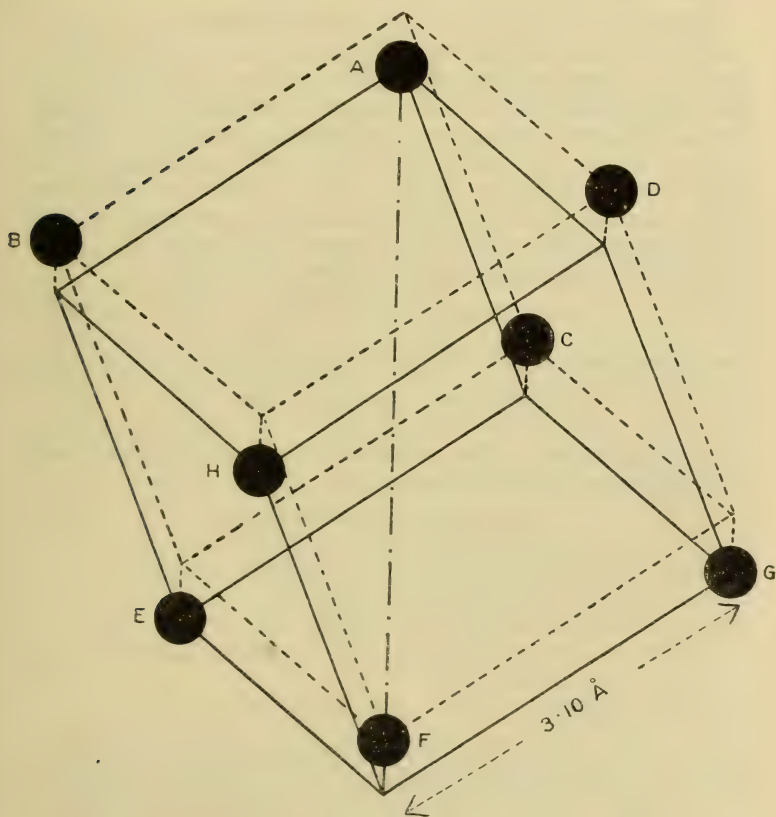
From considerations of symmetry, it will be seen that the atoms of the second lattice must lie in these diagonals. If they lay at the unoccupied corners of the first lattice, the structure would become a simple rhombohedral one. This will not fit in with the observed facts, but if the atoms of the

R 2

second lattice are all displaced from these corners along the diagonals in the same direction by a distance equal to ·074 of the length of a diagonal of one of the small cells, all the observed facts can be explained. This structure is shown in fig. 2, in which, for the sake of clearness, one only of the small cells is shown.

The Arrangement and Spacing of the Planes.

(*a*) (111) *planes*.   (B C D, E G H, fig. 2.)

Parallel to the (111) face, the planes containing the atoms occur in pairs. The planes belonging to one of the lattices divide the distance between those belonging to the other in the ratio $0.389 : 0.611$. The planes belonging to one lattice form a first-order spectrum at a glancing-angle of 4° 26′, but those belonging to the second lattice add a contribution to this spectrum, differing in phase by $2\pi \times 0.389$ or 140° from that from the first set, thus reducing the intensity of the first-order spectrum. On this assumption, taking the intensities of a normal set of spectra to be in the ratio

$$100 : 34 : 14 : 7 : 4,$$

the intensities of the first four orders should be

$$11.7 : 20.6 : 10.5 : 0.2 : 3.8.$$

If the intensity of the second-order spectrum is put equal to 100, the calculated ratios are

$$57 : 100 : 51 : 1.4 : 18.$$

The *observed* intensities have the ratios

$$60 : 100 : 48 : 0 : 15,$$

which is quite as close an agreement as can be expected.

(*b*) (100) *planes*.

The planes occur in pairs containing equal numbers of atoms. The spacing of the pairs is $0.074 : 0.926$. Thus the contributions to the first-order spectrum from the two sets of planes differ in phase only by about 36°. This will correspond to a nearly normal series of spectra, the intensities falling off rather more rapidly, which is, in fact, what was observed. The intensities of the spectra from this plane show clearly that the structure cannot be similar to that of the diamond.

(c) (110) *planes.*

The planes are again in pairs, each plane containing an equal number of atoms. The spacing is $0.141 : 0.859$. The intensities of the first three orders should have the ratio

$$100 : 17 : 1.$$

The observed ratio was about

$$100 : 20 : 0.$$

(d) (1$\bar{1}$0) *planes.*

These planes are parallel to the trigonal axis. They are evenly spaced, and should show a normal sequence of spectra. No certain third-order spectrum was found, but the glancing angle is rather large, and even the normal intensity will be very small.

(e) (11$\bar{1}$) *planes.* (A E G, B D F, fig. 2.)

The planes are in pairs, very nearly evenly spaced, the spacing being in the ratio $0.463 : 0.537$. For the first-order spectrum, the phase-difference between the contributions from the two set of planes is $167°$. The first-order spectrum should, therefore, be very small. No first order could be observed at all. The structure assumed approximates to that of a simple rhombohedral lattice, for which the glancing angle for the first-order spectrum for the (11$\bar{1}$) planes should be double the angle for the face-centred lattice. Thus the spectra from the (11$\bar{1}$) face confirm the conclusion that the atoms of the second lattice must lie very close to the unoccupied corners of the first lattice, and not somewhere near the middle of the diagonals of the small cells, as would be the case for a structure approximating to that of diamond.

Accuracy of determination of Position of the Atoms.

The planes parallel to the (111) face occur in pairs, and it is from the spacing of these planes that the relative positions of the atoms in the crystal are determined. The accuracy with which the spacing ratio of these pairs of planes can be determined depends on the accuracy with which the relative intensities of the spectra of different orders can be measured, on our knowledge of the intensities of the orders of the spectra from a series of equally-spaced planes, and also on the actual spacing of the planes under consideration, since a

small change in the spacing has a far greater effect on the relative intensities in some positions than in others. In the present experiments, the intensities of the orders were measured roughly by the method of sweeping the crystal round at a constant speed *, and for the first three orders are probably known to within about 10 per cent. The fourth order was too faint to be observed at all, and, although an undoubted fifth order was found, its intensity cannot be considered as accurately known. The intensities of a series of normal spectra were taken as

$$100 : 34 : 14 : 7 : 4.$$

These figures are based on comparisons of some measurements on rock salt and on galena, and probably only represent very roughly the normal intensities from antimony. The only planes in this crystal which are evenly spaced are so close together that the higher-order spectra occur at large angles, and are therefore faint, so that no reliable intensity measurements could be made for them.

Assuming the normal intensities stated above, and calculating the intensities of three series of pairs of planes spaced so that the phase-differences, δ, between the two sets for the first-order spectra are 135°, 140°, and 145° respectively, we get, taking the intensity of the second-order spectrum in each case as 100,

$$\delta = 135° \quad \ldots\ldots \quad 86 : 100 : 71 : \ 0 \ : 20$$
$$\delta = 140° \quad \ldots\ldots \quad 57 : 100 : 51 : 1·4 : 18$$
$$\delta = 145° \quad \ldots\ldots \quad 39 : 100 : 38 : 3·5 : 17.$$

The observed intensities were

$$60 : 100 : 48 : 0 : 15$$

Supposing the intensities to have been measured to within 10 per cent., it will be seen that the value of δ can hardly vary by more than 2° on either side of 140° without causing intensity changes greater than the errors of observation.

Assuming now a different normal intensity law, supposing the intensities to be inversely proportional to the square of the order of the spectrum, which gives a ratio

$$100 : 25 : 11·1 : 6·25 : 4,$$

* W. H. Bragg, Phil. Mag., May 1914, p. 881.

the corresponding calculated intensities are

$$\delta = 135° \quad \ldots \ldots \quad 116 : 100 : 76 : \ 0 \ : 27$$
$$\delta = 140° \quad \ldots \ldots \quad 79 : 100 : 56 : 1\cdot3 : 26$$
$$\delta = 145° \quad \ldots \ldots \quad 54 : 100 : 42 : 4\cdot2 : 24.$$

The most likely value of δ is now 143°, but the general "fit" is not so good. Making this large alteration in the assumed normal intensity series only makes 3° difference in the probable value of δ. But it is practically certain that the true normal intensity series is much more nearly the first series than the second, and we can take as the probable value of δ

$$\delta = 140° \pm 2°$$

which gives a range of only 0·062 Å, within which the Antimony atoms of the second lattice may be displaced along the diagonals of the first lattice.

Distances between the Atoms.

Any particular atom lies in one of the (111) planes, and is equidistant from three atoms in each of the (111) planes on either side of it. The three atoms in one plane are, however, nearer the given atom than those in the other plane. The distance between the centres of two atoms, such as A and B in fig. 2, in the close pair of planes, which is the closest distance of approach of two antimony atoms, is 2·87 Å with a probable error of $\pm 0\cdot01$ Å., assuming the limits of error for δ stated above; and this can, perhaps, be considered as the "atomic diameter" of antimony. For the wider pairs of planes the closest distance of approach of two atomic centres, such as B and E, is 3·37 Å.

The planes thus occur in pairs in which the atoms approach one another closely, the pairs being separated by a wider spacing. It should be noted that the very good cleavage of antimony is parallel to these pairs of planes.

In conclusion, we wish to express our thanks to Prof. C. A Edwards, of Manchester University, who kindly supplied us with some excellent specimens of crystalline antimony, and to Prof. W. L. Bragg, who suggested the work, and to whom we are indebted for much helpful advice during its progress.

XXVII. *The Spectrum of Hydrogen Positive Rays. By* G. P. THOMSON, *M.A., Fellow and Lecturer Corpus Christi College, Cambridge* *.

[Plate IV.]

1. INTRODUCTORY.

AS is well known, hydrogen gives rise to two spectra. One, the Balmer series, is a group of lines of which only a small number are easily obtainable under ordinary conditions and whose frequencies follow a simple law ; the other, the so-called second or many-lined spectrum, consists of a large number of lines whose frequencies have not yet been reduced to any law.

The theoretical researches of Bohr make it seem very probable that the Balmer series is produced by the neutralization of a positively charged hydrogen atom by an electron moving through successive orbits. If this is true, it would seem natural to ascribe the more complicated second spectrum to the neutralization of the more complicated molecule. Stark† has obtained results from the spectra of different parts of the striæ of the positive column in a hydrogen-filled discharge tube, which lead him to the same conclusion, but the evidence is not so direct as could be desired.

On the other hand, Fabry and Buisson ‡ from measurements of the width of spectral lines came to the conclusion that the second spectrum was atomic in origin ; while Wolfke § showed that a formula closely resembling that of Bohr could be obtained for the Balmer series on the assumption that it was due to the molecule. In addition, there is the difficulty, which will be dealt with more fully later, that, according to both Stark ‖ and Wilsar ¶, the second spectrum of hydrogen shows no Döppler effect when hydrogen positive rays are examined in the direction of their motion ; while it is well known that when the positive rays of hydrogen are analysed electro-magnetically by Sir J. J. Thomson's method, a considerable proportion generally consists of rapidly moving hydrogen molecules with a positive charge.

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2. Method of Experiment.

In order to obtain direct evidence on these questions, it occurred to the author that it might be possible to combine the electro-magnetic analysis of the positive rays with an investigation of their spectrum. The method first tried was to analyse a narrow pencil of positive rays by magnetic and electric fields in the ordinary way (see 'Rays of Positive Electricity,' Sir J. J. Thomson, p. 20), and then examine the spectra of the various constituents. It was found, however, that the light obtainable from a pencil sufficiently small to give sharp resolution was totally inadequate for spectroscopic investigation.

It was therefore decided to make use of the fact that by changing the conditions in the discharge tube it is possible to vary the proportion of atoms to molecules in the positive rays over a wide range.

The apparatus used is illustrated in fig. 1. A pencil of positive rays from the discharge tube " A " passed

Fig. 1.
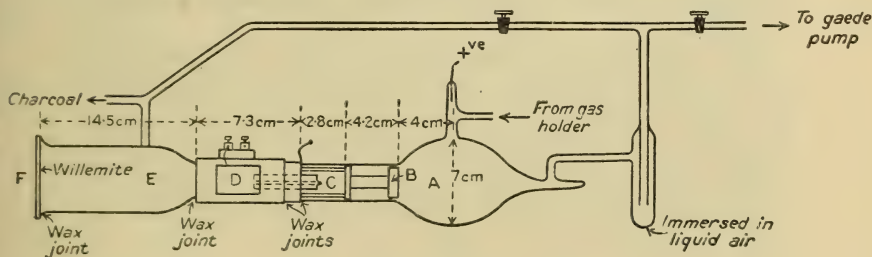
through an aluminium tube of 8 mm. diameter inserted in the cathode " B," the end of the tube and the cathode being crossed by a network of aluminium wires. The positive rays then passed into the observation chamber " C," through the glass walls of which they could be examined in a Hilger direct reading spectroscope. They then impinged on the end of a fine copper tube (bore ·35 mm.); those of the rays which passed down this were deflected by electrostatic and magnetic fields produced between the plates " D," and thus all corresponding to the same value of e/m became generators of one parabolic cone. After passing through the chamber " E," in which the pressure was reduced to the lowest possible amount by the use of charcoal cooled by liquid air, they struck the willemite-covered glass plate " F,"

on which they showed in a darkened room as bright parabolic arcs, one for each value of e/m. The method of experiment was so to adjust the conditions in the discharge tube that one of the two parabolas, corresponding to the atoms and molecules respectively, was as bright as possible in comparison with the other—then to take a photograph of the spectrum of the rays in the observation-chamber.

In order to secure the purity of the hydrogen, a slow steam of gas was passed into the discharge tube through a capillary during the whole of the exposure, and exhausted at the other end by a Gaede pump; to prevent mercury vapour from the pump diffusing back into the apparatus, a mercury trap was fitted, as shown in fig. 1, and kept cool with liquid air. It was found necessary after any alteration which involved admitting air into the apparatus, to pass a stream of gas in this manner, with the discharge passing, for some hours before the impurities in the tube were driven off—a result shown by the change in colour of the positive rays from a greyish hue to a deep pink. The hydrogen used was obtained by the electrolysis of barium hydroxide and kept in a glass container dried with phosphorus pentoxide.

The discharge was produced by means of an induction coil, and the voltage, as measured by the equivalent spark-gap, was in the neighbourhood of 15,000 volts. The exposures used were $2\frac{3}{4}$–$5\frac{1}{2}$ hrs.; the plates Imperial Flashlight. These are not sensitive beyond the blue, but it was found that panchromatic plates would have required too long an exposure.

3. RESULTS.

It was found that the nature of the positive rays was very sensitive to slight changes in the form of the discharge tube, and in the position of the cathodes in the neck of the tube. In addition, there was a well-marked pressure-variation, the proportion of atomic to molecular rays being markedly greater at the higher pressures.

Atoms.

The highest proportion of atoms was obtained with a tube of the dimensions shown in fig. 2. With this tube the molecular parabola was quite invisible at the higher pressures (dark space less than half across the tube). A photograph taken under these conditions is shown in Pl. IV. No. 1. It will be seen that the only lines visible are two of the

Balmer series H_β and H_γ (H_α does not appear, as the plates used were not sensitive to the red). From this it seems certain that the Balmer series is due to the hydrogen atom.

Fig. 2.
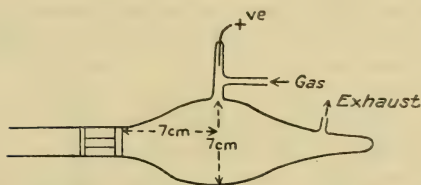
It is harder to deduce the electrical condition of the atoms which are giving out this light. In the positive rays there are, besides the positively charged particles, particles which have become neutralized, and even some which have acquired a negative charge. There are thus three kinds of particles and four types of change of state—namely, neutralization of positive and negatively charged particles and the corresponding ionizations. Since these are all going on simultaneously, any of these changes or conditions may be the cause of the emission of light. In view, however, of the excess of neutral and positively charged particles in the positive rays, it seems natural to suppose that the emission of the Balmer series is caused either by the neutralization of the positively charged atom, or by its collisions with other particles without neutralization, or by the splitting off of an electron from the neutral atom. From theoretical considerations the second is very improbable, owing to the smallness of the nucleus, whose characteristic frequencies, if any, would be expected to be of an order far beyond those of the visible spectrum. It would theoretically be possible to decide between the other two alternatives by sweeping all the charged particles out of a beam of positive rays by an electric or magnetic field, and examining how the luminosity re-established itself further along the beam. It would be necessary, however, to separate the "resting" from the "moving" spectrum, as the existence of the former, due presumably to the dissociation of the molecules of the gas in the observation-chamber by the impact of the rays, would mask the effect. Bohr's theory suggests strongly that it is the neutralization which causes the emission of light, but the point cannot be regarded as quite conclusively settled. In addition there is the possibility (*cf.* the phenomenon of resonance potential)

that some of the emission may be due to the partial separation of an electron from the atom and its return to the normal position.

Molecules.

It was never found possible to get a state of discharge in which the positive rays were exclusively molecular. At very low pressures indeed, the atomic parabola became almost invisible in some cases, but at these pressures the light in the observation-chamber was too faint for spectroscopic examination. The best that could be done was with the larger discharge tube (fig. 3). With the dark space about half across the tube this showed a marked excess of molecules over atoms as determined by the brightness on the willemite screen. Since it is known that such a screen is considerably more sensitive to atoms of hydrogen than to molecules, it is probable that in these experiments there was really a very large excess of molecules. A spectrograph

Fig. 3.
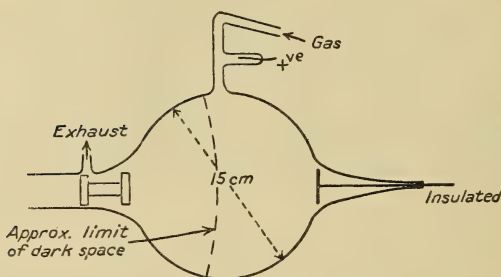
taken under these conditions is shown in Pl. IV. No. 2, the dark space being as shown in fig. 3. It will be seen that the second spectrum is clearly shown, though the H_β line is still the brightest on the plate. This is not surprising when we consider that the light of the Balmer series is concentrated into very few lines relative to that of the secondary spectrum. The brightness of the second spectrum in this case, as compared with the former plate—in which indeed it was invisible,—leaves no doubt that the secondary spectrum is caused by the hydrogen molecule. This result is confirmed by the results of experiments with another discharge tube (fig. 1), in which increasing proportions of molecules

in the rays corresponded with increasing brightness of the second spectrum.

Since hydrogen in the normal state does not absorb the second spectrum, the latter cannot be due to collisions of neutral molecules which do not result in ionization ; but beyond this there is at present no sufficient evidence to determine the state of charge of the molecules before or after the collisions which lead to its emission.

4. The "Resting" Spectrum.

It is clear from an inspection of Pl. IV. No. 1, that when atoms only are present in the positive rays, the second spectrum occurs only very faintly, if at all. It is probable, however, that even in this case it is not entirely absent (a very faint blackening can be detected on the negative of No. 1 between H_β and H_γ, though there is no trace of any definite lines), and is presumably due to the rays exciting the spectrum of the gas through which they pass (the "resting" spectrum of Stark). When molecules are present the second spectrum occurs in considerable quantities, and one would naturally expect it to show the Döppler effect if examined along the direction of motion of the rays. Stark and Wilsar (*loc. cit.*) have found that the second spectrum shows no such effect. To account for this, one of two suppositions must be made. Either, which seems rather improbable, the second spectrum is only emitted as the result of collisions between molecules moving comparatively slowly with respect to each other—*i. e.*, rays near the end of their path ; or Stark and Wilsar never got molecules in their positive rays at all. The second hypothesis seems the most likely. They used a narrow tube which is not favourable to the development of molecules, and in Stark's account of his experiments with the second spectrum the potential difference used in the discharge tube never seems to have exceeded 7500 volts. In all the work done at Cambridge on positive rays fairly powerful induction coils have been used.

When a discharge is produced by these means in a tube at the low pressures found favourable for the production of molecular rays, the potential difference is much greater than 7000 volts. Stark used a wide range of pressures, but it seems not improbable that his comparatively low-potential batteries are less effective in producing molecular rays than the coil discharges used in the Cambridge experiments.

5. Effect of Magnetic Field on the Discharges.

A curious phenomenon was noticed with the discharge tube illustrated in fig. 2. This tube gave only atomic rays under ordinary conditions except at very low pressures, and sometimes even then the molecule was barely visible. When, however, the discharge was influenced by an electromagnet held near it in a certain position, the molecular parabola would suddenly appear. This only happened over a certain range of pressure, and at the pressure at which Pl. IV. No. 1, was taken it had no effect. In addition to bringing out the molecular parabola the magnet always increased the deviation of the atomic parabola, and as this depends chiefly on the cathode fall of potential, it presumably made the tube go easier; while the atomic parabola was generally long and frequently beaded, indicating a wide range of velocities, the molecular parabola produced by the magnet was always short, being little more than a patch of light at the place corresponding to the greater velocity. The magnet had the effect of spreading out the negative glow, which was originally concentrated near the mouth of the anode tube, and bringing it forward towards the cathode. In addition to this effect the magnet would occasionally brighten the atom as well, but careful inspection showed that this was always due to a better centring of the beam of positive rays on to the fine tube, owing to slight deviations of the rays themselves by the magnet.

6. Intensity of Second Spectrum Lines.

The brighter lines in the second spectrum generally occur in groups of two or three, too close together to be separated with the dispersion used. It may, however, be of interest to note that lines (*e. g.*, the group near 4680) which Merton[*] found abnormally weak in a mixture of helium and hydrogen occur quite strongly in the positive rays. Unfortunately, the region examined does not contain any of the lines which Merton found intensified under his conditions.

* Proc. Roy. Soc. A, vol. xcvi. p. 382.

SUMMARY.

1. The Balmer series is produced when positively charged hydrogen *atoms* pass through hydrogen as positive rays.

2. The second spectrum is produced when positively charged hydrogen *molecules* pass through hydrogen as positive rays.

3. Stark and Wilson's failure to find the Döppler effect for the second spectrum of hydrogen is probably to be explained by there being no molecules in the positive rays they used.

4. In certain circumstances a great change can be made in the nature of the positive rays given by a discharge tube by subjecting it to a magnetic field.

In conclusion, I wish to express my sincere thanks to my father, Sir J. J. Thomson, for his interest and advice during the progress of the work described above.

XXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

December 17th, 1919.—Mr. G. W. Lamplugh, F.R.S., President, in the Chair.

THE following communication was read :—

'A Rift-Valley in Western Persia.' By Prof. S. James Shand, D.Sc., F.G.S.

Asmari Mountain, near the oilfields of Maidan-i-Naftun, in the Bakhtiari country of Western Persia, is an inlier of Oligocene limestone among the beds of the Fars System (Miocene), the latter consisting, in the lower part, of bedded gypsum with intercalated shales and a few thin limestones. The mountain is a whale-back, 16 miles long and 3 miles wide at the middle, formed by a simple symmetrical anticline plunging at both ends. The north-western end plunges rather steeply, and shows no abnormal structures ; but at the south-eastern end the fold has collapsed along its length for a distance of 3 miles, letting the gypsum-beds down into a trough in the limestone.

This trough is bounded by two main faults hading north-eastwards and south-westwards respectively, with an average hade of 20°, and marked by steep escarpments. The northern scarp, which lies practically along the axis of the anticline, is at one point 500 feet high ; but the southern one, being low down on the flank of the

anticline, is much less conspicuous. Besides these main faults, there are at least three other big faults parallel to them, which produce minor scarps within the valley; the valley-floor thus descends in terraces towards the south-west, besides having a general south-eastward inclination of some 10°. Uphill, towards the crest of the mountain, the downthrow of the limiting faults diminishes gradually to zero, and the valley dies out on the broad top of the anticline. Downhill, towards the plunging nose of the anticline, the trough is closed abruptly by a cross-fault nearly at right angles to the anticlinal axis. The length of the whole trough is $2\frac{1}{2}$ miles, and its width half a mile.

The northern boundary-fault at its maximum has a downthrow of about 500 feet, the parallel faults range from 150 to 200 feet, and the cross-fault throws about 100 feet.

The gypsiferous beds which once completely filled the trough have been partly removed by erosion, clearly revealing the fault-walls in the lower part of the valley. These fault-scarps in their lower portions are remarkably fresh, and show the smoothed and fluted surfaces produced by the friction of the sliding faces.

The drainage of the faulted region is curious in several respects. The only perennial stream that traverses the valley cuts sheer across it from side to side. Rising in the gypsum-beds on the north-eastern flank of the anticline, the stream turns south-westwards, and cuts right through the limestone in a deep cañon; the latter breaches the northern fault-scarp where the downthrow is greatest, and from here the bed of the stream lies in the gypsum of the valley-bottom, except for a short stretch between two faults, where the limestone-floor is again exposed to view. The stream finally breaks through the southern limestone-wall, and so makes its escape from the valley.

These conditions imply that the river assumed approximately its present direction when there was a cover of gypsiferous beds over the whole area, and that, although younger than the initiation of the faulting, it is older than the sculpturing of the inside of the fault-trough. The eastern end of the trough is again tapped by another and smaller stream with a precisely similar development.

It might be surmised from the excellent preservation of the fluted surfaces on the fault-scarps that the last movement took place at a very recent date, but the behaviour of the river in crossing the scarps does not favour this supposition. The succession of events appears to have been as follows:—

(1) Formation of the trough with gypsum-infilling by partial collapse of the anticline.

(2) Levelling of the gypsum surface and development of a stream across the position of the buried trough.

(3) The stream, cutting down through gypsum, discovers the faults, etches them out, develops subsequents along them, and thus gradually eats out the gypsum filling the rift, until the present topography results.
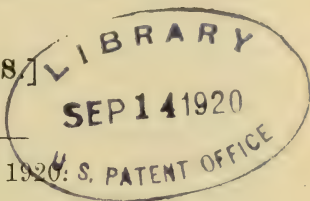
XXIX. *On the Application of Probabilities to the Movement of Gas-Molecules.* By Professor F. Y. EDGEWORTH, *F.B.A.**

THE following is an attempt to vary, in the hope of elucidating, some arguments which the kinetic theory of gases derives from the Calculus of Probabilities.

A. Beginning with the simplest case, imagine an immense number of short perfectly elastic smooth cylindrical pistons of equal size but two varieties of density, the two sets equally numerous, moving in a perfectly smooth long straight horizontally placed groove, terminated at each extremity by a perfectly elastic barrier. The pistons are capable of passing each other. They may be conceived as *side-tracked* from time to time—say, each one after suffering a collision—and guided by smooth devious paths to be replaced without loss of velocity at random at some new point on the main line †. The instances in which more than two come together at once are so rare that they may be neglected. Negligible also is the length of the pistons in comparison with the average

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* Communicated by the Author.
† If the pistons are *not* capable of passing each other, their movements might still be sufficiently *independent* to generate the normal law by repeated collisions. The conception of corpuscles thus tethered may have some relevance to the vibrations of molecules within a solid.

interval between any two of them [*]. There are at first supposed to be no external forces. To investigate the ultimate distribution of velocities to which this system tends, three distinct lines of reasoning may be employed.

I. Among arguments accounting for the genesis of the normal law of error a foremost place seems due to the *rationale* adopted by Laplace (with reference to averages of observations). On that analogy we may expect that the velocity will be distributed according to the normal law [†], if it is a linear function of elements each of which may be regarded as a random specimen of a group distributed according to some definite law of frequency, say $\chi(U, u)$—not, in general, the same law for different elements. Consider the play of the system during an interval of time Δt so short that the deformation of the frequency-function through the occurrence of collisions is very slight. If a piston of mass M with velocity U overtakes one of mass m with velocity u [‡], the new velocity of the former may be written

$$U' = (M-m)U + 2mu ; \qquad (1)$$

if for brevity we take $M+m$ as the unit of mass. Now let the cylinder with velocity U make a second collision with one of mass m and velocity u_1. We have for the new velocity of the M corpuscle,

$$U'' = (M-m)U' + 2mu_1 = (M-m)U + 2m(M-m)u + 2mu_1 ; \qquad . \quad . \quad (2)$$

and so on. Since the frequency for the distribution of velocities may be treated as constant during Δt, the collisions tend to bring the distribution nearer to the normal [§]. If the frequency-function was $\chi(U, u)$ initially, let it become, in the interval Δt, $\chi + \Delta\chi$, or χ_1. By parity, in a second interval there will be a further approach to the

[*] If this assumption is not granted, it will be easy to make allowance in the formulæ for the length of a piston, supposed small (with reference to the mean free path), though not negligible.

[†] By the "normal law" of distribution (or "error") is here understood (conformity to) the function $\dfrac{1}{\sqrt{\pi}c}\exp.-\dfrac{x^2}{c^2}$, and the analogous expressions for higher dimensions : *e. g.* (3) and (5) below.

[‡] The frequency distribution is not altered by the collision of *like* molecules, since they simply exchange velocities.

[§] According to the general *Law of Error* as exhibited by the present writer in the 'Cambridge Philosophical Transactions' for 1905, vol. xx. *Cp.* 'Journal of the Royal Statistical Society,' Sept. 1906, and 'Philosophical Magazine,' 1889, vol. xxviii. p. 283 (article by Dr. Burton).

normal*. Accordingly χ_n, when n is indefinitely great, becomes normal.

There will, indeed, be *some* interdependence between the elements which constitute the set of velocities after a great number of collisions. But presumably this correlation will be of that slight degree which is not fatal to the approximate fulfilment of the normal law †. If N, the total number of molecules clashing with each other, is sufficiently large, any degree of approximation to the normal law can be secured. For consider any particular degree of approximation—say, that which is effected by a linear combination of a large number, ν (*e. g.* a thousand), of elements taken at random from an immense number N. And suppose a group numbering μ (*e. g.* a thousand) of compounds thus constituted, each out of a different set of elements. Such a group will be presented by the values of U (and likewise of u) after a certain number ($\log \nu / \log 2$) of collisions, if N, the number initially distributed according to *any* law of frequency, is sufficiently large. It suffices that $\mu\nu$ elements taken at random from among N should all be different—that is, that $\dfrac{N-1}{N} \times \dfrac{N-2}{N} \ldots \times \dfrac{N-\mu\nu}{N}$ should be very approximately $=1$. Since

$$\left(1 - \frac{1}{N}\right)\left(1 - \frac{2}{N}\right)\ldots\left(1 - \frac{\mu\nu}{N}\right) = 1 - \mu\nu(\mu\nu + 1)/2N \text{ nearly,}$$

the condition will be satisfied if $\mu^2\nu^2$ is small with respect to N (*e. g.* $\mu^2\nu^2$ a million million, and N a trillion). The law then will be approximately fulfilled by a group of velocities after a certain, not very great, number of collisions. With these let the remaining $N - \mu\nu$ velocities, after about the same number of collisions, now be grouped. So far as these superadded specimens are formed from entirely different sets (of the initial N) they render the grouping more approximately normal in the degree to be expected from the addition of independent observations. So far as the elements which go to the $N - \mu\nu$ velocities are not quite distinct, they will enhance the fulfilment

* At any time, say $\nu\Delta t$, after an epoch taken as initial, the velocities $u_1 u_2 \ldots$ successively encountered by an average piston of mass M occur with a frequency that is more nearly normal than were the corresponding velocities at the initial epoch; and accordingly the collisions at the later period are more conducive to the normal distribution of the U's.

† *Cp.* 'Journal of the Royal Statistical Society,' vol. lxix. (1906) p. 500, and vol. lxxxi. (1918) p. 624.

of the law in a less degree *. Altogether the N velocities resulting from numerous collisions will not be distributed so as to satisfy Prof. Pearson's criterion, if based on the supposition that they purported to be N *independent* observations †. But they will form a more nearly normal group than the $\mu\nu$ quite independent observations ‡.

From the preceding verification it appears § that U and u after numerous collisions will be distributed according to the law of frequency Nz, where

$$z = \frac{\sqrt{\mathrm{A}a}}{\pi} \exp.-(\mathrm{A}\mathrm{U}^2 + au^2). \quad . \quad . \quad . \quad (3)$$

The function z must fulfil the condition

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(\mathrm{M}\mathrm{U}^2 + mu^2)z\,d\mathrm{U}\,du = \mathrm{M}[\mathrm{U}^2] + m[u^2] = 2[\mathrm{T}], \quad (4)$$

using square brackets to denote mean values. Put for A, $\mathrm{M}/2[\mathrm{T}]$; and for a, $m/2[\mathrm{T}]$. These values satisfy the equation $\mathrm{M}/2\mathrm{A} + m/2a = 2[\mathrm{T}]$, derived from (4); and also a second *linear* equation derived from the condition that the velocity-distribution of that set of molecules which comes (once) into collision during the instant Δt should be the same just after as before collision. The number of pairs with velocities U and u before collision, viz.

$$\Delta t \mid \mathrm{U} - u \mid \Delta\mathrm{U}\Delta u \exp-(\mathrm{A}\mathrm{U}^2 + au^2),$$

is the same as the number with U' and u' after. Whence $\mathrm{A}\mathrm{U}^2 + au^2 = \mathrm{A}\mathrm{U}'^2 + au'^2$ (the other quantities on each side being equal, see (13)). Giving to U' and u' their values in

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* The imperfection would be of the kind described in Camb. Phil. Trans. *loc. cit.* p. 127, under the head "Relaxation of the Third Condition."

† *Cp.* Camb. Phil. Trans. *loc. cit.* p. 127, and *Enc. Brit.* "Probability," Art. 157.

‡ For the purpose of this verification the finite difference $\Delta\mathrm{U}$ (and likewise Δu), according to which the abscissa is graduated—being of the order $1/\sqrt{n}$, where n is the number of *perfectly independent* elements,—should here be much smaller than $1/\sqrt{\mu\nu}$ and much larger than $1/\sqrt{\mathrm{N}}$. (*Cp.* 'Journal of the Royal Statistical Society,' vol. lxxx. (1917) p. 427.)

§ It being assumed *à priori* (*cp.* below, § III.) that the distributions of U and u are *independent* (*cp.* Tait, Trans. Roy. Soc. Edinburgh, vol. xxxiii. (1886) p. 68. Otherwise we may start with the more general form $\quad z = \mathrm{J} \exp.-(\mathrm{A}\mathrm{U}^2 - 2\mathrm{C}\mathrm{U}u + \mathrm{B}u^2);\quad$ (5) and find from the given conditions that C is null.

U and u from (1) we have $Ma = mA$, the required second equation. Thus

$$z = \frac{1}{2\pi[T]} \exp. -\tfrac{1}{2} \frac{MU^2 + mu^2}{[T]}. \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

That is, supposing U and u to be measured from the centre of gravity. Otherwise it is proper to substitute for U, $(U) - v$ and for u, $(u) - v$, where v is the velocity of the centre of gravity supposed constant, and (U), (u) are the velocities measured (as v is) from a fixed point.

II. A second proof is based on the " H " theorem discovered by Boltzmann. " H " may be described as an "index," meaning a quantity which by its magnitude indicates, but does not measure, the magnitude of some other quantity [*]. An index may act either positively by always increasing with the increase and decreasing with the decrease of the thing indicated, or negatively by always varying in the direction opposite to that which it indicates. " H " is an index of the latter kind. It is a negative index of a certain probability which may be thus described :—Let $f(x)$ [†] be the frequency-function which represents the *ultimate* distribution of a set of observations numbering n, a large but finite number ; that is, the distribution which would be presented by averaging an indefinitely great number of sets each consisting of n observations, the outcome of unaltered conditions. Let P be the probability that a random specimen of a group numbering n would diverge from $f(x)$ to the extent at least that $f_1(x)$, any particular observed or assigned distribution of n observations, does diverge therefrom. Then " H " is an index of P ; decreasing with the increase of P, and conversely. For " H " is—or differs only by added or multiplied constants [‡] from—the negative of the logarithm of a certain probability ϕ which is a positive index of P [§].

The simplest example of " H " occurs when f degrades to a pair of frequencies such as the number of black balls and the number of white balls drawn in the course of n trials from a medley of black and white mixed in proportions $p:q$. The *ultimate* frequencies—those which would be presented

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[*] Compare the use of the term "index-number" in Statistics (*e. g.* by Bowley in his 'Elements of Statistics').

[†] *Mutatis mutandis* when the variation takes place in more than one dimension.

[‡] Accordingly, expressions for " H " differing by such constants are given by different writers.

[§] The index of an index is itself an index.

if an indefinitely large set of series each numbering n were averaged—are np and nq. For any particular series the chance that f_1, representing the observed number of black and white balls, should diverge from f by one compartment having an excess and the other a defect of exactly r is

$$\frac{n\,!}{(np+r)\,!\,\,(np-r)\,!}p^{np+r}q^{np-r}, \quad . \quad . \quad . \quad . \quad (7)$$

well known to be proportional to

$$\exp.-r^2/2npq, \text{ approximately *} . \quad . \quad . \quad . \quad (8)$$

That expression is the "ϕ" in this case †. Accordingly, $H=r^2/2npq$. A more complex case arises when the drawing is made from a medley containing balls of several colours. The (approximate) probability that a particular set of numbers (of balls of each colour) will be presented has for exponent a quadratic expression, χ^2, of which Professor Pearson has made splendid use ‡. This expression, an *alias* of H, is used by the present writer to determine the best values of the constants pertaining to a function of known form—given the values of strips of area (subtended by a curve) between certain points on the axis. The most probable values of the constants are those which minimise the expression for χ^2 obtained from the data §. A bolder stroke of inverse probability is now required : to determine not, as usual, the most probable constants ‖ for a function of

* See, *e. g.*, Todhunter, 'History of Probabilities,' p. 548.

† Note that ϕ itself is but an *index* of the quantity proper to *measure* the probability of a deviation as large as r occurring in n trials, namely (twice) the *integral* of ϕ between limits r and ∞, corresponding to the P in Pearson's *Criterion* of good fit. Accordingly, H may be viewed as a *positive* index of $1-P$.

‡ To measure, by means of a proper integration (see preceding note), the probability that a given distribution, f_1 (in our notation), is a fortuitous specimen of the frequency distribution f. See Phil. Mag , July 1900.

§ 'Journal of the Royal Statistical Society,' vol. lxxvii. (1913–14) p. 724 *et seqq.*, and vol. lxxx. (1916) pp. 471 & 485.

‖ The application of inverse probability to the determination of constants has been discussed at length by the present writer in the 'Journal of the Royal Statistical Society' for 1908. The analogy between the present argument and the more familiar reasoning there employed is brought out by regarding an undetermined (frequency-) function as a determinate function with very numerous undetermined constants.

The argument here summarized is believed to be in accordance with Boltzmann's reasoning about the " H " theorem (*Vorlesungen über Gastheorie* and *Weitere Bemerkungen über* . . . *Wärmetheorie, Sitzungs. Berichte der* . . . *Akademie der Wissenschaften*, vol. lxxvii.: Vienna) ; with the " considerations of probability " from which, according to Jeans ('Dynamical Theory of Gases,' ed. 2, p. 12), " the law of distribution of velocities could have been predicted."

known form, but to determine the most probable form of a function, consistent with certain data, that form for which a certain conditional probability becomes a maximum—namely, the probability that, if the proposed function represented the sought ultimate distribution, the given conditions would be fulfilled. One datum in the case before us is summarized by the equation $\iint f(U, u)\, dU\, du = \text{constant}$ (say unity, or else a given number of molecules); U and u being relative to the centre of gravity supposed at rest, the integration extending over all possible values of U and u. Another datum is furnished by the conservation of the energy of the system. Also it is known that "H" is approximately of the form $\iint f \log f\, dU\, du$ [*]. Accordingly, it is proper to minimise the expression

$$\iint f \log f dU\, du + j\left(\iint f dU\, du - \text{const.}\right) \\ + h\left(\iint f (MU^2 + mu^2) - \text{const.}\right), \quad . \quad (9)$$

where j and h are undeterminate multipliers. Varying (9), we have for the first term of expansion

$$\iint \partial f (\log f + 1 + j + h(MU^2 + mu^2)) = 0.$$

Whence it is deducible (the second term being positive) that

$$f(U, u) \equiv \text{Const. exp.} - h(MU^2 + mu^2). \quad . \quad . \quad (10)$$

More generally, the centre of gravity moving uniformly, there is a second datum, namely $MU + mu = \text{const.}$ But the only effect of this condition is to introduce into (9) a new term under the sign of integration, say $k(MU + mu)$, where k is a new constant. There will thus be introduced *first* powers of U and u into the exponent of f, which may be written

$$-h(MU^2 + mu^2) + k(MU + mu) + \text{const.,} \quad . \quad (11)$$

where h and k are to be determined from the given mean energy of the molecules and the given (constant) velocity of the system's centre of gravity.

The validity of this reasoning is confirmed by observing that the law of error itself, as applicable to statistics generally, is deducible by parity of reasoning. For instance,

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[*] By a generalization of the approximation whereby the exact expression (7) was reduced to (8). See Boltzmann, *Vorlesungen über Gastheorie*, Abschnitt iii. §§ 5, 6, & 8; Jeans, 'Dynamical Theory of Gases,' ed. 2, § 22; and other leading authorities.

let x be sum of m elements, each a random specimen of a group characterized by some definite law of frequency, not all the laws identical, but each having the same mean square of deviation, say $\frac{1}{2}c^2/m$ [*]. Then f, the sought frequency-function of x, is such that $\int_{-\infty}^{\infty} f \log f \, dx$ is a minimum, subject to the conditions $\int_{-\infty}^{\infty} f \, dx = \text{const.}$, and $\int_{-\infty}^{\infty} x^2 f \, dx = \frac{1}{2}c^2$. Whence (if the average is zero) by parity of reasoning $f(x)$ is proved to be of the form $A \exp. - x^2/c^2$.   Q. E. D.

III. The proof by way of the " H " theorem is sometimes introduced by a less complete proof which shows only that the normal distribution of velocities is *sufficient*, not that it is *necessary*, for stability [†]. This proof is readily adapted to the case of motion in one dimension.   Let $\mathrm{N}\mathrm{F}(\mathrm{U})$ represent the average number of pistons (of mass M) with velocity between U and $\mathrm{U} + \Delta\mathrm{U}$, say of the *class* U, which occur at any time between any two points on the line distant from each other by a unit of length; and let $f(u)$ be similarly defined.   Measure a short distance Δx from the position of every molecule of class U throughout a tract of unit length, to the right or left according as U > or < u, any assigned velocity.   Say $\mathrm{U} > u$: and put $\Delta x = \Delta t(\mathrm{U} - u)$, where Δt is an interval of time so short that the number of molecules making more than one collision during that instant may be neglected.   Then the expected number of collisions produced by a specimen of class U overtaking one of class u, during the instant Δt, is

$$\mathrm{N}\Delta t(\mathrm{U} - u)\,\Delta\mathrm{U}\,\Delta u\,\mathrm{F}(\mathrm{U})f(u). \quad . \quad . \quad (12)$$

That is the number of members lost to class U by collisions of that type during Δt.   Let the respective velocities resulting from such a collision be U' and u' $(u' > \mathrm{U}')$. When a molecule of class u' overtakes one of class U', the resulting velocities are the original u and U.   Accordingly [‡], the loss to class U through collisions of the first

* The reasoning is readily extended to the more general case in which the mean square increases with the number of the elements ; the elements have not all the same mean square, and are not measured from their mean value.

† *Cp.* Watson, ' Kinetic Theory of Gases,' § 14 *et seq.*

‡ See below, p. 258 (16).

type, in the time t, will be compensated by the gain to class U through collisions of the second type, if

$$\Delta t(\mathrm{U}-u)\,\Delta\mathrm{U}\,\Delta u\,\mathrm{F}(\mathrm{U})\,f(u)$$
$$= \Delta t(u'-\mathrm{U}')\,\Delta\mathrm{U}'\,\Delta u'\mathrm{F}(\mathrm{U}')f(u'). \quad . \quad (13)$$

Of the factors on each side $(\mathrm{U}-u)=(u'-\mathrm{U}')$, the colliding bodies being perfectly elastic; and $\Delta\mathrm{U}'\Delta u'$ is equatable to $\Delta\mathrm{U}\,\Delta u$ independently of the variables U and u [*]. Accordingly, the equation will be satisfied if

$$\mathrm{F}(\mathrm{U})f(u) \equiv \mathrm{F}(\mathrm{U}')f(u'), \quad . \quad . \quad . \quad (14)$$

consistently with the conservation of energy. This functional equation may be solved by putting $\Phi = \log \mathrm{F}$, $\phi = \log f$:

$$\Phi(\mathrm{U}) + \phi(u) \equiv \Phi(\mathrm{U}') + \phi(u'), \quad . \quad . \quad (15)$$

subject to the condition

$$\mathrm{M}\mathrm{U}^2 + mu^2 = \mathrm{M}\mathrm{U}'^2 + mu'^2.$$

The condition supplies the solution [†], viz. the left-hand side of the equation multiplied by a constant, evidently negative, say $-h$. That is, not taking account of the conservation of momentum; otherwise it is proper to add a term of the form $k(\mathrm{M}\mathrm{U}+mu)$. The constants may be determined by well-known considerations.

This reasoning has no claim to novelty. It is re-stated here only in order to draw attention to two points. One is the relation between this third argument and our first. Whereas the third argument does not prove that the normal distribution will be set up in a molecular medley, but only that if it is set up it will be maintained—this method of approach has hitherto been completed by the " H " theorem of Boltzmann. The error theory of Laplace is now suggested as an alternative complement.

Another point to which attention is called is the implied use of that sort of Probability which has been called in the 'Philosophical Magazine' " *à priori* " [‡] and elsewhere

* As may be shown by differentiating with respect to U' and u' the expression for U (1) and that for u; and more generally from the consideration adduced below (34).

† *Cp.* Jeans, 'Dynamical Theory of Gases,' p. 25, ed. 2. If (13) is obtained by the reasoning employed in the first argument to determine the *constants* for the normal function ((4) *et seq.*) the solution of (13) avails to prove that the function is *necessary*.

‡ See Phil. Mag. 1884, article by the present writer. The term " *à priori* " is infelicitous so far as it is sometimes used with a different connotation in the calculus of probabilities. As to the alternative designations, see article on " Probability," *Encyc. Brit.* (ed. 2) p. 377

" unverified " or, after Boole, " intellectual." An assumption of this kind was tacitly made in the preceding argument when it was taken for granted that the appearance (in consequence of collisions) of additional couples with velocities U' and u', $u' > $ U', within a distance of $(u' - $ U'$)\Delta t$ from each other, the slower M molecule *behind* the quicker one, was tantamount to, or attended with, the appearance of additional couples corresponding in all respects to the above description except that the slower body is now *before* the quicker one. The underlying assumption might perhaps be formulated as follows :—(16) A molecular chaos must present the same appearance, both as to the relative position of molecules and as to their velocities, whether contemplated from above or below. Thus corresponding to couples of the first type just now defined with M *behind* m, there are (on an average) at any time an equal number of couples in other respects similar but with M *before* m.

The preceding arguments are readily extended to the case in which there are several varieties of mass, each pertaining to a large set of cylindrical molecules.

B. Coming nearer to reality, let us next consider the random movements of disks on a plane.

I. The simplest case under this head—that in which the molecules are equal not only in volume but also in mass—has already served to introduce our first argument to readers of the ' Philosophical Magazine ' *. It has been shown that if a disk with velocities U and V overtake one with velocities u and v, the line joining the centres at the moment of impact making an angle θ with the axis of U and u, the new velocities of the former are as follows :

$$\left. \begin{array}{l} \text{U}' = \text{U} \sin^2 \theta - \text{V} \sin \theta \cos \theta + u \cos^2 \theta + v \cos \theta \sin \theta, \\ \text{V}' = - \text{U} \sin \theta \cos \theta + \text{V} \cos^2 \theta + u \cos \theta \sin \theta + v \sin^2 \theta. \end{array} \right\} \quad (17)$$

If now with these acquired velocities the said disk collide with a fresh disk of which the velocities are u_1 and v_1, the angle made by the centre-line with the axis of U being now θ_1, we shall have for the new velocity

$$\text{U}'' = \text{U}' \sin^2 \theta_1 - \text{V}' \sin \theta_1 \cos \theta_1$$
$$+ u_1 \cos^2 \theta_1 + v_1 \cos \theta_1 \sin \theta_1, \quad . \quad (18)$$

with a corresponding expression for V''; where for U'

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and V′ their values in U, V, u, r above given are to be substituted. It was thus shown that after many, say n, collisions the velocity of the disk under consideration, say $U^{(n)}$ and likewise $V^{(n)}$, is a linear function of numerous elements.

It is now to be added that the plurality of constituent elements is further secured in the more concrete case of disks differing in type : say, one large class of mass M, another of mass m. For then, after the first collision,

$$U' = (M - m)(U \cos^2 \theta + V \cos \theta \sin \theta) + U \sin^2 \theta$$
$$- V \sin \theta \cos \theta + 2m(u \cos^2 \theta + r \cos \theta \sin \theta), \quad (19)$$

with corresponding expression for V′. Accordingly, except in the limiting cases when M and m are very unequal or nearly equal, the ultimate velocity of any disk is largely made up of fragments of orders reduced, not only through repeated multiplication by powers and products of sines and cosines, but also by factors of the type $(M - m)^r$, where $M - m$ is a proper fraction. The penultimate constituents— the less remote progenitors—of the ultimate velocity do indeed bulk more largely. But in general, and except initially, they are themselves the product of numerous antecedent collisions, and are therefore on the way to normal distribution [*]. The system may be conceived as approaching that ultimate state by successive steps as in the simpler case [†], or rather more rapidly. As before, we may argue that the normal law in a general form will be set up ; and may determine the constants from the conservation of energy, and the condition that the velocity-distribution of the molecules which come into collision during Δt should be the same before and after collision. The frequency-function thus found may be written

$$\text{Const. exp.} - \tfrac{1}{2} T/[T]. \quad \quad \ldots \quad (20)$$

Here U, V and u, v are velocities relative to the centre of gravity—which is at rest or moving uniformly. The transformation required when the velocities relate to a fixed point has already been indicated [‡].

II. This conclusion is reached more quickly by the second argument. Putting $f(U, V, u, v)$ for the sought function, we have now to determine f so that the integral (over all possible values of the variables) of $f \log f$ should be a minimum—subject to the condition that the co-extensive

integral of f and of $f(M(U^2 + V^2) + m(u^2 + v^2))$ should be constant, and the two additional conditions that the integrals of $f(MU + mu)$ and that of $f(MV + mv)$ should each be constant. Varying f, as before, we find for the required function,

$$f \equiv \text{Const. exp.} -h(M(U^2 + V^2) + m(u^2 + v^2))$$
$$+ k(MU + mu) + l(MV + mv); \quad . \quad (21)$$

where the constants are to be determined from the data by familiar considerations.

III. The third argument purports to show that the loss to the contents of any class (U, V) through collisions with molecules of class (u, v) is repaired by collisions between molecules of certain other classes—provided that the distributions of velocities, say $F(U, V)$ and $f(u, v)$, are *normal*. Following the analogy of the simpler case, consider the *species* defined by an m molecule of class u occurring in such neighbourhood to an M molecule of class U that a collision will result within the time Δt. And let the species now be divided into *varieties* according to the relative orientation of the molecules at or on the eve of a collision, defined, say, by the angle θ which a line joining the point of contact makes with a horizontal axis.

Fig. 1.
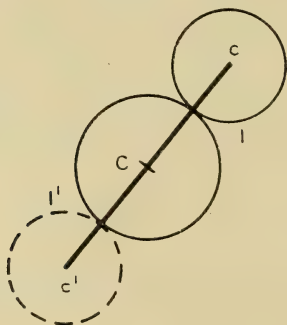
By parity of reasoning it may shown that the distribution will be stable if $F(U, V)f(u, v) \equiv F(U', V')f(u', v')$; or putting as before Φ for $\log F$, ϕ for $\log f$,

$$\Phi(U, V) + \phi(u, v) \equiv M(U'^2 + V'^2) + m(u'^2 + v'^2), \quad . \quad (22)$$

subject to the condition

$$M(U^2 + V^2) + m(u^2 + v^2) = M(U'^2 + V'^2) + m(u'^2 + v'^2).$$

As before, one side of the equation multiplied by a (negative) constant supplies the solution *.

That is, not taking account of the moments. When they are similarly treated, there is obtained for the required function one identical with (21).

The character of the reproductive collision may be seen by looking at figure 1 from the top of the page as if it were the bottom. If the velocities just after collision are reversed and the figure is then looked at from above, the circle with centre *c* which was at first overtaken now overtakes the other. The dotted circle with point of impact at I′ is meant to represent such a collision viewed from below. The argument involves an assumption of the kind exhibited in the simpler case (16), namely that (in a molecular medley) of the couples with respective velocities U, V and *u, v* there are (on average) as many with one molecule *before* as *behind* the other.

The arguments which have been employed with reference to collisions between disks of different masses may of course be narrowed to the case of perfectly similar disks, and may be extended to the case of more than two types of molecules, and to three dimensions.

C. We go on from Cartesian to Lagrangian co-ordinates, beginning with the case of two dimensions and two sets of molecules.

I. Let the generalized co-ordinate of a molecule for one set be $Q_1, Q_2 \ldots Q_m$; for another $q_1, q_2 \ldots q_n$; and the corresponding components of momentum $P_1, P_2 \ldots p_1, p_2 \ldots$ Let R be the impulsive force at the moment of collision between two molecules of different type—its direction being normal to the contour of each figure at the point of impact, say I. Let X be the abscissa of I with respect to fixed rectangular axes $= \Phi(Q_1, Q_2 \ldots Q_m)$, and likewise $Y = \Psi(Q_1, Q_2 \ldots Q_m)$. Let Φ_t and likewise Ψ_t denote the respective differential coefficients of Φ and Ψ with respect to Q_t. If θ is the angle made with the horizontal by the normal at the moment of collision, $R(\Phi_t \cos \theta + \Psi_t \sin \theta)$, say (23) $RL_t = (P_t - P'_t)$; where, R being positive, L is negative when $P' > P$. Like equations are obtainable for the other P's. Likewise for the *p*'s $R(\phi_t \cos \theta + \psi_t \sin \theta)$,

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* The argument may be more closely assimilated to that under head A by transforming to new axes, one making an angle θ with the horizontal and the other with the vertical. Only the velocities in the first of these directions, say W and *w*, will be changed by the collision, say to W′ and *w*′. $W - w = w' - W'$, as the argument requires. *Cp.* C. II. below.

say (24) $Rl_t = p'_t - p$; where l is negative when $p'_t < p_t$. One more equation connecting R with the P's and p's is obtained from the principle that the relative velocity of the two points of impact is the same (in absolute magnitude) before and after collision : say (25) $W - w = w' - W'$, both sides positive.   Now $W = L_1 Q_1 + L_2 Q_2 + \ldots + L_m Q_m = L_1(B_{11}P_1 + B_{12}P_2 + \ldots) + L_2(B_{21}P_1 + B_{22}P_2 + \ldots) + \ldots$; when for each of the Q's is substituted its value in terms of the p's *.   And W' is an analogous linear function of the *dashed* P's.   Rearranging and adding, we have $W + W' = (P_1 + P'_1)(L_1 B_{11} + L_2 B_{12} + \ldots) + (P_2 + P'_2)(L_1 B_{21} + L_2 B_{22} + \ldots)$. Likewise $(w + w')$ is expressible in terms of p's and b's. But by (25) $(W + W') - (w + w') = 0$.   And by (23) and (24) $P'_t = P_t - R L_t, p'_t = p_t + R l_t$.   Whence R is found as a *linear function* of the P's and p's.   Accordingly P'_t, what P_t becomes through the collision, is a linear function of the P's and p's. Likewise P''_t (the result of a fresh collision) is a linear function of those P's and p's, and of fresh p's themselves † the result of numerous previous collisions.   There is evidenced that plurality of components which, the composition being linear, tends to generate the law of error.

But a scruple may be raised with respect to the condition of *independence*.   That condition is threatened by the circumstance that the coefficients of the P's in the expressions for P_1, $P_2 \ldots$ (and likewise the coefficients of the p's in p_1, $p_2 \ldots$) are not, as usual in the statement of the law of error, *constants*, but *functions* of the co-ordinates which vary between successive collisions.   It is not necessary, however, for the genesis of the normal law that the " constants " in the linear function should be rigorously constant.   It suffices that they should be random specimens of a medley‡ , as the coefficients here may be regarded.

The distribution resulting from this jumble will be in a form which may be written $Z = J \exp \frac{1}{2} {}_1 T/[T]$; where J is a constant securing that the integral of Z between extreme limits is unity ; ${}_1 T$ is a quadratic function of the P's and p's with numerical coefficients § ; [T] is the mean energy of all the molecules (in a large unit of area).   To show the relation of ${}_1 T$ to T, the expression in terms of P's and p's for the mean energy of molecules having the same P's and p's but

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* *Cp.* Watson and Burbury, ' Generalised Co-ordinates,' § 7.

† *Cp.* note to p. 251 above.

‡ " Law of Error," Camb. Phil. Trans. 1906, p. 128.

§ As in the simpler cases, Cartesian (*x* and *y*) *co-ordinates* do not appear in the expression for P_1, P_2, etc., nor in the expression for the energy.

different Q's and q's, transform T so as to form a linear function of squares, say

$$C_1 \Pi_1^2 + C_2 \Pi_2^2 + \ldots C_m \Pi_m^2 + c_1 \pi_1^2 + \ldots c_n \pi_n^2 ; \quad . \quad (26)$$

where the coefficients are numerical. Then, as in the simpler case, $_1T$ must be of the form

$$_1C_1 \Pi_1^2 + \ldots + _1C_m \Pi_m^2 + _1c_1 \pi_1^2 + \ldots + _1c_n \pi_n^2,$$

and if
$$_1C_1 = C_1(m+n)/2[T], \ldots c_{11} = _1c_1(m+n)/2[T], \ldots$$

the condition analogous to (4) will be satisfied. Also as $_1T = _1T'$ (the mean energy of the set which has come into collision during Δt) the other equations for the constants must be satisfied (see (13) and (34)). Thus the distribution may be written

$$Z = J \exp -\tfrac{1}{2} \frac{m+n}{2} T/[T], \quad . \quad . \quad . \quad (27)$$

The complex molecules with different co-ordinates to which this distribution refers form a " universe," which may be divided into *genera* delimited by values of the co-ordinates. Consider first extensive genera, *e. g.* all the cases which have co-ordinates between Q_1 and $Q_1 + \alpha$, Q_2 and $Q_2 + \beta$, where α, β, etc. are considerable. If the normal law is *very well* fulfilled for the " universe " it must be *fairly well* fulfilled by those genera *. As the law becomes *still better* fulfilled for the universe it must become *very well* fulfilled for those genera. So by parity of reason it must be fairly well fulfilled for subordinate less extensive genera ; and so on. Ultimately the law must be fulfilled for every genus defined by neighbouring values of the co-ordinates Q_1 and $Q_1 + \Delta Q_1$, Q_2 and $Q_2 + \Delta Q_2 \ldots$. The mean energy for each such genus is presumably the same †.

II. The second argument gives at once the distribution in terms of the co-ordinates, with reference to each particular configuration which may be assumed by a pair of colliding molecules. Let T be the energy of a pair expressed in terms of the co-ordinates, and either the generalized velocities or the components of momentum ; and let P_1 be the momentum in the direction of a fixed axis x, and likewise

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* The constituents of the universe being taken at random from those genera, supposed few.

† The energy would be the same for any one molecule moving without collision through different *phases* defined by the varying values of the co-ordinates ; and there is no reason why it should not be the same for the *average* molecule in different phases.

P_2 in the direction y. Then, by reasoning of parity with that employed in the simpler cases, the required function is of the form

$$\text{Const. } \exp -h(T + kP_1 + lP_2). \quad . \quad . \quad . \quad (28)$$

Each genus being thus distributed normally, the universe which comprises all the genera must be so distributed, whence (27) can be deduced.

III. The assumptions involved by the third argument may be illustrated by a simple example. Let the molecules of one set be shaped each like a flat ruler with one side AIB in fig. 2 A rectilinear, but the other side not[*]. And let another

Fig. 2.
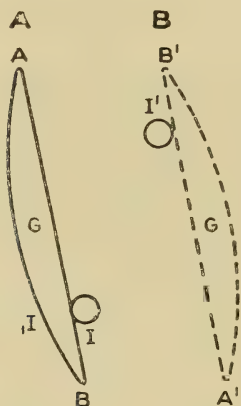
set of molecules consist of disks, both sets moving in the same plane. Fig. 2 A represents a collision between two such bodies. Say $U \cdot V$ are the velocity components for the centre of gravity of the ruler; Ω is the velocity of rotation about the centre of gravity; ϕ is the angle made by the straight line AB with the vertical; u and v are the (translational) velocities of the disk. If I is the point on the ruler which comes into contact with the disk, let the velocity of I just before impact resolved in the direction normal to the colliding surfaces be W, and that of

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[*] To secure that the velocities of the bar after a collision of type A might not be replenished by an impact *from behind*, as in the case of a symmetrical disk (above, p. 261). Impact from behind, say at $_1$I, is to be distinguished from the " back-hand " collision at I'.

the disk w. Let the velocities after collision be W' and w'—
say, $W > w, w' > W'$. Analogy with the simpler cases suggests
that we should equate

$$F(U, V, \Omega) f(u, v) \equiv F(U', V', \Omega') f(u', v'). \quad (29)$$

But there will not now be secured thereby the replenish-
ment of the class (U, V, Ω) by means of collisions between
molecules of the dotted classes. The sort of collision which
might be expected to act thus is shown by reversing the
velocities of the points of contact, and then looking at
the figure from above (16). The view thus obtained is
shown in fig. 2 B, where the disk has the post-collision
velocities u', v'; but the velocity of I' in the direction
perpendicular to A' B' is $U' \cos \phi + V' \sin \phi$ *minus* $c\Omega$,
where c is the perpendicular distance of the normal at
I from G, whereas in W the sign of $c\Omega$ is *plus*. The
relative velocity of the points of contact at (*i. e.* just before)
this back-hand collision is thus not the same as it was for the
collision shown in fig. 2 A. The reasoning before employed[*]
thus breaks down. The break is obviated by the assumption
that the class $(U, V, -\Omega)$ occurs as frequently in the medley
as the class $(U, V, +\Omega)$. We have then (30) $F(U, V, \Omega)$
$= F(U, V, -\Omega)$. What is lost to class (U, V, Ω) through
the collision shown by fig. 2 A is gained by the class
$(U', V', +\Omega')$. And by the postulate the content of that
class keeps equal to that of $(U', V', -\Omega')$. And collision
between molecules of the latter class and those of class
(u', v')—the collisions shown in fig. 2 B—results in the class
$(U, V, -\Omega)$. If then equation (29) is satisfied, what is lost
to class (U, V, Ω) through a back-hand collision will be
gained by class $(U, V, -\Omega)$[†]. But the contents of these
two classes are equal by (30). Therefore if equation (29) is
satisfied, the class (U, V, Ω)—and likewise any other class—
will not be increased or diminished by collisions with m mole-
cules of the class (u, v) and likewise not by collisions with
those of any other class.

The example may be generalized by supposing the ruler AB
to be connected by a hinge at B with another flat bar BC, and
that again with another link CD; while the disk is likewise
connected with a complicated mechanism. By parity of
reason, the velocities lost to any class $(\dot{Q}_1, \dot{Q}_2 \ldots)$ through a
direct collision with any class $(\dot{q}_1, \dot{q}_2 \ldots)$—each class of an

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[*] Above, (22).

[†] By analogy with the particular cases above or by the general
reasoning below (p. 267).

assigned *genus* (defined by the values of the Q's and *q's*)—will be restored by a back-hand collision of type B : granted postulates analogous to (16) and (30).

The new axiom may be stated thus (31) :—For any assigned values of the co-ordinates pertaining to a set of molecules, the class defined by particular values * of the velocities of the centre of gravity (or the corresponding momenta), and of the other components of velocity (or momentum), occurs with the same frequency as the class defined by the *reverse* of the components for the centre of gravity, together with the same values as before for the other components. Which frequency is the same as that of the class defined by retaining the components of velocity or momentum for the centre of gravity and *reversing* all the other components ; as follows from the received axiom that (32) the frequency of a class is not altered by changing the signs of *all* the components of velocity or momentum †.

To combine this datum with the leading equations analogous to (13) and (29), transform the co-ordinates so that one of them may be the abscissa of the centre of gravity of the molecules of mass M measured on an axis parallel to the normal with corresponding velocity $\bar{U}$ at the point of impact and another the ordinate thereto with corresponding velocity $\bar{V}$, and likewise for the molecules of mass m. Considering any *species* defined by the proximity of two molecules of assigned classes ‡, say $(\bar{U}, \bar{V}, \dot{Q}_1, \dot{Q}_2 \ldots)$ and $(\bar{u}, \bar{v}, \dot{q}_1, \dot{q}_2 \ldots)$, suppose the points of impact on the contour of the two molecules to be moving just before the collision with respective normal velocities W and w (say, $W > w$). Let these be changed by the collision to W' and w', the velocities of the points in a tangential direction remaining unchanged. By (32) the frequency of the species with the *dashed* components which results from the collision will be the same as the frequency of the species formed by *reversing all* those components. To secure that the loss to the original class $(\bar{U}, \bar{V}, + \dot{Q})$ through

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* *I. e.*, values between limits separated by small finite differences, *e. g.* $\dot{Q}$ and $\dot{Q} + \Delta \dot{Q}$.

† *Cp.* Burbury, 'Kinetic Theory of Gases,' ed. 2. p. 21; Bryan, "Report on Thermodynamics," Brit. Assoc. Report, 1891, p. 92. The generally admitted (32) is to be distinguished from the now proposed (31).

‡ Classes defined by velocities (or momenta) and species constituted by members of two classes within a certain proximity. (*Cp.* above, pp. 256, 260.)

collisions with $(\bar{u}, \bar{v}, + \dot{q}_1 \ldots)$ is the same as the loss to class $(\overline{\text{U}}', \overline{\text{V}}', -\dot{\text{Q}}_1 \ldots)$ from collision between members of that class and class $(\bar{u}', \bar{v}', -\dot{q}_1' \ldots)$ (w' reversed overtaking W$'$ reversed), that is, the gain to the class of $(\overline{\text{U}}, \overline{\text{V}}, -\dot{\text{Q}}_1 \ldots)$, we have—granted the postulate (31)—the condition

$$\Delta \text{Q}_1 \Delta \text{Q}_2 \ldots \Delta q_1 \Delta q_2 \ldots \Delta \text{U} \Delta \text{V} \Delta \dot{\text{Q}}_1 \Delta \dot{\text{Q}}_2 \ldots \Delta u \Delta v \Delta \dot{q}_1 \Delta \dot{q}_2 \ldots,$$
$$\text{W} - w \mid \text{F}(\text{Q}_1, \text{Q}_2 \ldots \overline{\text{U}}, \overline{\text{V}}, \dot{\text{Q}}_1, \dot{\text{Q}}_2 \ldots) f(q_1, q_2 \ldots \bar{u}, \bar{v}, \dot{q}_1, \dot{q}_2 \ldots),$$
$$\cdots \quad (33)$$

equal to the expression which is formed by *retaining* all the symbols relating to *co-ordinates* and affecting all the *velocities* with *dashes*. The equation may likewise be expressed in terms of the components of momentum, say

$$\text{MU, MV, P}_1, \text{P}_2 \ldots mu, mv, p_1, p_2 \ldots.$$

This equation relates to the *genus* (or pair of genera) which is defined by values of the co-ordinates between assigned values of Q_1 and $\text{Q}_1 + \Delta \text{Q}_1$, Q_2 and $\text{Q}_2 + \Delta \text{Q}_2 \ldots$ q_1 and $q_1 + \Delta q_1 \ldots$; which are the same on both sides of the equation, unaltered by the collision. F and f, as before, denote frequencies of classes, for the definition of which it is necessary now to specify the coordinates as well as the velocities;

$$\Delta \overline{\text{U}} \Delta \overline{\text{V}} \Delta \dot{\text{Q}}_1 \ldots \Delta u \Delta v \Delta \dot{q}_1 \ldots = \Delta \overline{\text{U}}' \Delta \overline{\text{V}}' \Delta \dot{\text{Q}}_1' \ldots \Delta \bar{u}' \Delta \bar{v}' \Delta \dot{\text{Q}}_1' \ldots$$
$$\cdots \quad (34);$$

since each P (and so each Q) is a *linear function* of P's *, and accordingly the right side of (34) = the left side multiplied by a constant—which constant cannot be other than unity. Also $(\text{W} - w) = w' - \text{W}'$. Thus (33) will be satisfied if

$$\text{F}(\text{Q}_1 \text{Q}_2 \ldots \overline{\text{U}} \overline{\text{V}} \dot{\text{Q}}_1 \ldots) f(q_1, q_2 \ldots \bar{u}, \bar{v}, \dot{q}_1 \ldots)$$
$$= \text{F}(\text{Q}_1 \text{Q}_2 \ldots \overline{\text{U}}' \overline{\text{V}}_1' \dot{\text{Q}}_1' \ldots) f(q_1, q_2 \ldots \bar{u}', \bar{v}', \dot{q}_1' \ldots); \quad (35)$$

subject to the condition that T$'$ the energy of the two molecules after the collision equals T what it was before. Whence, as before †, it is deduced that the required distribution is of the form J exp $-h$T, where T is a quadratic function either of the components of velocity or those of momentum. For the co-ordinates it is convenient to take, besides the velocity components of the centre of gravity,

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* As pointed out by Jeans, *op. cit.* p. 18.
† *Cp.* (15) and (22).

a third co-ordinate which does not figure in the expression for the energy, viz. the angle made with a fixed axis by an arbitrary line through the centre of gravity ; and for the remaining co-ordinates such as do not relate to points or lines fixed in space (but only to parts of the complex molecule) *.

The characteristic defect of the third argument, that it does not prove the *necessity* of the normal distribution, may, as before, be remedied by the *first* argument.

The analogues in three dimensions † of the preceding problems, and other generalizations not involving other principles of Probabilities, are here passed over.

D. So far we have supposed two molecules colliding with each other and separating with velocities determined by the laws of impact for perfectly elastic bodies. We are now to entertain the more general conception of an *encounter* ‡ between two molecules supposed to come within each other's *sphere of influence* and to be deflected from their previous path according to some unknown law of repulsion (perhaps preceded by attraction). Considering first the simple case of equal disks moving in a plane, we suppose the circles of influence to be so small and rare that the path of a molecule after leaving one of these circles, and likewise before entering it, is rectilinear, and that throughout a considerable space (in a large unit of area) there occur only molecules moving in free straight paths. The remainder of the unit area—a constant proportion—consists of regions within which the movements of the couples are correlated as Dr. Burbury

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* The energy will then be of the form

$$M\overline{U}^2 + m\overline{u}^2 + Mk^2\Omega^2 + T_1,$$

where Ω is the velocity of the molecule about its centre of gravity, k^2 involves co-ordinates other than that of which Ω is the differential coefficient. T_1, the remainder of the energy, is a quadratic function of the remaining velocities (or momenta) with coefficients involving the corresponding co-ordinates. The *signs* of the P''s for the back-hand collision are obtained by observing the signs of the L's and *l*'s in equations (23) and (24).

† Analogous to the view of the molecular system from above (16) is now the view in *any* direction. The configuration at a "back-hand" collision will now depend not only on the configuration, but also on the velocities of rotation about each centre of gravity, at the direct collision between two molecules.

‡ *Cp.* Watson, p. 36, Jeans, etc. A good representation of encounter is given by Clerk Maxwell in his ' Dynamical Theory of Gases : Collected Papers,' vol. ii. p. 42.

conceives [*]. We are now concerned only with the free molecules. Their number per unit area and their mean energy are to be considered constant.

I. The velocity (in either direction) of any one in particular may be considered as depending on an immense number of preceding velocities, as in the simpler examples. But the dependence is not now known to be linear. Let f be the function whereby u_r', the present velocity in the horizontal direction of any particular molecule, is connected with the velocities of n molecules at a prior epoch. Say

$$u_r' = f({}_1u_r,\ {}_2u_r \ldots {}_nu_r;\ {}_1v_r,\ {}_2v_r \ldots {}_nv_r),$$

where the variables involved in the functions are velocities at the prior epoch. Expanding f in ascending powers of the variable, write

$$u_r' = a_1\Sigma u_r + b_1\Sigma u_r^2 + c_1\Sigma u_r^3 + \ldots + a_2\Sigma v_r + b_2\Sigma v_r^2 + \ldots$$

+ terms involving combinations of the u's and of the v's *inter se*, and of the u's with the v's. Here the symbol Σ is for the moment used to denote *weighted* sums; since with respect to any particular value of u_r' a particular coefficient attaches to each u. Similarly interpreted,

$$u_r'^2 = a_1^2\Sigma u_r^2 + 2a_1^2\Sigma u_r u_s + b_1^2\Sigma u_r^4 + \ldots + a_2^2\Sigma v_r^2 + 2a_2^2\Sigma v_r v_s$$
$$+ b_2^2\Sigma v_r^4 + \ldots + 2a_1a_2\Sigma u_r v_s + \ldots.$$

But in forming the mean value of u', or any of its powers, it is proper to treat one value of u as on a par with another. Accordingly we may write

$$[u'^2] = a_1^2[\Sigma u^2] + 2a_1^2[\Sigma u_r u_s] + \ldots + a_2^2[\Sigma v^2] + \ldots$$
$$+ 2a_1a_2[\Sigma u_r v_s],$$

where Σ is interpreted as usual, and square brackets denote mean values. Put $\upsilon = u/n$, $\eta = v/n$, $A = na$,

$$[u'^2] = A_1^2[\Sigma \upsilon^2] + 2A_1^2[\Sigma \upsilon_r \eta_s] + \ldots A_2^2[\Sigma \eta^2] + \ldots$$
$$+ 2A_1A_2[\Sigma \upsilon_r \eta_s],$$

and we have (neglecting some quantities of the order $1/n$)

$$[u'^2] = A_1^2[\Sigma \upsilon^2] + 2A_1^2[\Sigma \upsilon_r \upsilon_s] + \ldots A_2^2[\Sigma \eta^2] + \ldots$$

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[*] According to his " Assumption B," ' Kinetic Theory of Gases,' p. 11 *et passim.* That within the spheres of influence the distribution of velocities must be normal may be concluded by the use of an argument like our *second*. Presumably the whole class of molecules within such regions may be broken up into species characterized by the stage of approach—some couples for instance at the initial stage, others as close together as possible, at the very acme of the encounter. To each stage there would pertain a different *coefficient of correlation*.

Of the terms on the right some disappear because affected with *first* powers of v and η, the *means* whereof are respectively zero, *e. g.*, $\Sigma v_r v_s$; others for that reason combined with the presumption that the v's and η's are *independent* [*], *e. g.*, $\Sigma v \eta$; others because the number of the combinations is of an inferior order compared with that of some which are retained, *e. g.*, Σv_1^4 as compared with $\Sigma v_r^2 v_s^2$ [†]. There are retained when n is large, only combinations equatable to powers of $[\Sigma v^2]$ and $[\Sigma \eta^2]$, say of k_1 and k_2. Thus

$$[u'^2] = A_1^2 k_1 + 2 B_1^2 k_1^2 + \ldots + A_2^2 k_2 + 2 B_2 k_2^2.$$

Also $[u'^2] = k_1$ (by the conservation of energy). Therefore

$$k_1 = A_1^2 k_1 + 2 B_1^2 k_1^2 + \ldots + A_2^2 k_2 + 2 B_2^2 k_2^2 + \ldots,$$

with a like equation for k_2.

Differentiating with respect to k_1 and k_2 separately, we find $A_1 = A_2 = 1$, and every other coefficient $= 0$. Thus u', and likewise v', is shown to be in effect a sum of numerous independently fluctuating, randomly selected constituents; and accordingly each of these velocities is distributed according to the normal law.

To generalize this reasoning: consider first a simplified example of two *correlated* co-ordinates. Imagine corpuscles each consisting of two links AB and BC, as in fig. 3; each

Fig. 3.
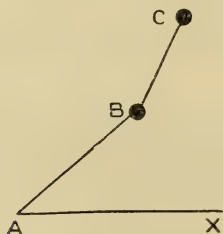
rod is of negligible mass, but there is a nucleus of mass m at the extremity of each, at B and at C. There are two degrees of freedom, the link BC turning about a joint at B,

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[*] *Cp.* Tait, cited above, p. 252. Clerk Maxwell's similar judgment (Phil. Mag. 1860) will surely not be questioned with respect to the *free* molecules here considered.

[†] For the proof of these propositions, see the proof of the *law of error* given by the present writer in Camb. Phil. Trans. *loc. cit.* Part I. § 1.

and the link AB turning about a fixed vertical pin at A ; the same pin for all the corpuscles, which move in horizontal planes that are indefinitely close to each other. Each nucleus repels any other within a minute circle of influence with a force depending on the *horizontal* distance only, according to some unknown law. Let the angles made by AB and BC with the horizontal be ϕ and ψ respectively. The present velocities of any molecule $\dot\phi'$ and $\dot\psi'$ are considered as each an undetermined function of previous ϕ's and ψ's ; the two velocities of any molecule among the progenitors being not now independent of each other. Identifying the mean energy of a molecule as deduced (by expansion of the functions) from that consideration with what it is as given by dynamical theory, we find by parity of reasoning that $\dot\phi'$, the present velocity of a molecule, is in effect the (weighted) sum of innumerable prior $\dot\phi$'s and $\dot\psi$'s, and likewise $\dot\psi'$, of $\dot\psi$'s and $\dot\phi$'s. Accordingly, the distribution of $\dot\phi'$ and $\dot\psi'$ is normal ; but as among the constituents, each pair, *e. g.*, $\dot\phi_r$ and $\dot\psi_r$ are now *correlated*, the exponent of the resulting error-function may be expected to involve the *product*, as well as the squares of velocities *.

As before, we may pass from the distribution of the " *universe* " to that of the *genus* †.

Parity of reasoning is applicable to molecular motion of the most general character, admitting movements of translation and other degrees of freedom.

II. The result is reached more readily by the *second* argument with regard to the *free* molecules moving (with any number of degrees of freedom) in the space outside the spheres of influence. We have now to determine the law of distribution *f*, so that $\Sigma f \log f$ should be a minimum, subject to the conditions that $\Sigma f = $ const., $\Sigma f \mathrm{T} = [\mathrm{T}]$, where Σ is used to denote integration with respect to all the *velocities* (or components of momentum), but *not* the co-ordinates. T is the quadratic expression in terms of the velocities (or components of momentum) for any assigned values of the co-ordinates, say

$$= \mathrm{A}_{11}\dot{\mathrm{Q}}_1{}^2 + 2\mathrm{A}_{12}\dot{\mathrm{Q}}_1\dot{\mathrm{Q}}_2 + \mathrm{A}_{22}\dot{\mathrm{Q}}_2{}^2 + \ldots + a_{11}\dot{q}_1{}^2 + 2a_{12}\dot{q}_1\dot{q}_2\ldots,$$

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* As to the formation of correlated compounds from correlated elements, and other propositions implied in this paragraph, see Camb. Phil. Trans. *loc. cit.* p. 116 *et seq.*

Cp. above, p. 263.

where the A's are, in general, functions of the co-ordinates Q_1, $Q_2 \ldots$; and the a's are likewise functions of the q's. Whence at once there is obtained for the f form J exp $- h$T. As before, we may pass from this expression for the law of distribution of the *genus* to that of the *universe* *.

III. The third argument in the simple form so far adopted is not applicable to cases in which the *co-ordinates* are changed by an encounter. Recourse must be had to that theorem of Liouville which leading writers have called in at an earlier stage.

E. It would be possible to advance further in other directions—in particular, where a field of force occurs—on the lines of the first and second arguments, without the aid of Hamiltonian Dynamics, by mere Probabilities.

XXX. *On the Permeability of Thin Fabrics and Films to Hydrogen and Helium.* By Prof. J. C. McLennan, F.R.S., and W. W. Shaver, B.A., *University of Toronto* †.

I. *Introduction.*

IN a recent paper by R. T. Elworthy‡ and V. F. Murray the diffusion of hydrogen and helium through thin rubber fabrics was discussed, and the results of measurements made by them on several samples of balloon fabrics were given. In these experiments the amount of gas diffusing through the fabrics was measured by a Shakespear Katharometer and by a Jamin Interferometer. As the method was one capable of wide application it was decided to use it in determining the permeability of liquid films to various gases, and the following paper describes some experiments made upon the passage of hydrogen and helium through soap films. The study of gas transfusion through membranous tissues is an important physiological problem, and it was thought on this account that it would be useful and might prove interesting to measure the rate of gas diffusion through films of various materials, with a view to formulating a more exact theory of the process of gas transfusion than exists at present.

II. *Preliminary Experiments.*

In order to test the apparatus and to acquire a working familiarity with the instruments, a preliminary study of the diffusion of hydrogen through the fabrics used by Elworthy and Murray was made. The apparatus used and the method of assembling it was the same as described in their paper. The fabrics used by them were inserted as a separating diaphragm in an air-tight drum-like vessel. Two gases were brought into this drum, one on either side of the fabric, and their transfusion was determined by tests on the gases by means of the instruments mentioned above. For a full description of the Shakespear apparatus the reader is referred to the paper by Elworthy and Murray. It will suffice here to say that this apparatus was made by the Cambridge Scientific Instrument Co., and that its principle is based on the variation in resistance of a heated platinum coil, constituting one branch of a Wheatstone Bridge circuit, when the gas mixture surrounding the cell has its thermal conductivity varied by changes in its component parts. The two methods adopted were (1) to pass a continuous stream of pure air and one of pure hydrogen on opposite sides of the fabric as a dividing diaphragm, and (2) to enclose a known quantity of pure air on one side and to pass a continuous stream of pure hydrogen past the other side of the fabric.

In the present experiments both methods were followed, but gas tests were made with the katharometer only. It was found that 20° C. was a more suitable temperature for working at than 15°·5 C. as previously used by Elworthy and Murray. The measurements obtained were made by keeping the permeameter and connexions in a thermostat at 20°·0 C., the variation in temperature being not more than 0°·2 C.

III. *Calibration.*

The katharometer used to detect small percentages of hydrogen or of helium in air had already been calibrated for both gases; but this calibration was checked by noting the galvanometer deflexions for a given sample of gas, deducing the percentage of helium or hydrogen present from the calibration curve and then checking the result by actually weighing a known volume of the sample studied. It was found that the values obtained by the latter method fitted in very closely with the calibration curve of Elworthy and Murray. It may be stated here that in their work it had

been well established that the curve obtained by plotting galvanometer deflexions against percentages of hydrogen or helium present in air was a straight line through the origin. The calibration showed that (1) 259 mm. deflexion on the scale 1 metre from the galvanometer represented 1 per cent. hydrogen in air, and (2) 163 mm. deflexion on the scale 1 metre from the galvanometer represented 1 per cent. of helium in air.

The following table gives a comparison of the results obtained in the present experiments with those obtained by Elworthy and Murray when using the same fabrics. In each case the permeability is given as being the number of litres of gas permeating 1 square metre of a fabric in 24 hours :—

TABLE I.

Fabric No.	Results obtained in this investigation. Temp. 20° C.		Results obtained by Elworthy and Murray. Temp. 15°·5 C.	
	Method I. Using Katharometer.	Method II. Using Katharometer.	Method I. Using Interferometer.	Method II. Using Katharometer.
*II. B	9·6	9·8	8·4	9·5
III. A ...	8·4	8·0	0	8·6
IV.	5·0	...	5·5	4·7
V. B	6·3	...	6·7	6·4
VI. A ...	8·0	...	...	8·1
VI. C......	7·8	7·5	...	8·1
XII.	5·4	...	...	...

IV. *Permeability of Films.*

After the preliminary experiments had been made, an attempt was made to employ the same method in making a determination of the transfusion of hydrogen and of helium through a soap film. Sir James Dewar † in a paper presented at a meeting of the Royal Institution of Great Britain in Jan. 1917, described many interesting experiments with long-lived soap bubbles and films, among them being a determination of what he calls " gas transference " through

* The fabric numbers refer to samples of balloon fabrics described in the papers by Elworthy and Murray.
† Dewar, Paper, "Soap Bubbles of Long Duration," presented at weekly meeting of the Royal Institution of Great Britain, Jan. 19, 1917.

a soap bubble, by blowing a hydrogen bubble in hydrogen and noting the decrease in diameter as time went on, due to the slight excess pressure inside the bubble. What he measured was the excess of the rate of gas diffusion outward over the rate inward through the film, and he found that as the soap bubble became thinner the gas transference became greater. In the present experiment the endeavour was to determine the actual rate of gas flow per square centimetre through the film, keeping the film as nearly constant in composition and thickness as possible.

V. *Description of Apparatus.*

A small cylindrical brass chamber (see fig. 1) was made for the film in two sections with a ground brass joint, which, when covered with soft wax and pressed together, made the vessel air-tight. Each section was 4·1 cm. in diameter and 7·0 cm. in height, having inlet and outlet tubes as shown in the diagram. The top section A, fig. 1, was closed by a window of plate glass, G, put on with hard wax, so that when a source of light was held directly over the chamber, its image in the film could be distinctly seen and in this way the character of the surface of the film—whether concave, convex, or plane—was known at once by the character of the image produced. Knowing the curvature of the film one could adjust the pressures of hydrogen and air on either side very accurately and so as to keep the film plane and therefore eliminate the diffusion due to excess pressure on either side. The brass ring C, fig. 1, supporting the film was 4·95 cm. in diameter, and ground down to a sharp edge. An annular channel, D, was made in the outer part of the supporting ring, and the whole soldered in the lower section of the film chamber, leaving about 0·6 cm. of the brass ring projecting above the wax surface. In this way the soft wax used in making the joint air-tight was prevented from contaminating the film and destroying its surface tension.

To overcome the difficulty of evaporation and drainage from the film, that is to keep its composition and thickness constant, the air and hydrogen used were both saturated with water vapour before entering the chamber, and, in addition, a means of adding solution to the film was provided in the following way. A bent tube, T, was inserted in the upper chamber as indicated in the diagram, having a thistle tube connected to the outer end by rubber tubing. A small amount of the same soap solution used in making the film was poured into the thistle tube and a drop of this was

allowed to fall on the film at short intervals (say, every two or three minutes), the flow being regulated by a clamp on the rubber tubing. The excess solution drained off the edges

Fig. 1.
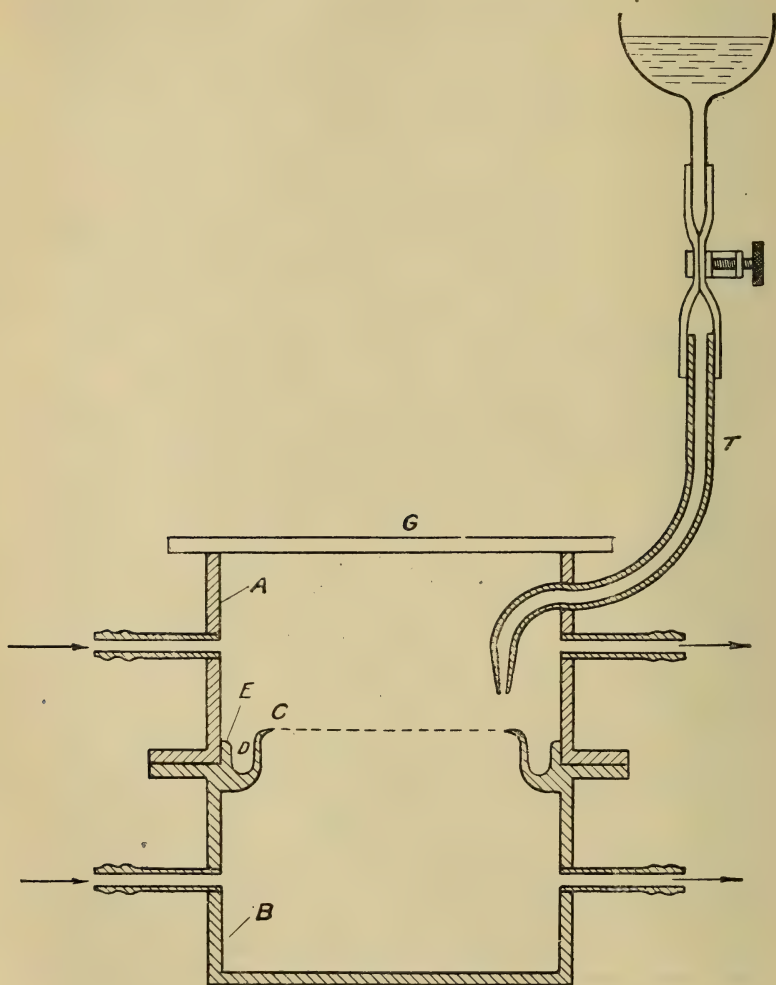
of the film into the lower section of the chamber. In this way the film was kept at a practically constant maximum thickness and the variations in diffusion due to changes in the film were eliminated as far as possible.

VI. *Air Circuit.*

The air was let in through a T-tube A (see fig. 2), which permitted the rate of flow to be varied by raising or lowering the water level. With any given level the pressure was adjusted so that the air always gently bubbled through the base of the T-tube. In its course through the system the air passed through a copper warming coil B and two tubes filled with cotton wool moistened with glycerine so as to eliminate all dust particles, as it was found that the introduction of dust particles soon caused the soap films to rupture. It was then bubbled through water and led through a gas-meter which measured the rate of flow. From the gas-meter the air, saturated with water vapour, was led through the lower section of the film chamber, D, sweeping out with it the hydrogen gas which diffused through the film. From there the air was dried in the phosphorus pentoxide tubes E and E′, and tested by the katharometer K, finally bubbling out through the water in H at a pressure of about 1 cm. of water.

VII. *Gas Circuit.*

The gas circuit shown in fig. 2 was somewhat similar, except that the gas was tested before entering the film chamber by a purity meter P, of the katharometer type,

Fig. 2.
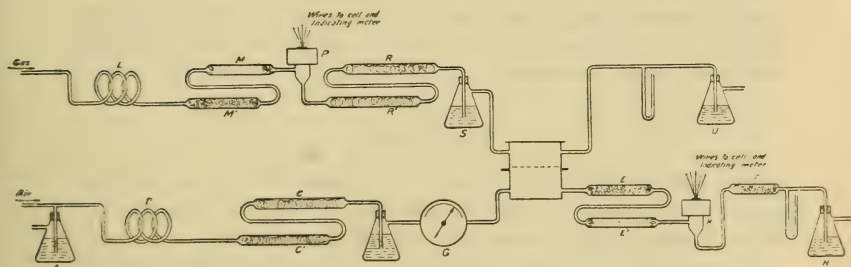
and then passed through the cotton wool tubes R and R′, bubbled through water in the bottle S, and thence to the film chamber, and, finally, bubbled out through water in U, at a pressure of about 1 cm. of water. The pressure of the gas in the circuit was altered very slightly by adjusting the tube U, so that the film surface remained plane. The rate of flow used was about 2 litres per hour.

VIII. *General Procedure.*

When readings were taken the air and the gas under test were allowed to flow past the film until the katharometer reading giving the percentage of gas in the air was steady. This required one half hour, and then readings were taken at two minute intervals for forty minutes, and note was taken of the rate of flow of air by means of the gas meter.   This ranged from 2 to 10 litres per hour.   After one set of readings was taken, if the film still remained intact, the rate of air flow was changed, and after conditions became steady again another set of results was obtained.   In this way as many as four sets of readings were taken without renewing the film.

IX. *Purity of Gases.*

The purity of the gases under test was in both cases comparatively high.   The hydrogen was obtained from a commercial supply which was guaranteed to be of 99 per cent. purity.   The helium used was first purified by passing it through a set of four charcoal tubes at the temperature of liquid air.   Its purity was tested by means of a quartz density balance, and found to be 99·2 per cent.

X. *Soap Solution.*

The soap solution used was one made up according to Boys' formula, and contained 2 per cent. sodium oleate, 24 per cent. glycerine, and 74 per cent. water, with a few drops of strong ammonia.

XI. *Results.*

The following are the results obtained.   The last column gives the number of cubic centimetres of gas transfusing through one square centimetre of film per hour.

The readings were taken at room temperature which varied slightly as shown in the table.   However, taking the average values obtained for the two gases, we find the ratio of the transfusion of helium to that of hydrogen to be 0·70.   In the case of balloon fabrics, Elworthy and Murray found this ratio to be 0·67.   Expressing the average results for hydrogen and helium in the case of a soap film in the same terms as the permeability of balloon fabrics, we find the permeability of films to these gases given by Elworthy and Murray for

TABLE II.

(a) *Hydrogen.*

Duration of film.	Temp.	Transfusion of gas in c.c. per sq. cm. of film per hour.
H. min.	°C.	
1 52	18·6	4·8
1 35	20·0	5·2
0 59	20·1	4·2
1 45	19·6	4·3
1 20	20·8	3·5
1 10	19·7	4·1
1 07	19·1	3·8
4 40	19·2	3·1
	19·1	3·1
	19·2	3·8
	19·1	3·6
	Average	4·0

(b) *Helium.*

3 41	18·4	3·0
	18·3	2·4
	18·0	3·1
5 15	19·5	2·2
	19·3	2·8
	18·7	2·8
	18·7	3·1
	Average	2·8

hydrogen to be 960 and for helium 670 litres per square metre per day. For the most highly porous balloon fabrics tested by Elworthy and Murray the transfusion of hydrogen was only about 10·0 litres per square metre per day, and of helium 7·1 litres per square metre per day. It is interesting to note that while soap films were very much more permeable to hydrogen and helium than were the balloon fabrics tested, the ratios of the permeabilities of both fabrics and films to the two gases were practically the same. This is the more interesting when it is considered that while in the case of the films the membrane was of the continuous type, in the case of the fabric there was a possibility of the diaphragm being discontinuous. It may be, however, that on account of the fabrics being " doped " the discontinuity referred to was negligible. In this case the process of transfusion of the gases through the substance of the fabric would probably be of the same nature as that of transfusion through the films.

XII. *Diffusion of Hydrogen through Wet and Dry Cotton Fabrics.*

Some experiments were made on the transfusion of hydrogen through a closely woven cotton fabric when wet and also when dry.   When this fabric was dry the gas diffused through it so rapidly that it was impossible to obtain a measure of the rate of transfusion with the katharometer. On the other hand, when the fabric was thoroughly wetted with distilled water it was found that the transfusion of hydrogen through it was so slow that it could not be detected with the katharometer, even when the rate of flow of the air past the fabric was reduced to as low a value as 2·4 litres per hour.

It was noted in the experiments on the transfusion of hydrogen through soap films that as soon as the film became thinner than the red-green stage the rate of diffusion rapidly increased.   It is evident, therefore, that the rate of diffusion depends very largely on the thickness of the films used.   In the case of the wet cotton fabrics the thickness of the water films filling up the interstices was very much greater than that of the soap films investigated.

XIII. *Summary of Results.*

1. The rate of diffusion of hydrogen through a series of balloon fabrics has been determined.

2. The permeability of soap films whose thickness corresponds to the red-green stage has been found for helium to be 670 litres per square metre per day and for hydrogen 960 litres per square metre per day at 20° C.

3. The rate of transfusion of helium through soap films has been shown to be 0·70 of that of hydrogen through similar films.

4. The diffusion of hydrogen through water films filling the interstices of a wet cotton fabric has been shown to be very low; with soap films showing interference colours the rate of diffusion of both hydrogen and helium was found to be considerable.

The Physical Laboratory,
    University of Toronto.
        May 15th, 1920.

XXXI. *On the Electrical Conductivity of Copper fused with Mica. By* Sub-Lieut. A. L. WILLIAMS, *R.N., with Introduction by* Prof. J. C. McLENNAN, *F.R.S.*[*]

[Plates V.–VII.]

INTRODUCTION.

WHILE acting as Scientific Adviser to the Admiralty, I had my attention drawn by Sub-Lieut. A. L. Williams, R.N., to some experiments made by him in the early part of 1919 at Cambridge, in which he found that samples of copper when fused with mica exhibited a remarkably large fall in resistance when gradually subjected to rising temperatures.

During a short furlough he was given an opportunity at the Admiralty Physical Laboratory, South Kensington, to develop this discovery and, on going back to duty, he left with me some notes embodying the results of his work. I have not had an opportunity of communicating with him again, but as the results are interesting it is thought they should be duly recorded. His experiments are described below, and accompanying them are some additional notes of results obtained at the University of Toronto by Miss Isabel Mackey and Miss I. Giles, who have followed up the subject still further.   J. C. McL.

A.

EXPERIMENTS BY SUB-LIEUT. A. L. WILLIAMS, R.N.

I. *Preparation.*

The samples for test were all prepared in the open on a piece of iron or copper plate—used as an anode—and a carbon rod as the cathode, the arc being struck at first between the plate and carbon, and then, when hot, to the mixture. The mica was first melted, then the copper added. In making up the samples studied, about equal proportions of copper and mica were used.

II. *Effect of Temperature.*

Resistance temperature measurements for two samples were made for a range of temperatures from 27° to 850° C. For sample A, the curves of which are attached, Graphs 1 and 2 (Pl. V.), the resistance fell from 16,000 ohms at 27° C., to 0·5 ohm at 850° C.

* Communicated by Prof. J. C. McLennan.

III. *Notes.*

(1) It was noted that the material was malleable at about 2000° C.

(2) A specimen piece was rolled at this temperature into a small rod 2·5 mm. in diameter for the purpose of ascertaining the specific resistance of the mixture. This was found to be as follows :—

> 25° C., Specific Resistance, 10,400 ohms.
> 30° C.,   „   „   8,000 ohms.

(3) An attempt was made to obtain a sample of the mixture in the form of a very thin film for delicate temperature measurements, etc., and it was found possible to squeeze it out to about 1/1000 of an inch between platinum foil. It was not possible, however, to separate the film from the foil; but two pieces of foil cemented together by this fine film were found to be extremely sensitive to heat. They quickly responded to the action of infra-red rays from an arc about one yard away, notwithstanding the comparatively large volume of platinum to be heated first.

It is thought that with suitable films of the copper-mica mixtures enclosed in hydrogen it may be possible to use them for signalling purposes. It is also suggested that these films may be used instead of wires in microphones for sound-ranging, as the changes of resistance, due to changes of temperature, are quite considerable, being some thousands of ohms per degree centigrade with some samples.

(4) Attempts were made to make thin sheets by mixing the copper-mica material, finely powdered, with fine carbon, in the form of cane-sugar, and driving off the water by heating. The resistance of the resulting material was extremely high, but very regular thin sheets could be obtained in this way. It is possible, when the density of this mixture is increased by compression in an hydraulic press, that it may be obtained in sheets, rods, or other forms having a moderate resistance and yet possessing a high resistance-temperature coefficient.

5. Attempts to cast the material in various forms were not successful, partly owing to the difficulty in working with the requisite high temperatures. The material, when molten, is absorbed by such porous substances as porcelain, and if glazed porcelain is used the glazing melts and mixes with the material. It is possible that castings could be obtained by using fused quartz as a moulding material.

6. Attempts were made to make up similar compounds with the following metals and mica:—

Tin. The metal vaporized at too low a temperature.
Silver. Did not combine.
Platinum. Did not combine.
Iron. Combined, but no resistance temperature measurements were made.

B.

Experiments by Miss Mackey.

I. *Experimental Arrangements.*

(*a*) The samples to be tested were all made in the open on a piece of iron plate used as an anode and a carbon rod as a cathode. The current was controlled by a large rheostat giving up to 30 amperes on the 110 D.C. circuit. An arc was struck between the plate and carbon and, when hot, the mica was melted and the other material added.

(*b*) A quartz tube closed at one end and covered with nichrome wire was used as a receptacle in which to melt the material and form it into a regular cylindrical shape for experimental work.

(*c*) A small electrical furnace was used to heat the material. It consisted of a circular porcelain foundation covered with wire and all was covered with asbestos except the two binding posts.

II. *Results.*

(a) *Mica and Copper.*—Mica and copper were fused on the iron plate into small lumps, and some of these were then finely ground into powder. No traces of mica or copper could be detected, only a uniform dull black powder. The powder was put into a quartz tube and heated, but this did not prove a satisfactory method of obtaining the mixture in the form of solid rods, as part of the mixture fused with the quartz, and it was found impossible to separate the two substances. When the quartz was broken, the copper-mica was found to be very brittle and not at all suitable for resistance measurements. Platinum wires were then fused into the ends of the copper-mica lumps which had not been powdered, and the variations in the resistances of these lumps were observed when they were raised to various temperatures.

Two different samples of copper and mica were tested in the furnace for variation in resistance with temperature (but only up to about 400° C.). In Case No. 1 (Graph No. 3), the resistance was found to vary from 4400 ohms to 300 ohms, while the temperature varied from 25° C. to 400° C. The specific gravity of the specimen was found to be 5·1, and as copper is given by 8·9, it will be seen that the specimen contained considerable mica.

Graph No. 3.

Temperature, ° C.	Resistance (Ohms).	Temperature, ° C.	Resistance (Ohms).
22	4,400	148	1,250
46	3,600	154	1,150
54	3,200	164	1,100
58·5	2,940	206	780
61	2,900	260	611
65·5	2,800	275	450
70	2,460	315	400
72	2,400	344	340
93	1,950	364	281
127	1,550		

In Case No. 2 (Graph No. 4) the variation in resistance was from 95,000 ohms to 3000 ohms, while the temperature changed from 100° C. to 400° C. The specific gravity was found to be 4·3.

Graph No. 4.

Temperature, ° C.	Resistance (Ohms).	Temperature, ° C.	Resistance (Ohms).
139	45,550	228	11,370
178	23,330	211	13,585
236	11,645	208	14,570
262	9,120	200	16,738
314	6,000	192	19,090
345	4,590	172	23,445
364	3,790	165	26,230
378	3,605	155	29,670
395	3,280	147	34,050
333	4,200	139	40,505
323	4,740	130	44,350
313	5,490	122	51,340
290	6,330	118	57,110
278	7,030	113	64,070
267	7,790	108	74,033
256	8,610	103	81,740
245	9,410	99	91,010
232	10,790		

From these results it would appear that an increase in the mica-content of the mixture raises the resistance at ordinary

temperature and causes the fall in resistance with temperature to be much more rapid.

While more brittle than copper, the copper-mica is not as brittle as iron-mica compounds described below. The hardness is almost the same as that of glass. X-ray photographs showed the composition to be quite homogeneous. The mixture was black with a dull metallic lustre.

(b) *Iron and Mica.*—Two mixtures were made as in the case of the copper and mica, and the temperatures and resistances were measured as before. In Case No. 1 (Graph No. 5) the resistance fell from 1300 ohms to 100 ohms on being heated from 25° C. to nearly 300° C.

Graph No. 5.

Temperature, ° C.	Resistance (Ohms).	Temperature, ° C.	Resistance (Ohms).
26	1,350	303	91
42	980	308	90
47·5	890	165	235
52·5	825	138	310
54	790	116	380
104	410	97	490
134	350	75	650
138	340	83	590
178	219	64	765
195	180	55	860
209	160	51	905
218	150	45	1,010
165	280	40	1,070
214	170	38	1,110
263	115	33·5	1,203
282	103	31	1,240
294	95		

In Case No. 2 (Graph No. 6) the resistance fell from 32,000 ohms on being heated from 160° C. to 380° C.

Graph No. 6.

Temperature, ° C.	Resistance (Ohms).	Temperature, ° C.	Resistance (Ohms).
250	6,100	294	3,380
228	9,050	282	3,900
280	3,870	255	5,970
318	2,410	242	7,350
335	1,980	231	8,440
344	1,780	222	10,380
360	1,550	214	11,720
377	1,280	204	15,750
360	1,550	197	15,900
336	1,980	187	19,550
322	2,360	175	25,210
309	2,730	164	32,100

The hardness was above that of glass, and the material was much more brittle than copper-mica and had more metallic lustre.   X-ray examinations showed the mixture to be homogeneous.   The specific gravity in Case No. 1 was 3·7, and in Case No. 2 was 4.   The specimens studied were quite irregular in shape, but from a rough examination of the sizes of the samples, it appeared that the sample which had the higher mica-content was the one which had the higher specific resistance.

(c) *Aluminium and Mica.* — No fusion was obtained between aluminium and mica.   The two seemed to remain entirely separate.

(d) *Antimony and Mica.*—The antimony when heated gave off dense clouds of vapour, leaving nothing to fuse with the mica.

(e) *Bismuth and Mica.*—The same results were obtained as with antimony.

(f) *Cobalt and Mica.*—Cobalt and mica were fused on the iron plate in the same manner as the copper and mica.   The cobalt-mica had a very dull black colour and was very brittle, but hard enough to scratch glass.   Platinum wires were fused in the ends with difficulty, and the resistance at ordinary temperatures was very great.   When heated red hot with a bunsen flame, a current of about ·020 ampere was obtained, using the 110 circuit.

(g) *Nickel and Mica.*—When nickel and mica were fused, the substance produced was very similar to cobalt-mica. When it was heated red hot, a current of about ·001 ampere was obtained, using the 110 circuit.

(h) *Manganese and Mica.*—Mica and manganese did not seem to mix at all.   In one test, the manganese was found to form a complete shell around the mica, and in other cases an X-ray photograph showed the two to be quite separate.

(i) *Silicon and Copper.*—It did not seem at all easy, if indeed possible, to fuse copper and silicon.   The two substances appeared to be quite separate after fusion.

(j) *Selenium and Copper.*—These fused quite readily and formed a dull black substance with very little or no lustre. The resistance was found at various temperatures and a graph, No. 8, drawn.   The specific gravity was 6·6, and the hardness less than that of glass.   With this mixture it will be seen that a discontinuity occurred in the resistance temperature measurements at about 150° C.   The explanation of this result does not appear evident at present.

GRAPH No. 8.

Temperature, °C.	Resistance (Ohms).	Temperature, °C.	Resistance (Ohms).
370	·219	124	·261
335	·207	115	·200
315	·200	108	·176
298	·188	104	·172
260	·173	101	·169
247	·164	98	·169
240	·164	95	·168
230	·162	92	·163
221	·157	90	·164
204	·152	87	·164
190	·147	84	·163
180	·139	80	·165
173	·136	78	·167
167	·136	65	·176
160	·135	61	·176
154	·130	59	·177
136	·333	58	·176
130	·317	44	·185
127	·300		

(k) *Ferro-Silicon.*—A sample of commercial ferro-silicon was also investigated. It was found to be very brittle and difficult to grind up into regular form for examination. In studying a sample, leading wires of iron were used, as platinum fused readily at the junction when the ferro-silicon was raised to a high temperature. When a graph was drawn between temperatures as abscissæ and resistance as ordinates, the result was a straight line showing that the resistance varied directly as the temperature, just as in the case of ordinary pure metals. (See Graph No. 7.)

GRAPH No. 7.

Temperature, °C.	Resistance (Ohms relative).	Temperature, °C.	Resistance (Ohms relative).
280	·092	148	·078
259	·089	139	·077
246	·088	126	·076
226	·085	118	·075
214	·084	109	·074
202	·083	96	·073
185	·082	84	·071
176	·081	79	·070
165	·079	71	·070

C.

EXPERIMENTS BY MISS GILES.

In these experiments a micrographic study was made of the plane polished surfaces of the fused copper-mica mixtures referred to above. These were made both when the mixtures

were at room temperatures and when their temperature was gradually raised by means of an electric furnace. The object in view was to see whether the fused mixtures possessed any crystalline structure, and if they did whether the increased conductivity observed with them on raising their temperature could be connected in any way with observable modifications in their crystal structure.

I. *Preparation of Specimens.*

In preparing these specimens they were first of all filed off to an approximately flat surface. The surfaces were then ground on a carborundum wheel, and after that on several successive grades of aloxite of increasing fineness. The grades used were those commercially known as Nos. 90, 150, 220, and 3F respectively. The polishing was then started with optical alundum and finished with jewellers' rouge. The two coarsest grades of aloxite were used on a flat metal plate, while the finer grades and the optical alundum were used on fine even linen fabric stretched over a smooth glass plate. The rouge was used on a piece of soft, smooth broadcloth stretched over a glass plate. The plates used were fastened on a horizontal revolving table rotated by a small electric motor. In some cases the surfaces were etched with nitric acid of various concentrations ranging from strengths of 10 per cent. to 25 per cent. and even to 50 per cent. Better results, however, were obtained by the use of ammonia in solution, with a specific gravity of about 0·93. With this solution the specimens were found to be uniformly etched by an attack of about one hour.

II. *Optical Equipment.*

The microscope used was one of the instruments especially designed by Bausch and Lomb for micrographic work. For normal illumination the type of illuminator used was the usual reflecting disk of thin cover glass. In this method the light was projected at right angles to the optical axis of the microscope, reflected from the cover glass along the optical axis of the system to the specimen, and then back through the microscope. For visual examination the source of light was a frosted electric light bulb, while for the photographic work a small carbon arc was used. The photographic plates used were rapid panchromatic, and the shorter wavelengths in the illuminating beam were cut out with a Wratten and Wainwright filter. Oblique, in place of normal illumination, was used in some cases.

III. *Results.*

When examined under the microscope different specimens were found to exhibit different appearances. Most samples appeared to be quite uniform in structure, while in some many little globules could be seen, which from their lustre appeared to be pure copper.

Specimens which possessed a high temperature coefficient were found both under high and low power magnification to show no change in structure, either by normal or oblique illumination, when heated to temperatures as high as 400° C.

Pl. VII. fig. 1 shows the appearance of a specimen at room temperatures with a magnification of 46. The resistance of this sample, which was 3200 ohms at 21° C., fell to 1600 when at 95° C. The structure of the specimen appeared very uniform, and no copper could be discerned in it judging by metallic lustre.

Pl. VII. fig. 2 shows the appearance of this specimen when etched with ammonia solution for an hour. As pure copper was found to require approximately about seven hours' exposure to ammonia to bring out its crystalline structure, the markings on the plate may be taken to indicate the boundaries between copper and mica or the constituents of the latter. The regularity of the markings would indicate that the copper and mica fused into an intimate and homogeneous mass.

A specimen, whose resistance at 100° C. was found to be 95,000 ohms and only 3000 ohms at 400° C., was polished and examined previous to etching it with ammonia, both with high-power and low-power magnification, and with oblique and direct illumination.

Pl. VII. fig. 3 shows its appearance when illuminated obliquely under a magnification of 46.

Pl. VII. figs. 4 & 5 show the same region when illuminated by normally reflected light under magnifications 46 and 205 respectively. The structure in this case, as will be seen, is quite different from that shown in Pl. VII. fig. 1.

With the sample illustrated by figs. 3, 4, and 5 there appeared to be a great many streaks of light and dark, bounded by straight lines running in all directions, while in other specimens there appeared to be nothing uniform in the shapes of the patches. The portions of the surface which are dark in Pl. VII. fig. 3 it will be seen are light in Pl.VII. fig. 4. In this specimen much detail was brought out with the low-power objective. It was therefore used among others with low magnification to study the effect of any increase in temperatures. A water-cell provided with

running water was placed between the specimen and the microscope objective, in order to cut off the heat from the objective, and the specimen was heated up to 400° C. No change could be discerned in the appearance of the etching.

Pl. VII. fig. 6 shows the appearance of a portion of the surface at a temperature of 350° C.

The specimen was then etched with the ammonia solution. Here, again, the surface was found to be marked by fine lines after an attack of about an hour, but no copper could be detected. It was heated again to 400° C. after etching, but no change in structure could be observed due to the rise in temperature.

IV. *Resistance-temperature coefficient of Glass.*

In studying these specimens one gained the impression that they possessed a number of the characteristics of glass. In most cases the specimens were very hard, and one could easily produce scratches on a glass plate with many of them. It is known, too, that many glasses when strongly heated become electrically conducting, and with a view of making a comparison between the behaviour of these specimens and that of a sample of glass, some measurements were made on the resistance of a rod of glass when its temperature was gradually raised.

In these experiments a rod of " Schmeltzglas " about 8·0 cm. long and 5·0 mm. in diameter was used. Short platinum wires were attached. These were then joined in circuit with the mains of the 110 volt d.c. circuit, and the glass portion was placed within an electric furnace. As the temperature rose observations were made on the current which passed and on the fall of potential between the ends of the glass rod, contact being made with the circuit at the platinum junctions.

In these observations practically no current was found to pass through the glass until a temperature of about 300° C. was reached. Even then the current was only of the order of 10^{-7} ampere, which showed that the resistance of the glass rod at this temperature was very high, practically about 10^9 ohms.

From this result it would appear that the high resistance temperature coefficient possessed by the fused copper-mica mixtures is something specific, and it does not appear that the remarkable property they exhibit finds a direct parallel in the behaviour of glass.

The Physical Laboratory,
        University of Toronto,
                May 15th, 1920.

XXXII. *On the Measurement of Changes in Resistance by a Valve Method. By* R. T. Beatty, *M.A., D.Sc., Lecturer in Physics, and* A. Gilmour, *M.Sc.,* 1851 *Exhibition Student, Queen's University, Belfast* [*].

WHEN a valve circuit is arranged, as in fig. 1, to generate oscillations, it is well known that on the insertion of a high resistance shunted by a condenser, in series with the grid, the oscillations will be broken up into equally spaced groups, and the groups thus formed will give rise to a note whose frequency will be equal to the number of interruptions per second.

If the frequency of the note be plotted against the grid resistance R (fig. 1) a curve is obtained showing decreasing frequency with increasing R, and when R is very large the sound in the telephone may only occur, perhaps, once per minute.

Fig. 1.
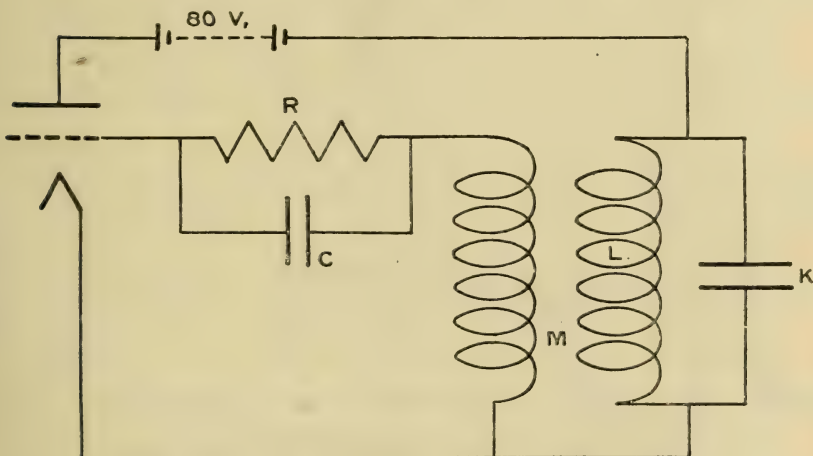
It is the purpose of this paper to show that such a curve only represents the final stages of a series of relations between R and the frequency f, and to exhibit these relations over a wide range of values of R.

Experimental Arrangements.

The experimental circuit used is shown in fig. 1. A receiving valve maintained oscillations in the main circuit LK. A variable liquid resistance R (copper sulphate solution in

glycerine) was placed in series with the grid and shunted by a condenser C. The mutual inductance was iron-cored. The oscillations were of audio frequency. When $K = C = R = 0$, $f = 420$ cycles.

In addition, a standard oscillation-circuit was set up which could be tuned to unison with the experimental circuit by varying the capacity of the main condenser. The standard circuit was carefully calibrated by means of tuning-forks and a curve drawn connecting capacity with frequency.

Results.

In fig. 2 the relation between f and R is shown for different values of the grid capacity C in the experimental circuit.

Fig. 2.
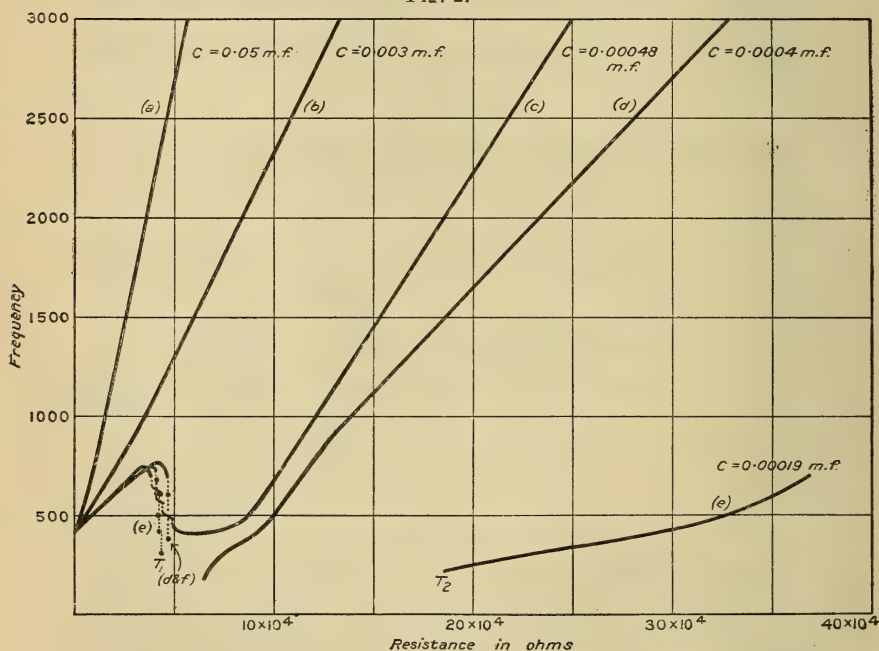
It will be seen that, as C decreases, the relation between f and R, at first approximately linear, becomes more involved. A hollow appears in the curve, and the frequency descends by a series of jumps to the bottom of this hollow, and rises again continuously as R is further increased. Curve (d) shows a separation into two parts with a silent region between them, extending from $R = 4 \cdot 8 \times 10^4 \omega$ to $R = 6 \cdot 7 \times 10^4 \omega$.

With further decrease in C the silent region spreads towards the right. Curve (*e*) shows a stage in its development. When C = 0 it extends from $R = 4 \cdot 8 \times 10^4 \omega$ to R = infinity.

At this stage it is evident that we have here a method of measuring resistance or changes in resistance. *Firstly,* using both circuits, we may insert the unknown resistance in R, and alter R and C till a suitable frequency is obtained in unison with the standard circuit. If, then, the unknown resistance be removed and R increased till the same frequency is again obtained, the required value can be found. *Secondly,* using the experimental circuit only, R may be varied till the sound in the telephone stops or starts— *i. e.*, till a border of a silent region is reached. These transition points are well defined, and precise measurements can be obtained. In fig. 2 (*e*), T_1 is the first transition point, T_2 the second, the region between them being silent.

The simplicity of the second method leads to inquiry into the possibility of displacing the transition points to positions suitable for dealing with resistances of any magnitude.

Fig. 3 shows the value of R required to reach a transition point when changes are made in K, C, or V*g* (potential applied

Fig. 3.
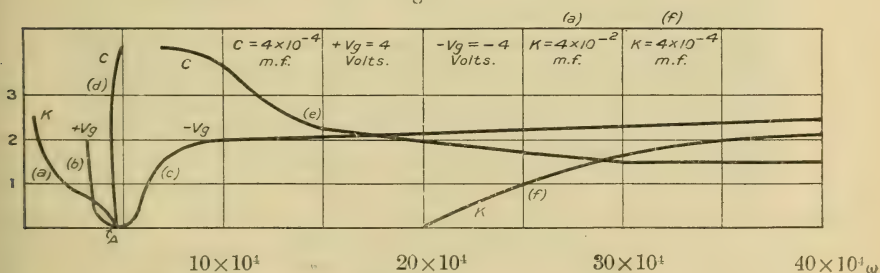
to grid). On passing, in the direction of increasing R, across any of the curves which meet at A, we pass from sound to silence. In the case of curves (*e*) and (*f*) we pass from silence to sound. In other words, the curves (*a*), (*b*), (*c*), (*d*) are loci of the first transition point T_1, while (*e*) and (*f*) refer to T_2. Each curve is labelled with the variable under consideration, the other variables being maintained at zero, except in the case of curve (*f*).

Movements of the first transition point T_1.

This point may be moved indefinitely to the left by increasing the main capacity K [curve (*a*)], or to the right

by inserting a battery in the grid circuit so as to keep the grid at a negative potential, $-Vg$, with regard to R [curve (c)]. Fig. 4 (h) also shows the effect of negative potential on the grid.

Fig. 4.
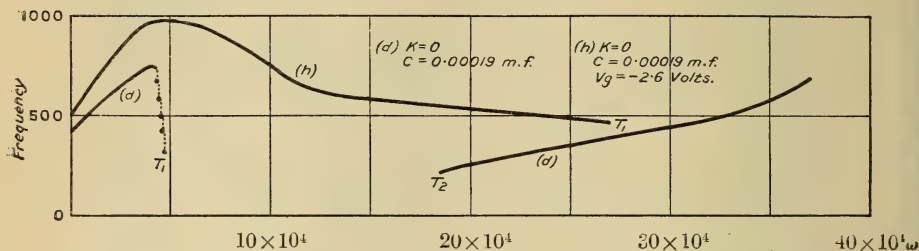
Increase in C has but little influence on T_1. As C increases, T_1 and T_2 approach each other and finally coincide. For values of C greater than this critical one no silent region exists [*cf.* fig. 2, curve (c)].

Measurement of the second transition point T_2.

When C=0, oscillations do not restart after the silent region is reached. As C increases, T_2 appears at a high value of R and travels to the left [fig. 3, curve (e)], finally coinciding with T_1 [curve (d)].

Thus a finite value of C is necessary for restarting. When, by using some value of C, T_2 is located anywhere on the diagram, it can be displaced by altering K or Vg. Fig. 3, curve (f), shows the effect of altering K, when $C=1.9 \times 10^{-4}$ m.f. [*cf.* fig. 5].

Fig. 5.
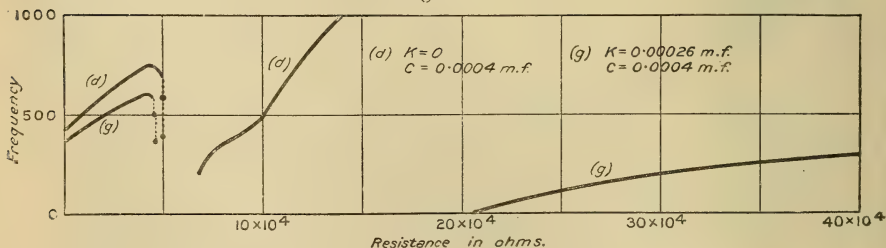
Examples of the application of the method.

(1) A selenium cell of the d'Albe pattern, of resistance 2×10^5 ohms, was used as the grid resistance. With $C=1.8 \times 10^{-4}$ m. f. the circuit functioned at the transition point T_2, and the light from a candle twenty feet distant was sufficient to cause a note in the previously silent telephone.

(2) With the same cell, and a potential of $-2\cdot3$ volts applied to the grid, the circuit functioned at the transition point T_1, where a change of resistance causes discontinuous changes in the frequency. By tuning the standard circuit to unison, a marked change in the number of beats per second caused by the two telephone notes could be produced by a candle at sixty feet.

(3) Similar results were obtained with a " Thalofide " cell.

Continuous change in frequency caused by change in resistance.

A convenient method of expressing the sensitiveness to change in resistance is to define the sensitiveness as $\partial f \div \dfrac{\partial R}{R}$ or $R . \dfrac{\partial f}{\partial R}$. Thus, along the continuous portions of the curves in fig. 2, for a given R the greatest sensitiveness occurs on the curve of the greatest slope; while along any straight part of a curve the sensitiveness increases with the resistance.

Increase in C causes the curves to slope more steeply. In fig. 2, curve (a), $\dfrac{\partial f}{\partial R} = \dfrac{1}{20}$. Hence, for a resistance of $5 \times 10^4 \omega$, the sensitiveness $= \dfrac{5 \times 10^4}{20} = 2500$—*i. e.*, if the two circuits be tuned to unison, one beat per second will be produced when the resistance changes by one part in 2500. Curve (a) has not been worked out beyond $f = 3000$, but the note continues to rise as R increases, and if the curve remains a straight line, a sensitiveness of 10,000 should be obtained with the selenium cell of resistance $2 \times 10^4 \omega$.

Comparison of capacities.

From fig. 3, curves (a), (e), (f), it is evident that an unknown capacity can readily be determined in terms of a known one by obtaining a transition point. The method is as applicable to condensers of a few cms. capacity as to those of the order of 1 m.f.

Further investigations.

A number of interesting phenomena take place in the neighbourhood of the transition points—such as, for example, the discontinuities in frequency which occur near T_1. These phenomena are under investigation, and a theoretical discussion of the results is reserved till further experimental results have been obtained.

XXXIII. *On the Character of the Light Radiations emitted by the Vapours of Magnesium, Copper, and Manganese under the Selective Actions of Thermo-chemical and Thermoelectrical Excitations.* *By* G. A. HEMSALECH*.

[Plates VIII. & IX.]

§ 1. *Introduction.*

THE flow of a heavy current of electricity through a plate of graphite is accompanied at high temperatures by the appearance of the red fringe. This phenomenon is caused by part of the heating current passing outside the plate as thermelectronic current through the strongly ionized vapours in the protected space. The spectroscopic effect produced by the thermelectronic current is quite distinct from that caused by the action of the plate temperature upon the chemical compounds which form the luminous vapour †. In fact the difference between these two effects is as striking as that which has been noted between the spectra emitted by the explosion region and the outer mantle of the air-coal gas flame. For the special case of iron vapour the results of my experiments leave no room for doubt that the character of the spectrum emitted by the luminous vapour in the protected space is identical with that observed in the outer mantles of flames. With regard to the more complex spectrum observed in the explosion region of the air-coal gas flame, I have attributed its origin to the decomposition or breaking up of the iron compound, owing to the existence of a strong chemical affinity between the iron atom and nitrogen‡. In like manner I have ascribed the origin of the fringe emission to the electrolytic decomposition of metal compounds by the thermelectronic current. We should, therefore, in accordance with these views, expect to observe some similarity between the spectra caused by chemical excitation in the Bunsen cone and those emitted under thermo-electrical excitation in the fringe, since each of these processes is supposed to involve the breaking up of a compound molecule. Thus we should anticipate that the characteristic cone lines (class III.) of iron, cobalt, nickel, &c. will be sensitive to the thermelectronic current and form part of the fringe emission, whereas at the same time the flame lines (classes I. and II.) of these elements would be observed in the luminous vapour beneath the fringe.

* Communicated by the Author.
† Hemsalech, Phil. Mag. ser. 6, vol. xxxix. p. 241 (1920).
‡ Hemsalech, Phil. Mag. ser. 6, vol. xxxiv. p. 229 (1917).

In order to verify the results of these considerations experimentally, it is necessary to fill the protected space with the vapour of the metal to be examined. This was accomplished by means of a very simple method based upon the observed fact that the vapours of any substance placed on the upper surface of the incandescent graphite plate pass automatically into the protected space beneath. In this way it has been possible to examine the spectra of a great many substances and study the relative effects of thermo-chemical and thermo-electrical excitations upon their bands and lines. The results of this investigation have also completely confirmed my anticipations with regard to the similarity between the characteristic emissions caused respectively by chemical and thermo-electrical excitations.

The present paper deals briefly with the observations and experiments which have led to the establishment of the new method, and with the application of the latter to the spectra of magnesium, copper, and manganese.

§ 2. *Observation of fringe emission with an unprotected plate of graphite.*

The experiments described in an earlier paper were made with graphite plates protected from excessive loss of heat through radiation by means of a cover of carborundum powder. Under these conditions the temperature of the under surface was found to be from $200°$ to $300°$ C. higher than when the plate was unprotected. Further, the carborundum powder employed contained many impurities, notably Ca, Al, K, Na, Sr, Mn, Fe, &c., and the protected space beneath the plate became filled with a great variety of highly ionized vapours in addition to those expelled by the graphite. The presence of these vapours was, however, found to be of great advantage, because it provided the opportunity of comparing the spectra of these elements with those emitted by them in the tube-furnace. The carbon tubes employed in my furnace work contained as impurities nearly all the same elements as the carborundum powder, and this fact proved to be invaluable for establishing the identity of the character of the emissions given by these substances in the carbon tube-furnace and in the luminous vapour beneath an electrically heated plate of graphite. But for the detailed investigation of the spectrum of some definite metal or other substance, it is of course essential to reduce the disturbing influence of the presence of impurities to a minimum. For this reason it is preferable to dispense

with the carborundum altogether whenever possible ; the loss of heat entailed thereby is compensated for by increasing the intensity of the heating current—an operation which involves the raising of the value of the potential gradient along the plate. It has not been possible to prepare a new set of temperature determinations for the unprotected plate, but it will be perfectly permissible for the purpose of the present investigation to assume a reduction of about 250° C. at the highest temperatures as compared with the protected plate. The dimensions of the graphite plates used in these experiments and the method of mounting them were the same as those already given in a preceding paper. A fresh plate was used for every observation.

It will be remembered that with a heating current of about 205 amperes the under surface of the protected plate gave a temperature of about 2700° C., and in its vicinity was seen the carbon band λ 3883. Now, with a heating current of the same intensity passing through an unprotected plate no sign of this band is observed beneath the plate, but a trace of it is found in the immediate vicinity of the upper surface. When the intensity of the heating current is raised to about 250 amperes, the red fringe emission is well developed on both sides of the plate ; in fact, the upper fringe passes to a greater distance from the surface than the lower one. In like manner the lines and bands of the luminous vapour which originates from the impurities expelled by the graphite (principally Ca, Sr, Li, Na, Fe) pass to a greater distance above the plate than below. This is of course caused by the convexion currents which rise up from the plate and carry these vapours through a certain distance before their luminous vibrations have ceased. About half of the total amount of luminous vapour which appears above the plate emanates from the under surface, whence it passes first into the protected space and then upwards round the edges. This latter fact may possibly explain the greater extension of the upper fringe ; for these strongly ionized vapours coming direct from the protected space would by virtue of their upward drift enable the thermelectronic current to spread over a greater vertical distance near the edge of the plate. This explanation for the greater extension of the upper fringe emission receives support by the observation that, when appreciable amounts (as indicated by the degree of development of the spectrum) of iron vapour are expelled from the graphite, the fringe emission always passes to a greater distance from the plate, as though vapour of this metal possessed a relatively high degree of conductivity for the thermelectronic current. In this connexion it is well to

state that graphite plates vary considerably with regard to the nature and quantity of impurities contained. Thus it often happens that of two plates, although cut from the same stratum, one will be quite free from iron, whereas the other will show a highly developed spectrum of this element. It is therefore essential, when comparing photographs of fringe emissions as given by different plates, to choose only such records as spectroscopically contain similar amounts of impurities.

What complications may arise through the presence of certain impurities is further illustrated by the fact that in their absence the fringe emission is but slightly affected by external magnetic fields. Thus, in the case of graphite plates free from spectroscopic traces of iron, but containing small amounts of Ca, Sr, and Ba, a magnetic field of from 1500 to 2000 c.g.s. units is required in order to appreciably displace the fringe emission. Much greater displacements are obtained in the presence of large amounts of iron vapour, derived from boiling iron metal on the top of the plate. The results of these new observations help to explain the relatively great displacements which I obtained for the fringe emission with feeble magnetic fields. The considerable amount of luminous vapours driven out by the carborundum and passing through the protected space beneath the plate formed a highly conducting medium through which the thermelectronic current was able to diffuse. Further, the swarms of electrified particles resulting probably from the breaking up of a potassium compound, and the true nature of which had then not yet been recognized, were largely instrumental in bringing about the drawn-out appearance of the red fringe emission. The positively charged particles are especially affected by magnetic forces, and on being drawn away from the plate the space through which they pass becomes strongly ionized. On this view the great displacements of the fringe emission would be caused by the diffusion downwards of the thermelectronic current, which, helped by the external magnetic field, would tend to follow the track of the electrified particles.

As a result of this new development of the subject, the explanation which I have given respecting the sharp outline of the red fringe and its spectrum emission becomes untenable, except perhaps in the case when free electrified particles are present; for in view of the small effect which magnetic forces have upon the fringe emission when only small amounts of ionized vapour are present, such as in the case with the unprotected plate, it seems hardly possible that the relatively feeble magnetic field due to the heating

current could have any influence in shaping the outline of the fringe. I am at present unable to offer a satisfactory explanation for this peculiarity of the red fringe emission, but wish to call attention to the fact that most luminous phenomena which owe their origin to the flow of an electric current at atmospheric pressure present a sharp outline, which they retain even when acted upon by magnetic forces or, mechanically, by air-currents. Thus the initial discharge which marks the path of the condenser current in a capacity spark passing between metal poles is a sharply-defined luminous band stretching across the space between the electrodes [*]. (The more diffused aureole which envelops the initial discharge is formed by luminous vapour of the metal, or more probably its compounds with oxygen and nitrogen. This part of the phenomenon develops at a later stage than the initial discharge and does not convey the electric current.) Again, the pilot spark and the luminous arcs formed when the oscillations in a self-induction spark are separated by means of an air-blast are all sharply defined [†]. But even when a strong magnetic field is acting upon a high-tension discharge, the drawn-out luminous figure thus produced presents a very sharp contour line along its outer edge [‡]; and, as I shall show in a subsequent communication, the path figures described by electrified potassium particles under the influence of magnetic forces are all characterized by their well-defined outlines. Thus it would seem that the sharp borders of these phenomena cannot be caused by the magnetic fields set up by the electric current ; there must be some other force which tends to keep the individual constituents of a stream of electrons or ions confined within certain definite bounds. But whatever the true explanation may be, the sharply-defined boundary surface of the red fringe is quite in keeping with the characteristic features of a luminous phenomenon, the origin of which can be traced back to the flow of an electric current.

Plate VIII. represents the red end of the fringe spectrum as obtained with an unprotected plate of graphite containing an unusual amount of calcium as impurity. The actual vertical distance to which the fringe and the luminous vapour rise may be gauged by comparison with the edge of the plate, which is 0·95 mm. across. The bright individual band $\lambda\,626$ which rises high above the plate coincides with

* Schuster and Hemsalech, Philos. Trans. Royal Society, vol. 193, pp. 189–213 (1899).
† Hemsalech, *Comptes Rendus de l'Académie des Sciences*, t. 111 p. 1103 (1905).
‡ Hemsalech, *ibid*. t. 152. p. 1086 (1911).

a similar band given by calcium in the outer mantles of
flames; the emission of this band is controlled by the
temperature of the plate. The lower red fringe extends
only to a very short distance from the plate; but the upper
fringe, thanks to the upward rush of relatively great
quantities of calcium vapour, attains about four times that
distance. Particular attention should be directed to the
abrupt extinction of the upper fringe bands in spite of the
upward motion of the vapours. This, as has already been
explained, is of course quite in accordance with the electrical
origin of the fringe; for were the emission of these bands
solely controlled by the plate temperature, they would, like
the great flame band, rise higher and die out only gradually.

§ 3. *Circulation of the luminous vapour round the plate of graphite.*

It was suggested in § 4 of my preceding paper that the
bluish vapour observed beneath a plate of graphite covered
with carborundum powder is caused by the cooling of the
luminous vapour at the boundary surface of the protected
space. When no carborundum or other substance is placed
on the graphite plate the bluish vapour is not observed;
hence, in the former case the vapours which filled the pro-
tected space must have in some way passed from the upper
surface of the graphite plate into the space below. Numerous
experiments were made in order to account for this fact, and
the following observations seem to throw some light on the

Fig. 1.

Striated appearance of bluish vapour.
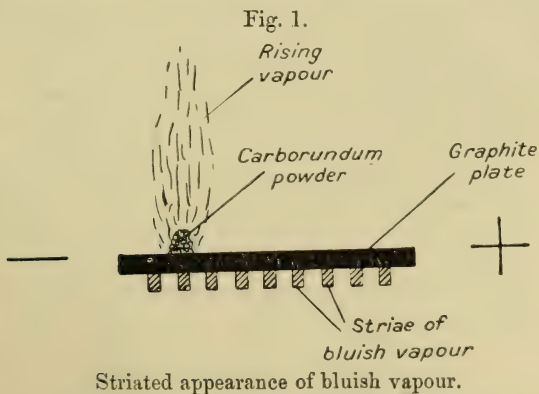
manner in which the displacement of the metal vapour is
accomplished. A small quantity of impure carborundum
powder was laid upon the negative end of the graphite plate
as shown in fig. 1. When the temperature of the latter was

raised to the necessary degree, there appeared in the place generally occupied by the continuous band of bluish vapour a long series of approximately equidistant bluish patches or striæ. No vapour was seen above the plate except that which rose vertically upwards from the small heap of carborundum. An upwards acting external magnetic field had apparently no effect upon the striation. When the small heap of carborundum was placed near the positive end of the plate the bluish striæ were observed only just beneath that end, and did not extend towards the opposite one. A contrary effect was observed with calcium carbide. A small quantity of this material placed upon the negative end produced only a short horizontal streak of bluish vapour beneath that end. When, however, a little calcium carbide was put near the positive end, flocculi of light grey vapour formed beneath, and appeared to move towards the negative end like a succession of closely-placed smoke puffs. When larger quantities of carborundum are placed upon the plate the individual striæ are merged into a continuous bluish band. Thus, when only a small heap of the substance is used the vapour proceeding from it follows a narrow track, the width of which is about equal to that of a stria. There can be little doubt that the bluish striæ are formed in a similar manner as the bluish vapour—namely, by the cooling of luminous vapour at the boundary surface of the protected space.

Further, the orderly arrangement of the striæ seems to indicate that the encounters with cool air as the luminous vapour moves towards the positive end of the graphite plate take place at regular intervals. This fact suggests that the particles concerned execute some uniform periodic motion, such as might result if the path of the luminous vapour proceeding from the small heap of carborundum formed a helix round the plate. A path of this kind could be conceived to be caused by the combined actions of the electric and the magnetic fields set up by the heating current. Let us consider the case of a negatively charged particle, such as might originate from the electrolytic decomposition of a compound molecule by the thermelectronic current in the upper fringe, moving along the top surface towards the positive end of the plate. In doing so the particle crosses lines of magnetic force, and is deviated in the direction of the magnetic south. Since the lines of magnetic force form closed oblongs round the plate, the particle in moving towards the south will tend to describe a similar figure ; but as it also moves under the action of the electric field in a

direction normal to the plane of this oblong, its path is not a closed one, but forms a flattened helix between the negative and positive ends of the graphite plate. If, instead of a single particle, there be an uninterrupted and abundant supply of them, such as would most likely be furnished by the thermelectronic current from the small heap of carborundum, the stream of particles would probably form a layer of appreciable depth; and their combined system of paths, each of which forms a helix, would wind itself round the graphite plate like a screw-thread. This path system would probably be confined to the region of the red fringe, for as soon as a particle has passed out of the latter, it will recombine to form a neutral molecule of luminous vapour. In those places where the helix passes near the border of the protected space or actually out of it, the electrified particles travelling along it will come into contact with relatively cool air and form a stria of bluish vapour. Evidently there will be as many striæ as there are turns in the helix. Hence, on this view, the ions as they move in the direction of the electric field are whirled round the plate of graphite by the magnetic field due to the heating current, and the bluish striæ represent those portions of a helical path which cross the boundary surface of the protected space.

§ 4. *Possible causes of the formation and downward drift of the luminous vapour in the protected space.*

It has been shown that the emission centres of the luminous vapour travel down to a considerable distance from the electrically heated plate of graphite, even when a strong magnetic force is acting upwards; in fact, they behave in this respect like neutral molecules. Their presence far down in the protected space cannot, therefore, be attributed solely to the action of the magnetic field established round the plate by the heating current. Without for the present attempting to find a definite solution of the problem, it may be useful, however, to call attention to one or two possible explanations. Thus the luminous vapour might originate from the recombination of metal and carbon atoms near the outer edges of the helical path, especially in those places where the force of affinity between the atoms is great enough to counteract the decomposing action of the thermelectronic current. If large quantities of ions pass through the fringe, it is conceivable that many of them will be pushed out of the fringe owing to overcrowding. Once out of the sphere of action of the thermelectronic current they will immediately reassociate to form neutral molecules, and their

downward drift would simply be caused mechanically by the continual expulsion of fresh ions from above. But against this explanation stands the fact that even with very small quantities of luminous vapours, such as are obtained with an unprotected plate of graphite, the emission centres still drift away from the plate downwards against strong magnetic forces. Since there can be no question in this case of a mechanical push due to overcrowding of the space, it seems to me that the only forces which can act upon the molecules of the luminous vapour are gravity and radiation pressure. In any theory concerning the downward drift of the emission centres in the protected space of a single plate resistance furnace the possible action of either of these two forces or of both will undoubtedly deserve serious consideration.

§ 5. *Practical application of the foregoing observations to the spectroscopic analysis of metal vapours.*

The fact that metal vapours originating from substances laid upon the top surface of the electrically heated plate of graphite pass automatically into the protected space beneath, at once provides a most convenient method of studying the spectroscopic or other properties which characterize these vapours at high temperatures. The experimental arrangements employed for this purpose may, on account of the *rôle* played by the graphite plate, be regarded as a *single plate resistance-furnace*, and will be referred to as such hereafter. Exhaustive trials have shown that practically any substance may be examined under these conditions by placing small quantities of it upon the plate, preferably in two places, one on either side of the slit image as indicated in fig. 2. The two portions of the substance should be not

Fig. 2.
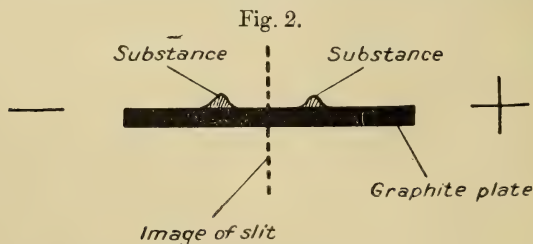
Method of observing spectrum of a substance with single plate resistance-furnace.

less than 10 mm. apart, in order to prevent the formation of a conducting deposit on the graphite surface between them.

If the substance be a metal which easily forms a carbide, such as Ca, Fe, Co, Ni, &c., and therefore adheres to the surface of the graphite plate, no covering with carborundum powder is required. In the case of a volatile metal, mineral, or rock, &c., it is often of advantage to first crush or in some other way subdivide the material, and place small quantities of it all over the plate, which is then covered with a $\frac{1}{8}$ in. thick layer of pure carborundum No. 80. But whenever possible the protecting layer should be dispensed with, as it always introduces lines and bands due to impurities contained in the carborundum. Such metals as copper and silver, which do not adhere to the graphite, may be prevented from rolling off the plate—they are of spheroidal shape in the molten state—by placing small pieces of graphite round them. Particular methods employed for the purpose of mounting and holding substances will be given in each case.

With the arrangement sketched in fig. 2 the spectrum of the vapours given off by the substance is of course observed both below and above the plate. But since the greater quantity of vapour is immediately carried upwards by convection, only a relatively small amount of it passes into the protected space. It is no doubt for this reason that the spectrum emission due to thermo-chemical excitation is brighter and passes to a much greater distance from the plate in the region above than in the protected space below. Also the emission due to thermo-electrical excitation, although in many cases appreciably feebler above the plate than below, passes to a greater height, probably owing to the upward rush round the edge of highly ionized vapours from below. For these reasons it is preferable to make all observations in the protected space beneath the plate, where, thanks to the more tranquil state of the vapours and the absence of convection currents, the two emissions are more sharply differentiated than above. Only doubtful cases with regard to lines caused by thermo-chemical excitation are for the sake of confirmation examined in the uprising vapour above the plate.

As usual an image of the incandescent plate and protected space below it is sharply focussed upon the slit of a spectrograph in such a way that the slit bisects the plate as marked in fig. 2. The resulting spectrum shows a continuous bright band caused by the edge of the incandescent graphite plate and, immediately below it, a sharply-defined region of short lines and bands which constitute the fringe emission (thermo-electrical excitation). Superposed

upon the latter, and passing much farther from the plate, is the spectrum caused by the action of heat upon chemical compounds of the elements contained in the substance under examination (thermo-chemical excitation).   The character of a light radiation can then be derived from the relative degree of its response to these two modes of excitation as indicated by the corresponding line intensities in the fringe and in the luminous vapour.

In order to facilitate the grouping of the lines according to character, the following three standard types based upon their relative appearance in fringe and luminous vapour have been adopted :—

First type. Long lines.   These constitute the so-called flame lines, which are emitted by the mantles of the various low- and high-temperature flames.   They are caused by the action of heat upon chemical compounds, and their intensities are controlled by the plate temperature. The thermelectronic current does not appear to affect these lines appreciably, and they generally pass far down from the under surface of the plate through the protected space, fading away gradually.

Second type. Tadpole lines.   These are specially sensitive to the thermelectronic current in the fringe and to a lesser degree also to thermo-chemical actions in the luminous vapour.   On account of this peculiarity these lines appear to consist of an intense head, to which is attached a long thin tail.   They are strongly emitted in the explosion region of the air-coal gas flame, but are either absent from, or appear only as mere traces in the hottest zone of this flame just above the cone.   They are generally brought out in the mantles of high-temperature flames.

Third type. Short lines.   The emission of these lines is almost entirely confined to the fringe ; only faint traces are in some cases observed under thermo-chemical excitation at very high temperatures.   They are, however, easily emitted under chemical excitation in the explosion region of the air-coal gas flame.

This classification naturally only serves as a guide in the establishment of the most probable character of a line, as in some cases it is difficult to decide into which category a line should be placed.   For this reason the relative intensity of each line has been recorded both for the fringe and the region just beneath it.

§ 6. *Magnesium.*

The substances examined were metallic magnesium, its chloride, sulphate, and oxide. In the case of the first three of these substances a protecting layer of pure carborundum No. 80 was employed. The oxide, on the other hand, was laid upon the plate as shown in fig. 2, without a covering. In order to prevent the lumps of oxide from moving when in the liquid state three small pieces of graphite were placed round each. The general character of the line spectrum is independent of the nature of the compound used, but on account of the high melting-point of the oxide and the fact that it can be used without a carborundum covering, this substance gives a brighter and better-developed spectrum than the more volatile materials. The relative intensities given in the following table are founded upon a photographic record obtained in this way with magnesium oxide.

	Single plate furnace.			Air-coal gas flame.		
λ.	Fringe (thermo-electrical excitation).	Luminous Vapour (thermo-chemical excitation at $2900°$ C.).	Type.	Cone (chemical excitation).	Mantle (thermo-chemical excitation at $1850°$ C.).	Capacity Spark (electrical excitation).
3829·35	6	000	tadpole	10	—	50
3832·30	8	00	,,	15	—	50
3838·29	10	0	,,	20	—	100
4571·10	$\frac{1}{2}$	$\frac{1}{3}$	long	5	5	3
5167·32	6	$\frac{1}{4}$	tadpole	7	—	12
5172·68	8	1	,,	8	—	15
5183·60	10	2	,,	10	—	20

The acting electric field in the vicinity of the plate was about $8 \frac{\text{volts}}{\text{cm.}}$ and the plate temperature, allowing for the absence of a carborundum cover, about $3000°$ C. The relative intensities under the heading "fringe" refer to that part of the vapour which radiates under the influence of the thermelectronic current, whereas those given under "luminous vapour" are controlled by the temperature prevailing just beneath the fringe, which has been assumed to be about $100°$ C. less than that of the plate. The scale of intensities is the same as that previously adopted [*]. Wavelengths are given in international units. In order to emphasize the significance of the results obtained with the single plate resistance-furnace the relative intensities of the

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[*] Hemsalech, Phil. Mag. vol. xxxiii. p. 9 (1917).

lines as observed by Dr. de Watteville in the cone and mantle of the air-coal gas flame *, and by me in the capacity spark †, have been added for comparison.

In addition to the line spectrum there also appeared certain bands, especially the one with head line at 5007·3. The bands are not affected in the fringe, but pass well down from the plate into the protected space and, like the flame line 4571, die out gradually.

The tabulated results bring to light a most important fact—namely, the triplet lines, which are strongly emitted under thermo-electrical excitation, are precisely those which are likewise strongly emitted under chemical excitation in the explosion region of the air-coal gas flame and under electrical excitation in a capacity spark. Again, the only line which from its character as a long line is evidently a temperature line is also the only one which is emitted by the mantle of the air-coal gas flame. In the capacity spark it is a relatively feeble line, and appears, if at all, to be but slightly affected by electric actions. The fact that the triplets at 3838 and 5184, although very intense in the cone of the air-coal gas flame, do not show in the mantle just above the cone is probably due to the temperature of this flame—namely 1850° C., being too low for their emission under thermo-chemical excitation. Even with the high temperature of the furnace they only come out as relatively faint lines below the fringe. There is no doubt that they will show in the oxy-acetylene flame, but no data are as yet available on this point. I have obtained them by simply burning a lump of magnesium metal in air, although in this case it is not quite certain whether and in how far the emission of these lines is controlled by the heat generated through combustion or by the chemical actions involved.

That the triplet lines of magnesium are particularly sensitive to electric actions will be further exemplified in a subsequent communication by the fact that with a two-plate furnace, in which a uniform electric field is established between two parallel plates, these lines always appear first at the cathode plate.

No trace of the spark line 4481, or of any line of the nebulous series, has been observed in the fringe or bluish vapour.

Pl. IX. *a* shows the ultra-violet triplet of magnesium in the fringe ; the long thin tails of these lines which represent those portions of the emission due to thermo-chemical

* De Watteville, 'Thèses de Doctorat,' Paris, p. 34 (1904).
† Hemsalech, 'Thèses de Doctorat, Paris, p. 92 (1901).

excitation, do not show in the reproduction on account of their great feebleness. It will, however, suffice to point out the sudden cessation of the electrically controlled emission at the lower border of the fringe, which, like that of the C bands and Ti lines, is in striking contrast to the more gradual fading away of the lines of Fe and Ca under the control of the plate temperature. As compared with the other two spectra *b* and *c* on Pl. IX., the fringe emission of magnesium extends to a relatively greater distance from the graphite plate. This is probably due to the presence of iron vapour, which, as already explained in § 2, seems to be a particularly good conductor of the thermelectronic current at high temperatures.

§ 7. *Copper.*

The metal as well as its oxide and chloride were employed both with and without a protecting layer of carborundum. The best results were, however, obtained with pieces of metallic copper on an unprotected plate of graphite. Since the metal boils already at about 2300° C. it became necessary, in order to prevent the boiling mass from being thrown off the plate, to adopt special precautions, and the following method was found to work satisfactorily. The pieces of metal, instead of being placed near the middle of the plate as sketched in fig. 2, were brought close up to the end faces of the clamping bars as shown in plan view, fig. 3. The

Fig. 3.
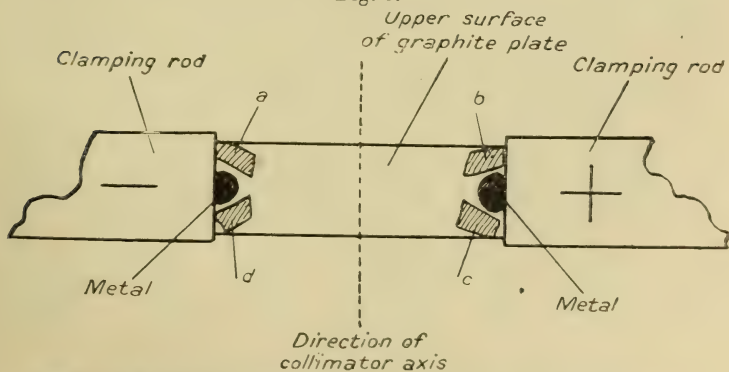
Method of obtaining spectrum of a metal having low boiling-point.

temperature here is considerably lower than near the middle of the plate, and the metal does not boil too violently. The lumps of copper were held in position by small pieces of

graphite a, b, c, d, care being taken to leave open a free passage towards the opposite end so as to enable the ionized vapours to creep along the surface of the plate under the impulse of the electric field due to the heating current. As before, the hottest part of the plate—namely, the middle, was focussed upon the collimator slit. Observations were made of the vapour on both sides of the plate.

The spectrum given by copper vapour under these conditions is composed of lines and bands; the latter are particularly well developed above the plate, and are probably due to oxidation of the metal, which is facilitated by the inrush of fresh air through convection. The band spectrum is practically identical with that observed for the same metal in the tube-furnace. With regard to the line spectrum the so-called flame lines are more intense above the plate than in the protected space beneath, but the electrically controlled lines have the same strength in the lower and upper red fringe, although in the latter they pass to a greater distance from the incandescent plate for reasons already explained in § 2.

The tabulated results refer to the emission of copper vapour in the protected space beneath the plate, and are founded upon a photographic record obtained in the manner described at a plate temperature of about 2900° C. The value of the acting electric field in the vicinity of the plate was $7 \cdot 5 \frac{\text{volts}}{\text{cms.}}$. The relative intensities of the copper lines in the air-coal gas flame, as observed by Dr. de Watteville *, and in the capacity spark as found by me † have been added for comparison.

λ.	Single plate furnace.			Air-coal gas flame.		Capacity Spark (electrical excitation).
	Fringe (thermo-electrical excitation).	Luminous Vapour (thermo-chemical excitation at 2800° C.).	Type.	Cone (chemical excitation).	Mantle (thermo-chemical excitation at 1850° C.).	
5105·58	6	6	long	10	10	8
5153·26	2	—	short	3	—	10
5218·20	3	—	short	5	—	15
5700·25	1	1	long	3	?	2
5782·16	3	3	long	10	10	5

Dr. de Watteville has also very kindly supplied me with copies of his original photographs of the flame spectrum of copper, which go to show that the two lines 5106 and 5782 are equally intense in cone and mantle. With regard to the

* De Watteville, *Thèses*, p. 31.
† Hemsalech, *Thèses*, p. 107.

line 5700, the presence of continuous ground and bands which in the mantle are stronger than in the cone has not permitted to decide whether or not this line is emitted by the mantle; for even if the intensity of this line in the mantle were the same as in the cone, it would hardly be possible to detect it for the reason just stated.

No other line of this element has been observed in the fringe or luminous vapour down to about λ 3800.

When comparing the results given by the single plate furnace with those obtained for the mantle of the air-coal gas flame, allowance must be made for the considerable difference in temperature between the two cases; for whereas the temperature of the mantle is only about 1850° C., that of the protected space near the fringe is probably in the neighbourhood of 2800° C. This great difference may well account for the fact that the visibility of the line 5700 in the protected space is not impeded by continuous ground to the same extent as in the air-coal gas flame. According to my results with the plate furnace, this line belongs most probably to type I., and I do not doubt that if a little oxygen were added to the air-coal gas mixture the intensity of the continuous ground would diminish and the line show up plainly. With regard to the remaining lines, the furnace results corroborate entirely Dr. de Watteville's observations respecting their character.

If now we compare the furnace results with those given by a capacity spark in which the emission of lines is predominantly caused by electrical excitation, the striking fact is brought out that the two lines which are most strongly emitted in the latter—namely 5153 and 5218—are precisely those which in the furnace are excited solely by the thermelectronic current. They are likewise emitted under chemical excitation in the cone, but are absent from the mantle; and the fact that no trace of them has been observed in the luminous vapour beneath the fringe goes to indicate that their emission is not stimulated by thermo-chemical excitation up to a high temperature. Thus, also in the case of copper, the spectroscopic effects produced by chemical excitation in the air-coal gas cone and by thermo-electrical excitation in the red fringe are the same.

Pl. IX. *b* represents the spectrum given by copper vapour in the protected space of the single plate furnace. Special attention is invited to the unmistakable contrast between the short lines in the fringe and the long lines in the luminous vapour, which fact so manifestly bears witness to the difference in origin between these two types of lines.

§ 8. *Manganese.*

Two pieces of the metal were laid upon the graphite plate as shown in fig. 2, and photographic observations made both with a protecting layer of pure carborundum and without. The tabulated results are based on an experiment made with an unprotected plate raised to a temperature of about 3000° C.; the acting electric field was about 8 $\frac{\text{volts}}{\text{cms.}}$. The relative intensities for the lines in the luminous vapour refer to the region situated just below the fringe, where the temperature will be slightly less than on the surface of the plate. No detailed results concerning the air-coal gas flame spectrum of this element are as yet available, but Dr. de Watteville very kindly placed at my disposal copies of his original photographs of this spectrum, from which I was able to derive the relative intensities of the manganese lines in cone and mantle. These results as well as the relative intensities in arc and spark for the lines of the same element according to Messrs. Exner and Haschek have been added for comparison.

	Single plate furnace.			Air-coal gas flame.			
λ.	Fringe (thermo-electrical excitation).	Luminous Vapour (thermo-chemical excitation at 2900° C.).	Type.	Cone (chemical excitation).	Mantle (thermo-chemical excitation at 1850° C.).	Arc.	Spark.
4018·09	2	1	tadpole	2	—	10	8
4030·80	10	10	long	10	10	100	20
4033·06	8	8	,,	10	10	100	20
4034·48	6	6	,,	8	8	50	10
4035·73	1	$\frac{1}{2}$	tadpole	?	?	6	8
4041·34	3	2	long?	4	—	20	10
4048·73	1	$\frac{3}{4}$	,, ?	2	—	8	7
4055·55	2	1	tadpole	3	—	4	8
4058·92	1	$\frac{1}{2}$	,,	2	—	4	6
4063·55	1	$\frac{1}{2}$	,,	1	—	5	6
4070·32	0	00	long?	0	—	4	3
4079· $\begin{cases} 20 \\ 43 \end{cases}$	2	1	tadpole	3	—	3	5
4082·92	1	0	,,	} 3	—	4	6
4083·62	1	0	,,		—	3	6
4235·31	2	000	,,	2	—	10	20
4257·65	00	—	short?	observation impeded		3	4
4265·92	0	—	,, ?	by bands		3	5
4754·05	4	$\frac{1}{2}$	tadpole	8	—		
4762·38	1	00	,,	2	—		
4766·41	$\frac{3}{4}$	000	,,	2	—		
4783·45	4	1	,,	8	—		
4823·52	4	1	,,	8	—		
5341·07	00	000	long	?	?		
5394·68	2	$1\frac{3}{4}$	,,	5	5		
5432·55	1	$\frac{3}{4}$	,,	4	4		

The following facts may be derived from these results :—
All lines which in the air-coal gas flame are equally strong
in cone and mantle, and therefore mark their character as
temperature lines, are of the " long " type in the furnace—
that is to say, their emission in the latter is, just as in the
flame, controlled by temperature. Again, all the lines of
the " tadpole " type which in the furnace are particularly
affected by thermo-electrical excitation are in the coal-gas
flame emitted solely by chemical excitation in the explosion
region. The three apparent exceptions—namely 4041,
4049, and 4070—which have been classed as long lines in
the furnace emission, are probably also of the tadpole type,
as may be expected from their relative intensities in fringe
and luminous vapour ; they are perhaps a little more
sensitive to temperature than most other lines of this type,
and would therefore occupy a position intermediate between
long lines and tadpole lines. Lastly, nearly all the tadpole
lines are enhanced in the spark as compared with the arc.
Special interest is attached to the line 4235, which is a
prominent spark line. Thermo-electrical excitation in the
fringe brings it out with intensity 2, whereas under almost
similar conditions of temperature just outside the fringe,
thermo-chemical excitation hardly stimulates its emission.
Naturally it is absent from the mantle of the air-coal gas
flame, but it is well brought out in the cone. Thus we find
also in the case of manganese a very close agreement
between the emission caused by chemical excitation in the
cone of the air-coal gas flame and that due to thermo-
electrical excitation in the red fringe of a single plate
furnace.

Pl. IX. *c* shows the enhancement in the red fringe of the
three blue lines of manganese.

§ 9. *Summary.*

1. With an electrically heated plate of graphite, which
is not covered with a layer of carborundum, the red fringe
appears on both sides. The upper fringe will often extend
to a greater distance from the plate than the lower one.
This is probably caused by the upward rush of conducting
vapours which are expelled from the under surface and pass
round the sides of the plate into the space above. §2.

2. In spite of the rapid upward motion of conducting
vapours above the plate, the border line of the upper fringe
is sharply defined and its spectrum emission stops abruptly
in marked contrast to that of the luminous vapour. §2.

3. In the absence of sufficient quantities of ionized vapours, strong magnetic fields of from 1500 to 2000 c.g.s. units must be applied in order to appreciably displace the red fringe emission. Consequently, the conclusion arrived at in § 8 of my preceding paper—namely, that the sharp outline presented by the red fringe and its spectrum emission are caused by the magnetic field due to the heating current—becomes untenable. Although no satisfactory alternative explanation of this peculiarity of the fringe is offered, it is pointed out that most luminous phenomena which owe their origin to the flow of an electric current at atmospheric pressure present a sharp outline.   § 2.

4. It is shown that the vapours which fill the protected space are in great part derived from substances placed upon the plate. The formation of striæ at the boundary surface of the protected space is interpreted as indicating that the vapours pass round the plate in a helical path. It is further suggested that such a path might be caused by the combined actions of the electric and magnetic fields set up respectively along and around the plate by the heating current.   § 3.

5. A short discussion concerning the probable cause of the downward drift of the luminous vapour in the protected space has led to the suggestion that it might be due either to gravity or radiation pressure, or possibly even to the combined action of both.   § 4.

6. A convenient method has been developed of readily ascertaining the relative sensitiveness of a spectrum line to thermo-chemical and thermo-electrical excitation. According to this method the character of a line is revealed by its relative intensity in fringe and luminous vapour. For the purpose of facilitating the grouping of lines having similar character three distinct types, based on their shape and appearance, have been adapted as standards—namely, long lines, tadpole lines, and short lines. The experimental arrangement underlying this method may be appropriately called a *single plate resistance-furnace*.   § 5.

7. An investigation of the spectrum lines emitted by the vapours of magnesium, copper, and manganese has brought out the fact that the line emissions due to thermo-electrical and to chemical excitation are both of the same type—namely, the lines most strongly affected by the therm-electronic current in the fringe are precisely those which are characteristic of the explosion region of the air-coal gas flame. Their sensitiveness to electrical stimulation is further illustrated by the fact that their emission is appreciably enhanced in a capacity spark.   §§ 6, 7, and 8.

8. The characteristic flame lines of magnesium, copper, and

manganese, which in the air-coal gas flame are emitted by the mantle above the cone, appear all as long lines in the single plate furnace. This fact confirms their status as temperature lines. §§ 6, 7, and 8.

§ 10. *Concluding Remarks.*

The very definite grouping of the spectrum lines of metal vapours according to character, as revealed by the selective actions of thermo-electrical and thermo-chemical excitation with the single plate resistance-furnace, makes it appear hopeful that the new method of spectroscopic analysis developed in the course of this investigation will be of some help in the search for related lines in the case of metals possessing complicated line spectra. Furthermore, the remarkable agreement which has been shown to exist between the spectroscopic effects produced by thermo-electrical and chemical excitations goes to mark out the single plate furnace as a valuable means of both checking and supplementing the results given by flames. In particular this type of furnace provides the possibility of singling out the characteristic line emission which accompanies the decomposition of a chemical compound under temperature conditions unattainable in flames. Thus at a very high temperature and with the aid of electric actions the plate furnace performs the same function as the air-coal gas flame at a comparatively low temperature with the help of chemical actions. In this respect the red fringe may be regarded as the electrical analogue of the explosion region; in both, the line emission by metal vapours is connected with the breaking up of compound molecules, but the manner in which this is brought about is probably different in each. The resulting luminous effects, however, are evidently of the same order in both, as has been so clearly established by these experiments.

The fact that an electric current or—what may be regarded as its equivalent—a drift of electrons travelling under the action of a relatively feeble electric field is capable of strongly exciting characteristic spectrum radiations in metal vapours, may have some important bearing on certain astrophysical problems. Thus it is conceivable that at the very high temperature prevailing in the lower strata of the chromosphere or in the reversing layer an electric field of only a very minute fraction of a volt per centimetre may suffice to stimulate spectroscopic effects comparable to those which the relatively much more intense electric fields of our laboratory furnaces produce at considerably lower temperatures.

Manchester, May 1920.

XXXIV. *Note on a very Convenient Method of Accurately Focussing and Adjusting the Image of a Laboratory Light Source upon the Slit of a Spectrograph. By* G. A. Hemsalech [*].

IT is often necessary in exact spectroscopic investigations to project by means of a lens a sharply defined image of the source of light upon the collimator slit, for the purpose of differentiating between the radiations emitted by various regions in the source. In this way Sir Norman Lockyer, to whom this most important method of spectroscopic observation is due, discovered the so-called long and short lines in the arc and spark. In order to make the requisite adjustments it generally suffices, especially in the case of such bright sources as the arc or spark, to observe the image on the slit and to move either the source or the lens until the image appears quite sharp. But in the case of a feeble source of light, such as an uncoloured flame, or a source which is limited in duration as, for example, a small high temperature plate resistance furnace, the usual method of adjusting the image on the slit becomes difficult and even impracticable. Having become confronted with this inconvenience in the course of my experiments with plate furnaces, I was led to try several alternative methods, and finally adopted one which not only entirely solved the difficulty for the furnace, but was also found to be equally well applicable to the flame, arc, or spark. This method is merely the converse of the old one, and consists in focussing the slit upon the source of light. It is really so simple that I have no doubt of it having already been used by others, but since I have not seen a record of it in any work on spectroscopy, and also in view of its unquestionable usefulness, I venture to give a short account of it for the benefit of those spectroscopists who may not yet be acquainted with it.

Let us suppose that the projection objective O has been centred with respect to the axis of the collimator by means of some suitable method, as, for example, the one I have given in my thesis [†], and that the slit S is at one of the foci of O. If a spark passing between the electrodes E and E' be placed at the conjugate focus of O its image will coincide with S. But conversely also an image of the slit S is formed at T coincident with the spark-gap. It is this image T which is observed and made to coincide with the tips of the electrodes E and E'. In practice the procedure adopted is as

follows : the slit S is illuminated by means of an ordinary incandescent lamp placed within 1 or 2 yards from the former. Its image T is then directly viewed by the unaided eye, or if greater accuracy be desired, by means of the small

Fig. 1.
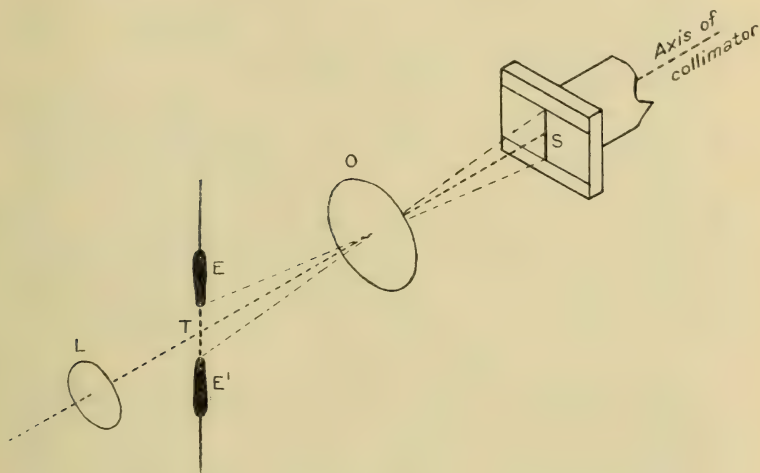
Illustrating method of focussing image of Light Source on slit of Spectrograph.

magnifying lens L. The electrodes E and E′ are then moved into position and adjusted until the slit image and spark-gap are seen to coincide. Any region of the spark-gap can in this way be brought into coincidence with any part of the slit image without much trouble. Accuracy of focus is tested by displacing the eye sideways, and the least deviation from coincidence will immediately reveal itself by a parallax effect between the slit image and the tips of the electrodes. If the source be a flame the orifice of the burner may be brought into coincidence with the slit image, or, if the region to be examined be too far above the burner a piece of wire held in that region will serve the purpose.

Evidently the same method applies when it is desired to adjust the position of the objective O. In this case the spark-gap between E and E′ is placed in line with the optic axis of the collimator at a distance from the slit which corresponds to the focal length of O and the size of image required. The slit image T is then made to coincide with the spark-gap by adjusting the position of the objective O.

Manchester, May 1920.

XXXV. *Heat-loss by Conduction in Explosions of Coal-gas and Air.* *By* W. T. DAVID, *M.A., D.Sc.**

IN this paper the results of experiments are given upon the heat-loss by conduction during the explosion and subsequent cooling of mixtures of coal-gas and air of various strengths contained in a closed vessel. From these results an approximate law of cooling by conduction of gases at high temperatures may be formulated.

The results of experiments upon the heat-loss by radiation in similar mixtures have already been published †, and in a subsequent paper these will be combined with the results given in the present paper. The combined results will give the total heat-loss during explosion and cooling, and it will therefore be possible to estimate the internal energy of the various gaseous mixtures experimented upon in terms of the gas temperature.

Method of Experiment.

The inflammable mixtures were contained in a cylindrical cast-iron vessel whose internal dimensions were 30 cm. in diameter and 30 cm. in length. It is shown in fig. 1. The pressures developed on firing the gaseous mixtures were measured by means of a Hopkinson optical indicator, which traced a continuous curve upon a revolving photographic film. From the pressure-curves thus obtained the mean gas temperatures were calculated by means of the equation $pv = R\theta$, after allowing for a small contraction of volume which takes place during the combustion of the gaseous mixtures.

The heat-loss by conduction was measured by means of a grid of highly polished silver sheet mounted upon a backing of linoleum and placed upon one of the end covers of the explosion vessel, as shown at A in fig. 1. The silver grid was connected with a reflecting galvanometer, by means of which a curve of rise of resistance of the grid as it was warmed up by contact with the hot gaseous mixtures was traced upon the same photographic film as that upon which the pressure-curve was traced.

The experimental arrangements were similar to those used by Hopkinson in connexion with his recording calorimeter for explosions ‡. The total heat-loss by conduction per
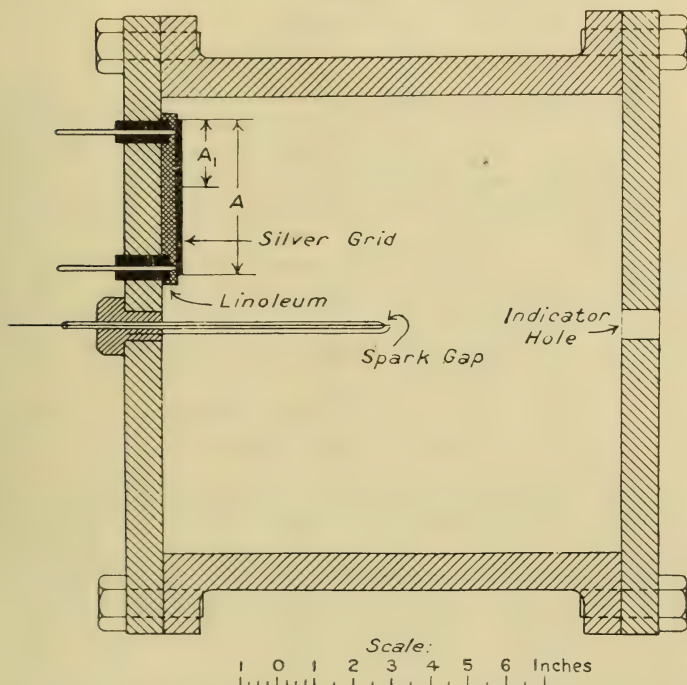
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* Communicated by the Author.
† Phil. Trans. Roy. Soc. A. vol. ccxi. p. 375.
‡ Proc. Roy. Soc. A. vol. lxxix. p. 79, p. 138.

sq. cm. of surface is equal to the amount of heat in the grid
per sq. cm. at that instant plus the amount which has passed
from the grid into the linoleum backing. The amount of

Fig. 1.

heat in the silver grid per sq. cm. at time t is equal to $C\theta$,
where C is the thermal capacity of the grid per sq. cm. and
θ is the rise of temperature of the grid at that instant. The
amount of heat which has passed into the backing at time t
may be calculated from the expression

$$2\sqrt{\frac{kct}{\pi}}\left\{\theta - \frac{1}{3}t\dot{\theta} + \frac{1}{5}\frac{t^2}{2!}\ddot{\theta} - \dots\right\},$$

where k and c are the thermal conductivity and thermal
capacity respectively of the linoleum, θ the rise of tempera-
ture of the surface of the linoleum (which may be assumed
to be equal to that of the grid) at time t, and $\dot{\theta}, \ddot{\theta} \dots$
differential coefficients of θ with regard to t.

The thermal conductivity and thermal capacity of the

linoleum were determined by subsidiary experiments. The values found were

$$k = 0\cdot00032$$

and

$$c = 0\cdot6,$$

and hence

$$\sqrt{\frac{kc}{\pi}} = 0\cdot008.$$

Grids made from polished silver and polished copper sheets of various thicknesses (and therefore of different thermal capacities) were experimented with. The thinnest grid used had a thermal capacity equivalent to $0\cdot0025$ grm. of water per sq. cm. and the thickest a thermal capacity equivalent to $0\cdot0118$ grm. of water. The results were very similar, although the proportions of the heat in the grids and in the backing at any instant were widely different. In view of this it is believed that the various constants determined by subsidiary experiments for the grid and the linoleum are of a good degree of accuracy.

Results of Experiments.

It was found that the heat-loss by conduction was not uniformly distributed over the interior surface of the vessel. Thus a grid of about 5 cm. diameter placed high up on one of the end covers (position A_1, fig. 1) gave results about 10 per cent. lower than those obtained with a grid of about 12 cm. diameter covering the top half of the end cover (position A, fig. 1). The explanation of this would appear to be that the smaller grid, on account of its position, was well out of the path of the main convection currents, whereas the lower part of the large grid was probably disturbed by these currents and consequently received more heat from the hot gaseous mixture than the small grid.

In the experiments about to be described the large grid was used, and it is thought that the measurements made with this grid may without serious error be taken as giving the mean value of the conduction-loss over the entire surface of the vessel.

The curves in fig. 2 relate to a $12\cdot4$ per cent. mixture of coal-gas and air. Curve T shows the mean gas temperature (as deduced from the pressure record) at various times after ignition. Curve G was taken from the record traced by the galvanometer and shows the heat in the grid per sq. cm. of its surface. Curve H shows the total heat which has passed

through each sq. cm. of the grid—that is, the heat in the grid together with that which has passed into the linoleum backing as calculated by means of the expression given above. The data from which these curves have been drawn are given in Table I. It will be noticed that at the moment

Fig. 2.
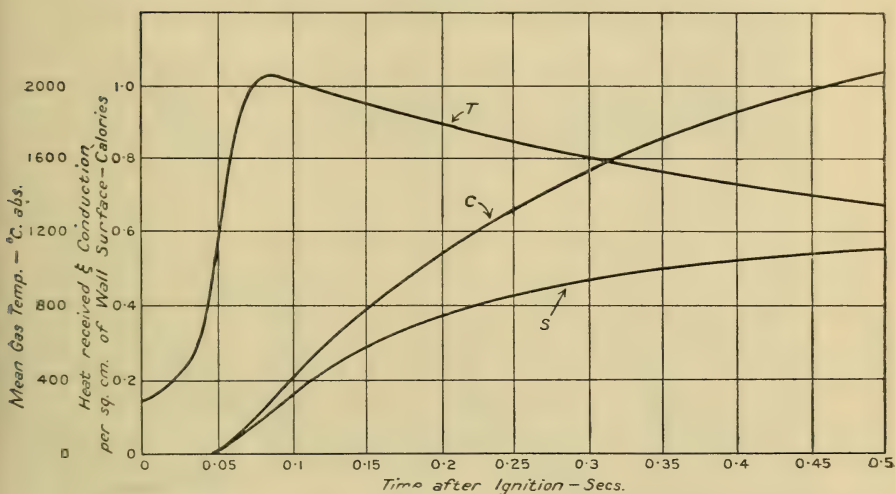
Curves showing Heat in Silver Grid per sq. cm. (S) and total Heat-loss by Conduction per sq. cm. of Wall-surface (C) in a 12·4 per cent. mixture of Coal-gas and Air.
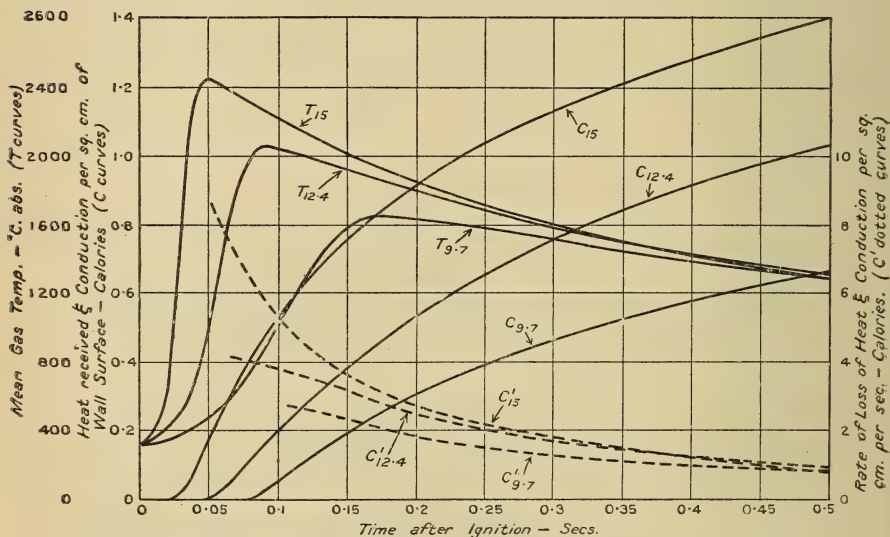
TABLE I.—Heat-loss by Conduction in a 12·4 per cent. mixture of Coal-gas and Air.

Time after Ignition (secs.).	Mean Gas Temp. (° C. abs.).	Rise of Temp. of polished Silver Grid (° C.).	Heat in polished Silver Grid per sq. cm. (Calories.)	Percentage Loss to Linoleum Backing.	Total Loss of Heat by Conduction per sq. cm. of surface. (Calories.)
0·08	2050 (max.temp.)	12·1	0·143	18·5	0·17
0·1	2030	14·5	0·171	20·5	0·21
0·15	1920	25·0	0·295	30·0	0·38
0·2	1800	31·5	0·372	44·0	0·53
0·25	1700	36·5	0·43	55·0	0·67
0·3	1610	40·0	0·472	63·0	0·77
0·4	1460	44·0	0·52	78·5	0·93
0·5	1330	46·5	0·548	91·5	1·05

of maximum temperature (2050° C. abs.), which occurs in this mixture at 0·08 sec. after ignition, the heat-loss by conduction amounts to 0·17 calorie per sq. cm., of which about 0·14 calorie is in the silver grid and about 0·03 calorie has passed into the linoleum backing. At 0·25 sec. after ignition, when the gas temperature has fallen to 1700° C. abs., the conduction loss is 0·67 calorie per sq. cm., of which 0·43 calorie is in the silver and 0·24 calorie has passed into the backing.

Similar experiments were made upon 15 per cent. and 9·7 per cent. mixtures of coal-gas and air. The results are given in fig. 3. Those for the 12·4 per cent. mixture are

Fig. 3.

Curves showing Heat-loss by Conduction per sq. cm. of Wall-surface in 15·0 per cent., 12·4 per cent., and 9·7 per cent. mixtures of Coal-gas and Air.

also given for purposes of comparison. The T-curves give the mean gas temperature in the different mixtures at various times after ignition. The C-curves give the heat-loss by conduction per sq. cm. of wall-surface; and the dotted C′-curves give the rate of heat-loss by conduction per sq. cm. per sec. Tables II., III., and IV. have been compiled from

these curves. They give the proportion of the heat of combustion of the coal-gas in the vessel which has been lost by conduction at various times after ignition.

TABLE II.—Heat-loss by Conduction in a 15 per cent. mixture of Coal-gas and Air.

Heat of Combustion of Coal-gas in Vessel = 16,300 calories.

Time after Ignition (secs.).	Mean Gas Temp. (° C. abs.).	Heat lost by Conduction per sq. cm. of Wall-surface. (Calories.)	Heat lost by Conduction expressed as a percentage of the Heat of Combustion of the Coal-gas in Vessel.
0·05	2440 (max.temp.)	0·19	5·1
0·1	2220	0·54	14·4
0·15	2020	0·76	20·3
0·2	1840	0·92	24·5
0·25	1710	1·04	27·7
0·3	1600	1·13	30·0
0·4	1430	1·29	34·4
0·5	1300	1·41	37·6

TABLE III.—Heat-loss by Conduction in a 12·4 per cent. mixture of Coal-gas and Air.

Heat of Combustion of Coal-gas in Vessel = 13,500 calories.

Time after Ignition (secs.).	Mean Gas Temp. (° C. abs.).	Heat lost by Conduction per sq. cm. of Wall-surface. (Calories.)	Heat lost by Conduction expressed as a percentage of the Heat of Combustion of the Coal-gas in Vessel.
0·08	2050 (max.temp.)	0·17	5·5
0·1	2030	0·21	6·8
0·15	1920	0·38	12·5
0·2	1800	0·53	17·4
0·25	1700	0·67	21·7
0·3	1610	0·77	25·0
0·4	1460	0·93	30·2
0·5	1330	1·05	34·0

TABLE IV.—Heat-loss by Conduction in a 9·7 per cent. mixture of Coal-gas and Air.

Heat of Combustion of Coal-gas in Vessel = 10,600 calories.

Time after Ignition (secs.).	Mean Gas Temp. (° C. abs.).	Heat lost by Conduction per sq. cm. of Wall-surface. (Calories.)	Heat lost by Conduction expressed as a percentage of the Heat of Combustion of the Coal-gas in Vessel.
0·18	1660 (max.temp.)	0·26	11·0
0·2	1650	0·31	12·8
0·25	1580	0·4	16·5
0·3	1520	0·47	19·4
0·4	1390	0·59	24·4
0·5	1310	0·67	27·7

The conduction-loss up to the moment of maximum temperature, it will be noticed, amounts to 5·1 per cent. of the heat of combustion in the 15 per cent. mixture, 5·5 per cent. in the 12·4 per cent. mixture, and 11·0 per cent. in the 9·7 per cent. mixture. The much greater proportion of the heat of combustion lost by conduction to the vessel-walls up to the moment of maximum temperature in the weakest mixture is due to the much greater "time of explosion" which occurs in this mixture; it amounts to 0·18 sec., whereas in the 15 per cent. mixture it was only 0·05 sec.

At 0·5 sec. after ignition the 15 per cent. mixture has lost by conduction about 38 per cent. of its heat of combustion. The 12·4 per cent. mixture at the same instant has lost about 34 per cent. and the 9·7 per cent. mixture about 28 per cent.
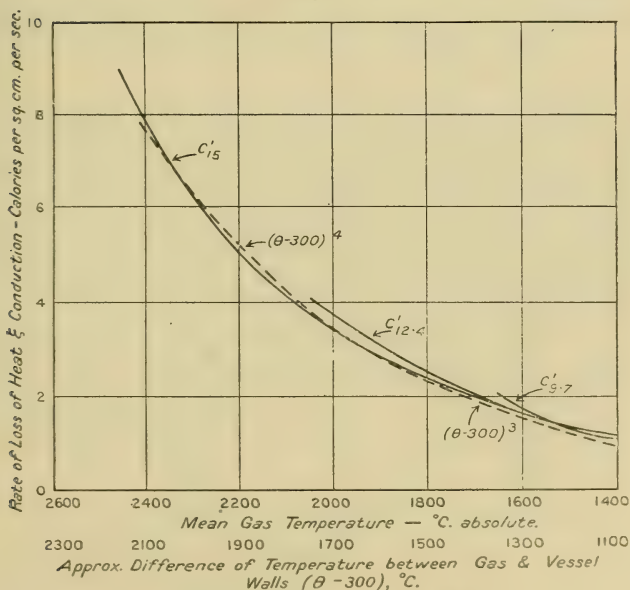
The curves in fig. 4 and data in Table V. show the rate at which heat-loss by conduction is proceeding during the cooling of the various mixtures after explosion. It will be noticed that the weaker mixtures in the initial stages of cooling lose heat by conduction rather more rapidly than the stronger mixtures when they have cooled to the same mean temperatures as the weaker mixtures have in this epoch *. This is probably mainly due to convection currents, which, having been set up during the explosion period, are more vigorous in the initial stages of cooling than in the later stages.

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* A similar result was obtained in an investigation into the radiation loss (Phil. Trans. A. vol. ccxi.).

TABLE V.—Rate of Heat-loss by Conduction in 15 per cent., 12·4 per cent., and 9·7 per cent. mixtures of Coal-gas and Air.

Mean Gas Temp. (° C. abs.).	Rate of Heat-loss by Conduction per sq. cm. of Wall-surface.—Calories per sec.		
	15 % Mixture.	12·4 % Mixture.	9·7 % Mixture.
2440	8·7		
2400	7·9		
2200	5·0		
2050	3·8	4·1	
2000	3·4	3·7	
1800	2·4	2·5	
1660	1·9	1·9	2·1
1600	1·7	1·7	1·8
1400	1·2	1·2	1·1

Fig. 4.

Curves showing Rate of Loss of Heat by Conduction per sq. cm. of Wall-surface per sec. in 15·0 per cent., 12·4 per cent., and 9·7 per cent. mixtures of Coal-gas and Air.

At temperatures above 2000° C. abs. the rate at which conduction-loss proceeds in the 15 per cent. mixture is roughly proportional to the fourth power of the difference in temperature between the gaseous mixture and the vessel-walls, while at temperatures below 2000° C. abs. the rate of loss is more nearly proportional to the third power of the temperature difference. That this is so will be seen from the dotted curve which, above 2000° C. abs., is proportional to the fourth power of the temperature difference and, below 2000° C. abs., is proportional to the third power of this difference.

The equation to the dotted curve is

$$\dot{C} = 4 \times 10^{-13}(\theta - \theta_\omega)^4$$

for temperatures above 2000° C. abs., and

$$\dot{C} = 7 \times 10^{-10}(\theta - \theta_\omega)^3$$

for temperatures below 2000° C. abs. Where

$\dot{C}$ = rate of loss by conduction in calories per sq. cm. of wall-surface per sec.,

θ = mean absolute temperature of the gaseous mixture,

and θ_ω = absolute temperature of the walls of the explosion vessel which in these experiments has been taken to be 300°.

The equations given above are sufficiently accurate for rough calculation, but on closer examination the law of cooling by conduction would appear to be more complicated. In the neighbourhood of 2400° C. abs. (when convection currents are probably somewhat vigorous) the rate of loss is proportional to the fifth power of the temperature difference, whereas in the neighbourhood of 1600° C. abs. it approaches proportionality to the square of the temperature difference. An inspection of the curve indicates that $\dot{C}$ is proportional to

$(\theta - \theta_\omega)^5$ in the neighbourhood of 2400° C. abs.,

$(\theta - \theta_\omega)^4$ „   „   „ 2100° C. abs.,

$(\theta - \theta_\omega)^3$ „   „   „ 1800° C. abs.,

and $(\theta - \theta_\omega)^2$ „   „   „ 1500° C. abs.

At still lower temperatures it is probable that C would become proportional to the temperature difference simply.

XXXVI. *On the Path of a Ray of Light in the Gravitation Field of the Sun.* By G. B. JEFFERY, *M.A., B.Sc., Fellow of University College, London* *.

IN a paper published in the May number of the ' Philosophical Magazine,' Prof. A. Anderson gives a modification of the usual theory of the motion of a planet under Einstein's theory from which he concludes that there should be no advance of the perihelion.

The particular integral of Einstein's contracted tensor equations for a particle of mass m at rest at the origin of polar co-ordinates gives for the line element in a plane through the origin

$$ds^2 = -\gamma^{-1}dr^2 - r^2 d\theta^2 + \gamma dt^2, \quad . \quad . \quad . \quad (1)$$

where $\gamma = 1 - 2m/r$.

For the propagation of light we have $ds = 0$, which gives

$$\gamma^{-1}\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2 = \gamma,$$

so that for a ray of light making an angle χ with the radius vector the velocity of propagation is v where

$$v = \gamma(\cos^2\chi + \gamma\sin^2\chi)^{-\frac{1}{2}}. \quad . \quad . \quad . \quad (2)$$

In order to avoid this dependence of the velocity of propagation upon the direction χ, it is usual to write $r = r_1 + m$ and to interpret r_1 as the actual measured radius vector †. Then, neglecting the square of m/r, the velocity of propagation becomes $1 - 2m/r_1$, and is independent of the direction. The problem thus becomes identical with that of the determination of the path of a ray of light in a medium of variable refractive index $u = 1 + 2m/r_1$.

This leads quite simply to the conclusion that a ray of light passing at a distance R from the Sun would be deflected through an angle $4m/\text{R}$.

Einstein's equations of motion for a planet give

$$\frac{d^2u}{d\theta^2} + u = \frac{m}{h^2} + 3mu^2, \quad . \quad . \quad . \quad (3)$$

where $u = 1/r$ and h is a constant.

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* Communicated by the Author.

† The introduction of r_1 is also defended on the ground that to the first order in m/r it reduces (1) to the form $ds^2 = -\gamma^{-1}(dr_1^2 + r_1^2 d\theta^2) + \gamma dt^2$, so that the scales of measurement along and perpendicular to the radius vector are the same.

If we write $u_1 = 1/r_1$, so that neglecting squares of m, $u = u_1(1 - mu_1)$ and substitute in (3), it is readily seen that to the same degree of approximation the last term disappears and we are left with the ordinary Newtonian equation giving no motion of the perihelion. This is Prof. Anderson's result. It would seem, however, that criticism might be directed against the introduction of the co-ordinate r_1 into the first problem rather than against its omission in the second. It is, therefore, of interest to inquire what the effect of the gravitational field would be upon the path of a ray of light if we regard r as the actual measured radius vector.

If we write $\theta' \equiv d\theta/dr$, then $\tan \chi = r\theta'$ and (2) becomes

$$v = \gamma \left\{ \frac{1 + r^2\theta'^2}{1 + \gamma r^2\theta'^2} \right\}^{\frac{1}{2}}$$

and the time between two points is

$$t = \int \gamma^{-1} \{1 + \gamma r^2\theta'^2\}^{\frac{1}{2}} \, dr,$$

where r, θ are given at both limits.

By Huyghens' principle t is stationary for small variations of the path. We have

$$\delta t = \int \frac{r^2\theta'}{\{1 + \gamma r^2\theta'^2\}^{\frac{1}{2}}} \, \delta\theta' \, dr$$

$$= \left| \frac{r^2\theta'\delta\theta}{\{1 + \gamma r^2\theta'^2\}^{\frac{1}{2}}} \right| - \int \frac{d}{dr} \left\{ \frac{r^2\theta'}{(1 + \gamma r^2\theta')^{\frac{1}{2}}} \right\} \delta\theta \, dr.$$

The first term taken between limits vanishes, and the vanishing of the integral for $\delta\theta$ arbitrary gives

$$r^4\theta'^2 = c^2(1 + \gamma r^2\theta'^2),$$

where c is a constant.

Writing $u = 1/r$, we have after differentiating

$$\frac{d^2u}{d\theta^2} + u = 3mu^2. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is interesting to compare this with the differential equation of planetary orbits. The first term on the right-hand side of (3) represents the ordinary Newtonian attraction, and the second the small Einstein correction. Equation (4) might then be interpreted by saying that a ray of light is not subject to the Newtonian attraction, but that the Einstein effect is the same as for a planet. The advance of

the perihelion of a planet and the deflexion of a ray of light thus appear, according to this view, as different manifestations of the same effect.

Solving (4) by successive approximations, we have, neglecting $(mu)^2$,

$$u = \frac{1}{R}\cos(\theta - \alpha) + \frac{2m}{R^2} - \frac{m}{R^2}\cos^2(\theta - \alpha),$$

where R, α are constants.

Putting $u = 0$, we obtain for the directions of the asymptotes, to the same degree of approximation,

$$\theta = \alpha \pm \left(\frac{\pi}{2} + \frac{2m}{R}\right).$$

Hence the ray is deflected through a total angle $4m/R$ which agrees with the usual theory.

It appears that the deflexion of a ray of light is the same whether we regard r or r_1 as the actual measured distances, but that the difference is important in the problem of the orbit of a planet.

XXXVII. *Variably Coupled Vibrations* : *Gravity-Elastic Combinations.*—II. *Both Masses and Periods Unequal.* *By* L. C. Jackson, *F.P.S.L., University College, Nottingham* *.

[Plate X.]

I. Introduction.

IN a previous paper † the author described a model of a coupled system consisting of a gravity pendulum and an elastic pendulum, the separate periods and the masses of the two being equal. The present paper deals with the same system for the case in which both the masses and periods of the two pendulums are different.

The model may thus be considered as analogous to the case of coupled electrical circuits, in which the inductances and periods are both different. The apparatus, though still the same in principle, has been entirely re-made and improvements effected in certain details, as experience showed them to be desirable. The chief points in which the present apparatus differs from the one previously described, are such

that we can now obtain simultaneous traces of the motion of each bob on the same photographic plate.

As the traces showed that the damping for the present arrangement was not negligible, it was thought desirable to take this into account in the theory.

The paper includes twenty-four photographic reproductions of the double traces obtained for the motions of the bobs under various conditions of starting and coupling.

II. Theory.

Equations of Motion and Coupling.

Using the notation of the previous paper, the equations of motion may be written :

$$\mathrm{M}\frac{d^2y}{dt^2} + \mathrm{M}m^2y = \mathrm{M}m^2\alpha z, \quad \ldots \quad \ldots \quad (1)$$

$$\mathrm{N}\frac{d^2z}{dt^2} + (\mathrm{N}n^2 + \mathrm{M}m^2\alpha^2)z = \mathrm{M}m^2\alpha y. \quad \ldots \quad (2)$$

Putting $\dfrac{\mathrm{M}}{\mathrm{N}} = \rho$, $\dfrac{m^2}{n^2} = \eta$ and inserting the frictional term $2k\dfrac{dy}{dt}$ in the first, we have

$$\frac{d^2y}{dt^2} + 2k\frac{dy}{dt} + m^2y = m^2\alpha z$$

$$\frac{d^2z}{dt^2} + \left(\frac{m^2}{\eta} + \rho m^2\alpha^2\right)z = m^2\alpha\rho y.$$

If $m^2\alpha$ is put equal to a and $\dfrac{m^2}{\eta} + \rho m^2\alpha^2$ equal to b, we have :

$$\frac{d^2y}{dt^2} + 2k\frac{dy}{dt} + m^2y = az, \quad \ldots \quad (3)$$

$$\frac{d^2z}{dt^2} + bz = a\rho y. \quad \ldots \quad \ldots \quad (4)$$

From (3) and (4) we may write for the coefficient of coupling γ,

$$\gamma^2 = \frac{\alpha^2\rho}{\dfrac{1}{\eta} + \rho\alpha^2}. \quad \ldots \quad \ldots \quad (5)$$

To solve (3) and (4), try in (4)

$$z = e^{xt}.$$

This gives

$$y = \frac{x^2 + b}{a\rho} e^{xt}. \qquad . \quad . \quad . \quad . \quad . \quad (6)$$

Put (6) in (3); then we obtain the auxiliary equation in x

$$x^4 + 2kx^3 + (b+m^2)x^2 + 2kbx + m^2b - a^2\rho = 0. \quad . \quad (7)$$

This is a complete equation of the fourth degree, but since k is small compared with the coefficients of x^2 and x, we may assume a solution in the form

$$x = -r \pm ip \quad \text{or} \quad -s \pm iq, \quad . \quad . \quad . \quad (8)$$

where r and s are small quantities whose squares are negligible.

Thus we have the equivalent equation

$$(x + r - ip)(x + r + ip)(x + s - iq)(x + s + iq) = 0,$$

or
$$x^4 + 2(r+s)x^3 + (p^2 + q^2 + r^2 + s^2 + 4rs)x^2$$
$$+ 2(p^2s + q^2r + r^2s + rs^2)x + (p^2 + r^2)(q^2 + s^2) = 0.$$
$$. \quad . \quad . \quad (9)$$

This, on omitting the negligible quantities, becomes the approximate equation sufficiently accurate for the present purpose

$$x^4 + 2(r+s)x^3 + (p^2 + q^2)x^2 + 2(p^2s + q^2r)x + p^2q^2 = 0. \quad (10)$$

The comparison of coefficients in (7) and (10) yields

$$r + s = k, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$p^2 + q^2 = b + m^2, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$p^2s + q^2r = kb, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$p^2q^2 = m^2b - a^2\rho. \quad . \quad . \quad . \quad . \quad (14)$$

From (12) and (14) we may eliminate q^2 and obtain a biquadratic for p^2, whose roots may be called p^2 and q^2. We thus find

$$\left. \begin{array}{l} 2p^2 = b + m^2 + \sqrt{\{(b-m^2)^2 + 4a^2\rho\}} \\ 2q^2 = b + m^2 - \sqrt{\{(b-m^2)^2 + 4a^2\rho\}} \end{array} \right\}. \quad . \quad (15)$$

(11) and (13) give

$$r = \frac{p^2 - b}{p^2 - q^2} \cdot k \qquad s = \frac{b - q^2}{p^2 - q^2} \cdot k,$$

Z 2

and by the use of (15) these become

$$r = \frac{m^2 - b + \sqrt{(b - m^2)^2 + 4a^2\rho}}{2\sqrt{\{(b - m^2)^2 + 4a^2\rho\}}} \cdot k, \quad . \quad . \quad (16)$$

$$s = \frac{b - m^2 + \sqrt{\{(b - m^2) + 4a^2\rho\}}}{2\sqrt{\{(b - m^2)^2 + 4a^2\rho\}}} \cdot k. \quad . \quad . \quad (17)$$

Using (6) and (8), and introducing the usual constants, the general solution may be written in the form

$$z = e^{-rt}(Ae^{pit} + Be^{-pit}) + e^{-st}(Ce^{qit} + De^{-qit}), \quad . \quad (18)$$

and

$$y = \frac{-p^2 + b}{a\rho} e^{-rt}(Ae^{pit} + Be^{-pit}) + \frac{-q^2 + b}{a\rho}(Ce^{qit} + De^{-qit})$$

$$+ \frac{2pri}{a\rho} e^{-rt}(-Ae^{pit} + Be^{-pit}) + \frac{2qsi}{a\rho}(-Ce^{qit} + De^{-qit}). \quad (19)$$

If small quantities are further neglected, these will simplify to

$$z = Ee^{-rt}\sin(pt + \epsilon) + Fe^{-st}\sin(qt + \phi), \quad . \quad . \quad (20)$$

and $\quad y = Ge^{-rt}\sin(pt + \epsilon) + He^{-st}\sin(qt + \phi). \quad . \quad (21)$

(21) and (22) are equations representing two superposed simple harmonic vibrations, of which the frequency ratio is

$$\frac{p}{q} = \left[\frac{b + m^2 + \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}}{b + m^2 - \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}}\right]^{\frac{1}{2}} \cdot \cdot \cdot \quad (22)$$

Initial Conditions.

Let us consider now the form of the general solutions (20) and (21) for various conditions of starting the vibrations of the pendulums.

(i.) *Upper bob struck.*

We may here write

$$y = 0, \quad z = 0, \quad \frac{dy}{dt} = 0, \quad \frac{dz}{dt} = v \text{ for } t = 0. \quad . \quad (23)$$

Introducing these conditions in (20) and (21) and into the

differentiations of these with respect to the time, we find

$$\left. \begin{array}{l} 0 = \mathrm{E} \sin \epsilon + \mathrm{F} \sin \phi \\ 0 = \mathrm{G} \sin \epsilon + \mathrm{H} \sin \phi \end{array} \right\}, \quad \cdots \quad (24)$$

$$\left. \begin{array}{l} v = \mathrm{E}p \cos \epsilon + \mathrm{F}q \cos \phi \\ 0 = \mathrm{G}p \cos \epsilon + \mathrm{H}q \cos \phi \end{array} \right\} \quad \cdots \quad (25)$$

Equations (24) and (25) are satisfied by

$$\epsilon = 0, \quad \phi = 0. \quad \cdots \quad (26)$$

Then from (18), (19), and (21), we have

$$\left. \begin{array}{l} \mathrm{G} = \dfrac{-p^2 + b}{a\rho} \cdot \mathrm{E} = \dfrac{b - m^2 - \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}}{2a\rho} \\[2mm] \mathrm{H} = \dfrac{-q^2 + b}{a\rho} \cdot \mathrm{F} = \dfrac{b - m^2 + \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}}{2a\rho}. \end{array} \right\} \quad (27)$$

(26) and (27) in (25) give

$$\left. \begin{array}{l} v = \mathrm{E}p + \mathrm{F}q \\ 0 = \mathrm{G}p + \mathrm{H}q \end{array} \right\}, \quad \cdots \quad (28)$$

whence

$$\left. \begin{array}{l} \mathrm{E} = \dfrac{-q^2 + b}{p(-q^2 + p^2)} \cdot v \\[2mm] \mathrm{F} = \dfrac{-p^2 + b}{q(-q^2 + p^2)} \cdot v \end{array} \right\} \quad \cdots \quad (29)$$

Thus we see that the ratios of the amplitudes of the quick and slow motions for the y and z vibrations respectively are given by

$$\left. \begin{array}{l} \dfrac{\mathrm{G}}{\mathrm{H}} = \dfrac{-q}{p} = - \left[\dfrac{b + m^2 - \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}}{b + m^2 + \sqrt{\{(b - m^2)^2 + 4a^2\rho\}}} \right]^{\frac{1}{2}} \\[3mm] \dfrac{\mathrm{E}}{\mathrm{F}} = \dfrac{(b - m^2 + \sqrt{\{(b - m^2)^2 + 4a^2\rho\}})(b + m^2 - \sqrt{\{(b - m^2)^2 + 4a^2\rho\}})^{\frac{1}{2}}}{(b - m^2 - \sqrt{\{(b - m^2)^2 + 4a^2\rho\}})(b + m^2 + \sqrt{\{(b - m^2)^2 + 4a^2\rho\}})^{\frac{1}{2}}} \end{array} \right\}, \quad (30)$$

or writing δ for $\sqrt{\{(b - m^2)^2 + 4a^2\rho\}}$

$$\left. \begin{array}{l} \dfrac{\mathrm{G}}{\mathrm{H}} = - \left[\dfrac{b + m^2 - \delta}{b + m^2 + \delta} \right]^{\frac{1}{2}} \\[3mm] \dfrac{\mathrm{E}}{\mathrm{F}} = \dfrac{(b - m^2 + \delta)(b + m^2 - \delta)^{\frac{1}{2}}}{(b - m^2 - \delta)(b + m^2 + \delta)^{\frac{1}{2}}} \end{array} \right\} \quad \cdots \quad (31)$$

(ii.) *Lower bob struck.*

We may here write

$$y=0, \quad z=0, \quad \frac{dy}{dt}=v, \quad \frac{dz}{dt}=0 \text{ for } t=0.$$

Then, proceeding as before, we find

$$\left. \begin{array}{l} 0=\mathrm{E}\sin\epsilon+\mathrm{F}\sin\phi \\ 0=\mathrm{G}\sin\epsilon+\mathrm{H}\sin\phi \end{array} \right\}, \quad \cdots \quad (32)$$

$$\left. \begin{array}{l} 0=\mathrm{E}p\cos\epsilon+\mathrm{F}q\cos\phi \\ v=\mathrm{G}p\cos\epsilon+\mathrm{H}q\cos\phi \end{array} \right\} \cdots \quad (33)$$

Equations (32) and (33) are satisfied by

$$\epsilon=0, \qquad \phi=0. \quad \cdots \quad (34)$$

From (27) and (34) in (33) we obtain

$$0=\mathrm{E}p+\mathrm{F}q,$$
$$v=\mathrm{G}p+\mathrm{H}q,$$

whence

$$\left. \begin{array}{l} \mathrm{E}=\dfrac{a\rho}{p(-p^2+q^2)}\cdot v \\[2mm] \mathrm{F}=-\dfrac{a\rho}{q(-p^2+q^2)}\cdot v \end{array} \right\} \quad \cdots \quad (35)$$

Thus we see that the ratios of the amplitudes of the quick and slow motions for the y and z vibrations respectively are given by

$$\left. \begin{array}{l} \dfrac{\mathrm{G}}{\mathrm{H}}=\dfrac{-q(-p^2+b)}{p(-q^2+b)}=-\dfrac{(b+m^2+\delta)(b+m^2-\delta)^{\frac{1}{2}}}{(b+m^2-\delta)(b+m^2+\delta)^{\frac{1}{3}}} \\[3mm] \dfrac{\mathrm{E}}{\mathrm{F}}=\dfrac{-q}{p}=-\left[\dfrac{b+m^2-\delta}{b+m^2+\delta}\right]^{\frac{1}{3}} \end{array} \right\} \cdot (36)$$

(iii.) *Upper bob displaced; lower bob free.*

We may here write

$$y=af, \quad z=f, \quad \frac{dy}{dt}=0, \quad \frac{dz}{dt}=0 \text{ for } t=0.$$

Then, proceeding as before, we find

$$\left. \begin{array}{l} f=\mathrm{E}\sin\epsilon+\mathrm{F}\sin\phi \\ af=\mathrm{G}\sin\epsilon+\mathrm{H}\sin\phi \end{array} \right\}, \quad \cdots \quad (37)$$

$$\left. \begin{array}{l} 0=\mathrm{E}p\cos\epsilon+\mathrm{F}q\cos\phi \\ 0=\mathrm{G}p\cos\epsilon+\mathrm{H}q\cos\phi \end{array} \right\} \quad \cdots \quad (38)$$

(37) and (38) are satisfied by

$$\epsilon = \frac{\pi}{2}, \qquad \phi = \frac{\pi}{2}, \quad . \quad . \quad . \quad . \quad (39)$$

From (27) and (39) in (37) we obtain

$$j = E + F,$$
$$\alpha f = G + H,$$

whence

$$\left. \begin{aligned} \frac{G}{H} &= \frac{(b - m^2 + \delta) - 2a\alpha\rho}{2a\alpha\rho - (b - m^2 - \delta)} \\ \frac{E}{F} &= \frac{(b - m^2 + \delta) - 2a\alpha\rho}{2a\alpha\rho - (b - m^2 - \delta)} \end{aligned} \right\} \cdot \quad . \quad . \quad . \quad (40)$$

Note $\dfrac{E}{F} = \dfrac{G}{H}$.

(iv.) *Lower bob displaced; upper bob free.*

We may here write

$$y = f, \quad z = \frac{\alpha^2 \rho}{\dfrac{1}{\eta} + \alpha^2 \rho} \cdot j, \quad \frac{dy}{dt} = 0, \quad \frac{dz}{dt} = 0 \text{ for } t = 0.$$

Then, proceeding as before, we obtain

$$\left. \begin{aligned} \frac{\alpha^2 \rho}{\left(\dfrac{1}{\eta} + \alpha^2 \rho \right)} \cdot f &= E \sin \epsilon + F \sin \phi \\ f &= G \sin \epsilon + H \sin \phi \end{aligned} \right\}, \quad . \quad . \quad (41)$$

$$\left. \begin{aligned} 0 &= Ep \cos \epsilon + Fq \cos \phi \\ 0 &= Gp \cos \epsilon + Hq \cos \phi \end{aligned} \right\} \cdot \quad . \quad . \quad (42)$$

Equations (41) and (42) are satisfied by

$$\epsilon = \frac{\pi}{2}, \qquad \phi = \frac{\pi}{2}. \quad . \quad . \quad . \quad . \quad (43)$$

From (27) and (43) in (41) we obtain

$$1 \frac{\alpha^2 \rho f}{\eta + \alpha^2 \rho} = E + F,$$
$$f = G + H,$$

whence

$$\frac{G}{H} = \frac{\left\{ 2a\left(\frac{1}{\eta} + \alpha^2\rho\right) - \alpha^2(b - m^2 + \delta) \right\} \left\{ b - m^2 - \delta \right\}}{\left\{ \alpha^2(b - m^2 - \delta) - 2a\left(\frac{1}{\eta} + \alpha^2\rho\right) \right\} \left\{ b - m^2 + \delta \right\}}$$

$$\frac{E}{F} = \frac{2a\left(\frac{1}{\eta} + \alpha^2\rho\right) - \alpha^2(b - m^2 + \delta)}{\alpha^2(b - m^2 - \delta) - 2a\left(\frac{1}{\eta} + \alpha^2\rho\right)} \quad \cdot \quad (44)$$

III. Relations among Variables.

The relations between the coupling γ and either the values of α (the ratio of the distance from the base of the elastic pendulum to the point of suspension of the gravity pendulum to the whole length of the elastic pendulum) or the ratio of the frequencies of the superposed simple harmonic vibrations, i. e. p/q, may be more conveniently visualised by means of a graph.

In fig. 1 the graph showing the relation between γ and α is plotted for the three cases given in the Tables I. to III., a separate graph being needed for each combination of ρ and η.

Table I.—Masses $3:2$, Periods $12:7$.

Coupling γ. Per cent.	Length Ratio a.	Frequency Ratio p/q.
0	0	1·339
29·01	0·324	1·563
36·72	0·422	1·682
43·74	0·520	1·839
50·25	0·618	2·014

Table II.—Masses $1:1$, Periods $12:13$.

Coupling γ. Per cent.	Length Ratio a.	Frequency Ratio p/q.
0	0	1·041
22·81	0·225	1·266
31·95	0·324	1·393
40·22	0·422	1·539
54·10	0·618	1·862

Fig. 1.
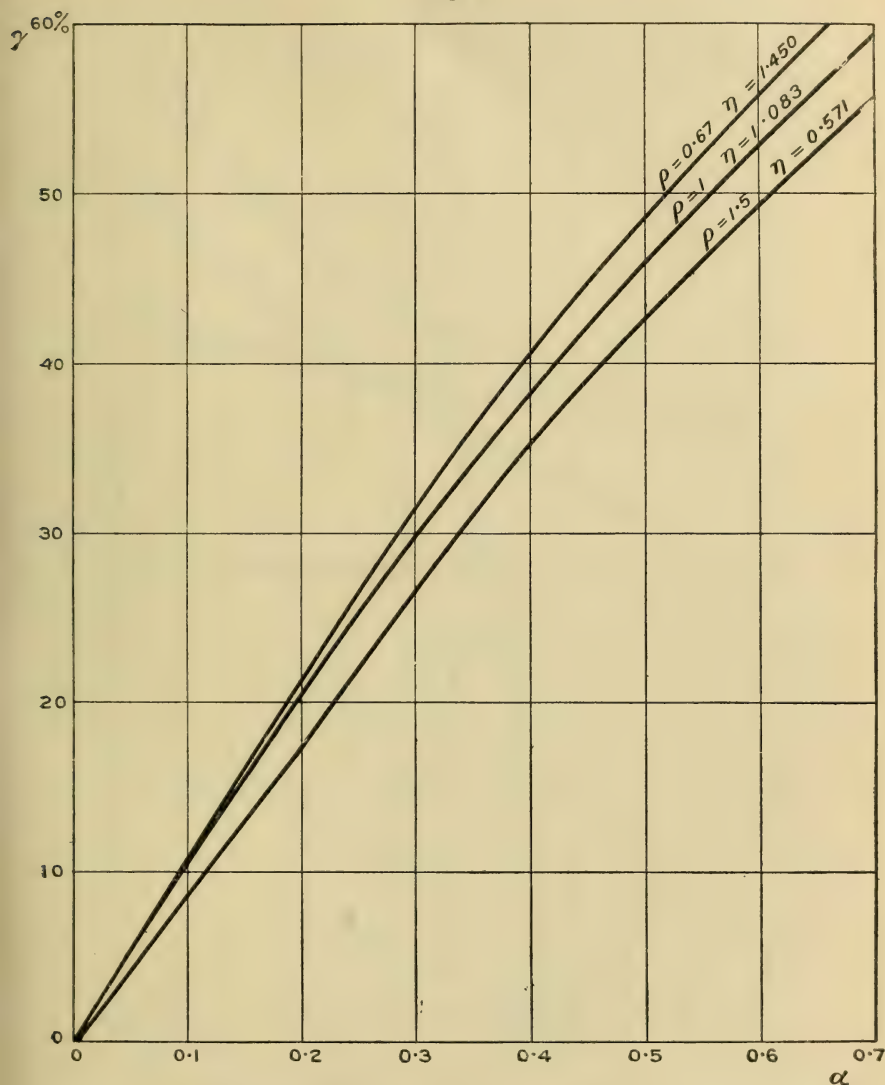
TABLE III.—Masses $2:3$, Periods $4:7$.

Coupling γ. Per cent.	Length Ratio a.	Frequency Ratio p/q.
0	0	1·311
12·69	0·127	1·338
18·68	0·176	1·353
23·62	0·225	1·372
28·09	0·274	1·393

Fig. 2 is a graph showing the relation between γ and p/q.

Fig. 2.
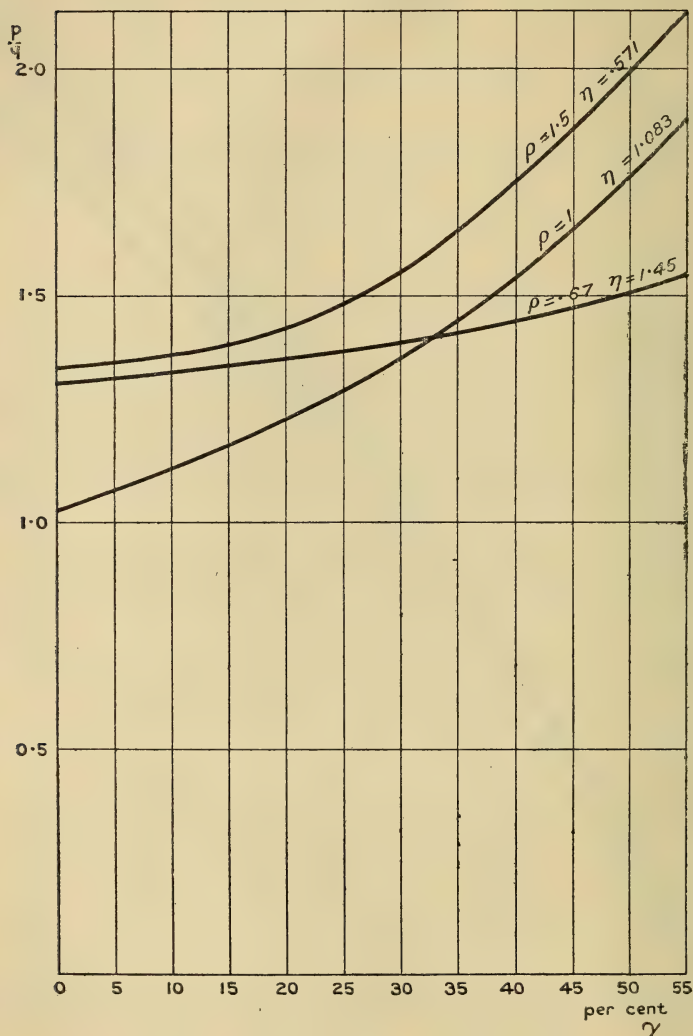
IV. Experimental Arrangements and Results.

The apparatus used by the author consists of a gravity pendulum coupled to an elastic pendulum, the motions of the two being recorded photographically. Fig. 3 is a general view of the arrangement. For the purpose of recording the vibrations, each bob carries a small electric lamp and means

for focussing a spot of light therefrom on a photographic plate, B, placed sensitive side uppermost in a frame which can be moved uniformly in a direction perpendicular to the motion of the pendulums. The experiment is performed in a dark room and the plate developed immediately.

Fig. 3.
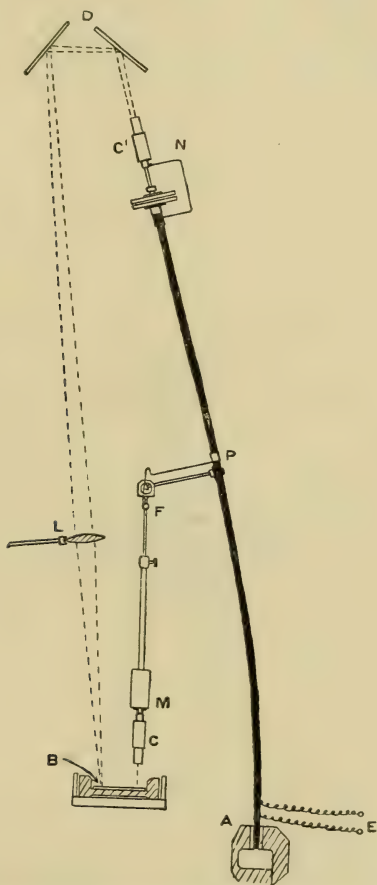
The elastic pendulum consists of an oak lath clamped in a vice at A and carrying a bob of special construction at its upper end. The details of the latter can be seen from fig. 4, which is shown partly in section. The end of the lath S is fitted with a brass cap carrying a screw T. This screw serves for the purpose both of clamping the lead weights R between washers, as shown, and of forming the central

contact of the small lamp-holder G. The light from the
lamp U passes through the pinhole V and the lens W,
thereby allowing a spot of light to be focussed on the photo
plate by means of the mirrors D and the lens L (fig. 3).
The mirrors D can be adjusted to any angle with one
another, and can be clamped in such a position on a hori-
zontal slide that they occupy the correct position relative to
N, the latter movement being necessary, as the equilibrium
position of N varies with the distance of the point of sus-
pension of the gravity pendulum M from the base of the lath.

Fig. 4.
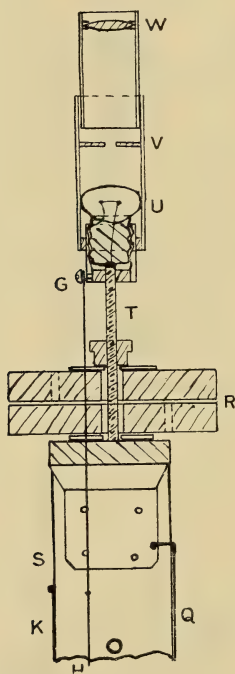
The gravity pendulum consists of a steel rod which can
slide in a steel tube carrying a cylindrical lead bob which
supports the optical arrangements. These latter are exactly
similar to those of the bob N. The gravity pendulum swings
on a knife edge attached to the rod P, which screws into the
lath at various distances along its axis.

The electrical connexions are as follows :—A wire is
fastened to each side of the lath throughout its whole length,
while a third wire (GH in fig. 4) runs down the back of the

lath. One side wire is connected to the brass cap of the lath, and hence to the central contact of the lamp-holder, while the upper end of the other wire is free. The current enters by the wire GH (which is bent into a rectangular form at N to avoid the lead weights—see fig. 3) and passes through the lamp U and down the side wire Q to the point P, where it passes to the lamp in M *via* a clip on the lath, and special leads to the base of M. The spiral leads to and from the lamp to the insulator F are not shown in fig. 3 for clearness. To avoid interfering with the swinging of M, the leads from the clips to F are bent into a circular form near the knife edge. The current returns through a second clip and down the side wire K to the battery at E.

The masses of the lead weights which can be attached to N are such that each is approximately equal to half that of M. Thus the ratio of the masses, and with it the ratio of the periods of M and N, can be altered within certain limits.

Figs. 1–24 (Pl. X.) are reproductions of the traces obtained with the apparatus under various conditions. It should be noted that while the trace of the lower bob gives the actual amplitude of the vibrations of this pendulum, the trace of the upper bob is proportional but not equal to the actual amplitude of its vibrations, owing to the occurrence of a proportionality factor due to the reflexion of the light at the mirrors D and its passage through the lens L. The proportionality factor is the same in any pair of photos, but is not in general the same for any two photos selected at random.

The reproductions are arranged in pairs, one for the upper bob displaced, and the other for the lower bob displaced as initial conditions, and each with the same coupling. The dependence of the details of the traces on the initial conditions is thus strikingly illustrated in certain cases.

Figs. 1–8 (Pl. X.) are traces obtained for the case in which the ratio of the masses ρ was $3:2$, and that of the frequencies η $7:12$. Except in figs. 4 and 8, the traces of the lower bob are seen to be very nearly simple sine curves, the amplitude of the second component vibration being so small as not to affect the curve appreciably, while the traces of the motion of the upper bob are throughout complex, showing distinctly the existence of the two superposed vibrations.

Figs. 4 and 8 show component vibrations, the frequencies of which are very nearly as $2:1$, the characteristic kink of the $2:1$ curve showing plainly. Comparison with Table I.

shows that the agreement between theory and experiment is satisfactory.

Figs 9–16 (Pl. X.) are traces obtained for the case $\rho = 1$ and $\eta = 1.083$. The figures show clearly the phenomenon of beats with a progressive increase in the difference between the frequencies of the component vibrations.

Figs. 17–24 (Pl. X.) are traces obtained for the case $\rho = 0.67$ and $\eta = 1.45$. They show well the dependence of the traces on the initial conditions, the trace of the bob which was started being in this case almost a simple sine curve throughout, while the other trace is complex. The figures show that the bob which is first started can have a very considerable amplitude of vibration without producing any great amplitude in the coupled vibration of the other bob.

V. Summary.

1. In the present paper, the mathematical theory of a coupled system consisting of a gravity and an elastic pendulum is developed for the general case, in which the masses and periods of the two pendulums were both unequal.

2. The paper is illustrated by 24 photographic reproductions of the double traces obtained for the motions of the pendulums under various conditions of starting and coupling.

3. This mechanical case possesses features analogous to the electrical case of coupled circuits of which both the inductances and periods are unequal and can be used to illustrate the latter.

Physical Department,
University College, Nottingham,
June 10th, 1920.

XXXVIII. *Advance of Perihelion of a Planet.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN the May number of the 'Philosophical Magazine,' Prof. Anderson, applying the transformation,

$$r = r_1 \left(1 + \frac{m}{2r_1} \right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

to the equations for the motion of a planet

$$\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 = c^2 - 1 + \frac{2m}{r} + \frac{2mh^2}{r^3}, \quad \text{(ii.)}$$

$$r^2\frac{d\theta}{ds} = h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

reaches equations from which he argues that no motion of perihelion is to be expected, but only non-constancy in the rate of description of areas, although he does not appear to show where the supposed fallacy in Einstein's argument lies. Now the small additional term $\frac{2mh^2}{r^3}$ in (ii.) which is introduced by Einstein's theory is of order $\left(\frac{m}{r}\right)^2$ (for h will be of the same order as in Newtonian mechanics, where $h = \sqrt{ma(1-e^2)}$); and therefore, as Prof. Anderson is admittedly neglecting squares of m — i. e. terms of order $\left(\frac{m}{r}\right)^2$,—it is to be expected that (i.) will transform (ii.) into the ordinary Newtonian equation

$$\left(\frac{dr_1}{ds}\right)^2 + r_1^2\left(\frac{d\theta}{ds}\right)^2 = c^2 - 1 + \frac{2m}{r_1}, \quad . \quad . \quad \text{(iv.)}$$

where $c^2 - 1$ is identified with $-\frac{m}{a}$. In fact, we are not making use of Einstein's theory at all, and the equation

$$r_1^2\left(1 + \frac{2m}{r_1}\right)\frac{d\theta}{ds} = h, \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

which Prof. Anderson obtains by applying transformation (i.) to (iii.) has no more significance than it would have if we were treating the problem on purely Newtonian lines.

It is perhaps of interest to note that if we substitute for r from (i.) in (ii.) and (iii.) and do not neglect terms in $\left(\frac{m}{r}\right)^2$ we obtain, as is to be expected, an equation of motion giving the advance of perihelion. Equations (ii.) and (iii.)

when combined give

$$\left(\frac{h}{r^2}\frac{dr}{d\theta}\right)^2 + \frac{h^2}{r^2} = c^2 - 1 + \frac{2m}{r} + \frac{2mh^2}{r^3}, \quad . \quad . \quad \text{(vi.)}$$

and then using (i.) and neglecting terms of order higher than $\left(\dfrac{m}{r_1}\right)^2$ we obtain after reduction

$$\frac{h^2}{r_1{}^4}\left(\frac{dr_1}{d\theta}\right)^2 + \frac{h^2}{r_1{}^2} = c^2 - 1 + c^2\frac{4m}{r_1} - \frac{2m}{r_1} + \frac{6m^2}{r_1}, \quad . \quad \text{(vii.)}$$

or writing $u = \dfrac{1}{r_1}$, and differentiating with respect to θ,

$$\frac{d^2u}{d\theta^2} + u = \frac{m}{h^2}(2c^2 - 1) + \frac{6m^2}{h^2}u. \quad . \quad . \quad \text{(viii.)}$$

If we identify c^2 with $1 - \dfrac{m}{a}$, and note that $\dfrac{2m^2}{ah^2}$ and $\dfrac{6m^2}{h^2}u$ are second order terms, we obtain as an approximate solution:

$$u = \frac{m}{h^2}\Big(1 + e\cos(\theta - \varpi)\Big), \quad . \quad . \quad . \quad \text{(ix.)}$$

as in Newtonian mechanics, and proceeding to a second approximation on the usual lines, integrating and neglecting terms which will have no appreciable effect in the solution, we have:

$$u = \frac{m}{h^2}\Big(1 + e\cos(\theta - \varpi) + \frac{3m^2}{h^2}\cdot e\cdot\theta\cdot\sin(\theta - \varpi)\Big)$$

$$= \frac{m}{h^2}\Big(1 + e\cos(\theta - \varpi - \delta\varpi)\Big),$$

where $\dfrac{\delta\varpi}{\theta} = \dfrac{3m^2}{h^2}$ and gives the advance in perihelion per revolution.

Yours faithfully,
E. S. Pearson.

Trinity College,
Cambridge.

XXXIX. *The Ignition of Gases at Reduced Pressures by Impulsive Electric Sparks.* By W. M. THORNTON, *Professor of Electrical Engineering in Armstrong College, Newcastle-on-Tyne*[*].

1. *Introduction.*

IGNITION by discharge across a fixed spark-gap is a complex function of the nature of the gas, the mode of production of the spark, and the gas pressure. The discharge is intermittent[†] and in part oscillatory, the first spark of the train being a bright active capacity discharge, the remainder tailing off in brightness and igniting power. Paterson and Campbell's researches deal fully with most of the variables. Their result that the first spark of the train alone can determine ignition is of the first importance. The object of the present work was to examine whether the singular variations of inflammability previously observed in coal gas[‡] were regular phenomena of ignition of gases at reduced pressure, and if so to determine their cause.

A large induction-coil was used, with the primary condenser short-circuited, and the current broken by a switch of very rapid action. Since the speed and nature of the primary break is copied in the manner of rise of the secondary voltage, a clean rapid separation by a large quick-break switch gives a sharper and higher voltage than a break made by a slow scraping contact, and ignition phenomena are known to depend upon the rapidity of break. Platinum poles 2 millimetres diameter with rounded ends were used throughout and kept bright.

The gases examined were confined to hydrogen, methane, ethane and propane, carbon monoxide, and coal gas as a mixture of some of these.

2. *Nature of Disruptive Sparks.*

Ionization in gases has three well-marked stages which occur in succession as the electric field is increased; an approach to saturation, the electronic state, and ionization by collision. The last begins with values of X/p, volts per centimetre per millimetre of mercury pressure, greater than 50. Higher values than this were used here, at least twice as great. Before the electronic state is reached the current

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[*] Communicated by the Author.
[†] C. C. Paterson and N. Campbell, Proc. Phys. Soc. vol. xxxi. Part IV. June 15, 1919, p. 177.
See also J. D. Morgan, 'Electric Spark Ignition,' Chap. II.
[‡] "The Reaction between Gas and Pole in the Electrical Ignition of Gaseous Mixture," Proc. Roy. Soc. A, vol. xcii. p. 16 (1915).

is known to be carried by ions, with a group of molecules surrounding each, which groups become smaller as the field and velocity of ions increase until there is a state of free electrons in equilibrium with inert molecules. Above this ionization is caused by collision of electrons, moving with very high velocity in the electric field, with molecules. This then is the state in which, on the eventual passage of a spark, ignition occurs. The molecules of combustible gas and air in and near an electric arc are both, according to the work of Lowry * and Haber and Koenig †, ionized by contact with it. They then form groups in which electric recombination occurs. When in the present case of disruptive discharge there is a complete bridge of ions between the poles, a spark passes and ignition may or may not follow. The dividing line is extremely sharp. A change of one per cent. of the primary current frequently converts a spark, apparently brilliant but still inert, into one that gives certain ignition. Something more than ionization is needed. There is a critical intensity of spark, that is a certain number of ions produced *per second* to ensure ignition. Time enters as a principal factor as it has been shown to do with the slower transient arcs which form circuit break sparks.

The spectrum of disruptive sparks contains lines both of the gas and material of the poles, but the latter lines are secondary and arise from finely divided metal carried over by the first current rush from the poles. There is, however, as seen by the luminosity, intense energy of vibration as well as translational energy of electrons in the spark, and to start an explosion of gas certainly requires a finite liberation of energy at the source, first in the spark and then by combustion of the gas, sufficient to continue the latter by self-ignition after the spark ceases.

3. *Ignition by Disruptive Sparks.*

There is then in ignition by jump sparks the following sequence of events. First, ionization leading up to ionization by collision probably of all gases present, increasing until a spark passes which releases the electrostatic energy at the terminals, and by introducing a conducting path across the gap allows a current to pass equal to the momentary resultant voltage divided by the resistance of the high-tension windings of the coil. Around this current there is a magnetic field, which as the induced voltage impulse dies down decays with oscillations and prolongs the duration of the spark.

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* T. M. Lowry, J. C. S. 101. p. 1152 (1912) ; Faraday Soc. ix. p. 189 (1913).

† Haber and Koenig, *Zeitsch. Electrochem.* xiii. p. 725 (1907); xiv. p. 689 (1908).

4. *Pressure and Temperature in the Spark.*

The temperature of a disruptive spark, like that of an arc, is probably not the same throughout. Towards the positive pole the spark is brighter. This brightness falls off as the pressure is reduced and eventually forms a glow corresponding to the positive column in a vacuum-tube. In a steady arc the heat is greatest at the positive pole, and the temperature is at most that of vaporization of the electrode. The observation * that the first spark of an oscillatory series passes through air and the succeeding sparks through the vapour of the metal of the electrodes, indicates that this initial spark has a higher voltage gradient and temperature than those following. A higher temperature would to some extent explain the fact, quoted in § 1, that this first spark has greater power of ignition than the others; it certainly has a higher voltage gradient. When the circuit is inductive the metal lines appear in the spectrum of the first spark also. Apart from energy, all records of ignition show that the discharge of a condenser with relatively low inductance in series has greater activity as a source of ignition than a single jump spark from an induction-coil.

From photographs of spark discharge the actual breakdown which constitutes a disruptive spark takes place along a localized narrow chain of ions. The volume of the spark as such does not appear to be inversely proportional to the pressure but is more nearly constant. Thus the lower the pressure the fewer the number of molecules affected. Haschek and Mache's conclusion † that pressures of 60 to 120 atmospheres occur in induction-coil spark discharge can be taken to indicate transient temperatures higher than those of the steady carbon arc. The pressures in condenser discharge sparks have been estimated ‡ to approach 1000 atmospheres, and these sparks pit platinum freely, single induction-coil discharge does not. The temperatures in disruptive spark discharge are in any case much higher than are required for ignition by a steady source of heat.

At pressures lower than atmospheric the rise of pressure in the spark and the temperature of discharge fall steadily. If ignition depended upon temperature alone it should increase in difficulty as the pressure is reduced until a temperature is reached where a gas could not transmit flame.

When ignition is by hot wires, inflammation is obtained at pressures as low as 10 centimetres of mercury, or 0·13 of an

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* Schuster and Hemsalech, Phil. Trans. vol. cxciii. p. 189 (1899).
† Wied. *Ann.* lxviii. p. 740 (1899).
‡ Sir J. J. Thomson, ' Conduction through Gases,' p. 517.

atmosphere. In the present case it was never obtained
below 0·25 atmosphere. In vacuum-tubes the temperature
of the bright bands of the striated positive column is about
100° C., too low in any case to ignite gas. At some point
about an eighth of an atmosphere ignition appears to fail,
but the fact that with different kinds of ignition the lower
limiting pressure may change from 0·13 to 0·4 of an atmo-
sphere shows that the argument of a simple thermal limit to
ignition will not hold. That there is thermal effect cannot
be doubted, and the hyperbolic form of some of the curves
suggests that in certain cases it may be more marked than
others, but the singular variations, from which no mixtures
are free, show clearly that there are reactions other than
thermal between the spark and gas which profoundly modify
the process of ignition, especially of the simpler gases such as
hydrogen and methane.

5. *General nature of results.*

The curves of figs. 1 to 6 have as ordinates the magnitude of
the primary current which when broken gives a secondary
spark just causing ignition.

Considering figs. 1 to 6 as a whole, and remembering
that the secondary voltage of a transformer having an open
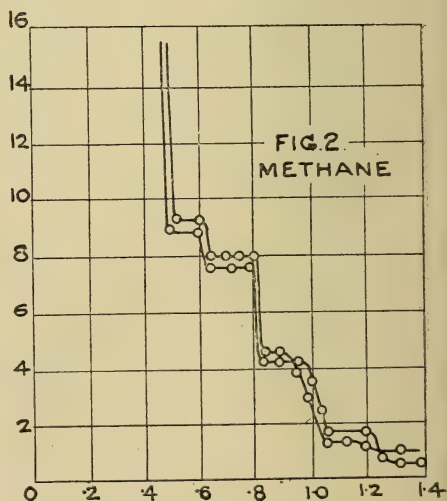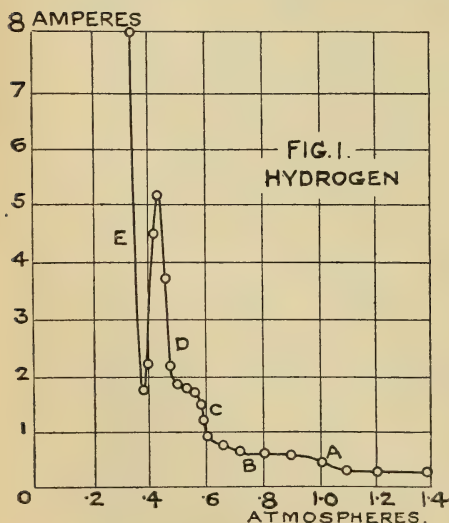
magnetic circuit and carrying a small current is proportional
to this primary current, the first observation is that as the
gas pressure is lowered difficulty of ignition rises, on account

partly of the lower thermal energy per unit volume of the mixture. The curves were all obtained with the same break, and the causes of any singularities are to be looked for in the gas and not in the spark alone. The second significant
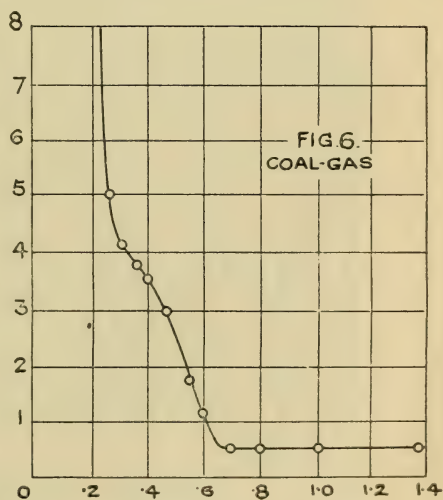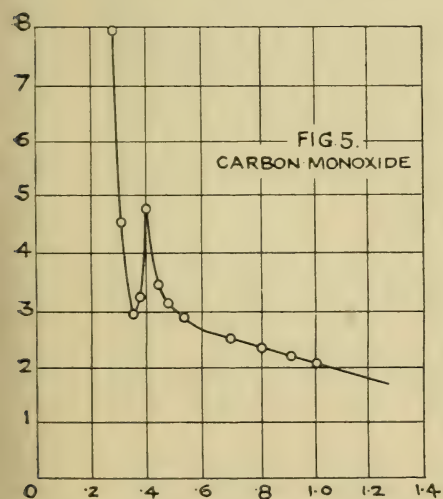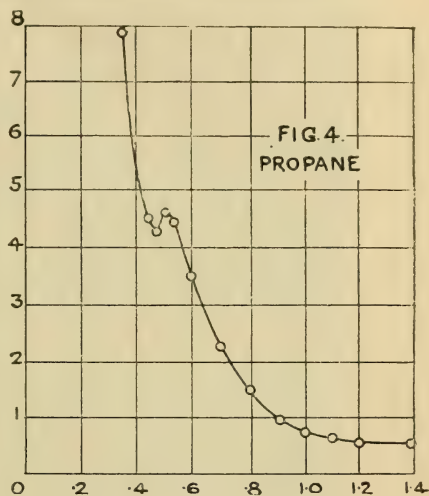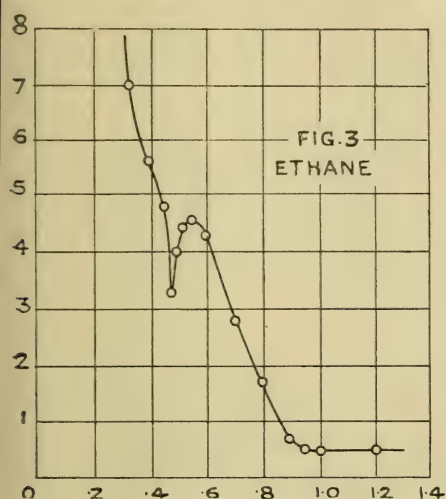
feature is that all the curves have sudden changes or points of inflexion at about 0·4 of an atmosphere. Now it has been shown elsewhere that this pressure is a critical one in all ignition by transient sources, as distinct from hot wires, and since there is ionization in all these cases and no other electrical action

that might give rise to singularities of the kind observed, the inference is that there is a change of type of ion, from clusters of molecules to the electronic state for example, or of numbers of ions, which retards ignition, finally in the case of methane, partially in hydrogen and the other paraffins, and gives rise to the point of inflexion in coal-gas. The evidence of the next two sections supports the view that any such critical points depend more on group formation than upon duration of spark, though in ignition by transient arcs the latter undoubtedly has great influence. But the first and most decisive condition is that the temperature of the point from which the spark starts should be sufficient to permit discharge of ions from the heated surface under the momentary high voltage gradient, and this discharge appears to have a critical value at ·4 of an atmosphere.

6. *Hydrogen.*

The points on the curve of fig. 1 are the results of many observations of explosions. There are in the curve five distinct stages. Here as in steady arc phenomena atmospheric pressure is a point of transition. In passing through it the current is doubled. There is from A to B no change in the current. It then begins to rise, slowly at first, suddenly at C, approaches another steady state and then goes through a violent fluctuation in the neighbourhood of 0·4 atm., reaching the limit of inflammability at a little over 0·3 of an atmosphere. This well-marked oscillation of inflammability of hydrogen at low pressures has been previously observed in the ignition of coal gas by condenser discharge sparks*, but the approach to it was then smooth. It does not occur in hot-wire ignition†. The two steps from A to B and C to D do not occur in break-spark ignition of hydrogen. There is no sudden change of the chemical or thermal properties of the mixture as a whole to account for them. They appear to be a consequence of critical relations between time of molecular contact in collision and time of action of the spark, of the same nature as the steps in methane.

From the values of the ratio e/m clusters of molecules are known to be formed around an electric charge and can to some extent be identified. The groups change in size by the successive loss of molecules, and it is in the integral relations

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* "The Reaction between Gas and Pole," *loc. cit.* fig. 5.
† "The Ignition of Gases by Hot Wires," Phil. Mag. vol. xxxviii. p. 628 (Nov. 1919).

between the numbers of molecules in such groups that the observed sudden stages in ignition are here considered to arise.

There are in hydrogen-air mixtures two such possibilities, the clusters may be of hydrogen molecules around an activated oxygen molecule, or the reverse. The molecules through which the spark immediately passes may even be dissociated by its extremely high temperature so that, as in arcs, transient groups in which there are atoms may be formed. The ratios of collision frequency between hydrogen molecules in a mixture can be varied in two ways, by changing the proportion of gas to air, or by changing the pressure of a mixture of fixed composition. A variation of action which takes place as a consequence of change of pressure can be expressed in terms of the corresponding variation of composition. There was no *a priori* reason to expect that such a mode of interpretation would explain the salient points of the ignition curves, but it appears on making the comparison that there is a suggestive coincidence of this nature.

The composition of the mixture was 29·2 per cent. of hydrogen by volume in air, giving the proportion $H_2 + O$. By raising the proportion of hydrogen a series of mixtures is obtained in which the ratio of combustible gas to oxygen has the values of the natural numbers in succession. Taking the collision frequency in the $H_2 + O$ mixture at atmospheric pressure as unity that in the other mixtures is given below.

TABLE I.

Mixture.	Per cent. in Air.	Ratio of collision frequencies.	Observed steps at
$H_2 + O$	29·2	1·0	1·0
$2H_2 + O$	45·2	0·64	·6
$3H_2 + O$	55·2	0·53	—
$4H_2 + O$	62·2	0·47	·48
$5H_2 + O$	67·4	0·43	—
$6H_2 + O$	70·2	0·41	·4
$8H_2 + O$	76·8	0·38	·38
$10H_2 + O$	80·7	0·36	—

The third column is the pressure in atmospheres which has the same ratio of collision frequency or partial pressure as the mixtures in the second column at atmospheric pressures.

On the other hand, the ratio may be reduced by lowering the proportion of hydrogen to oxygen as follows:—

Table II.

Mixture.	Per cent. in Air.	Collision frequency.
$O + H_2$	29·2	1·0
$O_2 + H_2$	17·1	0·58
$O_3 + H_2$	12·1	0·41
$O_4 + H_2$	9·35	0·32
$O_5 + H_2$	7·12	0·26
$O_6 + H_2$	6·44	0·22

Certain of the numbers in the third column of Table I. are close to those in Table II., so that in the event of these coinciding with the critical stages in ignition it would be difficult to discriminate between them. The curve rises suddenly at 1·0, 0·6, 0·48, falls through a mean value at about 0·4 and has a minimum at 0·38. The evidence is if anything in favour of Table I., that is, of ignition rising suddenly in difficulty with each added molecule of hydrogen. This is in general agreement with the facts of ignition by condenser discharge sparks, which passes through critical rising steps when the proportions of hydrogen in air are 29·2, 45·2, 55·2, and 70 per cent.*

And in all kinds of ignition by direct sparks previously examined excess of oxygen is favourable to electrical ignition, though it is not to final combustion, while excess of hydrogen retards it. It is therefore improbable in the above argument that the sudden jumps of difficulty of ignition are due to excess of oxygen, though they may be to excess of hydrogen.

7. *Methane.*

The curve of fig. 2 has similar points of interest. There are steps at 1·0, 0·8, 0·6, and 0·45 atmosphere. The mixture for perfect combustion taking air as 4·85 times the contained oxygen is 9·35 per cent. Proceeding as in hydrogen we have:—

Table III.

Mixture.	Per cent. in Air.	Ratios.	Observed steps at.
$CH_4 + O_5'$	7·64	1·22	1·25
$CH_4 + O_4$	9·35	1·0	1·0
$CH_4 + O_3$	12·0	0·78	0·8
$CH_4 + O_2$	17·1	0·54	0·6
$2CH_4 + O_3$	21·6	0·43	0·45

* "The Ignition of Gases by Condenser Discharge Sparks," Proc. Roy. Soc. A, vol. xci. p. 17 (1914).

There is here an agreement between the possible ratios and the pressures at which steps were observed which is on the whole too close to be accidental. It is possible that the slower rate of initial combination of methane and oxygen is favourable to the production of these well-marked stages. Similar steps have been shown to coincide when ignition is by condenser discharge.

An action of this kind is not to be expected, though it cannot be ruled out as impossible, when ignition proceeds by general bombardment over the wave-front as in an established travelling flame. It is most likely to occur when in addition to the normal time of combination of the two gases another element is introduced, in this case the time of duration of the spark and of the ionization that leads up to it.

The explanation now offered why the electrical spark impulse necessary for igniting gas changes suddenly when the proportion of gas to oxygen goes through certain values, is that in the passage of a spark ions necessary for chemical combination are formed, and that before these have recombined electrically and become inert, combustion has begun. The proportions of gas and oxygen in the upper and lower limit mixtures show* that in these mixtures there is a sudden change of inflammability determined solely by the ratios of the numbers of oxygen atoms to one of combustible gas. What is now found is that when the source of ignition has a very short duration these steps occur whenever the proportion of oxygen atoms to combustible gas passes through integral values such as the first few natural numbers.

Change of gas pressure has the same effect on the rate of group formation as change of proportion of the mixture. From a purely electric point of view steps might occur when the conductivity of the sparking path changed suddenly. It is only possible to imagine such a change taking place after chemical combination has begun, but if the rate of development of the latter is so slow that a definite time of duration of spark is necessary to allow it to work up to a state of self-ignition, it might appear to have an electrical origin and to explain Paterson and Campbell's stepped ignition curves as depending on an instantaneous change of capacity, but the origin of their steps and those now observed would be the same.

* "The Limits of Inflammability of Gaseous Mixtures," Phil. Mag. vol. xxxiii. February 1917, p. 190.

8. *Ethane and Propane, and the cause of their oscillation.*

When there are no singularities such as those first dis-
cussed there is the oscillation of inflammability found in
the neighbourhood of 0·4 atmosphere pressure. Such a
variation has been observed in the case of ignition by
transient arcs and it is there much more pronounced than in
figs. 3 and 4, for ethane and propane. As the pressure
is lowered the arc goes through a remarkable change of
condition and is for a time unstable. Its length and dura-
tion suddenly diminish almost with discontinuity. As the
pressure is still further reduced the arc again lengthens and
changes type from a sharply defined discharge to a glow.
This eventually extends so that when the mechanical break
is about one and a half centimetres the arc persists as a
brightly luminous though cool discharge, showing striations
or pulsations of brightness as it is drawn out.

From examination of some eight hundred photographs of
transient arcs at low pressure it became evident that as the
pressure is reduced the temperature of the point of the cathode
from which the arc starts is lowered until a point is reached
where it is insufficient to start a discharge of metallic vapour
or of large ions through which the arc can be maintained.
The extreme suddenness with which this state is reached
resembles that observed by Sir J. J. Thomson at lower
pressures*, where a small change of cathode temperature
suffices to lower the current to a hundredth of its previous
value. This point corresponds to an increase of difficulty of
ignition because of the smaller size and less duration of
the arc.

Following this period of inaction there appears with almost
equal suddenness a discharge similar to an arc but without
the distinctive features of one started by a hot cathode.
It is rather the commencement of the positive glow and is a
relatively low-temperature discharge in which ionization is
active. Disruptive spark discharge at low pressure does not
show any such changes of length, the product of spark length
and pressure is constant. When, however, the spark-gap is
fixed and small the magnitude of the primary current is a
measure of the current in the spark, and the temperature of
the points as affected by the magnitude of the current changes
with it. So far as this is the case the action is not unlike
that of a transient arc.

The ordinates of the curves of ignition of ethane and
propane show sudden fluctuations at nearly the same point.

* 'Conduction of Electricity through Gases,' p. 480.

That of ethane is a definite increase of inflammability, that of propane is not more than an indication of its presence. The propane curve is otherwise an approach to the hyperbolic form associated with ignition by condenser discharge at low pressures.

Comparing the hydrogen and methane curves in view of the above, the commencement of the glow stage, which is probably that of ionization by collision rising suddenly to saturation, is seen to be unfavourable to the ignition of methane, favourable to that of hydrogen. Now according to Bone's accepted theory[*], the combustion of methane proceeds by the successive addition of atoms of oxygen to the hydrogen of the molecule. In the normal high-temperature arc or spark oxygen is dissociated and atomic oxygen is free to combine and start self-ignition. As the pressure is reduced and the sparks become cooler there is less of this action and in the glow discharge high-temperature dissociation will almost cease. There are then present molecules and free electrons, a state which is perhaps less favourable to combination than when oxygen is atomic.

On the other hand, Bone has shown that "in explosion flames hydrogen is directly burnt to steam as the result of trimolecular impacts," and a phase in which there is ionization of molecules of gas by collision with electrons without dissociation is favourable to such an action. It has been shown elsewhere that as the gases rise in the paraffin series ignition, which became suddenly more difficult in the step from hydrogen to methane, becomes easier, and that pentane approaches hydrogen in sensitiveness and type. Ethane and propane are intermediate, and it is not difficult to follow the transition from the methane curve of fig. 2, by that of ethane to that of propane, falling in towards the origin and showing, though to a much smaller extent, the fluctuation so marked in hydrogen.

9. *Carbon Monoxide.*

The curious cusp in fig. 5 has been found in carbon monoxide with more than one kind of ignition. It is a sudden but not permanent increase of difficulty of ignition occurring at much the same pressure as the change first discussed. It would appear to depend more upon the variation of spark intensity, or temperature of the pole at the

[*] W. A. Bone and others, "Gaseous Combustion at High Pressures," Phil. Trans. ser. A, vol. 215. p. 304.

point of sparking, than upon anything else; in this resembling the oscillation of hydrogen at the same pressure. The cause of this has been discussed in § 8.

10. *Coal Gas.*

This is a mixture containing about 50 per cent. hydrogen, 35 per cent. methane, 10 to 15 per cent. carbon monoxide. Its curve of ignition, fig. 6, shows clearly the influence of hydrogen and methane but not of carbon monoxide. The magnitude of the currents and the shape of the curve at pressures not much below atmospheric resemble hydrogen. The straight part of the curve is a mean line through the methane steps. The point of inflexion occurs at the same pressure as the oscillations in hydrogen and carbon monoxide, and gives to the curve a form similar to that of the pressure-volume curve of a gas at the critical temperature. In the present case the analogue of temperature is the reciprocal of time of duration of the igniting impulse. The curve is of interest in showing the modification of the hydrogen type by methane, though the gas in all essentials behaves as hydrogen.

11. *Conclusions.*

Ignition by impulsive sparks is on the whole more difficult at low pressures, in this differing from ignition by hot wires. In hydrogen and methane the increase of difficulty takes place by well-marked steps or stages. In ethane and propane these do not occur, but there is an oscillation of the curve, found also in hydrogen and carbon monoxide. This appears to be associated with the temperature of the sparking point during the passage of the spark. It has been shown previously that at pressures well above atmospheric sudden changes of inflammability occur when ignition is by impulsive sparks or condenser discharge. It is now found that there are such steps at reduced pressures and that there is a close agreement between the partial pressures corresponding to the points at which oxygen has ratios to the mass of combustible gas expressed by successive natural numbers, and the pressures at which sudden changes of inflammability occur.

XL. *The Variation of the Specific Heat of a Gas with Temperature.* By GEORGE W. TODD, *M.A.(Cantab.), D.Sc.(Birm.), Professor of Experimental Physics, Armstrong College, Newcastle-on-Tyne* [*].

THE criticisms which are frequently brought up against the principle of the equipartition of energy among the degrees of freedom of the molecules of a gas are the experimental observations (a) that the molecular heat varies with the temperature when it should be $C = \dfrac{\partial}{\partial \theta}\left(\dfrac{n}{2} R\theta\right) = \dfrac{n}{2} R$, and (b) that the ratio of the specific heats of a gas also varies with the temperature when it should agree with the equation $\gamma = 1 + \dfrac{2}{n}$, n being the number of degrees of freedom. It is often argued that since one cannot have a fractional degree of freedom, then if C and γ do change with temperature, the changes should take place in steps.

It will be shown that the criticisms are unjust and that the principle will account for the available experimental facts, as well as does the quantum theory which discards altogether the equipartition principle.

The Specific Heat at Constant Volume.

Adopting a method of treatment similar to that used in previous papers [†], we will assume that the gas molecules have three degrees of freedom so long as their velocities are below a critical value. Above this critical value we assume that the collisions result in added degrees of freedom (*e. g.* rotation produced). Let the number of degrees of freedom added be q.

The number of molecules per c.c. with velocities between c and $c + dc$ is

$$\frac{4}{\sqrt{\pi}} N \left(\frac{m}{2R\theta}\right)^{3/2} e^{-\frac{mc^2}{2R\theta}} c^2 . dc,$$

where the symbols have their usual significance.

The translational energy of these molecules is therefore

$$\frac{2}{\sqrt{\pi}} \mathrm{N}m \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} e^{-\frac{mc^2}{2\mathrm{R}\theta}} c^4 \, . \, dc.$$

So that the kinetic energy of molecules in 1 c.c. having velocities greater than a critical value c is

$$\frac{2}{\sqrt{\pi}} \mathrm{N}m \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} \int_c^\infty \phi \, . \, dc, \quad \text{where } \phi = e^{-\frac{mc^2}{2\mathrm{R}\theta}} \, . \, c^4.$$

The total energy of these molecules is

$$\frac{3+q}{3} \frac{2}{\sqrt{\pi}} \mathrm{N}m \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} \int_c^\infty \phi \, . \, dc.$$

The translational energy of molecules in 1 c.c. with velocities less than c is

$$\frac{2}{\sqrt{\pi}} \mathrm{N}m \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} \int_0^c \phi \, . \, dc,$$

and since by hypothesis these have only three degrees of freedom, this is also their total energy.

Hence the *total energy of 1 c.c.* of the gas is

$$(\mathrm{T}o) = \frac{2}{\sqrt{\pi}} \mathrm{N}m \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} \left\{ \frac{3+q}{3} \int_c^\infty \phi \, . \, dc + \int_0^c \phi \, . \, dc \right\} . \quad (1)$$

It follows that the *Specific Heat at Constant Volume* will be given by

$$\mathrm{K}_v = \frac{\partial}{\partial\theta}\left(\frac{\mathrm{T}o}{\mathrm{N}m}\right)$$

$$= \frac{2}{\sqrt{\pi}} \frac{\partial}{\partial\theta} \left\{ \left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2} \left(\frac{3+q}{3} \int_c^\infty \phi \, . \, dc + \int_0^c \phi \, . \, dc\right) \right\}. \quad (2)$$

When $q=0$, the equation becomes

$$\mathrm{K}_v = \frac{2}{\sqrt{\pi}} \frac{\partial}{\partial\theta} \left\{ \frac{2\mathrm{R}\theta}{m} \frac{3\sqrt{\pi}}{8} \right\} = \frac{3}{2} \frac{\mathrm{R}}{m},$$

which is the usual expression for a monatomic gas.

Now the integral

$$\int \phi \, . \, dc = \left(\frac{2\mathrm{R}\theta}{m}\right)^{5/2} \int e^{-x^2} x^4 dx, \quad \text{where } x = c\sqrt{\frac{m}{2\mathrm{R}\theta}},$$

so that

$$\int_c^{\infty} \phi \cdot dc = \left(\frac{2R\theta}{m}\right)^{5/2} \left\{ \frac{1}{2} x^3 e^{-x^2} + \frac{3}{4} x e^{-x^2} + \frac{3}{4} \int_x^{\infty} e^{-x^2} \cdot dx \right\}$$

$$= \left(\frac{2R\theta}{m}\right)^{5/2} \left\{ \frac{1}{2} x^3 e^{-x^2} + \frac{3}{4} x e^{-x^2} + \frac{3}{8} \frac{1}{x} e^{-x^2} \right\}^*.$$

The integral

$$\int_0^c \phi \cdot dc = \int_0^{\infty} \phi \cdot dc - \int_c^{\infty} \phi \cdot dc$$

$$= \left(\frac{2R\theta}{m}\right)^{5/2} \left(\frac{3\sqrt{\pi}}{8} - \frac{1}{2} x^3 e^{-x^2} - \frac{3}{4} x e^{-x^2} - \frac{3}{8} \frac{1}{x} e^{-x^2} \right).$$

Equation (2) now becomes

$$K_v = \frac{2}{\sqrt{\pi}} \frac{\partial}{\partial \theta} \left[\frac{2R\theta}{m} \left\{ \frac{3\sqrt{\pi}}{8} \right. \right.$$

$$\left. + \frac{q}{3} \left(\frac{1}{2} x^3 e^{-x^2} + \frac{3}{4} x e^{-x^2} + \frac{3}{8} \frac{1}{x} e^{-x^2} \right) \right\} \Bigg]$$

$$= \frac{3}{2} \frac{R}{m} \left[1 + \frac{8qE}{3\sqrt{\pi}} e^{-\frac{E}{\theta}} \left\{ \frac{1}{6} E^{\frac{3}{2}} \theta^{-\frac{5}{2}} + \frac{1}{6} E^{\frac{1}{2}} \theta^{-\frac{3}{2}} \right. \right.$$

$$\left. \left. + \frac{3}{16} E^{-\frac{1}{2}} \theta^{-\frac{1}{2}} + \frac{3}{16} E^{-\frac{3}{2}} \theta^{\frac{1}{2}} \right\} \right] \quad . \quad . \quad (3)$$

where $\qquad E = \frac{mc^2}{2R}.$

Eucken [†] has determined experimentally the molecular heat of hydrogen at low temperatures, and he obtains the very important result that at very low temperatures the gas behaves as if it were monatomic. Some of his values are given below :—

θ abs. ...	35	40	45	50	60	65	70	80	90	100	110	196·5	273
mol. ht....	2·98	2·98	3·00	3·01	2·99	3·04	3·10	3·14	3·26	3·42	3·62	4·39	4·84

If we put $E = 625$ and $q = 2$ in equation (3), we get the following results :—

θ abs.	9	36	64	81	100	121	144	196	256
$K_v \div \left(\frac{3}{2} \frac{R}{m}\right)$.	1·000	1·000	1·009	1·043	1·113	1·215	1·335	1·542	1·677

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* See Todd & Owen, Phil. Mag. vol. xxxvii. p. 227.

† Eucken, *Sitzungsber. kön. preuss. Akad. Wissenschaft.* 1912.

These figures give the continuous line in fig. 1, and Eucken's experimental values are shown as small circles.

Fig. 1.
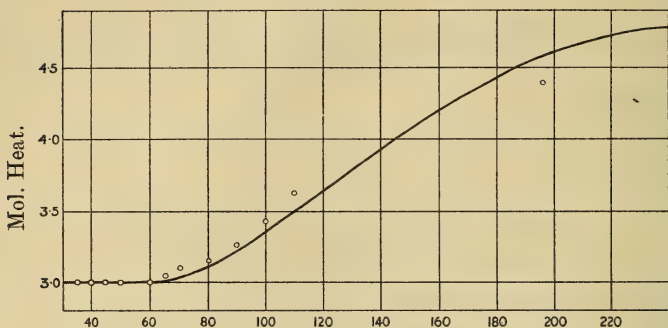
The agreement is good. Of course, if further degrees of freedom develop at higher critical molecular velocities, the expression for K_v will be modified, and the theoretical curve, instead of running asymptotically to the value representing five degrees of freedom for every molecule, would go on rising. The development of further degrees of freedom would explain Bjerrum's [*] values for hydrogen at very high temperatures.

The Ratio of the Specific Heats.

Whatever we assume about the number of degrees of freedom of the gas molecules, the ratio of the increase in translational energy to the increase in total energy of the gas molecules is

$$\frac{\Delta(\text{T}r)}{\Delta(\text{T}o)} = \frac{3}{2}(\gamma - 1),$$

where γ is the ratio of the specific heats of the gas.

If every molecule has the same number $(3 + q)$ of degrees of freedom, then

$$\frac{\Delta(\text{T}r)}{\Delta(\text{T}o)} = \frac{3}{3 + q},$$

so that $\quad \frac{3}{2}(\gamma - 1) = \frac{3}{3 + q}, \quad$ or $\quad \gamma = 1 + \frac{2}{3 + q}.$

[*] Bjerrum, *Zeit. f. Electroch.* xvii. (1911), and xviii. (1912).

Take our case. The increase in translational energy for a rise of $1°$ C. is

$$\Delta(\mathrm{T}r) = \frac{2}{\sqrt{\pi}}\mathrm{N}m\left(\frac{m}{2\mathrm{R}(\theta+1)}\right)^{3/2}\int_0^\infty \phi_{\theta+1}\,.\,dc$$
$$- \frac{2}{\sqrt{\pi}}\mathrm{N}m\left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2}\int_0^\infty \phi_\theta\,.\,dc$$
$$= \frac{3}{2}\mathrm{N}\mathrm{R}.$$

The increase in total energy for a rise of $1°$ C. is

$$\Delta(\mathrm{T}o) = \frac{2}{\sqrt{\pi}}\mathrm{N}m\left(\frac{m}{2\mathrm{R}(\theta+1)}\right)^{3/2}\left[\frac{3+q}{3}\int_c^\infty \phi_{\theta+1}\,.\,dc + \int_0^c \phi_{\theta+1}\,.\,dc\right]$$
$$- \frac{2}{\sqrt{\pi}}\mathrm{N}m\left(\frac{m}{2\mathrm{R}\theta}\right)^{3/2}\left[\frac{3+q}{3}\int_c^\infty \phi\,.\,dc + \int_0^c \phi_\theta\,.\,dc\right]$$
$$= \frac{3}{2}\mathrm{N}\mathrm{R} + \frac{4q\mathrm{N}\mathrm{R}}{3\sqrt{\pi}}\left[(\theta+1)\left(\frac{1}{2}x_1^3 e^{-x_1^2} + \frac{3}{4}x_1 e^{-x_1^2}\right.\right.$$
$$\left.\left. + \frac{3}{8}\frac{1}{x_1}e^{-x_1^2}\right) - \theta\left(\frac{1}{2}x^3 e^{-x^2} + \frac{3}{4}x e^{-x^2} + \frac{3}{8}\frac{1}{x}e^{-x^2}\right)\right].$$

Therefore

$$\frac{\Delta(\mathrm{T}r)}{\Delta(\mathrm{T}o)} = \frac{3}{3+\dfrac{8q}{3\sqrt{\pi}}\left[(\theta+1)(x_1\text{ terms})-\theta(x\text{ terms})\right]},$$

and

$$\gamma = 1 + \frac{2}{3+\dfrac{8q}{3\sqrt{\pi}}\left[(\theta+1)(x_1\text{ terms})-\theta(x\text{ terms})\right]}. \quad (4)$$

We are now in a position to calculate the values of γ for hydrogen at low temperatures. Putting $\mathrm{E}=625$, we find

$$(\theta+1)(x_1\text{ terms}) = e^{-\frac{625}{\theta+1}}\left\{7800(\theta+1)^{-\frac{1}{2}}\right.$$
$$\left. + 18\cdot75(\theta+1)^{\frac{1}{2}} + \cdot015(\theta+1)^{\frac{3}{2}}\right\},$$

and a similar expression for $\theta(x\text{ terms})$, the only change being θ for $(\theta+1)$. After substituting these values in equation (4), we obtain the following table :—

Calculated values of γ for hydrogen at low temperatures.

θ abs.	25	81	100	121	144	169	225
Υ	1·666	1·645	1·608	1·545	1·498	1·458	1·408

The change in γ with the absolute temperature θ is shown

in fig. 2.   Unfortunately there are no experimental figures
to put beside these calculated values.

Fig. 2.
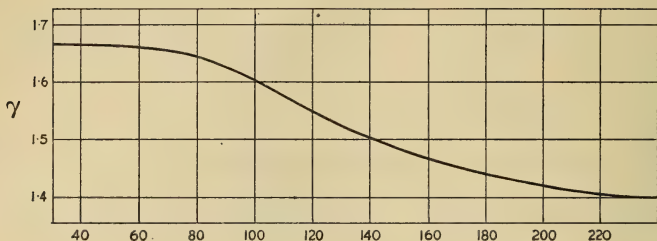
Apparently hydrogen is the only gas for which there are
experimentally determined values of the molecular heat at
low temperatures.   It will be interesting to see, when the
data become available, whether the kinetic theory will
suffice for other gases and to see whether any relations
exist between their critical energies and their physical or
chemical properties.

Armstrong College,
    Newcastle-on-Tyne,
        April, 1920.

XLI. *A Vapour Pressure Equation* *.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

1.   IN the paper by George W. Todd and S. P. Owen on
      "A Vapour Pressure Equation," which appeared
in the November issue of the Philosophical Magazine, the
authors developed the equation

$$N_v = N_1 e^{-\frac{B}{\theta}} \left(1 + \frac{B}{\theta}\right), \quad . \quad . \quad . \quad . \quad (1)$$

and from the fact that $N_v \propto p$ and $N_1 \propto \rho$ at a given absolute
temperature they obtained the equation

$$p = A\rho e^{-\frac{B}{\theta}} \left(1 + \frac{B}{\theta}\right). \quad . \quad . \quad . \quad . \quad (2)$$

It must be remembered that p is a function of both N_v and

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θ, while ρ is a function of N_1 only. Therefore A must be a function (approximately $R\theta$) of θ. Equation (1), however, may be put in the form

$$\rho_v = \rho_1 e^{-\frac{B}{\theta}} \left(1 + \frac{B}{\theta}\right), \quad . \quad . \quad . \quad . \quad (3)$$

where ρ_1 and ρ_v are the densities of liquid and vapour respectively.

2. Since $B = \dfrac{mc_1^2}{2R}$ and at the critical temperature, $\rho_v = \rho_1$, it follows from equation (3) that at this temperature $\dfrac{mc_1^2}{2R} = 0$. Hence c_1 must be a function of the temperature and cannot bear a definite relation to the molecular velocity at the critical temperature.

3. The agreement of the equation deduced with observed data cannot therefore be considered as justifying the original assumptions since additional assumptions are introduced. Considering the equation purely as an empirical one, the agreement with observation does not appear sufficiently good to make it of value.

<div align="center">Respectfully,</div>

Department of Commerce,
  Bureau of Standards,
    April 15, 1920.

Cyril H. Meyers,
  Assistant Physicist.

XLII. *On the Theory of Electrocapillarity* : I. *By* Alexander Frumkin [*].

Symbols used throughout this communication :—

    P is the ionic solution pressure.

    p is the osmotic pressure.

    γ is the surface-tension.

    ϵ is the electric charge on unit surface.

    ψ is the potential difference between a decinormal calomel electrode and the mercury in the solution.

THE classical theory of electrocapillarity of Lippman-Helmholtz, which considered the process of polarization as the charge of a condenser, led to the following equation of the electrocapillary curve

$$\frac{\partial \gamma}{\partial \psi} = \epsilon. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to this theory, the maximum surface-tension corresponds to the zero of the potential difference between the mercury and the solution. The experimental investigations of Rothmund[*], Smith[†], and Gouy[‡] have shown that this relation cannot hold generally: solutions of electrolytes which give complex salts with mercury show anomalies; the maximum of the electrocapillary curve is depressed and displaced from its normal position so as to correspond to greater values of ψ (see fig. 1, where the electrocapillary curves of $n/1$ KNO_3 and $n/1$ KI are drawn).

Fig. 1.

I.—$n/1$ KNO_3.   II.—$n/1$ KI.
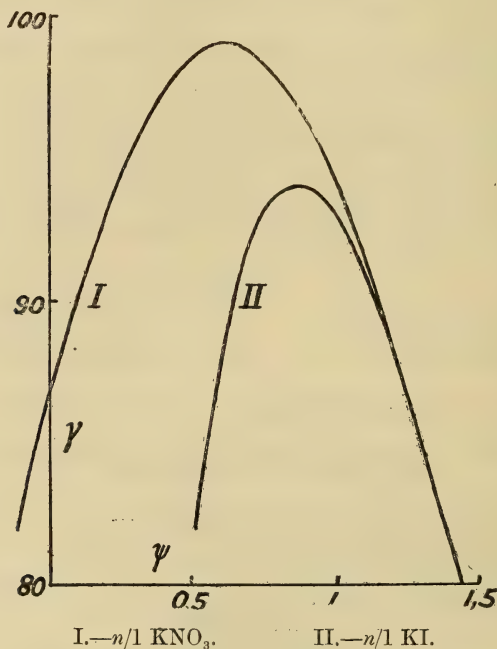
Nernst[§] showed that equation (1) may also be deduced from his "osmotic" theory of potential differences. To explain the observed anomalies, Nernst conjectured that the ions which form the double layer may have an influence on

* *Zeit. phys. Chem.* xv. p. 1 (1894).
† Phil. Trans. A. cxciii. p. 83 (1900).
‡ *Ann. chim. phys.* (7) xxix. p. 145 (1903).
§ Wied. *Ann.* lviii. (1896), *Beilage*; *Zeit. Electrochemie*, vii. p. 253 (1900).

the surface-tension independent of their electric charges and not involved in equation (1).

Freundlich [*] and Gouy [†] directed their attention to the importance of adsorption phenomena in the study of electrocapillarity. According to Gouy, ϵ is zero at the maximum of the electrocapillary curve, but there may be a potential difference between the solution and the mercury, caused by adsorbed layers of ions. I shall try to show that this point of view is the correct one and that it is incompatible with Nernst's theory of ionic solution pressure. First, we must consider the problem of the dropping electrode.

With the object of explaining the mechanism of working of a dropping electrode, the Lippman-Helmholtz theory assumes a constant quantity of electricity to be on an insulated mass of mercury; therefore the charge on unit surface and the potential difference between the solution and mercury both decrease with increase of surface. But Palmaer's [‡] experimental investigations, in agreement with Nernst's theory, have shown that the primary effect of a dropping electrode is to change the concentration of ions of mercury in the solution. If $P > p$, the potential difference between mercury and solution and the charge of the mercury surface are both negative; when the mercury surface is increased ions enter into the solution and the potential of mercury therefore increases. If $P < p$, the potential difference and the charge of the mercury are positive, by surface increase ions of mercury are removed from the solution and the potential of mercury decreases. Finally, if $P = p$—" null " solution—the potential difference and the charge of the mercury are zero, surface increase does not influence the concentration of ions of mercury, and the potential of a dropping electrode has the same value as the potential of a still one. The potential of every dropping electrode is bound to approach, independently of p, the same value, when the rate of surface increase becomes infinite; practically we obtain the limit value, as Paschen [§] has shown, if the end of the continuous part of the jet is in the surface of the solution.

Thus, if Nernst's " osmotic " theory were exact, Paschen's dropping electrodes and Palmaer's null solutions would give us a method of measuring absolute potentials not influenced

[*] *Kapillarchemie*, p. 184.
[†] *C. R.* cxlvi. p. 622 (1908); cxxxi. p. 939 (1900).
[‡] *Zeit. phys. Chem.* xxv. p. 265 (1898); xxviii. p. 257 (1899); xxxvi. p. 664 (1901); lix. p. 129 (1907).
[§] *Wied. Ann.* xli. p. 42 (1890); xliii. p. 585 (1891).

by the anomalies of the electrocapillary curves. But the investigations of Paschen, and especially those of Smith and Moss[*], have shown that the potential of the dropping electrode corresponds to the maximum of the electrocapillary curve even in the case of anomalous curves of electrolytes forming complex salts. The only attempt to explain quantitatively this coincidence, which we shall call with Smith and Moss Paschen's relation, was made by Krueger[†]. Krueger assumes that on the mercury surface there occurs adsorption of mercury salt and arrives at the following equation :

$$\frac{\partial \gamma}{\partial \psi} = \epsilon + F(k-1)c\delta,$$

where F is 96541 coulombs, k the distribution coefficient of mercury salt between the surface-layer and the bulk of the solution, c the concentration of mercury salt in the solution, and δ the thickness of the surface-layer. Let us compare two solutions like KI and KCl at equal values of ψ : the concentration of mercury in the KI solution will be much higher on account of the complex salt which HgI_2 gives with KI ; the term $F(k-1)c\delta$ will have a considerable value and cause the observed anomaly of the electrocapillary curve.

The maximum corresponds to a value of ψ which makes ϵ equal to $-F(k-1)c\delta$; the quantity of mercury salt adsorbed on unit surface therefore exactly corresponds to the quantity of mercury which entered the solution in the form of ions when the surface was increased by unity. It is obvious that under these conditions surface increase does not produce any change of concentration and the solution is a "null" one. Further, the negative value of ϵ increases with increasing stability of the corresponding complex salts, and accordingly the maximum corresponds to greater values of ψ, *i. e.* it is displaced to the right.

Krueger's reasoning is quite correct, but, as we shall show later, his supplementary term is probably much too small to account for the anomalies observed ; at any rate, Krueger's theory is not applicable to the anomalous curves of organic substances which Gouy[‡] has discovered. A suitable example of these curves may give the electrocapillary curve

[*] Phil. Mag. (6) xv. p. 478 (1908).
[†] *Nachr. d. Ges. d. Wiss. Göttingen Math.-phys. Klasse*, 1904, p. 33 ; *Zeit. Electr.* xix. p. 681 (1913).
[‡] *Ann. chim. phys.* (8) viii. p. 291, and ix. p. 75 (1906).

of $n/1\,Na_2SO_4$ saturated with paraldehyde (fig. 2, I.). The middle part of the curve is here cut away and the maximum is displaced to the left. Other organic substances, like pyrogallic acid, give curves with a maximum displaced to the right (fig. 2, II.). The potential difference solution / mercury

Fig. 2.
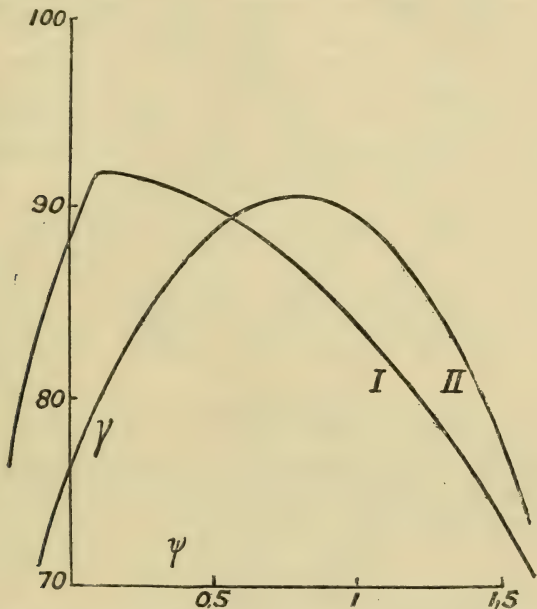
I.—Na_2SO_4+paraldehyde.　　II.—Na_2SO_4+pyrogallic acid.

does not change when paraldehyde or pyrogallic acid is added to the solution, no complex salts are therefore formed and Krueger's supplementary term must vanish. Besides, this term can cause only a displacement of the maximum to the right and never one to the left, as we usually observe in solutions of organic substances.

We shall show that Paschen's relation still holds with these solutions and that this relation can be deduced from purely thermodynamical considerations without any special assumptions as to the nature of the observed anomalies. With this purpose let us consider the classical demonstration of equation (1).

Let us suppose that a drop of mercury and an electrode, reversible for an anion, are immersed in a solution. We shall assume the concentration of the corresponding anion to be great as compared with the concentration of ions of mercury.

In consequence we may assume that the potential of the electrode remains constant when the potential of the mercury or its surface area is varied. Between the mercury and the electrode an electromotive force is inserted.

Let c be the concentration of mercury in the solution in gram-equivalents per c.cm., s the surface area of the mercury, ψ the potential difference between the electrode and the mercury, and E the quantity of electricity which has passed through the solution from the electrode to the mercury since a certain moment. Independently of the original composition of the solution the state of the system is wholly determined by the quantities s and ψ. If we increase s by ds and E by dE, the work performed will be

$$d\mathrm{A} = \gamma ds + \dot{\psi}d\mathrm{E} = \left(\gamma + \psi\frac{\partial \mathrm{E}}{\partial s}\right)ds + \psi\frac{\partial \mathrm{E}}{\partial \psi}d\psi,$$

whence

$$\frac{\partial\left(\gamma + \psi\dfrac{\partial \mathrm{E}}{\partial s}\right)}{\partial \psi} = \frac{\partial\left(\psi\dfrac{\partial \mathrm{E}}{\partial \psi}\right)}{\partial s}$$

and

$$\frac{\partial \gamma}{\partial \psi} + \frac{\partial \mathrm{E}}{\partial s} = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let us now consider the change in potential of an insulated mercury mass by surface increase.

Since now dE is zero,

$$\frac{\partial \mathrm{E}}{\partial s}ds + \frac{\partial \mathrm{E}}{\partial \psi}d\psi = 0$$

and

$$\frac{\partial \gamma}{\partial s} = -\frac{\dfrac{\partial \mathrm{E}}{\partial s}}{\dfrac{\partial \mathrm{E}}{\partial \psi}} = \frac{\dfrac{\partial \gamma}{\partial \psi}}{\dfrac{\partial \mathrm{E}}{\partial \psi}};$$

$\dfrac{\partial \mathrm{E}}{\partial \psi}$ is the quantity of electricity which must pass through the solution to increase ψ by unity. This quantity is partly spent in changing the concentration of the solution, partly in charging the double layer

$$\frac{\partial \mathrm{E}}{\partial \psi} = \left(\frac{\partial \mathrm{E}}{\partial \psi}\right)_{s=0} + \int_0^s \frac{\partial^2 \mathrm{E}}{\partial s \partial \psi}ds = -v\mathrm{F}\frac{\partial c}{\partial \psi} - \int_0^s \frac{\partial^2 \gamma}{\partial \psi^2}ds,$$

whence

$$\frac{\partial \psi}{\partial s} = \frac{-\dfrac{\partial \gamma}{\partial \psi}}{v\mathrm{F}\dfrac{\partial c}{\partial \psi} + \displaystyle\int_0^s \frac{\partial^2 \gamma}{\partial \psi^2}ds}, \quad . \quad . \quad . \quad (3)$$

v being the volume of the solution.

If $\dfrac{\partial \gamma}{\partial \psi}$ is zero, $\dfrac{\partial \psi}{\partial s}$ must also be zero, consequently, if the concentration of ions of mercury in the solution corresponds to the maximum value of the surface-tension, the potential of an insulated mercury mass does not change when its surface is increased, *i. e.* such a solution is a "null" one.

The denominator of the right-hand side of equation (3) is always negative ; in fact, $\dfrac{\partial c}{\partial \psi} < 0$, and as Gouy's [*] numerous determinations have shown $\dfrac{\partial^2 \gamma}{\partial \psi^2} < 0$; $\dfrac{\partial \psi}{\partial s}$ and $\dfrac{\partial \gamma}{\partial \psi}$ are therefore quantities of the same sign and the potential of mercury approaches, when its surface is increased, the value which corresponds to the maximum surface-tension.

Up to the present, we have considered a solution of uniform composition, depending on the value of s ; if matters were adequate to our supposition, we could, by increasing the surface, approach the maximum of the electrocapillary curve as closely as we wished and thus convert the solution into a "null" one.

In reality a dropping electrode changes the composition of the solution only in its immediate neighbourhood and a steady state soon results, determined by the rate of increase of the surface and by the rate of diffusion. If the concentration of mercury in the solution is low and the end of the continuous part of the jet is just in the surface of the solution, the influence of diffusion nearly vanishes and the potential of the dropping electrode must correspond to the maximum of the electrocapillary curve.

To verify this inference I measured both quantities in different solutions of organic substances with anomalous electrocapillary curves. The results are given in Table I. Column I. contains the maximum E.M.F., determined with a sensitive capillary electrometer of the form used by Gouy, the large mercury electrode being immersed in a $n/10$ solution of KCl; column II. the E.M.F. of the cell: Paschen dropping electrode solution/decinormal calomel electrode, both in volts.

Table I.

	I.	II.
$n/1$ NaCl + paraldehyde (saturated)............	0·225	0·216
$n/1$ NaCl + ethyl acetate ,, ...	0·257	0·259
$n/1$ NaCl + isoamyl alcohol ,, ...	0·307	0·315
$n/4$ HCl + metachloraniline ,, ...	0·612	0·582
$n/1$ NaCl + pyrogallic acid (M)	0·809	0·770
$n/2$ KCN + ,, ,, ,, ...	0·900	0·889

[*] *Ann. chim. phys.* (7) xxix. p. 230 (1903).

We see that, in spite of the great difference in the positions of the maxima, Paschen's relation always holds within the limits of experimental error.

Let us now examine two circumstances which can cause an apparent contradiction with Paschen's law.

(1) Let us suppose that there is in the solution a very active substance, which even at low concentrations displaces the maximum of the electrocapillary curve. Every mercury drop adsorbs and removes from the solution a certain quantity of the active substance. Its concentration in the immediate neighbourhood of the dropping electrode must be less than the concentration of the original solution, and therefore the potential of the dropping electrode has a less displaced value than that one which corresponds to the maximum of the electrocapillary curve, as determined by the capillary electrometer.

This discrepancy may be of importance only if the concentration of the active substance is very low, at any rate, when the concentrations of all components of the solution (ions of mercury of course excepted) are high enough, it vanishes as we see from Table I.

(2) With the capillary electrometer we measure the static values of the surface-tension which correspond to an equilibrium of the distribution of all components between the surface-layer and the bulk of the solution. If this equilibrium has not time to establish itself while the drop is being formed, there must be a discrepancy between the data as given by the dropping electrode and the capillary electrometer. We may expect this discrepancy to be especially great in the case of solutions which contain a small quantity of an active substance in presence of a great excess of an inactive one. Such solutions, according to Gouy *, show "electrocapillary viscosity," *i. e.* the meniscus of the capillary electrometer follows the variations of pressure and potential with some delay, and there is a perceptible difference between the surface-tension of a fresh meniscus and the final value of surface-tension. In fact, Palmaer's "null" solution $0 \cdot 1 \, n$ KCl $+ 0 \cdot 01 \, n$ KCN, which shows electrocapillary viscosity, shows also a contradiction with Paschen's relation: the dropping electrode potential is here $0 \cdot 574$ volt, in good agreement with the position of the maximum of the electrocapillary curve of pure $0 \cdot 1 \, n$ KCl $(0 \cdot 57)$, whereas a curve plotted from the final surface-tension values of $0 \cdot 1 \, n$ KCl $+ 0 \cdot 01 \, n$ KCN has a maximum corresponding to $0 \cdot 64$ volt. A fresh meniscus gives data which are included

* *Ann. chim. phys.* (7) xxix. p. 239 (1903).

between these two limits. Obviously in such a case equation (2) cannot be verified by means of a dropping electrode, and it would be advisable to use a slowly increasing surface.

Let us now consider the transition from equation (2) to the classical equation (1). We shall admit that the change of the potential difference solution / mercury caused by surface increase, depends only on the change of the concentration of mercury. This is not quite correct, as the value of the potential difference may also be influenced by other components of the solution, but as $d\psi$ is proportional to $\dfrac{dc}{c}$ and the concentration of mercury in the solution is very small as compared with the concentrations of other components, we may neglect their influence.

Let us suppose that there are M gram-equivalents of mercury in the solution when s and E are zero ; if a quantity of electricity equal to E passes through the solution $\dfrac{E}{F}$ gram-equivalents of mercury are removed from the solution ; likewise $\dfrac{\epsilon}{F} + \Gamma_{Hg}$ gram-equivalents are removed if the surface is increased by unity, where Γ_{Hg} is the excess of mercury in gr.eq. per cm.[2] of the dividing * surface ; where

$$c = \frac{M - \dfrac{E}{F} - \int_0^s \left(\dfrac{\epsilon}{F} + \Gamma_{Hg} \right) ds}{v}$$

and

$$\left(\frac{\partial E}{\partial s} \right)_\psi = -\epsilon - \Gamma_{Hg} F.$$

On substituting this value of $\dfrac{\partial E}{\partial s}$ in (2) we obtain

$$\frac{\partial \gamma}{\partial \psi} = \epsilon + \Gamma_{Hg} F, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

an equation which can be regarded as a generalized equation of Krueger.

It is easy to show that the second term of the right-hand side of equation (4) may sometimes be of importance. Let us consider a drop of zinc amalgam immersed in a solution of zinc sulphate. In the solution and in the surface-layer

* The position of the dividing surface is chosen as to make Γ_{H_2O} zero.

there are ions of two kinds: $Zn^{..}$ and SO_4'', so that we can put

$$\epsilon = (-\Gamma_{Zn^{..}} + \Gamma_{SO_4''})F ;$$

further

$$\Gamma_{Zn} = \Gamma_{Zn^{..}} + \Gamma_{ZnSO_4},$$

and if we neglect the influence of undissociated molecules

$$\Gamma_{Zn} = \Gamma_{Zn^{..}},$$

whence

$$\frac{\partial \gamma}{\partial \psi} = \Gamma_{SO_4''}F \; *. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

With the help of this equation we can calculate the maximum possible value which $\dfrac{\partial \gamma}{\partial \psi}$ can have when zinc amalgam is immersed in $n/1000$ $ZnSO_4$. The amalgam is negatively charged, in the surface-layer there is therefore a *deficiency* of SO_4'' ions. We may assume the thickness of the double layer to be approximately equal to 10^{-7} cm. The absolute value of $T_{SO_4''}$ is at any rate less than 10^{-7} cm. $\times 10^{-6}$ gr. eq./c.cm. $= 10^{-13}$ gr. eq./cm.^{2}; this corresponds to a value of $\dfrac{\partial \gamma}{\partial \psi}$ equal to 10^{-8} coulomb/cm.$^2 = 10^{-1}$ dyne/volt cm., which can be neglected. The surface-tension of a zinc amalgam immersed in a dilute solution of a zinc salt does not depend therefore on its potential, nor, in consequence, on the concentration of the solution. In this particular case $\dfrac{\partial \gamma}{\partial \psi}$ is zero because the quantities ϵ and $\Gamma_{Hg}F$ have equal absolute values and opposite signs.

Let us suppose now that in the solution there is a great excess of a salt with another cation, for instance, Na_2SO_4, then

$$\epsilon = -(\Gamma_{Na^.} - \Gamma_{Zn^{..}} + \Gamma_{SO_4''})F,$$

or, if the concentration of $ZnSO_4$ is low as compared with that of Na_2SO_4,

$$\epsilon = (-\Gamma_{Na^.} + \Gamma_{SO_4''})F.$$

As there is now an *excess* of $Na^.$ in the surface-layer, the value of ϵ is no longer limited and the surface-tension will vary with ψ and in consequence with the concentration of $ZnSO_4$. To verify this inference I measured with the

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* The reasoning above is not quite correct, the concentration of $Zn^{..}$ being, contrary to the assumption we have made previously, of the same order of magnitude as the concentration of SO_4''. Nevertheless, as it is easy to show, equation (5) holds if we denote by ψ the potential difference between an imaginary SO_4'' electrode and the zinc electrode. Besides that does not affect the following considerations.

capillary electrometer the surface-tension of a zinc amalgam in solutions of $ZnSO_4$ and Na_2SO_4. The results are given in Table II. (the maximum surface-tension between mercury and water is assumed to be 100).

TABLE II.

n. $ZnSO_4$	91·4
$1/1000\,n$. $ZnSO_4$	91·2
n. $ZnSO_4 + n$. Na_2SO_4	91·0
$1/1000n$. $ZnSO_4 + n$. Na_2SO_4	89·8

The experimental values are in agreement with the theory; unfortunately, the lack of mobility of the meniscus does not allow of rendering these measurements more accurate or of extending them to still more dilute solutions. Let us now consider the mechanism of working of a dropping electrode in these solutions. To simplify the problem we may neglect the presence of SO_4'' ions. If a drop of amalgam is immersed in a solution of zinc sulphate, zinc ions enter the solution, but, as no other ions are present, they must remain in the double layer to counterbalance the negative charge of the amalgam. The formation of a new surface is therefore not accompanied by any change of concentration, and the potential of a dropping electrode is equal to the potential of a still one. The conditions are quite different when there is in the solution a great excess of sodium ions; these take the place of the zinc ions in the double layer, and the zinc ions enter the bulk of the solution. Thus, in presence of an excess of sodium ions the formation of a new surface lowers the concentration of sodium ions and increases the concentration of zinc ions. The result is an alteration of the potential.

Table III. contains the potential difference between dropping and still amalgam in different solutions of $ZnSO_4$ and Na_2SO_4, the amalgam jet being surrounded by a hydrogen atmosphere.

TABLE III.

$0·001n$. $ZnSO_4$	0·003 volt
$0·001n$. $ZnSO_4 + n$. Na_2SO_4	0·037 ,,
$0·0001n$. $ZnSO_4$	0·011 ,,
$0·0001n$. $ZnSO_4 + n$. Na_2SO_4	0·055 ,,

We see that according to the theory, the addition of Na_2SO_4 greatly increases the potential difference; the small potential difference observed without Na_2SO_4 is due probably to the presence of SO_4'' ions, which we neglected in our

reasoning. Thus the term ΓF is of importance if the double layer is built up by the same ions whose concentration determines the value of the potential difference, but so far as we are dealing with pure mercury its influence is probably very small. In fact, along nearly the whole of the electrocapillary curve the mercury concentration in the solution is very low as compared with the concentration of other ions. If we suppose with Krueger that the anomalies of the electrocapillary curves of anorganic electrolytes are due to the adsorption of mercury, we must assume that salts of mercury are much more adsorbed at the mercury surface than any other known substances. Thus, the addition of $n/100$ KI to $n/1$ Na_2SO_4 lowers the surface-tension which corresponds to $\psi = 0.6$ volt by 5 per cent. To produce such a lowering effect, a very active substance like amyl alcohol ought to be present at a concentration as high as $M/10$, whereas the corresponding concentration of mercury in the solution, as we may easily calculate with the help of Nernst's formula from the experimental data of Abegg and Sherill[*], is 10^{-16}. Therefore it seems to me reasonable to admit that the lowering effect is not caused by the mercury salts, but by the KI (viz. by I'), whose concentration is high enough.

Krueger quotes in favour of his theory that the anomaly of the electrocapillary curves increases with increasing stability of the corresponding complex salts, *i. e.* with the concentration of mercury in the solution at constant potential; but it is easy to show that this relation does not hold. In fact, the stability of complex salts increases in the following order: nitrates, sulphates, iodides, cyanides, whereas the maximum surface-tension of normal solutions are: KNO_3, 98.95; K_2SO_4, 100.17; KI, 94.0; KCN, 96.6.

In the following we will make the probable assumption that the adsorbability of mercury salts is a quantity of the same order of magnitude as that of other substances and neglect the term $\Gamma_{Hg}F$. Equation (4) becomes then identical with the classical equation (1)

$$\frac{\partial \gamma}{\partial \psi} = \epsilon, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\epsilon = (\Gamma_{Anions} - \Gamma_{Cations})F.$$

In equation (1) ϵ is a function of ψ, whose form is determined by the composition of the solution.

In particular, the value of ψ which makes ϵ zero may vary between very wide limits (0.2 v.–1 v.).

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[*] Abegg's *Handbuch der anorganischen Chemie*, Bd. ii. Abt. 2, p. 648.

When mercury comes in contact with the solution, ions of mercury will enter the solution if $\epsilon < 0$, although their osmotic pressure may be greater than the ionic solution pressure of mercury; if $\epsilon > 0$, they will be removed from the solution, their osmotic pressure may thereby be less than the ionic solution pressure. Thus we see that, whilst the value of the potential difference between the solution and the mercury is determined only by the osmotic pressure of ions of mercury, contrary to Nernst's theory the direction of the reaction

$$2\mathrm{Hg} \underset{\longrightarrow}{\overset{\longleftarrow}{}} \mathrm{Hg_2}^{\cdot\cdot} + 2\theta,$$

which takes place when a new surface is formed, depends on the sign of ϵ, and therefore on all active components of the solution.

Also, contrary to Nernst's theory, the existence of a potential difference between solution and mercury is not at all connected with the exchange of ions of mercury. In fact, if the concentration of the ions of mercury corresponds to the zero value of ϵ, no ions at all are exchanged when a new surface is formed ; the potential difference which we must assume between solution and mercury to account for the displacement of the maximum can be caused only by adsorbed layers of anions and cations : we are justified in calling it adsorption potential difference.

In conclusion, I gladly take this opportunity of expressing my gratitude to Professor A. Sakhanow for the interest he has taken in the progress of this work.

Laboratory of Physical Chemistry,
    The University, Odessa.

XLIII. *On the Theory of Electrocapillarity* : II.
By Alexander Frumkin [*].

AS Gibbs has stated, there exists a simple relation between the adsorbed quantity of a substance and the lowering effect on the surface-tension, expressed by the equation

$$\Gamma = -\frac{c}{\mathrm{R T}}\frac{\partial \gamma}{\partial c}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where Γ is the excess of the solute in gram-mols. per cm.^{2} of the dividing surface, c the concentration of the solute, and γ the surface-tension.

Lewis's [*] investigations have shown that lowering of surface-tension at a liquid/liquid interface is really accompanied by adsorption, but the observed value of T was nearly always much greater than the calculated one. Only non-electrolytes of a small molecular weight like caffeine gave satisfactory results. Lewis supposed that the observed discrepancy is due to gelatinization and to electrical effects. Unfortunately, the accuracy of Lewis's method was very limited; further experimental investigations would be of great interest.

The reasoning of Gibbs neglects the electric charge of the dividing surface. Gouy [†] showed that an analogous equation may be deduced for charged surfaces, if the potential difference between the two phases remains constant when the concentration of the active substance is varied. Gouy deduced therefrom that the electrocapillary curve of a solution becomes larger with increasing dilution by a constant quantity, independent of the value of γ. We will show that, using Gibbs's equation, it is possible to calculate the horizontal distance between the ascending and descending branches of electrocapillary curves at different concentrations, and that the calculated values are in fair agreement with the observed ones. We must first consider what form Gibbs's

Fig. 1.
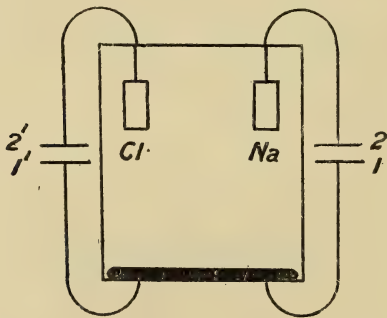
equation will have if we take separate account of the absorption of the anion and the cation. For this purpose let us use an arrangement already employed by Chapman [‡] (fig. 1). A mercury drop and two electrodes from Na and Cl are

* Phil. Mag. (6) xv. p. 499 (1908); xvii. p. 466 (1909); *Zeit. phys. Chem.* lxxiii. p. 129 (1910).

† *Journ. de Phys.* (3) x. p. 245 (1901).

‡ Phil. Mag. (6) xxv. p. 475 (1913).

immersed in a solution of NaCl. The electrodes are connected with the mercury by means of two condensers. The potential differences between the solution and the Hg, Na, and Cl electrodes are respectively ψ, ψ_1, ψ_2. The quantity of electricity which has passed through the solution since a certain moment from 1 to 2 is E_1, and from 1' to 2' E_2. The concentration of the NaCl, which we shall assume to be completely dissociated, is c and the surface area of the mercury s. The state of the solution is wholly determined by the values of ψ, c, and s. If we increase s by ds, keeping ψ and c constant, and c by dc keeping ψ and s constant, the work performed will be

$$d\mathrm{A} = \left[\gamma + (\psi - \psi_1)\frac{\partial \mathrm{E}_1}{\partial s} + (\psi - \psi_2)\frac{\partial \mathrm{E}_2}{\partial s} \right] ds$$
$$+ \left[(\psi - \psi_1)\frac{\partial \mathrm{E}_1}{\partial c} + (\psi - \psi_2)\frac{\partial \mathrm{E}_2}{\partial c} \right] dc,$$

whence, as ψ_1 and ψ_2 are functions of c and ψ, but not of s,

$$\frac{\partial \gamma}{\partial c} - \frac{\partial \psi_1}{\partial c}\frac{\partial \mathrm{E}_1}{\partial s} - \frac{\partial \psi_2}{\partial c}\frac{\partial \mathrm{E}_2}{\partial s} = 0, \quad \cdots \quad (2)$$

where

$$-\frac{\partial \psi_1}{\partial c} = \frac{\partial \psi_2}{\partial c} = \frac{\mathrm{RT}}{c\mathrm{F}}. \quad \cdots \cdots \quad (3)$$

When a quantity of electricity equal to $\dfrac{\partial \mathrm{E}_1}{\partial s}ds$ passes from 1 to 2, $\dfrac{1}{\mathrm{F}}\dfrac{\partial \mathrm{E}_1}{\partial s}ds$ gram-equivalents Na enter the solution and as many gr. eq. Hg are removed from it; likewise, when a quantity of electricity equal to $\dfrac{\partial \mathrm{E}_2}{\partial s}ds$ passes from 1' to 2', $\dfrac{1}{\mathrm{F}}\dfrac{\partial \mathrm{E}_2}{\partial s}ds$ gr. eq. Hg and as many gr. eq. Cl are removed from the solution. On the other hand, when the surface is increased by ds, E_1 and E_2 being constant, $\Gamma_{\mathrm{Na}}ds$, $\Gamma_{\mathrm{Cl}}ds$, and $\dfrac{\epsilon}{\mathrm{F}}ds$ gr. eq. Na, Cl, and Hg respectively, are removed from the solution; in consequence, as ψ and c must remain constant during the increase of s,

$$\left. \begin{array}{l} \Gamma_{\mathrm{Na}} = \dfrac{1}{\mathrm{F}}\dfrac{\partial \mathrm{E}_1}{\partial s}, \quad \Gamma_{\mathrm{Cl}} = -\dfrac{1}{\mathrm{F}}\dfrac{\partial \mathrm{E}_2}{\partial s}, \\[2ex] \dfrac{\epsilon}{\mathrm{F}} = -\dfrac{1}{\mathrm{F}}\left(\dfrac{\partial \mathrm{E}_1}{\partial s} + \dfrac{\partial \mathrm{E}_2}{\partial s}\right) = -\Gamma_{\mathrm{Na}} + \Gamma_{\mathrm{Cl}} \end{array} \right\} \quad \cdots \quad (4)$$

On substituting the values of $\dfrac{\partial E_1}{\partial s}$, $\dfrac{\partial E_2}{\partial s}$, $\dfrac{\partial \psi_1}{\partial c}$, and $\dfrac{\partial \psi_2}{\partial c}$ from (3) and (4) in (2) we obtain

$$\frac{c}{RT}\frac{\partial \gamma}{\partial c} = -(\Gamma_{N_a} + \Gamma_{Cl}), \quad . \quad . \quad . \quad (5)$$

i. e. Gibbs's equation.

Let us now suppose that the valency of the anion is n_A and the valency of the cation n_K; instead of (3) we must put

$$\frac{\partial \psi_1}{\partial c} = \frac{RT}{n_K c F}; \quad \frac{\partial \psi_2}{\partial c} = -\frac{RT}{n_A c F}.$$

If we express the quantities Γ in gr. eq. per cm.^{2} equation (4) will keep its form, hence

$$\frac{c}{RT}\frac{\partial \gamma}{\partial c} = -\left(\frac{\Gamma}{n}\right)_A - \left(\frac{\Gamma}{n}\right)_K. \quad . \quad . \quad . \quad (5\,a)$$

Let us compare ($5\,a$) with the equation of the electro-capillary curve

$$\frac{1}{F}\frac{\partial \gamma}{\partial \psi} = \Gamma_A - \Gamma_K.$$

I. *Descending branch.*

The mercury is charged negatively. In the surface-layer there is an excess of cations and a deficiency of anions, so that Γ_A has a negative value; the absolute value of Γ_A is at any rate less than $c\delta$, where δ is the thickness of the surface-layer and may be neglected if the solution is a dilute one [*]. This agrees very well with experiment, as the form of the descending branch, at a certain distance from the maximum, does not depend on the nature of the anion. In consequence we may put $\Gamma_A = 0$, whence

$$\frac{\partial \gamma}{\partial \psi} = \frac{n_K F}{RT}\frac{\partial \gamma}{\partial \log c}.$$

The integral of this equation is

$$\gamma = f\left(\psi + \frac{RT}{n_K F}\log c\right). \quad . \quad . \quad . \quad . \quad (6)$$

If $\gamma_1 = \gamma_2$,

$$\psi_1 + \frac{RT}{n_K F}\log c_1 = \psi_2 + \frac{RT}{n_K F}\log c_2,$$

whence

$$\psi_2 - \psi_1 = \frac{RT}{n_K F}\log \frac{c_1}{c_2}. \quad . \quad . \quad . \quad . \quad (7)$$

In consequence, the horizontal distance between the descending

[*] In fact, if $c = n/100$, $c\delta$ will be of the order 10^{-12} gr. eq./cm.^{2}, whereas the quantity $\dfrac{c}{RT}\dfrac{\partial \gamma}{\partial c}$ is of the order 10^{-10} gr. eq./cm.^{2}.

branches of two solutions, whose concentrations are c_1 and c_2, is $0.057 \log_{10} \frac{c_1}{c_2}$ ($t = 15°$) for a monovalent cation and $0.029 \log_{10} \frac{c_1}{c_2}$ for a bivalent one. If we take account of the incomplete dissociation, we must replace c by αc, where α is the degree of dissociation. In Table I. are given the values of $\psi_2 - \psi_1$ which correspond to different values of γ (the maximum surface-tension between mercury and water is assumed to be 100). The measurements were carried out with a capillary electrometer as described by Gouy [*], the large mercury electrode being always immersed in a $n/10$ solution of KCl.

Let us now denote by ψ the potential difference between the mercury in the decinormal calomel electrode and the mercury in the capillary tube, by i the value of the current which passes through the capillary electrometer, and by w its internal resistance. Then, obviously $\psi =$ applied E.M.F. $- iw$. The value of w was calculated, that of i determined

Fig. 2.
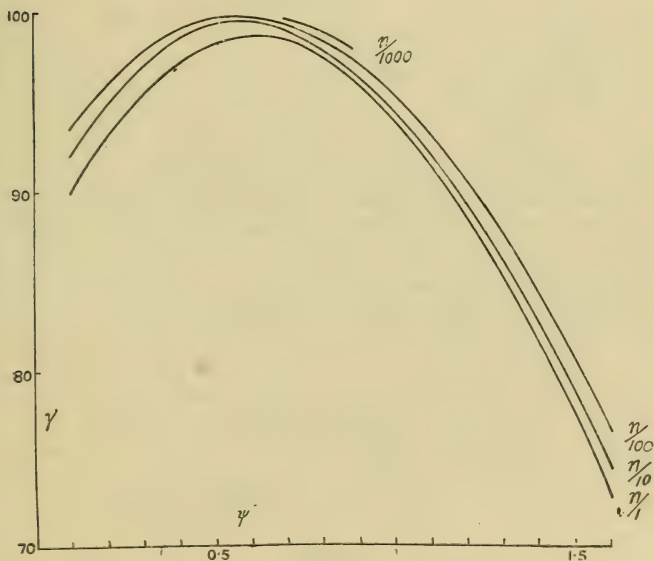
with an Edelmann string galvanometer. The term iw could be neglected at higher concentrations, but with $n/1000$ solutions it amounted to 0.01 volt and more. The electro-capillary curves of KNO_3 are plotted on fig. 2.

* *Ann. chim. phys.* (7) xxix. p. 178 (1903).

2 C 2

TABLE I.

KNO$_3$. $t = 15°$ (fig. 2).

γ.	$n - 1/10\,n$.	$1/10\,n - 1/100\,n$.	$1/100\,n - 1/1000\,n$.
99.0	...	0.045	0.049
98.0	0.037	0.051	...
95.0	0.021	0.052	...
90.0	0.022	0.048	...
85.0	0.025	0.051	...
80.0	0.035	0.052	...
75.0	0.035	...	...
$\dfrac{RT}{F} \lg \dfrac{\alpha_1 c_1}{\alpha_2 c_2}$	0.051	0.054	0.056

Ba(NO$_3$)$_2$. $t = 15°$.

γ.	$1/10\,n - 1/100\,n$.	$1/100\,n - 1/1000\,n$.
99.0	0.020	0.032
98.0	0.020	0.027
97.0	0.023	0.029
95.0	0.026	...
90.0	0.022	...
86.0	0.025	...
$\dfrac{RT}{2F} \lg \dfrac{\alpha_1 c_1}{\alpha_2 c_2}$	...	0.028

We see thus that the observed values of $\psi_2 - \psi_1$ are in a satisfactory agreement with the calculated ones, except for normal solutions. At higher concentrations the term T_A may be of importance, or perhaps in this case Gibbs's equation is no longer valid.

Let us now consider a zinc amalgam, immersed in a solution of zinc sulphate. Here

$$\psi = \text{const.} - \frac{RT}{nF} \log c,$$

whence

$$\psi + \frac{RT}{nF} \log c = \text{const.},$$

and

$$\gamma = \text{const.},$$

i. e. the surface-tension of the amalgam does not vary with the concentration of the solution, a result which we have already obtained in a different way.

II. *Ascending branch.*

Applying to the ascending branch a reasoning similar to the above, *i. e.* assuming T_K to be zero, we obtain the equation

$$\gamma = f\left(\psi - \frac{RT}{n_A F}\log c\right),$$

whence

$$\psi_2 - \psi_1 = -\frac{RT}{n_A F}\log\frac{c_1}{c_2}.$$

It appears that in reality, especially with active * electrolytes, the assumption $T_K = 0$ does not hold for the ascending branch and that there is an excess of both anions and cations in the surface-layer, when $\dfrac{\partial \gamma}{\partial \psi}$ is positive. We are induced to admit this if we consider :—

(1) *The position of the maximum.*—In solutions of electrolytes with an active anion like Br′, I′, CN′, SCN′, the maximum is displaced to the right, as compared with solutions of electrolytes with an inactive anion, like $NO_3′$, $SO_4″$, OH′. Thus the maximum surface-tension in $n/10$ KNO_3 corresponds to $\psi = 0.57$ volt, in $n/1$ KNO_2 to $\psi = 0.61$, and in $n/1$ KI to $\psi = 0.87$. Let us consider the portion of the electrocapillary curve of $n/1$ KI between 0.57 and 0.87 volt, supposing that the first value of ψ really corresponds to the zero potential difference between mercury and solution. If $0.57 < \psi < 0.87$, $\epsilon > 0$, and, in consequence, the potential of the mercury must be higher than the potential of the nearest layer of the solution; as the whole potential difference between solution and mercury is positive, the potential in the surface-layer must vary with the distance from the mercury surface in a way shown by fig. 3. The rise of potential can be caused only by free positive charges, and in consequence we must assume an excess of anions immediately at the mercury surface and at some distance from it an excess of cations, a circumstance which has already been pointed out by Gouy †.

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* We call an electrolyte active if it gives an electrocapillary curve with a depressed maximum. The activity of anorganic electrolytes depends on the anion.

† *C. R.* cxxxi. p. 939 (1900).

Fig. 3.
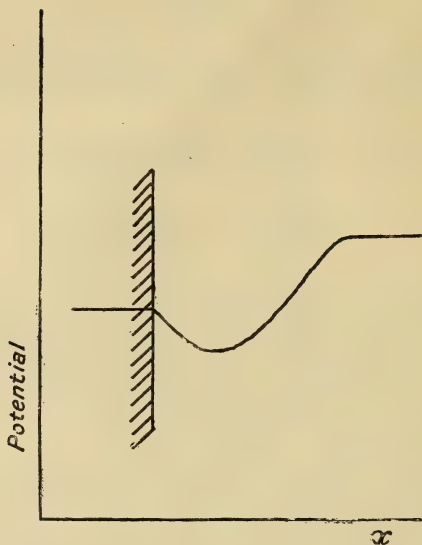
(2) *Salts with active cations.*—Gouy [*] has shown that similar to the active anions Br′, I′, CN′, there exist active cations like $N(C_2H_5)_4$, $S(CH_3)_3$. The electrocapillary curves of salts of these anions have a normal ascending branch and an altered descending one. For instance, the ascending branch of a solution of $[N(C_2H_5)_4]_2SO_4$ coincides with the ascending branch of a solution of Na_2SO_4, whilst the descending branch of $[N(C_2H_5)_4]_2SO_4$ is considerably depressed. But if the anion is active, the activity of the cation manifests itself in the ascending branch as well as in the descending one. Thus, comparing the electrocapillary curve of two salts with an active anion like $N(C_2H_5)_4Br$ and KBr, we see that their ascending branches are different. We must, therefore, admit that in presence of an active anion, the cation is adsorbed even in the ascending branch.

(3) *The value of the horizontal displacement of the ascending branch.*—If $T_K > 0$,

$$\frac{n_A F}{RT} \frac{\partial \gamma}{\partial \log c} > \frac{\partial \gamma}{\partial \psi},$$

and the horizontal distance between the ascending branches of two solutions whose concentrations are c_1 and c_2 must be greater than $\dfrac{RT}{n_A F} \log \dfrac{c_2}{c_1}$.

* *Ann. chim. phys.* (8) ix. p. 87 (1906).

The experimental determination of $\psi_2 - \psi_1$ presents some difficulties caused by the lack of mobility of the capillary meniscus, especially at low concentrations. The results obtained do not pretend therefore to a high degree of accuracy. Nevertheless, we may see from Table II. that the value of the displacement with SO_4'' and Cl' is approximately equal to $\dfrac{RT}{n_A F} \log \dfrac{c_2}{c_1}$ at low concentrations, whereas with an active anion like I' much greater displacements are observed. The same phenomenon is shown to a less degree with the Cl' ion in a concentrated solution.

The data for H_2SO_4 were obtained in the same way as the data for KNO_3 and $Ba(NO_3)_2$ in Table I., a correction for the potential difference between H_2SO_4 and the $n/10$ KCl of the calomel electrode being made ; the approximate data for NaCl and KI were calculated from the measurements of Gouy [*].

TABLE II.

H_2SO_4. $t = 20°$.

γ.	$n-1/10\ n$.	$1/10\ n-1/100\ n$.
95·0	0·042	0·031
90·0	0·038	0·028
85·0	0·032	0·022
80·0	0·027	0·023
75·0	0·027	0·023
70·0	0·027	...

NaCl. $t = 18°$.

90·0	0·09	0·05

KI. $t = 18°$.

90·0	0·15	0·11
75·0	0·09	...

III. *The maximum.*

In the neighbourhood of the maximum T_A and T_K are quantities of the same order of magnitude, and no definite inference can be drawn from (5 *a*). A very interesting attempt to find out the equation of that portion of the electro-capillary curve was made by Chapman [†]. Assuming that the ions in the surface-layer are in equilibrium under the

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[*] *Ann. chim. phys.* (7) xxix. p. 145 (1903).
[†] *Loc. cit.*

influence of osmotic and electrostatic forces, he calculated the distribution of potential in the surface-layer and the value of ϵ for a given potential difference between mercury and solution. The resulting equation of the electrocapillary curve is

$$\gamma_{\text{Max.}} - \gamma = \frac{2RT}{F} \sqrt{\frac{Kp}{2\pi}} \left(e^{\frac{FV}{4RT}} - e^{-\frac{FV}{4RT}} \right)^2, \quad . \quad . \quad (8)$$

where K is the specific inductive capacity of water, p the osmotic pressure of the ions in the bulk of the solution, and $V = \psi - \psi_{\text{Max.}}$. As Chapman's reasoning involves the assumption that the ions in the double layer behave like perfect gases, equation (8) especially at higher concentrations can be used only for small absolute values of V. It seemed to me therefore of interest to test eq. (8) in the neighbourhood of the maximum. Table III. contains the experimental values of $\gamma_{\text{Max.}} - \gamma$ in C.G.S. units for KCl, KNO_3, and Na_2SO_4, and the values calculated by means of equation (8), assuming $K = 81$, $t = 18°$, and $p = \alpha cRT$, where α is the degree of dissociation of KNO_3. Moreover, Table III. contains values of $\gamma_{\text{Max.}} - \gamma$ calculated by means of the classical formula

$$\gamma_{\text{Max.}} - \gamma = aV^2, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

a being determined from the value of $\gamma_{\text{Max.}} - \gamma$ which correspond to $V = 1$ volt.

Table III. shows a very great discrepancy between the calculated and the observed values: the influence of concentration is much less pronounced, as it ought to be according to (8); moreover, $\gamma_{\text{Max.}} - \gamma$ is approximately proportional to V^2. Thus, the results of experiment are unfavourable to Chapman's assumption concerning the conditions of the equilibrium in the double layer. As Chapman's reasoning is thermodynamically correct, equation (8) must be in agreement with (6). In fact, for great values of V, we have

$$\gamma_{\text{Max.}} - \gamma = \frac{2RT}{F} \sqrt{\frac{Kp}{2\pi}} e^{\frac{FV}{2RT}} = \text{const.} \sqrt{c} \, e^{\frac{FV}{2RT}} = \text{const.} \, e^{\frac{F}{2RT}\left(V + \frac{RT}{F}\lg c\right)}.$$

With the help of equation (5 a) we may calculate the value of absorption of any ions, except those of mercury, as we cannot vary their concentration without varying ψ. It is easy to give to the equation of the electrocapillary curve

$$\frac{\partial \gamma}{\partial \psi} = \epsilon + \Gamma_{\text{Hg}} F$$

TABLE III.

Calcul. by means of (8). KNO₃.			
V $\quad$ c	0·05 v.	0·1 v.	0·15 v.
n.	2·67	13·8	...
$n/10$.	0·96	4·96	...
$n/100$.	0·32	1·67	5·57
$n/1000$.	0·10	0·54	1·79

Calcul. by means of (9). KNO₃.			
V $\quad$ c	0 05 v.	0·1 v.	0·15 v.
n.	0·28	1·14	...
$n/10$.	0·26	1·03	...
$n/100$.	0·22	0·90	2·02

Observed KNO₃.			
V $\quad$ c	0·05 v.	0·1 v.	0·15 v.
n.	0·34	1·36	...
$n/10$.	0·29	1·20	...
$n/100$.	0·25	0·98	2·3

Observed KCl.			
V $\quad$ c	0·05 v.	0·1 v.	0·15 v.
$n/10$.	0·43	1·38	...
$n/100$.	...	0·85	2·2
$n/1000$.	0·37	...	...

Observed Na₂SO₄.			
V $\quad$ c	0·05 v.	0·1 v.	0·15 v.
$n/10$.	0·34	1·35	...
$n/100$.	0·34	1·0	2·35

the form of an equation of adsorption of mercury ions. In fact, let us put

$$d\psi = -\frac{RT}{nF}\frac{dc}{c},$$

then

$$\frac{c}{RT}\frac{\partial\gamma}{\partial c} = -\frac{1}{n}\left(\frac{\epsilon}{F} + \Gamma_{Hg}\right),$$

a formula quite analogous to (5 a).

Laboratory of Physical Chemistry,
    The University, Odessa.

P.S.—After this paper was already forwarded to the editors we received here Gouy's article (*Ann. Phys.* (9) viii. p. 129, 1917), where similar considerations are developed.

XLIV. *An Improved Design for the Friction Cones of Searle's Apparatus for the Mechanical Equivalent of Heat. By* H. P. Waran, *M.A., Government Scholar of the University of Madras* *.

IN Dr. Searle's well-known apparatus we have two cones of gun-metal, one inside the other, ground to a good fit so that by rotating the outer cone about the inner the friction between them converts the work done into heat, and it is estimated by noting the temperature rise of water contained in the inner cone. Though the apparatus is extraordinarily efficient for its size and simplicity, yet it is not without a few drawbacks. The present modification is an attempt to get over them.

The thickness of the walls of each of the metal cones is about 3 mm., and the heat generated by friction at the surface of contact has to be conducted through this thickness of metal before it can raise the temperature of the water. And in an ordinary laboratory experiment to minimise the effects of heat loss due to radiation the temperature rise is kept very low, and consequently the temperature gradient in the metal is small and the rate of conduction of heat to the water is slow. Further, the employment of water with its low conductivity of heat as the liquid to absorb the heat, makes the situation only worse. In the presence of these drawbacks very vigorous stirring of the water in the inner cone is essential to ensure a rapid equalization of temperature throughout the system, and in that stirring probably we are adding an amount of unmeasurable work and consequently heat to the system, which is probably very small. Further, this is an extra operation the experimenter has to do very efficiently, in addition to his duties of turning the wheel at a steady rate with one hand and noting down the thermometer reading with the other.

The following is an improved design for the cones calculated to overcome the above disadvantages.

As will be evident from the diagram, the inner cone I is made open at the bottom, and has, in addition, a few helical grooves G cut on the contact surface of the inner cone, these grooves terminating in a ring-channel S cut near the top of the cone. From this channel a few holes are drilled sloping inwards into the cone. The grooves G are cut sloping upwards in the direction of rotation of the outer cone. Further, for the liquid in the cones any essential oil of known specific heat and large conductivity for heat is

* Communicated by the Author.

used in preference to water. These comprise in brief the essential points of the improved design. If we look into the action of these improved cones we shall see that, as an effect of the rotation of the outer cone, the oil in the cup is

Fig. 1.
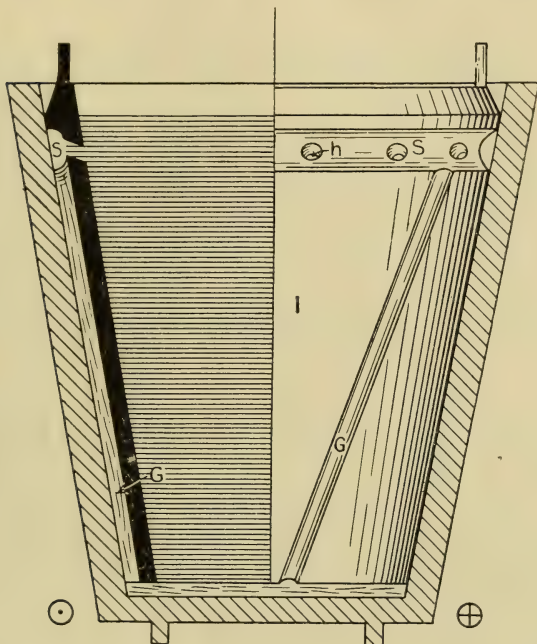
forced up through the grooves G on to the channel S and through the holes h back into the inner chamber again. Thus the liquid is stirred efficiently and automatically and a liquid of high conductivity brought into intimate contact with the surface where the heat is generated by friction, thus ensuring a uniform rise of temperature of the whole system in the minimum of time. The liquid also gives a steady and uniform lubrication for the friction surfaces, and in a class-room the experiment can be done by an average student solely by himself, without any extra aid to stir the liquid or to observe and take down the readings of the thermometer. This modification has also the great advantage that it can be directly introduced on all the existing type of millions of the apparatus already in use.

The Cavendish Laboratory,
        Cambridge.

XLV. *Notices respecting New Books.*

Collected Scientific Papers. By Professor JOHN HENRY POYNTING, F.R.S. Pp. xxxii+768. Cambridge University Press. 1920. 37s. 6d. net.

PROBABLY few are aware of the wide range of studies covered by Poynting's researches. His fame was made in 1884 by papers on the transfer of energy in the Electromagnetic Field (Phil. Trans. Roy. Soc. A) and on electric currents and the electric and magnetic induction in the surrounding medium (Phil. Trans. 1888). The Poynting vector specifies the direction and magnitude of flow of the energy in an electromagnetic field; it is at right angles to both the electric and magnetic forces, and is proportional to the product of these forces and the sine of the angle between them. This vector has taken an important position in any modern theory; and it may be said also from the practical point of view that no clear idea of the propagation of energy in wireless telegraphy could have been obtained without it.

But in three other directions at least Poynting made investigations of fundamental importance. In 1887 his attention was concentrated on the phenomena of change of state, and at other times he came back to this and the allied problems of osmotic pressure. He showed thermodynamically that vapour pressure must increase with isothermal increase of pressure; that the lowering of freezing-point with pressure must depend upon whether both phases are subject to the pressure or one phase alone. Experiments on this latter point did not bear out very well his theoretic conclusions, but there is no doubt that he was on the right lines; the difficulty was in trying to reproduce the theoretical conditions. With regard to the former point it is now known to be one example of a very general theory of pressure-influence in connexion with which much theoretical and experimental work has been done.

Much more importance attaches to his investigations concerning the pressure of radiation. Along with Dr. Guy Barlow he established the existence of a tangential force when light is incident upon an absorbing surface, and also the existence of a torque when light passes through a prism. In 1910 he showed that a radiating body recoils from the radiation it emits.

His fourth main subject was that of gravitation. First (1878–1891) he undertook a difficult investigation into the mean density of the earth using a balance method. Although his method was in the end overshadowed by the exceedingly neat method adopted by C. V. Boys, yet his extreme skill and perseverance overcame many of the difficulties which were minimised in the later method. He also sought whether the attraction between two quartz crystals depends upon their orientation; no difference was

detected. And lastly, in conjunction with Dr. Phillips, he showed that gravitation is independent of temperature ; at least to within 1 part in a thousand-million between 15° and 100° C.

This brief summary has referred only to investigations of physical interest. The papers here reprinted include one on the Drunkenness statistics of the large towns in England and Wales ; and one on a comparison of the fluctuations in the price of wheat and in the cotton and silk imports into Great Britain ; and also twenty-five addresses and general articles. In all, seventy communications are reproduced.

Poynting was above all an experimental philosopher. Although he had a theoretical equipment of a high order he was somewhat afraid of theoretical results unless well tested experimentally.

The present volume is a memorial one edited by Drs. Shakespear and Guy Barlow. It contains biographical notices by Sir J. Thomson, Sir O. Lodge, and Sir Joseph Larmor.

It is a worthy memorial ; it will make better known to all the work of a man who was one of the least assertive of men ; but who by his quiet and pertinacious labours (with a body enfeebled by disease) has enriched the world.

The Concept of Nature. Tarner Lectures delivered in Trinity College, November 1919. By A. N. WHITEHEAD. Cambridge University Press.

PROFESSOR WHITEHEAD asks us to regard this book as a companion to his recently published *Enquiry concerning the Principles of Natural Knowledge* (see Phil. Mag. June 1920). The two books are independent, but they supplement one another. It is quite clear why he wishes us to do so. In the *Enquiry* he accepted, not uncritically, the principle of relativity, and particularly the expression given to it by Minkowski in his concept of a four-dimensional universe constituted of events. The purpose of the *Enquiry* was to demonstrate the fundamental character of the event, to show how events are related and measurable, how objects are derived from them and to settle in the form of a definition what an event and what an object is. His book, however, was hardly published before we were all discussing the new general relativity of Einstein. It is not surprising therefore that Professor Whitehead has taken the opportunity of the Tarner Lectures to make his own position in regard to the generalized principle clear.

Without being at all unreceptive to the new theory, and while accepting its particular applications, the new formula for gravitation for example, he is very anxious to dissociate himself from the extremist interpretation. His keen philosophic vision warns him lest a position of absolute negativity towards independent objective reality should bring upon physical science a similar impasse to that which Hume's scepticism brought upon philosophy.

I refer to the insistence by Einstein on the impossibility of presenting the reality of nature in any purely objective form, that is, in any form which does not take account of the observer and his system of reference. Professor Whitehead will give up absolute space and absolute time, he has no need of material or stuff, the hypothetical ether of the physicists he dismisses with scant respect, but he must have an ether, an ether of events, if, as he holds, the universe consists of events. His scientific instinct will not let him entertain the possibility of a purely subjective reality. To proclaim monads as the real atoms of nature would signify for him the death of physical science. " There is now reigning in philosophy and in science an apathetic acquiescence in the conclusion that no coherent account can be given of nature as it is disclosed to us in sense-awareness, without dragging in its relations to mind." To counteract this is the inspiring motive of this book. On one definite point only it joins issue directly with Einstein. Professor Whitehead will not have the bending of space. The gravitational field is not in his view equivalent to the curvature of space in the field. Otherwise he accepts the new formulation and does not challenge the experimental tests by which it is confirmed.

The first two chapters, entitled " Nature and Thought " and " The Bifurcation of Nature," are introductory and meant to lead us to the central problem. In the five chapters which follow,— " Time," " The Method of Extensive Abstraction," " Space and Motion," " Congruence," and " Objects,"—the author is completely at home, using his own peculiar method, working at what he has happily named the organization of thought. The two last chapters,—" Summary " and " The Ultimate Physical Concepts,"— are additions which, we are told, formed no part of the original course. They emphasize the conclusion in regard to Einstein's general relativity.

By the bifurcation of nature, Professor Whitehead means the division of the science of nature into two classes of entities, those disclosed to sense-awareness, and those disclosed to conceptual thought. Materialism he rejects outright. It is so absurdly inadequate that it is becoming matter of amazement that the scientific opinion of the last century should have taken it, almost universally, as axiomatic. On the other hand, he is vigorous in denouncing metaphysics. A metaphysics of reality is, in his view, completely out of place in the philosophy of science. " It is like throwing a match into the powder magazine. It blows up the whole arena." Philosophy of science is the philosophy of the *thing perceived*, while metaphysics confuses everything by embracing within one reality both perceiver and perceived.

The whole book is valuable therefore in the indication it gives us of the line along which the issue is likely to be joined by physicists who agree in accepting the principle of relativity and yet disagree profoundly in its interpretation. The line of demarcation will be

metaphysics in Professor Whitehead's meaning of the term. For according to Einstein, not only is it impossible to denote any reality save in the terms of some observer's observation, but also when you abstract from the observer and his system of reference there is nothing to denote. If there be, what is it? Shall we say, for example, that colour is sense-awareness and relative to the observer, while the conceptual entity, the light waves of a certain amplitude and frequency, is not relative? We are at once brought to book by the fact that the essential character of this entity is its dimensions, and dimensions depend on the relative movement of systems of reference and vary with their acceleration. If it is not the dimensions what is it that is absolute in this entity? You find you must answer and you can give no definite answer. You fall back on the indefinite something or other I know not what. Einstein says there is nothing.

I find in Professor Whitehead's discussion of the theory he accepts, namely, that space-time is four-dimensional, a great deal that puzzles me and even seems at times incongruous. It suggests to me that he is putting new wine into old bottles. A four-dimensional space-time is the groundwork of his concept of nature. Yet he is continually talking about " instantaneous space " " timeless spaces " " time systems," these last being apparently interchangeable without affecting the space. It leaves me wondering whether his four dimensions mean anything more than that time and space are never dissociated. I will give an actual illustration. On p. 97 he says " the meaning of saying that Cambridge in the appropriate instantaneous space at 10 o'clock this morning for that instant is 52 miles from London at 11 o'clock this morning in the appropriate instantaneous space for that instant beats me entirely." A little further on, after discussing the boundaries of events, he says (p. 100) " Thus the boundary of a duration consists of two momentary three-dimensional spaces." Now have we not here precisely the difference between Professor Whitehead and Einstein? It could hardly be more complete. For Einstein there is no appropriate instantaneous space for any moment, and no momentary three-dimensional space boundary of any duration. Time and space are solidary. The only meaning you can give to the statement that 52 miles in space separate Cambridge from London is that the train journey occupies an hour, the light journey (if you are in a position to see London from Cambridge) an infinitesimal fraction of a second. In fact I find in this example the essential meaning of Einstein. Reduce the time interval to zero and there is nothing, not only no time but also no space.

I will conclude with one word concerning the relation of metaphysics to physical science. Probably I have already given myself away and shown that I come under Professor Whitehead's censure as one who confuses the problem of the thing perceived with the problem of the perceiver. The philosophy of science

stands to gain and not to lose by insisting that every scientific fact is what it is, always for some observer in some system of reference, and that every description of scientific fact must take the observer and his system into account as factors. If this be metaphysics, science has nothing to fear from it, but everything to fear from disregarding it. There is, however, a metaphysics which brings sterility alike to philosophy and to science. This is the affirmation of an existence which is not what it is to any observer. It is named in philosophy the thing-in-itself and physical science has no need of it.

I have only to add that the central portion of the book is certainly difficult but the whole is in the author's inimitable style and bright throughout with his wonderful humour.

H. Wildon Carr.

A Treatise on Gyrostatics and Rotational Motion.
By Andrew Gray, F.R.S. (Macmillan & Co. £2 2s. net.)

Prof. Gray has produced in this volume a very complete account of gyrostatics, which will be welcomed by students of applied mathematics and technical students generally. All who are engaged in the study of this subject will be grateful to the author for bringing together in such an attractive form the many interesting matters set forth in the pages of this book.

Following the discussion of elementary principles in the earlier chapters, a number of illustrations of the practical applications of gyrostatic action are given. The reader is also provided with a concise treatment of elliptic integrals, with the numerical solution of problems relating to rotating bodies. The numerical examples occurring in various parts of the book will be especially valuable, and should do much to encourage further investigation. In succeeding chapters the author gives an exhaustive treatment of the general dynamics of rotating systems, and a comprehensive discussion of more advanced gyrostatic problems, including the whirling of shafts and chains.

We are glad to commend this excellent and authoritative treatise, the work of one who has done much towards the development of this branch of science. It is to be hoped that Prof. Gray will find it possible to issue in the near future the supplementary volume dealing with gyrostatic devices of use in engineering and naval and military affairs.

The excellence of the printing and diagrams should not be overlooked. The book is well produced, has a useful index, and as a work of reference will be found indispensable to all interested in this fascinating subject.

XLVI. *On the Scattering of Light by Unsymmetrical Atoms and Molecules.* By Sir J. J. Thomson, *O.M., P.R.S.*[*]

WHEN the arrangement of the electrons in an atom
is quite symmetrical, the displacement of an electron
due to an external force will always be in the direction
of that force and the ratio of the displacement to the
force will be independent of the direction of the force.
These are the conditions postulated in the investigations
hitherto given of the scattering of light by small particles,
and we know that when they are fulfilled and the incident
light is plane polarized the intensity of the scattered light
vanishes along the direction of the electric force in the
incident light. When the incident light is not polarized,
the scattered light when observed in a direction at right
angles to the incident light is completely polarized.

These results, however, will not hold when the atom
is unsymmetrical and the displacement of an electron is
not necessarily in the direction of the disturbing force.
We shall see that under these conditions the intensity
of the scattered light does not vanish in any direction :
it, however, varies with the direction, and experiments on
the law of variation such as those made by Lord Rayleigh
give valuable information about the structure of the atom.

Suppose that OA, OB, OC are three directions in an
atom, at right angles to each other such that the electrons

can be displaced along any one of them without causing displacements along the other two.

Suppose that when the electrons are displaced by distances ξ, η, ζ parallel to OA, OB, OC respectively, the restoring forces are respectively $A\xi$, $B\eta$, $C\zeta$; then, if F_1, F_2, F_3 are the forces acting on an electron in these directions, the equations for ξ, η, ζ are respectively

$$m\frac{d^2\xi}{dt^2} + A\xi = F_1,$$

$$m\frac{d^2\eta}{dt^2} + B\eta = F_2,$$

$$m\frac{d^2\zeta}{dt^2} + C\zeta = F_3.$$

If the applied forces vary as ϵ^{ipt} the solutions are

$$\xi = \frac{F_1}{A - mp^2}, \quad \eta = \frac{F_2}{B - mp^2}, \quad \zeta = \frac{F_5}{C - mp^2}.$$

When A, B, C are small compared with mp^2,

$$\xi = \frac{-F_1}{mp^2}, \quad \eta = \frac{-F_2}{mp^2}, \quad \zeta = \frac{-F_3}{mp^2},$$

and

$$\frac{\xi}{F_1} = \frac{\eta}{F_2} = \frac{\zeta}{F_3}.$$

The electron is thus displaced along the direction of the force and the usual theory will apply. Thus, as long as the frequency of the incident vibrations is large compared with the free frequencies of the electrons, the system of electrons will behave as if it were quite symmetrical and the light will be scattered in accordance with the usual theory. When however A, B, C cannot be neglected in comparison with mp^2, we see that unless $A = B = C$ the direction of the displacement will not be that of the force and the theory requires modification.

Let A, B, C be the points where the axes OA, OB, OC of an atom cut a sphere of unit radius; X, Y, Z the points where this sphere is cut by three fixed axes OX, OY, OZ: let us calculate the displacements along these axes of an electron acted on by a force Z parallel to OZ.

With the notation indicated by the figure, the direction cosines of OC with respect to the fixed axes are

$$\sin \theta \cos \psi, \quad \sin \theta \sin \psi, \quad \cos \theta \, ;$$

Fig. 1.
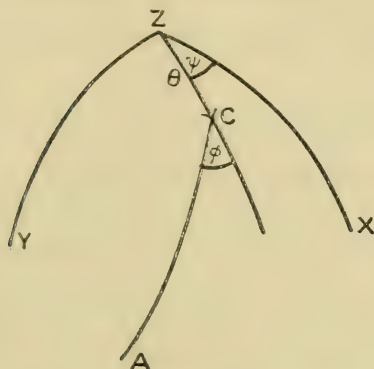
the direction cosines of OA are

$$\cos \theta \cos \psi \cos \phi - \sin \phi \sin \psi,$$
$$\cos \theta \sin \psi \cos \phi + \sin \phi \cos \psi,$$
$$- \sin \theta \cos \phi \, ;$$

those of OB are

$$-\cos \theta \cos \psi \sin \phi - \cos \phi \sin \psi,$$
$$-\cos \theta \sin \psi \sin \phi + \cos \phi \cos \psi,$$
$$\sin \theta \sin \phi.$$

Thus the components of Z along OA, OB, OC are

$$F_1 = - Z \sin \theta \cos \phi, \quad F_2 = Z \sin \theta \sin \phi, \quad F_3 = Z \cos \theta.$$

ξ, η, ζ, the displacements of the electron along OA, OB, OC due to these forces, are given by

$$\xi = -\frac{Z \sin \theta \cos \phi}{A - mp^2}, \quad \eta = \frac{Z \sin \theta \sin \phi}{B - mp^2}, \quad \zeta = \frac{Z \cos \theta}{C - mp^2}.$$

2 D 2

If x, y, z are the displacements of the electron parallel to OX, OY, OZ,

$$x = \xi (\cos \theta \cos \psi \cos \phi - \sin \phi \sin \psi)$$
$$- \eta (\cos \theta \cos \psi \sin \phi + \cos \phi \sin \psi) + \zeta \sin \theta \cos \psi$$
$$= Z \left[\sin \theta \cos \theta \cos \psi (c - a \cos^2 \phi - b \sin^2 \phi) \right.$$
$$\left. + (a - b) \sin \theta \sin \psi \sin \phi \cos \phi \right],$$

where

$$a = \frac{1}{A - mp^2}, \quad b = \frac{1}{B - mp^2}, \quad c = \frac{1}{C - mp^2};$$

$$y = Z \left[\sin \theta \cos \theta \sin \psi (c - a \cos^2 \phi - b \sin^2 \phi) \right.$$
$$\left. + (a - b) \sin \theta \cos \psi \sin \phi \cos \phi \right];$$

$$z = Z (c \cos^2 \theta + b \sin^2 \theta \sin^2 \phi + a \sin^2 \theta \cos^2 \phi).$$

If Z varies as ϵ^{ipt}, the components of the acceleration of the electron will be $-p^2 x$, $-p^2 y$, $-p^2 z$ respectively. If α, β, γ are the components at a time t of the magnetic force at a point P due to the motion of an electron whose distance from P is r, then when r is large compared with the wavelength of the light,

$$\alpha = \frac{e}{r} \{jn - km\}, \quad \beta = \frac{e}{r} \{kl - hn\}, \quad \gamma = \frac{e}{r} \{hm - jl\},$$

where l, m, n are the direction cosines of the line joining the electron to P, and h, j, k are the components of the acceleration of the electron at the time $t - \dfrac{r}{c}$, where c is the velocity of light and e the charge on the electron.

The energy per unit volume of the scattered light at P is equal to

$$\frac{1}{4\pi}(\alpha^2 + \beta^2 + \gamma^2)$$
$$= \frac{1}{4\pi} \frac{e^2}{r^2} \{h^2 + j^2 + k^2 - (lh + mj + nk)^2\}. \quad . \quad . \quad (1)$$

Now h, j, k are respectively $-p^2 x$, $-p^2 y$, $-p^2 z$ when x, y, z have the values given above. Substituting these values in (1) we get the energy in the scattered light from a single atom. We cannot observe the effect of a single atom or molecule; we must take the sum of the effects due to a large number of molecules with all possible values for θ, ϕ, ψ. When the atoms are uniformly orientated

in all directions the average values are as follows :—

$$h^2 = \frac{1}{30} Z^2 p^4(\overline{a-b}^2 + \overline{b-c}^2 + \overline{c-a}^2) = j^2 = p^4 f Z^2, \quad \text{say} ;$$

$$k^2 = \frac{1}{15} Z^2 p^4(3(a^2 + b^2 + c^2) + 2ab + 2ac + 2bc) = p^4 g Z^2 ;$$

$$hj = hk = jk = 0.$$

The energy of the scattered light per unit volume at P is thus equal to

$$\frac{1}{4\pi} \frac{e^2}{r^2} p^4 Z^2 \{ g(l^2 + m^2) + f(l^2 + m^2 + 2n^2) \} ;$$

since f and g are positive quantities, this expression cannot vanish whatever may be the values of l, m, n unless $f = 0$, *i. e.* unless $a = b = c$: this requires the system of electrons to be quite symmetrical.

We may write the expression for the energy in the scattered light in the form

$$\frac{1}{4\pi} \frac{e^2}{r^2} p^4 Z^2 \{ 2f + (g-f) \sin^2 \vartheta \},$$

where ϑ is the angle between the direction in which the scattered light is observed and the direction of the electric force in the incident light.

Since $g-f$ is positive, the energy is a minimum when $\theta = 0$ and a maximum when $\theta = \pi/2$.

The ratio of the minimum to the maximum energy is $2f/(f+g)$; this is equal to

$$\frac{2(a^2 + b^2 + c^2 - ab - ac - bc)}{4(a^2 + b^2 + c^2) + ab + ac + bc}. \quad \cdots \quad (2)$$

If a, b, c are positive the greatest value for this ratio is $1/2$ when $ab + ac + bc = 0$; so that two out of the three quantities a, b, c must vanish. When the incident light has the same period as one of the free vibrations of the atom, mp^2 will equal one of the three quantities A, B, C, so that either a, b, c will be infinite : in this case the minimum value of the intensity is one-half the maximum value. For still greater frequencies the values of one or more of the quantities a, b, c might be negative, and in such a case the minimum intensity might be more than half the maximum.

Hitherto we have been considering polarized light. If the incident light is not polarized the intensity of the light scattered in any direction can be found as follows :—Let OI be the direction of the incident light, OP that of the

scattered light, OZ the direction of the electric force in the incident light; IZ is always equal to $\pi/2$.

The intensity of the scattered light is, as we have just seen, proportional to

$$2f + (g-f) \sin^2 \theta.$$

But

$$\cos \theta = \cos PZ = \sin \phi \cos \psi.$$

Fig. 2.
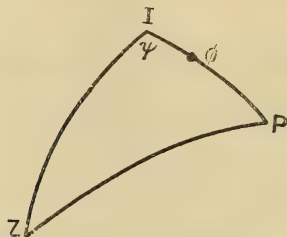
If $\phi = $ PI, $\psi = $ PIZ.

Hence the intensity of the scattered light is proportional to

$$f + g - (g-f) \sin^2 \phi \cos^2 \psi.$$

If the light is not polarized and all values of ψ are equally probable, the mean value of $\cos^2 \psi$ is $1/2$. So that the intensity of the scattered light is

$$f + g - \tfrac{1}{2}(g-f) \sin^2 \phi.$$

Since g is greater than f the intensity is greatest when $\phi = 0$, when it is equal to $f+g$, and least when $\phi = \pi/2$, when it is equal to $\tfrac{1}{2}(3f+g)$; since f is positive the minimum intensity is always greater than $(f+g)/2$, and thus always greater than half the maximum energy. For the symmetrical atom $f = 0$ and the minimum intensity of the scattered light is one-half the maximum.

Another point of difference between the scattering of light by symmetrical and unsymmetrical atoms occurs when the distances between the scattering atoms are small compared with the wave-length of the light. With symmetrical atoms or isolated electrons the scattered light reaching a point P will be in the same phase from whichever atom it may proceed; so that if there are N atoms the intensity of the magnetic force will be proportional to N and the intensity of the scattered light will be proportional to N^2. In the case of unsymmetrical atoms, though they may be packed close together, the phase of

the scattered light reaching P from one atom need not be the same as that reaching it from another atom. For this phase depends to some extent on the orientation of the atom. Hence if the orientation of these atoms is quite irregular, the phase of part of the light scattered by different atoms will also be quite irregular, and in calculating the intensity of this part of the light we have to add the intensities of the light scattered by the different atoms, and not, as in the case of the symmetrical atom, add the magnetic forces and take the square of this sum as proportional to the energy. Thus the energy in this part of the light will be proportional to the number of atoms and not to the square of the number. It must be remembered, however, that even with unsymmetrical atoms the phase of every part of the scattered light cannot be made to change sign by altering the orientation of the atom.

If we refer to the equations on p. 396, we see that the part of the light arising from the accelerations along x and y can be made to do so, but that depending on the acceleration along z cannot : hence part of the light scattered by N unsymmetrical atoms will be proportional to N^2 and another part to N. The light due to the acceleration parallel to z vanishes along the axis of Z—that is, along the direction of the electric force in the incident light ; so that in this direction the scattered light would be proportional to N. In other directions there would be a part proportional to the square of the number of atoms, provided the linear dimensions of the space occupied by these atoms were not large compared with the wave-length of the light. For large volumes we see, by Huyghens' principle, that the intensity of this part of the scattered light would be comparable with that scattered by the atoms contained in a layer whose thickness was of the order of the wave-length.

To see the conditions necessary for this statement to be true, we notice that the magnetic force in the scattered light at a point whose distance r from any of the atoms is a large multiple of the wave-length is given by an expression of the form

$$\frac{1}{r}\left\{ a \cos \frac{2\pi}{\lambda}\left(vt-(lx_1+my_1+nz_1)\right) \right.$$
$$\left. + a \cos \frac{2\pi}{\lambda}\left(vt-(lx_2+my_2+nz_2)\right)+\ldots \right\},$$

where x_r, y_r, z_r are the co-ordinates of one of the atoms, and l, m, n are constant.

The energy being proportional to the square of the magnetic force is of the form

$$\frac{a^2}{r^2}\left\{ \Sigma \cos^2\frac{2\pi}{\lambda}\left(vt-(lx_r+my_r+nz_r)\right)\right.$$

$$\left. + 2\Sigma\Sigma \cos\frac{2\pi}{\lambda}\left(vt-(lx_r+my_r+nz_r)\right)\cos\frac{2\pi}{\lambda}\left(vt-(lx_s+my_s+nz_s)\right)\right\},$$

where there are n terms under the single summation and $n \cdot (n-1)/2$ under the double, n being the number of atoms. The average value over a considerable time is

$$\frac{a^2}{2r^2}\left\{ n + 2\Sigma\Sigma\cos\frac{2\pi}{\lambda}\left(l(x_r-x_s)+m(y_r-y_s)+n(z_r-z_s)\right)\right\}.$$

If x_r-x_s, y_r-y_s, z_r-z_s are all small compared with λ, each of the cosines will be unity and the energy will be proportional to

$$n+2 \cdot \frac{n \cdot (n-1)}{2}, \text{ or to } n^2.$$

If the atoms are arranged in a lattice, so that x_r-x_s, y_r-y_s, z_r-z_s are always integral multiples of constants a, b, c, then for certain values of l, m, n the angles will be all multiples of 2π, and the energy in the directions corresponding to these values will be proportional to n^2. If, however, there is not this regular crystalline arrangement of the atoms, but, as in a gas, the atoms are distributed at random, we can easily see that, when the space containing the atoms is bounded by planes, the magnitude of the term involving the cosines is comparable with the square of the number of atoms in a layer whose thickness is proportional to the wave-length, and thus, when the atoms occupy a considerable volume, becomes small compared with n; so that we may take the scattering due to a gas or a liquid as proportional to the number of atoms.

From equation (2) we see that if we know the values of a, b, c we can calculate the ratio of the minimum to the maximum intensity of scattered polarized light; and since we can calculate these values when we know the arrangement of the electrons in an atom we have a method, and a very powerful one, of testing any theories of the constitution of the atom; for Lord Rayleigh has shown that the variations of the intensity of the scattered light in different directions can be determined with considerable accuracy, and that the magnitudes of these variations vary considerably with the nature of the atom.

We shall therefore proceed to find the values of a, b, c for

some specified type of atoms. The method of calculation will depend upon whether we suppose that the electrons in the undisturbed atom are describing circular orbits, or whether they are in equilibrium under a complex type of force. We shall begin with the first supposition, and consider the effect produced by a small disturbing force $X \cos qt$ acting parallel to x in the plane of the orbit, the orbit being described under the action of a central force equal to $\mu r/(r^2+d^2)^{\frac{3}{2}}$; where r is the distance from a point in the plane of the orbit, and d a constant. If d vanishes, we have the law of the inverse square; it is convenient, however, to take the more general law, for we shall require it when we consider molecules where there is more than one centre of positive electricity.

The orbits we shall consider are those which are approximately circular. Consider first the undisturbed orbits. The circular orbit is represented by

$$x = a \cos (nt+\epsilon), \quad y = a \sin (nt+\epsilon),$$

where

$$\mu = n^2(a^2+d^2)^{\frac{3}{2}}.$$

If the orbit is not circular, but only approximately so, and if $r=a+\xi$, where ξ is a small quantity, we can easily show that

$$\frac{d^2\xi}{dt^2} + \left(4 - \frac{3a^2}{D^2}\right)n^2\xi = 0,$$

where

$$D^2 = a^2 + d^2;$$

if $p^2 = 4 - 3a^2/D^2$, we see that we may write

$$r = a - ae \cos \{p(nt+\epsilon) - \omega\},$$

where e is small.

The values of x and y for an orbit of this type are represented if

$$\phi = nt+\epsilon, \quad \psi = (p-1)(nt+\epsilon) - \omega, \quad \chi = (p+1)(nt+\epsilon) - \omega$$

by the expressions

$$x = a \cos \phi - k_1 ae \cos \psi + k_2 ae \cos \chi,$$

$$y = a \sin \phi + k_1 ae \sin \psi + k_2 ae \sin \chi,$$

where

$$k_1 = \frac{1}{2} + \frac{1}{p}, \quad k_2 = \frac{1}{p} - \frac{1}{2}.$$

Following the methods of the Planetary Theory, we shall

suppose that when the force $X \cos qt$ acts on the electron x and y are still represented by equations of this type, but that the parameters are variable and are functions of the time which it is our object to determine. If $\dfrac{\partial}{\partial t}$ denotes differentiation with regard to the time only so far as the time enters into these parameters, and if we take the more general case where the electron is acted on by disturbing forces X', Y' parallel to the axes of x and y respectively, we have by the principle of Instantaneous Orbits

$$\frac{\partial x}{\partial t} = 0, \quad \frac{\partial y}{\partial t} = 0,$$

$$\frac{\partial x'}{\partial t} = X', \quad \frac{\partial y'}{\partial t} = Y',$$

where $x' = \dfrac{dx}{dt}$, $y' = \dfrac{dy}{dt}$, the parameters being considered constant for these differentiations; the mass of the electron has been taken as unity. From the equation $\partial x / \partial t = 0$ we get

$$0 = \frac{da}{dt} \cos \phi - \frac{d\epsilon}{dt} a \sin \phi - \frac{d}{dt}(ae) . \{k_1 \cos \psi - k_2 \cos \chi\}$$
$$- ae \frac{d\omega}{dt} (k_1 \sin \psi - k_2 \sin \chi).$$

In the coefficient of $d\epsilon/dt$ terms which are small compared with $a \sin \phi$ have been omitted.

From $\dfrac{\partial y}{\partial t} = 0$ we get

$$0 = \frac{da}{dt} \sin \phi + a \cos \phi . \frac{d\epsilon}{dt} + \frac{d}{dt}(ae)(k_1 \sin \psi + k_2 \sin \chi)$$
$$- ae \frac{d\omega}{dt}(k_1 \cos \psi + k_2 \cos \chi).$$

From $\dfrac{\partial y'}{\partial t} = Y'$,

$$Y' = \frac{da}{dt} \left\{ n + a \frac{dn}{da} \right\} \cos \phi - an \sin \phi \frac{d\epsilon}{dt}$$
$$+ \frac{d}{dt}(ae)((p-1)nk_1 \cos \psi + (p+1)nk_2 \cos \chi)$$
$$+ ae \frac{d\omega}{dt}((p-1)nk_1 \sin \psi + (p+1)nk_2 \sin \chi).$$

From $\dfrac{\partial x'}{\partial t} = X'$,

$$X = -\frac{da}{dt}\left\{ n + a\frac{dn}{da} \right\}\sin\phi - an\cos\phi \cdot \frac{d\epsilon}{dt}$$
$$+ \frac{d}{dt}(ae)((p-1)nk_1\sin\psi - (p+1)nk_2\sin\chi)$$
$$- ae\frac{d\omega}{dt}((p-1)nk_1\cos\psi - (p+1)nk_2\cos\chi).$$

From these and from the equation

$$n^2 = \frac{\mu}{(a^2 + d^2)^{\frac{3}{2}}},$$

we get

$$\frac{da}{dt} = \frac{2}{np^2}(Y'\cos\phi - X'\sin\phi),$$

$$\frac{d\epsilon}{dt} = -\frac{2}{np^2a}(Y'\sin\phi + X'\cos\phi),$$

$$\frac{de}{dt} = \frac{1}{nap}\{Y'(k_2\cos\chi + k_1\cos\psi) + X'(k_1\sin\psi - k_2\sin\chi)\},$$

$$e\frac{d\omega}{dt} = \frac{1}{nap}\{Y'(k_2\sin\chi + k_1\sin\psi) + X'(k_2\cos\chi - k_1\cos\psi)\}.$$

The third and fourth of these equations are equivalent to

$$\frac{d}{dt}(e\cos\omega) = \frac{1}{nap}\{Y'(k_2\cos\chi' + k_1\cos\psi')$$
$$+ X'(k_1\sin\psi' - k_2\sin\chi')\},$$

$$\frac{d}{dt}(e\sin\omega) = \frac{1}{nap}\{Y'(k_2\sin\chi' + k_1\sin\psi')$$
$$+ X'(k_2\cos\chi' - k_1\cos\psi')\},$$

where

$$\psi' = (p-1)(nt+\epsilon), \quad \chi' = (p+1)(nt+\epsilon).$$

Take the case when $Y' = 0$, $X' = X \cos qt$.
Then, integrating these equations, we get

$$a = a_0 + \frac{X}{np^2}\left\{\frac{\cos(q+n)t}{q+n} - \frac{\cos(q-n)t}{q-n}\right\},$$

$$\epsilon = -\frac{X}{nap^2}\left\{\frac{\sin(q+n)t}{q+n} + \frac{\sin(q-n)t}{q-n}\right\},$$

$$e \cos \omega = \frac{X}{2nap}\left\{k_2\left(\frac{\cos(\overline{p+1}\,n+q)t}{(p+1)n+q} + \frac{\cos(\overline{p+1}\,n-q)t}{(p+1)n-q}\right)\right.$$
$$\left. - k_1\left(\frac{\cos(\overline{p-1}\,n+q)t}{(p-1)n+q} + \frac{\cos(\overline{p-1}\,n-q)t}{(p-1)n-q}\right)\right\}.$$

$$e \sin \omega = \frac{X}{2nap}\left\{k_2\left(\frac{\sin(\overline{p+1}\,n+q)t}{(p+1)n+q} + \frac{\sin(\overline{p+1}\,n-q)t}{(p+1)n-q}\right)\right.$$
$$\left. - k_1\left(\frac{\sin(\overline{p-1}\,n+q)t}{(p-1)n+q} + \frac{\sin(\overline{p-1}\,n-q)t}{(p-1)n-q}\right)\right\}.$$

Substituting these values in the expression for x, we find that

$$x = X \cos qt\left\{\frac{2}{p^2(n^2-q^2)} + \frac{k_1^2.(p-1)}{p\{n^2(p-1)^2-q^2\}} + \frac{k_2^2(p+1)}{p\{n^2(p+1)^2-q^2\}}\right\}$$
$$- X \cos(2n+q)t . \frac{k_1 k_2}{p^2n^2-(n+q)^2}$$
$$- X \cos(2n-q)t . \frac{k_1 k_2}{p^2n^2-(n-q)^2}$$
$$+ a_0 \cos nt.$$

To calculate the intensity of the scattered light of the same colour as the incident we need only consider the term containing $\cos pt$. As this term is proportional to the applied force, we see that an electron rotating in an orbit acts, so far as its contribution to specific inductive capacity is concerned, like a statical system, where the displacement of the electron is proportional to the force. Hence for forces in the plane of the electron we have, using the notation of p. 396,

$$a = b = \frac{2}{p^2(n^2-q^2)} + \frac{k_1^2(p-1)}{p\{n^2(p-1)^2-q^2\}} + \frac{k_2^2(p+1)}{p\{n^2(p+1)^2-q^2\}},$$

where

$$k_1 = \frac{1}{2} + \frac{1}{p}, \quad k_2 = \frac{1}{p} - \frac{1}{2}.$$

If a force $Z \cos qt$ acts at right angles to the plane of the orbit, which we may suppose described under the influence

Fig. 3.
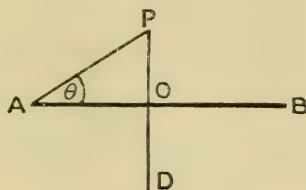
of two positive charges at A and B, the plane of the orbit bisecting AB at right angles, we have

$$\frac{d^2z}{dt^2} + \frac{\mu}{D^3}(1 - 3\cos^2\theta)z = Z\cos qt,$$

where $\theta = \angle \text{PAO}$ in the steady orbit;

i. e., $\quad \dfrac{d^2z}{dt^2} + n^2(1 - 3\cos^2\theta)z = Z\cos qt,$

$$z = \frac{Z\cos pt}{n^2(1 - 3\cos^2\theta) - q^2}:$$

hence

$$c = \frac{1}{n^2(1 - 3\cos^2\theta) - q^2}.$$

Since $a/D = \sin\theta,$

$$p^2 = 4 - 3\sin^2\theta = 1 + 3\cos^2\theta.$$

Knowing the value of $a, b, c,$ we can by equation (2) on p. 397 calculate the ratio of the minimum to the maximum intensity of the scattered polarized light.

Let us now take some special cases. The first is that of an electron describing an orbit under the attraction of a positive charge : here the charge will be in the plane of the orbit, so that $\theta = \pi/2,\ p = 1,$

$$a = b = \frac{2}{n^2 - q^2} + \frac{1}{2}\frac{1}{4n^2 - q^2},$$

$$c = \frac{1}{n^2 - q^2};$$

or when q is small compared with $n,$

$$a = b = \frac{1}{n^2}(2 + \tfrac{1}{8}),$$

$$c = \frac{1}{n^2}.$$

Hence

$$\frac{2(a^2 + b^2 + c^2 - ab - ac - bc)}{4(a^2 + b^2 + c^2) + ab + ac + bc} = \frac{5}{98}.$$

So that by equation (2), p. 397, the minimum intensity would in this case be about 5 per cent. of the maximum.

Let us take next the case of an electron describing a circular orbit under the attraction of two equal positive charges, the plane of the orbit bisecting at right angles the line joining the charges; we have found the values of a, b, c as functions of θ.

We see from the expression for c that there cannot be a state of stable steady motion unless $1 - 3 \cos^2 \theta$ is positive; so that θ must be between $90°$ and $54° \ 42'$. We have already considered the case when $\theta = 90°$. The values of σ, the ratio of the minimum to the maximum intensity, for some intermediate values of θ are given in the following table :—

$\theta.$		σ in per cent.
80	....	22
70	....	16
60	....	·46
58	....	2
55	....	50

We have supposed hitherto that only one electron was describing a circular orbit, and with a law of force of the type we have assumed it is easy to show that if we have more than one electron travelling round the same circle steady motion is unstable. For take the case of two electrons travelling round a circle of radius a: the steady motion, if possible, will be one where the two electrons are at opposite ends of a diameter. If r_1, r_2, θ_1, θ_2 are the co-ordinates of the two electrons when disturbed, we may put

$$r_1 = a + x_1, \quad r_2 = a + x_2, \quad \theta_1 = nt + y_1, \quad \theta_2 = nt + \pi + y_2,$$

where x_1, x_2, y_1, y_2 are small quantities.

The equations of motion are

$$\frac{d^2 r_1}{dt^2} - r_1 \left(\frac{d\theta_1}{dt}\right)^2 = -\frac{\mu r_1}{(r_1^2 + d^2)^{\frac{3}{2}}} + P_1,$$

$$\frac{1}{r_1} \frac{d}{dt}\left(r_1^2 \frac{d\theta_1}{dt}\right) = \Theta_1,$$

where P and Θ are the radial and tangential forces exerted

by the second electron on the first. We find, by a simple calculation, that

$$P_1 = \frac{e^2}{4a^2}\left(1 - \frac{1}{a}(x_1 + x_2)\right),$$

$$\Theta_1 = \frac{e^2}{8a^3}(y_2 - y_1).$$

Hence for the steady motion we have

$$-an^2 = -\frac{\mu a}{D^3} + \frac{e^2}{4a^2},$$

or $$n^2 = \frac{\mu}{D^3} - \frac{e^2}{4a^3};$$

and for x and y we have

$$\frac{d^2 x_1}{dt^2} - x_1 n^2 - 2an\frac{dy_1}{dt} = -\frac{\mu x_1}{D^3}\left(1 - \frac{3a^2}{D^2}\right) - \frac{e^2}{4a^3}(x_1 + x_2),$$

$$a\frac{d^2 y_1}{dt^2} + 2n\frac{dx_1}{dt} = \frac{e^2}{8a^2}(y_2 - y_1),$$

with similar equations for x_2, y_2.

From these we get

$$\frac{d^2(x_1 + x_2)}{dt^2} - (x_1 + x_2)n^2 - 2an\left(\frac{dy_1}{dt} + \frac{dy_2}{dt}\right)$$
$$= -(x_1 + x_2)\left\{\frac{\mu}{D^3}\left(1 - \frac{3a^2}{D^2}\right) + \frac{e^2}{2a^3}\right\},$$

$$a\frac{d^2(y_1 + y_2)}{dt^2} + 2n\frac{d}{dt}(x_1 + x_2) = 0.$$

The solution of these equations is,

if $$q^2 = 3n^2 + \frac{\mu}{D^3}\left(1 - \frac{3a^2}{D^2}\right) + \frac{e^2}{2a^3},$$

$$x_1 + x_2 = A\cos(qt + \epsilon),$$

$$y_1 + y_2 = B - \frac{2n}{qa}A\sin(qt + \epsilon).$$

If $$\xi = x_1 - x_2, \quad \eta = y_1 - y_2,$$

we have

$$\frac{d^2\xi}{dt^2} - \xi\left(n^2 - \frac{\mu}{D^3}\left(1 - \frac{3a^2}{D^2}\right)\right) - 2an\frac{d\eta}{dt} = 0,$$

$$a\frac{d^2\eta}{dt^2} + 2n\frac{d\xi}{dt} = -\frac{e^2}{4a^2}\eta;$$

or supposing ξ and η to vary as ϵ^{ipt}, we have

$$\left\{ p^2 + n^2 - \frac{\mu}{D^3}\left(1 - \frac{3a^2}{D^2}\right) \right\} \left\{ p^2 - \frac{e^2}{4a^3} \right\} = 4n^2p^2,$$

a quadratic equation in p^2. We have seen, p. 405, that for the equilibrium to be stable for displacements at right angles to the plane of the orbit $1 - 3\cos^2\theta$ must be positive, where θ is the angle between the line joining the electron to a positive charge and the normal to the plane of the orbit. Since $a/D = \sin\theta$, $1 - 3a^2/D^2 = 1 - 3\sin^2\theta$; and this is negative if $1 - 3\cos^2\theta$ is positive. Hence $n^2 - \frac{\mu}{D^2}(1 - 3\sin^2\theta)$ must be positive, so that the two values of p^2 given by this equation must have opposite signs; thus one value of p^2 must be negative, so that the steady motion will be unstable.

Thus if the two electrons repel each other, the system sometimes supposed to represent an atom of helium with two electrons revolving at the same distance from a central positive charge cannot be stable, nor can one when there are two electrons revolving in a circle midway between two positive charges, which is sometimes supposed to represent the constitution of the hydrogen molecule. If we make the extravagant assumption that the two electrons do not repel each other, the problem is the same as that of the single electron already discussed : the steady motion would be stable, and since the relative values of a, b, c would be the same as for a single electron the ratio of the minimum to the maximum intensity of the scattered polarized light would be that given in the table on p. 406.

If the hydrogen molecule is a system like that represented in fig. 3, with two positive charges and two electrons at the corners of a rhombus, we see by considering the equilibrium of one of the positive charges that θ must be $60°$; so that the ratio of the minimum to the maximum intensity of scattered polarized light would only be ·4 per cent. Lord Rayleigh's experiments show, however, that for hydrogen the ratio is at least ten times greater.

We shall now go on to consider the case when the electrons, instead of revolving in circular orbits, are in equilibrium under forces between the positive charges and the electrons which do not, at the distances which separate the positive charges from the outer ring of electrons, vary inversely as the square of the distance, but at these distances may vanish and change from attractions to repulsions.

If there is only one electron in the atom, the atom would

have a finite electrical moment measured by the product of the charge on the electron and its distance from the positive charge. The atoms would " set " under the action of an external force, and under such a force the collection of atoms would have a finite electrical moment and therefore a specific inductive capacity greater than unity. If it were not for the collisions between the atoms their axes would all point in the direction of the electric force and the moment would be independent of the strength of the electric field. These axes are, however, knocked out of line by the collisions between the atoms, so that the resultant moment diminishes as these collisions increase ; in fact, we can show that the resultant moment and therefore the excess of the specific inductive capacity over unity will, on account of this effect, vary inversely as the absolute temperature of the gas. There are gases such as water vapour and the vapours of various alcohols which vary in this way ; but the specific inductive capacity of gases such as hydrogen, helium, nitrogen, or oxygen varies much less rapidly with the temperature, showing that in the normal state the atoms or molecules of these gases have no finite electrical moment.

One form of such an atom is that of a double charge at the centre A with an electron on either side of it. If such an electron is acted on by a force X at right angles to the line joining the central charge to the electrons, then, if δx is the displacement of either electron in the direction of this force and d the distance of an electron from the central charge, we see that

$$\frac{e^2}{4d^2} \delta x = X e \cdot d,$$

or $\qquad 2e \delta x = 8d^3 X.$

Now $2e \delta x$ is the electrical moment of the atom when it is exposed to the electric force, and thus $8d^3$ is proportional to the quantity we have denoted on page 397 by a ; if the axis of y is also at right angles to the line joining the central charge to the electron, $b = a$.

We must now consider the effect of a force along the line of electrons : if δz is the displacement caused by a force Z acting in this direction, $2e^2 F$ the force exerted by the central charge on an electron, we see that

$$Z e = 2e^2 \frac{dF}{dz} \cdot \delta z.$$

Let
$$\frac{d\mathrm{F}}{dz} = \frac{\beta}{d} \cdot \mathrm{F}$$

when $z=d$, then
$$2e \cdot \delta z = \frac{\mathrm{Z}d}{\beta \mathrm{F}};$$

and from the equilibrium of the system, we have
$$2e^2 \mathrm{F} = \frac{e^2}{4d^2}.$$

Hence
$$2e\,\delta z = \frac{8d^3\,\mathrm{Z}}{\beta}.$$

Hence $c = 8d^3/\beta$ and $a = b = 8d^3.$

The ratio of the minimum to the maximum intensity of the scattered light is therefore, by equation (2), equal to
$$\frac{2(\beta-1)^2}{9\beta^2 + 2\beta + 4}.$$

Another system of which the hydrogen molecule may be taken as a type is that of two positive charges A and B and two electrons C and D, arranged as in fig. 3.

If the plane of the system be taken as the plane of x, y, then, if δz is the displacement of an electron due to a force Z at right angles to the plane of xy, we have, by taking moments about AB,
$$\frac{e^2}{\mathrm{CD}^2} \cdot \delta z = \mathrm{Z}e \tfrac{1}{2}\mathrm{CD},$$

or $2e \cdot \delta z = \mathrm{Z} \cdot \mathrm{CD}^3;$

thus c is proportional to CD^3.

If the system is acted on by a force X parallel to AB, and if $e^2\mathrm{F}$ is the force between a positive charge and an electron,
$$2e^2 \frac{d}{dx}\left(\mathrm{F}\,\frac{x}{r}\right)\delta x = \mathrm{X}e,$$

where r is the distance between the positive charge and an electron, from this we get, if we put $\dfrac{d\mathrm{F}}{dr} = \dfrac{\beta}{r}\mathrm{F}$, where F and r have the values corresponding to the undisturbed position,
$$2e \cdot \frac{\mathrm{F}}{r}\left(1 - (1-\beta)\cos^2\theta\right)\delta x = \mathrm{X},$$

or $2e\,\delta x = \dfrac{\mathrm{X}r}{\mathrm{F}\left(1 - (1-\beta)\cos^2\theta\right)}.$

For the equilibrium of the system,

$$2F \sin \theta = \frac{1}{CD^2},$$

or

$$\frac{F}{r} = \frac{1}{CD^3}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence

$$2e \, \delta x = X \cdot \frac{CD^3}{1-(1-\beta)\cos^2 \theta}.$$

Hence

$$a = \frac{CD^3}{1-(1-\beta)\cos^2 \theta}.$$

Similarly we may show that if δy is the displacement parallel to CD caused by a force acting in this direction,

$$2e \, \delta y = Y \cdot \frac{CD^3}{1-(1-\beta)\sin^2 \theta}.$$

Hence

$$b = \frac{CD^3}{1-(1-\beta)\sin^2 \theta}.$$

From these values of a, b, c we find that σ the ratio, expressed as a percentage, of the minimum to the maximum intensity of the scattered polarized light, is for a series of values of β and θ given by the following table :—

	$\theta = 90°$.	$\theta = 60°$ or $30°$.	$\theta = 45°$.
	σ.	σ.	σ.
	per cent.	per cent.	per cent.
$\beta = 0$	50	19	4·5
$\beta = \cdot 5$	7	2·5	1
$\beta = 1$	0	0	0
$\beta = 1\cdot5$	1·8	1	·7
$\beta = 2$	4·5	3·3	2·4
$\beta = 3$	8·8	7·2	7
$\beta = 4$	11·5	11	11

We can apply these results to check the validity of any assumed law of force between the positive charge and an electron in the following way :—Suppose that when the distance of the electron from the positive charge is r, the attraction between them is equal to

$$\frac{e^2}{r^2} \phi(x),$$

where $x = c/r$, c being a constant. $\phi(x)$ must possess the

2 E 2

following properties: (i.) when $x = 0$, *i. e.* when r is infinite, $\phi(x) = 1$; and (ii.) $\phi(x)$ must be of the form which will give rise to the Balmer series in the hydrogen spectrum. These conditions are not sufficient to determine $\phi(x)$. We shall show, however, that it is possible to write down an expression for ϕ which will satisfy these conditions, and in addition lead to the scattering of polarized light in a way consistent with Lord Rayleigh's experiments.

Taking the case of a hydrogen molecule, we see from equation (3) that if x_1 be the value of x in the hydrogen molecule

$$\phi(x_1) = \frac{1}{8 \sin^3 \theta},$$

and if the electrons and positive charges are at the corners of a square $\theta = \pi/4$, so that in this case

$$\phi(x_1) = \frac{1}{2 \sqrt{2}}.$$

Since when $x = x_1$, $\dfrac{d\mathrm{F}}{dr} = \dfrac{\beta}{r} \mathrm{F}$,

where F is the force, we see, putting

$$\mathrm{F} = \frac{e^2}{r^2} \phi(x),$$

that $\beta = -x \left(\dfrac{2}{x} + \dfrac{\phi'(x)}{\phi(x)} \right)$ when $x = x_1$.

Assume $\phi(x) = \dfrac{d}{dx} \left\{ x \cos^2 x + \dfrac{\sin^2 x}{x^2} \right\}.$

This satisfies the condition that $\phi(x) = 1$ when $x = 0$, and it is of the form which would correspond to a Balmer's series (see J. J. Thomson, Phil. Mag. April 1919).

From the condition

$$\phi(x_1) = \frac{1}{2 \sqrt{2}},$$

I find by the method of trial and error that $x_1 = \cdot 58$, and substituting this value of x in the expression for β, I find $\beta = \cdot 3$ approximately. This gives a scattering of a little less than 3 per cent.; according to Lord Rayleigh's experiments the scattering is a little less than 4 per cent.

Other expressions for ϕ could be assumed which would also be in agreement with experiment as far as the scattering goes.

It has been urged against the idea of a value of force not varying inversely as the square of the distance that the scattering of the α particles indicates a force of this type. The scattering of the α particles, however, practically all takes place at distances from the centre very small compared with the distance of the electrons which scatter the light or affect the emission of visible light ; and it is quite possible that the law should be the inverse square both at distances which are very large compared with c and again at distances which are very small compared with it, and yet be quite of a different character when r is comparable with c—in fact, the law expressed by the value of ϕ given above is at both very great and very small distances that of the inverse square.

XLVII. *On the Relative Ionization Potentials of Gases as observed in Thermionic Valves.* By G. Stead, *M.A.*, and B. S. Gossling, *M.A.*[*]

Preliminary Note.—The observations described in this paper were made during the summer of 1917, in connexion with the improvement of thermionic valves of a type in which the action was in considerable measure dependent on ionization. They are now published with the permission of the Admiralty.

(1) *Method employed.*—Some of the earlier methods [†] of determining the ionization potentials of gases have been the subject of criticism as indicating, not the appearance of positive ions, but some other effect such as photo-electric emission of electrons from the electrodes whose intended function was to collect the positive ions when formed. In the experiments here described the method used was similar to that employed by Bazzoni [‡], and consists in observing the effects of the presence of gas on the form of curves representing the variation of the current leaving an incandescent cathode with change in the potential applied to the collecting electrodes. When no gas is present, the chief factor determining the value of the space-current is the modification of the collecting field due to the applied potential by the addition

of the field due to the electrons at the time in transit across the space. (Space-charge effect.) If the electrons are projected with negligible velocity from an equipotential cathode, it can be shown[*] that the current will vary as the 3/2 power of the applied voltage up to the point when the current reaches a saturation value dependent on the temperature of the cathode, as shown in fig. 1. The current-voltage characteristics of tubes in which the voltage is great enough for the corrections for initial velocity and for variation in the

Fig. 1.
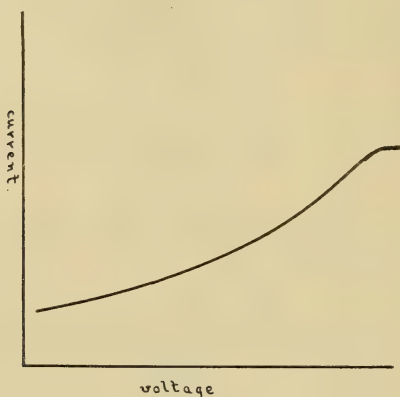
potential of the starting point on the cathode surface to be negligible, afford ample and accurate confirmation of this theory, which has further been applied with uniform success in the design of more complicated instruments, such as high-voltage thermionic valves.

When, however, the applied voltage is limited to low values, as in the case of the investigation of ionization effects, the effects of initial velocity and variation along the cathode are no longer to be neglected. In these experiments the same cathode heated to approximately the same temperature was used throughout. The results therefore indicate values of the ionization potential relative to any one of the gases observed taken as standard. It is, however, necessary to assume that replacement of one gas by another does not give rise to serious changes in the contact potential between the emitting and collecting electrodes.

The tube used was a three-electrode valve of the well-known form, the cold electrodes being connected together for the purposes of the experiments. Next the tungsten

filament there was a spiral molybdenum wire of diameter 0·4 mm. coiled into a helix of diameter 4·5 mm., having four or five convolutions per cm. length. Outside this was a nickel cylinder 10 mm. in diameter. In such a tube if the vacuum is high enough for the effects of ionization to be inappreciable, it is necessary to apply a potential of some 60 volts to the combined collecting electrodes in order to reach the saturation value of the space-current when the cathode is, as in these experiments, hot enough to give a saturation current of 30 milliamperes. The lower parts of the current-voltage curve, well away from this saturation value, are observed to have a form sensibly independent of the cathode temperature, but showing a slight bodily movement, not accompanied by change of form, in the negative direction parallel to the potential axis when the temperature is increased.

This movement is ascribable in some measure to increase in the average velocity of projection of the electrons constituting the current, but in large part also to increase of the length of the active part of the filament owing to a closer approach to the negative end of the filament by the point where the filament surface, in spite of the cooling effect of the end supports, first becomes hot enough to emit.

If, however, gas is present in considerable quantity, a point can be found, by giving to the applied potential a

Fig. 2

voltage.
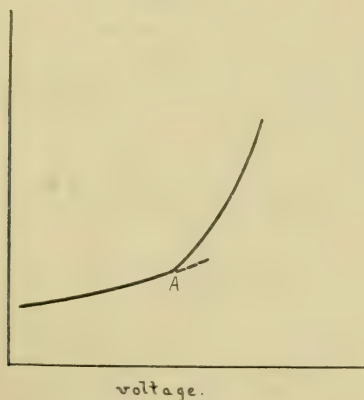
suitable value dependent on the gas used, where there is a marked departure from the form of the high-vacuum characteristic, an upward turn of the curve making its appearance, as shown at A in fig. 2. The high-vacuum

characteristic is reproduced in the lower parts of the curve; but the subsequent upward turn indicates, of course, that the higher applied potentials are competent to produce a larger current than in the high-vacuum case. In view of Langmuir's theory of the effect of the space-charge it seems difficult to account for this larger current except by the assumption that positive ions have appeared in the neighbourhood of the cathode. Positive ions would be expected to produce just such an effect as is observed, for they would tend to neutralize the opposing field due to the electrons in transit, and so permit the passage of a larger electron current for any given value of the applied voltage. As Professor Sir J. J. Thomson * has pointed out in a slightly different connexion, a very small proportion of positive ions produces a marked effect on the field by reason of their low velocity and consequent large contribution to the space-charge in their neighbourhood.

(2) *Discussion of Method.*—As mentioned above, some of the methods which have been used in attempts to measure ionization potentials are open to the serious objection that they fail to distinguish between the picking up of positive ions by the collecting electrodes and the photo-electric emission of negative electricity from these electrodes. The method described in the present paper is free from this objection, as the collecting electrodes are always at a positive potential with respect to the filament, and their function is to *collect* electrons, so that photo-electric *emission* of electrons would diminish rather than increase the current. If photo-electric emission from the filament itself is supposed to occur, this will merely slightly increase the saturation current from the filament, and will have no influence whatever on the current through the tube.

There remains the possibility that the sudden increase in the slope of the current-voltage curve is due to the production of positive ions, not by the thermions from the filament, but by more rapidly moving photo-electrons emitted by either the filament or the collecting electrodes under the influence of ultra-violet radiations from the gas molecules. Such a view, however, appears to be inconsistent with the quantum relation $Ve = h\nu$, for this relation not only determines the frequency of the ultra-violet light necessary to cause an emission

* Roy. Inst. Lecture, " Engineering," 103. p. 563 (1917). Proc. R. Inst. xxii. p. 175 (1917).

of electrons having energy equal to Ve, but also determines the energy which the bombarding electrons must have in order to stimulate the gas molecules to radiate ultra-violet light of frequency ν. In other words, if the quantum relation holds, the photo-electrons could never possess more energy than the thermally emitted electrons which are responsible for the radiation of the ultra-violet light, so that photo-electric emission could not cause positive ions to appear until the velocity of the thermions was sufficient to cause ionization of the gas.

Finally it is to be noticed that the value of the current through the tube at the critical point is of the order of 5 milliamperes, and this in itself appears to render any photo-electric explanation very improbable, unless the marked increase in currents of this magnitude is taken as representing a photo-electric emission far larger than any hitherto described.

(3) *Experimental Results.*—The method here described for the determination of ionization potentials has been applied to six different gases, with the following results :—

Mercury vapour	10·8	volts.
Argon	12·5	,,
Hydrogen	15	,,
Carbon monoxide	15	,,
Nitrogen	17·2	,,
Helium	20·8	,,

The numbers given in the above table represent the difference of potential between the anode and the *negative* end of the filament, and have not been corrected in any way. A short discussion of the necessary corrections is given in Section (4) below. Specimen curves showing the relation between current and voltage for each of the six gases are shown in figs. 3 and 4.

A certain amount of advantage is obtained by plotting the logarithm of the current against the logarithm of the applied voltage, as the initial part of the curve, before ionization sets in, is determined by the 3/2 power of the voltage, so that it becomes a straight line when plotted logarithmically. The line ceases to be straight when positive ions begin to appear. The curves of fig. 4 are re-plotted logarithmically in fig. 5.

Fig. 3.

Current-voltage curves for valves containing argon, hydrogen and helium.
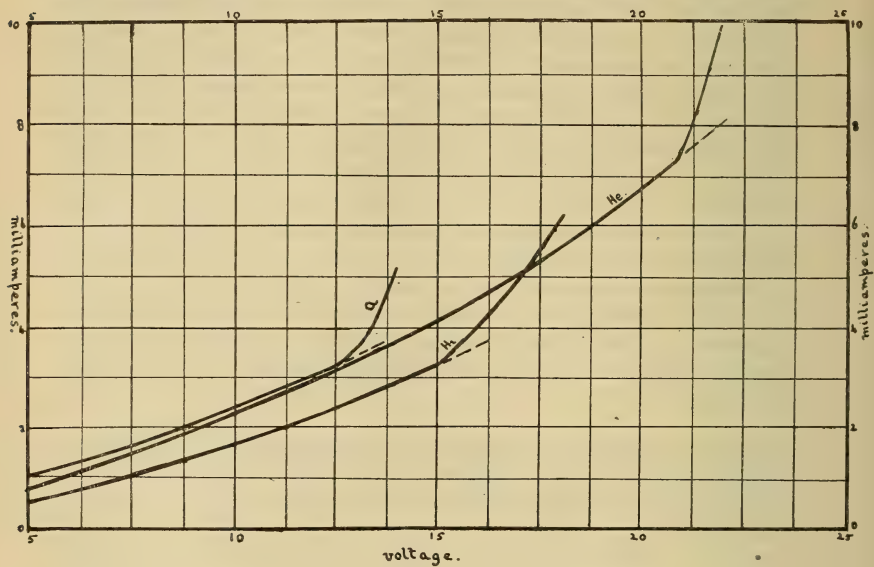
Fig. 4.

Current-voltage curves for valves containing mercury vapour, carbon monoxide, and nitrogen.

Fig. 5.

Logarithmic current-voltage curves for mercury, carbon monoxide and nitrogen.
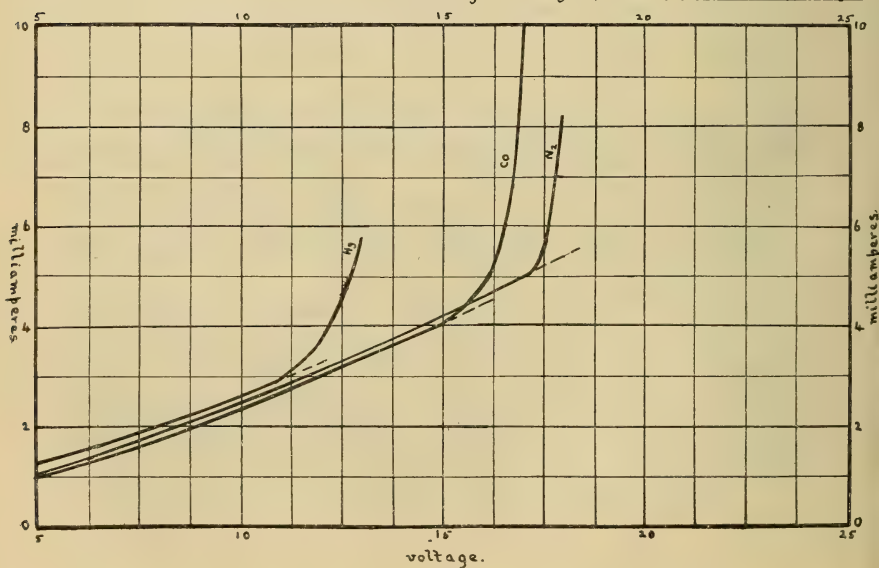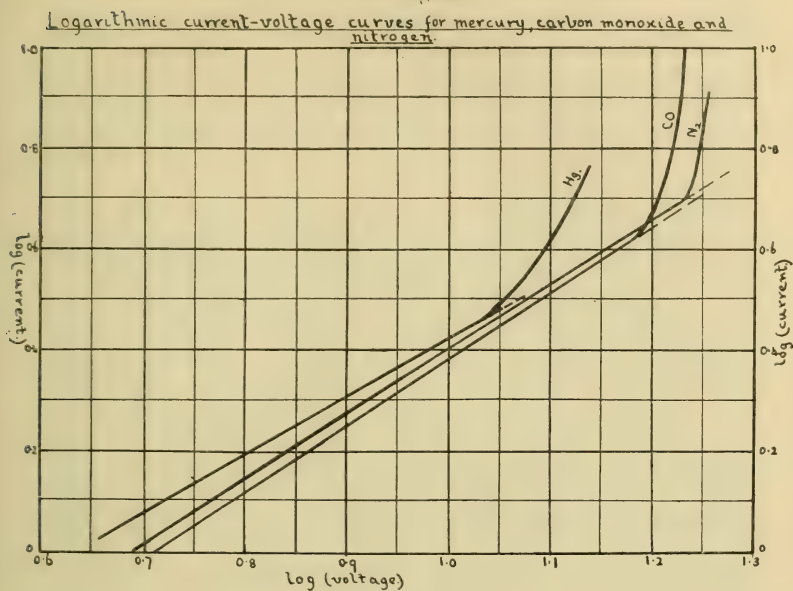
Fig. 6.

Current-voltage curves for filament in nitrogen at various pressures.
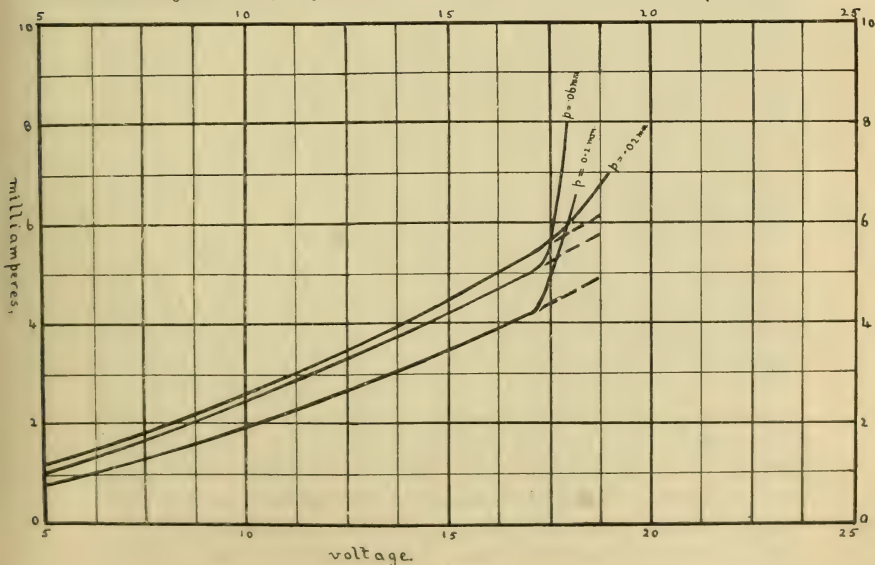
Experiments have been made with most of the six gases over a considerable range of pressure, and it has been shown that the critical point in the curve, for any given gas, occurs at a voltage which is sensibly independent of the pressure. The change of slope at the critical point is, of course, dependent on the gas pressure, and becomes less marked as the pressure is diminished, but otherwise there is no alteration. This is brought out clearly in fig. 6.

In all the experiments the valve used was highly exhausted by means of a Gaede rotary pump, followed by charcoal cooled by liquid air. During the evacuation the valve was baked at a temperature of about 400° C. for at least an hour, and the cold electrodes were subjected to sufficient electron bombardment to raise them to a red heat, in order to remove occluded gas. The gas to be experimented upon was then introduced in as pure a state as possible. The argon used was prepared from liquid air residues by sparking with oxygen over caustic potash, the excess of oxygen being finally removed by means of phosphorus. The argon when examined spectroscopically appeared to be free from nitrogen. Hydrogen was prepared by the electrolysis of a solution of barium hydroxide in water. Nitrogen from air was tried, but for most of the experiments it was prepared by mixing strong solutions of ammonium chloride and sodium nitrite and warming the mixture. Carbon monoxide was obtained by the action of strong sulphuric acid on formic acid, and also by heating nickel carbonyl. The helium used was obtained from Thomas Tyrer & Co., Ltd., and was purified by being left in contact with charcoal cooled by liquid air for a considerable time. In all cases mercury vapour was excluded by placing between the valve and the pump a U-tube immersed in liquid air. When mercury vapour itself was being studied this liquid air was removed after the valve had been thoroughly evacuated.

It may be remarked that, from the point of view of experiments on valves, and other apparatus in which a hot cathode is used, a knowledge of ionization potentials is often of great service, as the presence of a given gas in a sealed valve may frequently be detected by measuring the ionization potential in this way. Moreover, the test is quite sensitive. Thus the presence of mercury vapour is readily shown, even when it cannot be detected spectroscopically. Of course the conditions in a valve are not good for spectroscopic observation, as the discharge obtained through the bulb by means of an induction-coil is not very bright, but, nevertheless, this gives some idea of the sensitiveness of the ionization test. Again,

many valves which nominally contain helium, or nitrogen, give ionization voltages of about 15 after they have been in use for a short time. This indicates the presence of electrode gas, consisting probably of a mixture of carbon compounds and hydrogen, and shows that the bombardment of the anode and grid during the evacuation has not been carried far enough.

(4) *Corrections.*—The values of the ionization potentials obtained by the method here described require some correction, owing to the fact that the filament of a valve is not all at the same potential, nor at the same temperature, whilst correction is also necessary for the initial velocities of the emitted electrons, and for any contact potential difference which may exist between the filament and the collecting electrodes. As already remarked, the potential differences recorded are between the anode and the *negative* end of the filament, *i. e.*, they are the *maximum* potential difference in the valve. As a matter of fact the number of electrons which fall through this maximum difference of potential is entirely negligible, owing to the cooling of the ends of the filament by the leads. The magnitude of the cooling effect due to the leads has been fully discussed by one of the writers in a previous paper[*]; and it appears that if a point is taken on the negative limb of the filament such that the electron emission from it (per cm.) is one-tenth of that from the hottest part of the filament, then the potential difference between this point and the negative end is about 0·3 volt for filaments of the diameter used. The fraction 1/10 is of course chosen arbitrarily, but it probably gives the order of the quantity to be *subtracted* from the measured voltage to allow for the cooling due to the leads.

As regards the correction for the initial velocity of the electrons, it has been shown[†] that the average kinetic energy of the *emitted* electrons is equal to $2k\mathrm{T}$, where T is the absolute temperature of the filament and k is Boltzmann's constant. Now the average kinetic energy of the electrons *within the filament* is the same as that of a gas molecule at the same temperature, viz. $\frac{3}{2}k\mathrm{T}$. In the experiments here considered the value of T for the central part of the filament was about 2500° K., and at this temperature the value of $\frac{3}{2}k\mathrm{T}$, expressed in equivalent volts, is about 0·33. Hence $2k\mathrm{T}$ is equivalent to about 0·44 volt. At the point on the filament,

[*] Stead, Journal of Inst. Elect. Engineers, vol. lviii. Jan. 1920, p. 107.
[†] O. W. Richardson, 'Emission of Electricity from Hot Bodies,' pp. 140, 141.

considered in the previous paragraph, where the electron emission is one-tenth of that corresponding to the central part of the filament, the temperature would be considerably lower than 2500° K., and the correction would be reduced from 0·44 volt to about 0·40 volt. This correction must be *added* to the measured voltage, and it is seen to be almost compensated for by the amount (0·3 volt) to be subtracted on account of the non-uniformity of potential along the filament. It is to be observed that the velocities of the electrons emitted from a hot filament are distributed according to Maxwell's law, and the correction of 0·4 volt applies only to those electrons which are emitted with the average velocity corresponding to the given filament temperature. According to Maxwell's law of distribution an appreciable number of electrons, some 10 per cent. in fact, must come off with a velocity corresponding to at least one volt. It is clear that both this effect and also the want of uniformity of the potential of the filament must tend to make the position of the critical point in the current-voltage curves less sharply defined, and diminish the accuracy with which the ionization potential can be determined. Goucher[*] has overcome one of these difficulties by using as a source of electrons a platinum thimble heated to the required temperature by the radiation from a spiral of tungsten wire inside it, the tungsten wire being itself heated by an electric current. Such a source would not be satisfactory for the experiments here described because only a comparatively low temperature of the platinum is possible, and hence the electron emission is very small compared with that here employed.

The whole question of the contact difference of potential between a hot filament and a cold anode in a moderate or high vacuum appears to be obscure at the present time, and much work remains to be done before the correction to be applied to ionization potentials on this account can be computed with any degree of confidence. It seems quite likely, however, that a correction of the order of 0·5 volt may be necessary[†].

(5) *Discussion of Results.*—All these experiments on ionization potentials were carried out in May, June, and July, 1917, with the exception of those on helium, which were not undertaken until September 1917. Some of the

[*] Physical Review, viii. p. 561 (1916).

[†] Richardson, 'Emission of Electricity from Hot Bodies'; Stoekle, Phys. Rev., viii. p. 534 (1916).

results obtained were not in agreement with the values generally accepted at that time. Thus the ionization potentials of hydrogen and nitrogen, as measured by the Franck and Hertz method, came out at about 11 volts and 8 volts respectively, and for mercury vapour opinion was divided between 4·9 volts and about 10·5 volts. By a modification of the Franck and Hertz method, designed to eliminate photo-electric effects, Davis and Goucher * have established the fact that no appreciable ionization occurs in mercury vapour under 10 volts. In the same paper Davis and Goucher came to the conclusion that ionization occurs in hydrogen at about 11 volts, but that a second type of ionization sets in at about 15·8 volts. Shortly after the appearance of Davis and Goucher's paper Bishop † published an account of some experiments on hydrogen in which he confirmed Davis and Goucher's result that a second (and stronger) ionization appears in hydrogen at between 15 and 16 volts. The higher value agrees with the value of the ionization potential of hydrogen as determined by the method described in the present paper. No trace of ionization at 11 volts, however, appears in a valve containing hydrogen.

The only measurements of the ionization potential of nitrogen which are in agreement with the value here given (17·2 volts) are those made by Davis and Goucher ‡, and more recently by H. D. Smyth §. These observers have come to the conclusion that the true ionization potential of nitrogen is between 17 and 18 volts, and not about 8 volts, as had been previously supposed.

The value 12·5 volts for argon is in agreement with the result given by McLennan in the Physical Review for July 1917, but very recently Horton and Davies ‖ have come to the conclusion that ionization does not occur in argon until about 15 volts, and Rentschler ¶ gives the value 17 volts. It is very difficult to reconcile this with the behaviour of argon in valves, in which it is hardly possible to avoid the conclusion that strong ionization occurs at about 12·5 volts.

The result (20·8 volts) obtained for the ionization potential

* Physical Review, August 1917, p. 101.
† Phys. Rev., September 1917, p. 244.
‡ Phys. Rev., January 1919.
§ Phys. Rev. xiv. p. 409 (1919).
‖ Proc. Roy. Soc. vol. xcvii. A. p. 1 (1920).
¶ Phys. Rev. xiv. p. 503 (1919).

of helium is in agreement with that of most other observers[*], except Horton and Davies[†], who have recently found a higher value, as in the case of argon. Richardson and Bazzoni[‡] deduced a value of 29 volts from a consideration of the ultra-violet spectrum of helium.

As regards carbon monoxide, the value, 15 volts, here given at present lacks confirmation by other observers. Hughes and Dixon[§], employing a method of the Franck and Hertz type, obtained the value 7·2 volts. It seems probable that, as in the case of nitrogen, this low value represents a photo-electric effect, rather than the true ionization potential. At any rate there is no measurable ionization, in a valve containing carbon monoxide, below about 15 volts.

It may be of interest to note that the increase in slope of the current-voltage curve which occurs at the critical point is not accompanied by any visible radiation. The conditions for observing a faint glow between the electrodes are, however, not good, on account of the glare from the filament. All workers with soft valves are familiar with the fact that when the anode voltage exceeds a certain value a general glow suddenly fills the bulb, but the appearance of this general glow must on no account be confused with the critical point which has been taken by the writers to denote the formation of positive ions by collision. The general glow sets in at a much higher voltage than the critical point— usually not less than twice the voltage corresponding to the critical point. Moreover, whilst the position of the critical point is independent of the form of the electrodes and of the gas pressure, and nearly independent of the filament temperature, the potential at which the general glow appears depends very much on all these factors. Thus, in an audion type valve, with plane anodes and grids, the general glow occurs much more readily than in a cylindrical type valve, and the appearance of the general glow depends so much on the gas pressure that a rough estimate of the softness of a valve may be made by observing the voltage at which the glow appears. Again, if a current-voltage curve is plotted up to a potential at which the general glow appears, there is at this point a complete discontinuity, the current suddenly jumping to many times its previous

  * McLennan, Phys. Rev., July 1917, p. 84. Bazzoni, *loc. cit.*, and others.
  † Proc. Roy. Soc. vol. xcvii. A, p. 408.
  ‡ Phil. Mag. xxxiv. p. 285 (1917).
  § Phys. Rev., November 1917.

value without, apparently, passing through any of the intermediate values. If the potential is now gradually lowered there is a marked hysteresis effect, and the general glow suddenly disappears at a potential considerably lower than that at which it appeared. The disappearance of the general glow is accompanied by a sudden and discontinuous fall in the current. This behaviour is in marked contrast to the behaviour at the critical point. At this latter point there may be a discontinuity in the slope of the curve, but there is certainly no sudden jump in current without passing through intermediate values. Also there is little or no genuine hysteresis, the only observable effect being that the portion of the curve dependent on the 3/2 power of the voltage may be slightly displaced, but not the position of the critical point. This displacement is probably due to some change in the surface of the filament resulting from its bombardment with positive ions.

The point at which the general glow appears also shows up in ordinary three-electrode valve characteristics as a sudden discontinuity in the value of the current, the occurrence of which makes the adjustment of some " soft " valves troublesome.

(6) *Summary.*—A simple method is described of determining the differences of potential which are necessary to cause positive ions to be produced in soft thermionic valves. This method has been applied to six different gases, viz.: mercury vapour, argon, hydrogen, carbon monoxide, nitrogen, and helium.

The work was carried out in the Cavendish Laboratory, and the writers wish to express their best thanks to Professor Sir J. J. Thomson.

Note added September 3, 1920.

Since the above was written another valve method of determining ionization potentials has been described by Hodgson and Palmer [*]. For mercury vapour, nitrogen, and helium these observers obtained results substantially in agreement with those given in the present paper, but for argon a higher value (16·6 volts) was obtained.

[*] Radio Review, vol. i. Aug. 1920, p. 525.

XLVIII. *Optical Rotation, Optical Isomerism, and the Ring-Electron.* By H. STANLEY ALLEN, *M.A., D.Sc., University of Edinburgh* [*].

Introduction.

WHEN a beam of plane-polarized light passes through certain pure liquids and even certain vapours, there is produced a rotation of the plane of polarization, which implies that there must be some asymmetry in the molecule of the substance concerned. This asymmetry has been studied mainly from the chemical side, the difference between isomeric molecules of the same structure being explained by a different arrangement of atoms in space. On the physical side progress has been less satisfactory, and although a formal connexion between optical rotation and the electromagnetic theory of light was established by Drude [†], it is only recently that successful attempts have been made to explain why asymmetry in molecular structure should involve difference in the velocity of propagation of circularly polarized light. In this paper the subject is approached from a somewhat different standpoint from that usually adopted, for it is assumed that the electron, in addition to its electrostatic action, behaves like a current circulating in a closed ring, and consequently acts as a small magnet. This conception involves a modification of prevailing views, both as regards the action of light on a system of electrons, and also as regards the constitution of the molecule. The paper therefore divides naturally into two parts. The first is concerned with the propagation of an electromagnetic wave through an assemblage of ring-electrons, whilst the second (which may prove of more interest to the chemist) deals with the question of the arrangement of the electrons in the molecule of an optically active substance, assuming the theory of the "cubical atom" developed by G. N. Lewis [‡] and Irving Langmuir [§].

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[*] Communicated by the Author.
[†] Drude, ' The Theory of Optics,' part ii. Chapters vi. & viii.
[‡] G. N. Lewis, Journ. Amer Chem. Soc. vol. xxxviii. p. 762 (1916).
[§] I. Langmuir, Journ. Amer. Chem. Soc. vol. xli. pp. 868, 1543 1919).

Part I.

Optical Rotation.

Rotation of the plane of polarization of light by a pure liquid or a vapour has presented serious difficulties to the theoretical physicist. Drude and Voigt have shown what type of electromagnetic equations are required to account for the rotation, but " there is no satisfactory representation of the mechanism by means of which an asymmetrical molecular structure turns the plane of polarization " *. In the ordinary theory of dispersion the equation of motion of an electron (mass m, charge e) is of the form

$$m \frac{\partial^2 \xi}{\partial t^2} = e \mathrm{X} - \frac{4\pi e^2}{\theta} \, \xi,$$

where ξ is the x-component of the displacement from the equilibrium position, X is the x-component of the exterior electric force, and the last term represents the restoring force called into play by the displacement of the electron. Drude includes also a frictional term which represents a force retarding the vibrations. In an isotropic medium the only possible extension of the equation is by the introduction of a term of the form $ef'\left(\dfrac{\partial \mathrm{Y}}{\partial z} - \dfrac{\partial \mathrm{Z}}{\partial y}\right)$. By combining the equations thus modified with Maxwell's equations for the electromagnetic field, it can be shown that when plane-polarized light falls on the medium, two waves are propagated through it with different velocities, the first representing right-handed circular polarization, the second left-handed circular polarization. The superposition of the two waves yields a plane-polarized wave in which the plane of polarization rotates through a definite angle for each unit length of optical path. The terms which have been added to the equations may be taken to represent a torsional electric force. Drude gives a graphical representation by conceiving that because of the molecular structure the paths of the electrons are not short straight lines, but short helices twisted in the same direction, with their axes directed at random in space. " A rifle bullet lying in its rifle barrel would be displaced in a similar manner along the barrel both by a pulling and twisting force. But if we take the dimensions of a single electron to be very small, we exclude the possibility of a constraint which would enable a couple to cause a motion in one direction. We must in that case draw the conclusion

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* Schuster, 'The Theory of Optics,' § 162, 1904 edition.

that the vibrations of the electron which give rise to the rotatory effect are motions of systems of electrons united together by certain forces which are such that a couple of electric forces produces a displacement of the positive electrons in one direction or of the negative electrons in the opposite direction along the axis of the couple" (Schuster).

In the last few years several mathematical physicists, notably Born * and Gray †, have developed the latter hypothesis, and have shown that the optical activity of liquids and gases can be explained by regarding the molecules as coupled systems. Born views a molecule as a system of coupled electrons, the coupling and the restoring forces being identical. In the paper by Gray the atom is looked upon as a particle of dielectric. The atoms are coupled according to the ordinary laws for a doublet, and the restoring force on an electron is not identical with the coupling, but may be influenced by it.

To the present writer it appears that a simpler and more realistic mental picture of optical activity may be obtained by abandoning the limitation that the dimensions of the electron must be very small, and employing the ring-electron or "magneton" of A. L. Parson ‡. Such an electron vibrating backwards and forwards along a straight line seems admirably adapted to replace the electron moving in a spiral path as imagined by Drude.

The Ring-Electron.

The ring-electron may be looked upon as a charge of negative electricity distributed continuously around a ring which rotates on its axis with high speed, and therefore behaves like a small magnet. In an important paper on the electromagnetic mass of the Parson magneton, Webster § has shown that the ratio of the radius of the cross-section of the ring to that of the ring itself is extremely minute, and that most of the energy and momentum of the field are concentrated very closely around the ring. Thus, to a first approximation, the ring-electron may be regarded as a current in a circular wire of negligible thickness. In a later paper ‖ it is shown that the gyroscopic effect of the magneton

* Born, *Phys. Zeitschr.* vol. xvi. p. 251 (1915); *Ann. der Physik,* vol. lv. p. 177 (1918).

† Gray, Phys. Rev. vol vii. p. 472 (1916).

‡ A. L. Parson, "A Magneton Theory of the Structure of the Atom," Smithsonian Misc. Coll. No. 2371, Nov. 1915.

§ Webster, Phys. Rev. vol. ix. p. 484 (1917).

‖ Webster, Phys. Rev. vol. ix. p. 561 (1917).

is exactly the same as for an electron of the classical type moving in an orbit equal in size to the ring with a speed equal to that of the electricity of the ring. These results simplify very greatly the consideration of problems connected with the ring-electron.

In the case of an ordinary electron exposed to light, the incident vibrations of the light bring about forced vibrations through the action of the electric vector in the wave-front. With the modification here proposed, the effects are more complicated, for the ring-electron will be acted upon both by the electric and magnetic vectors. Any rotation of the plane of the ring, which may be produced by the magnetic force of the light-wave, will be neglected. There is a more important effect due to the alternating electromotive force acting round the ring and producing changes in the magnetic moment of the equivalent magnet. Consider a fixed ring-electron, the axis of the ring being parallel to the axis of x. When this is exposed to a light-wave, there will be an electromotive force * in the ring given by

$$E = -\frac{d}{dt}\iint \alpha dS = -\iint c\left(\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}\right)dS$$
$$= -Ac\left(\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}\right), \text{ approximately,}$$

where A is the area of the ring. If this alternating E.M.F. be represented by $E_0 \cos pt$, there will be round the ring an induced current differing in phase by $\frac{\pi}{2}$ from the electromotive force, and represented by $\frac{E_0 \sin pt}{Lp}$. The magnetic moment of the electron will be increased by an amount $\frac{AE_0 \sin pt}{Lp}$, and in consequence there will be a mechanical force acting upon the electron proportional to this increase and to the space variation of the controlling magnetic field. Thus the equation of motion of the electron will contain a term of the form $ef''\left(\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}\right)$ required by Drude's theory, the coefficient ef'' being proportional to A^2/L, and depending also on the character of the magnetic field due to the remainder of the molecule or to any external magnetic system. It then follows, as shown by Drude, that there will be two

* Following Drude, E, α, β, γ are in electromagnetic units, whilst e, X, Y, Z are in electrostatic units.

circularly polarized waves travelling through the medium with different velocities, according as the rotation is right-handed or left-handed, and in consequence the plane of polarization will rotate uniformly about the direction of propagation of the light, the amount of the rotation per unit length being

$$\delta = 2\pi^2 f/\lambda^2,$$

where λ is the wave-length of the light (in vacuum),

and
$$f = \Sigma \frac{\theta f' N}{1 - \left(\dfrac{\tau_h}{\tau}\right)^2}.$$

Here N denotes the number of electrons of the type considered, in unit volume, τ is $1/2\pi$ times the period of vibration of the light, and τ_h is $1/2\pi$ times the natural free period of the electron.

It is not claimed that the foregoing discussion gives a complete account of the behaviour of ring-electrons under the influence of light-waves. There are other actions which may be briefly referred to. In connexion with the magnetic rotation of the plane of polarization, Drude has given a theory based on the hypothesis of molecular currents, as conceived by Ampère and Weber. It is assumed that these molecular currents are made parallel to one another by the action of the external field. Drude points out that the displacement of the molecular current when a light-wave falls upon it, produces a displacement of the magnetic lines of force which arise from it, so that a peculiar induction effect takes place. It is to be observed that this theory calls for rotations of opposite sign on opposite sides of an absorption band. It would seem that a complete theory of the action of light-waves on an assemblage of ring-electrons would have to take into consideration also the "Hall effect," which has been found to yield a satisfactory explanation of rotatory dispersion in a magnetic field. Thus the hypothesis of the Hall effect explains the result that the rotation is in the same direction on opposite sides of the absorption band in the case of sodium vapour, and also predicts an effect when the rays of light are perpendicular to the lines of magnetic force. I have discussed elsewhere * the possibility of accounting for the Zeeman effect by means of the ring-electron.

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* H. S. Allen, Proc. Phys. Soc. Lond. vol. xxxi. p. 49 (1919).

Part II.

Optical Isomerism.

In the theory of atomic structure first put forward by G. N. Lewis and afterwards developed by Langmuir, the electrons, instead of rotating in rings as in Bohr's theory, are supposed to occupy, or to oscillate about, positions which are fixed in space with reference to the atomic nucleus. This fixity of the electrons is a characteristic feature of the magneton theory of the atom advanced by Parson—a theory which has not met with the recognition it merited, partly because it is based on the notion of a positive sphere, partly because Parson did not accept the atomic numbers of Moseley, which are now regarded as being determined not merely in a relative but also in an absolute sense. The magneton, or ring-electron, makes it possible to have stationary electrons. The most stable groupings of electrons, according to Lewis and Langmuir, are (1) the *pair*, as illustrated in the helium atom, (2) the *octet*, or group of eight electrons arranged approximately at the corners of a cube. Parson showed that such a group of eight magnetons formed a system possessing very low magnetic energy and producing a very weak external field. This assumption is in agreement with the " rule of eight," to which I have drawn attention in connexion with atomic and molecular numbers *. The number of unit electric charges in the atomic nuclei of related atoms or molecules frequently differs by 8 or a multiple of 8.

In the formation of chemical compounds only an even number of electrons can be held in common. " Two octets may hold 1, 2 or sometimes even 3 pairs of electrons in common. A stable pair and an octet may hold a pair of electrons in common. An octet may share an even number of its electrons with 1, 2, 3 or 4 other octets. No electrons

Fig. 1.
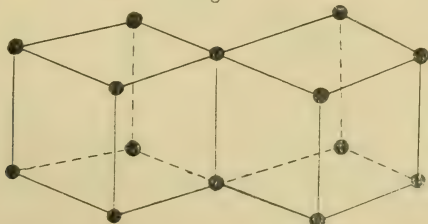
can form parts of more than two octets " (Langmuir, Postulate 11). Thus the single bond commonly used in graphical formulæ involves two electrons held in common by two atoms (fig. 1); the double bond implies that four electrons

* H. S. Allen, Trans. Chem. Soc. vol. cxiii. p. 389 (1918).

are held conjointly by two atoms (fig. 2). According to a suggestion made by Lewis and adopted by Langmuir, the electrons, which are held in common between two octets or an octet and a stable pair, are drawn together to form pairs,

Fig. 2.

perhaps by the action of magnetic forces. Thus in methane (CH_4) the 8 electrons are located in pairs at the 4 corners of a tetrahedron, each hydrogen nucleus being held by one pair.

On this view, dextro- and lævo-rotatory forms of a compound may be represented, as I have pointed out previously [*], by mirror images as in fig. 3. In this diagram the letters N and S may be supposed to indicate the polarity of the exposed face of the ring-electron.

Fig. 3.
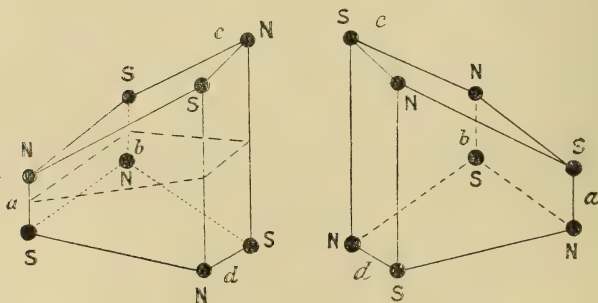
A suggestion has been made by W. E. Garner [†] that a large number of optical isomerides may possibly exist amongst organic compounds in consequence of the right-handed or

* 'Nature,' vol. cv. p. 71 (1920).

† W. E. Garner, 'Nature,' vol. civ. p. 661 (1920); vol. cv. p. 171 (1920). See also letters from A. E. Oxley, *id.* vol. cv. pp. 105, 231 (1920).

left-handed rotation of a valency electron around the direction of a chemical bond. This suggestion does not receive support from the arrangement shown in the figure which seems to yield exactly the same number of isomerides as the ordinary structural formulæ. It is true that it is possible to reverse *in the diagram* the magnetic polarity of one or more pairs of electrons, but even if the arrangements so obtained were stable, it is doubtful whether they would represent different isomerides. If such a reversal of the magnetic polarity were accompanied by a change in the nature of the compound, it does not seem possible to explain the phenomenon of free mobility about a single bond which is assumed in stereochemistry. It should, however, be mentioned that although the prevailing view is that the single bond between carbon atoms does not fix the positions of the atoms connected by it as regards rotation about the common axis, the contrary opinion has been supported by Aberson (Cohen, 'Organic Chemistry for Advanced Students,' pp. 116, 133).

This raises a question in the theory of the cubical atom which requires further elucidation. It is clear from fig. 3 that the electrons associated with group *a* are related to the electrons of group *b* in a manner different from that in which they are related to the electrons of *c* or *d*. Lewis assumes that each pair of electrons is drawn together so as to represent a single corner of "the model of the tetrahedral carbon atom which has been of such signal utility throughout the whole of organic chemistry." But even if the electrons in a pair are drawn closer together than in the diagram, the lines joining the centres of the pairs are oriented differently when *a* and *b* are compared with *c* and *d*. The difficulty might be got over by supposing the electrons in a pair to rotate about a point midway between them, or in the case of the ring-electron one electron might be supposed to move over the other, giving the arrangement
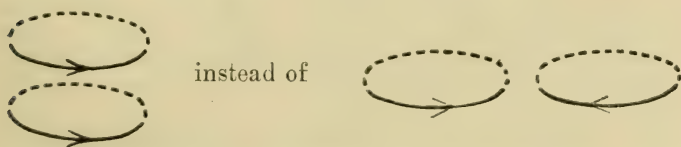
Dr. Langmuir has been kind enough to express his views on this question in a letter to the author. "When a pair of electrons acts as a bond between two adjacent atoms, the relationship between the two electrons has certainly become changed. The very fact that we never have one or three

electrons held in common between two atoms is proof that the electrons in the pair are bound into a kind of unit, in which the relationship between the two electrons is very different from that between two adjacent electrons in the neon atom . . . . In practically all the compounds of carbon, there are eight electrons arranged around the kernel of the carbon atom, but these electrons are gathered into four pairs, each pair constituting a unit or bond between the carbon atom and atoms surrounding it. The nature of this unit is evidently closely related to that of the pair of electrons in the helium atom and hydrogen molecule, and my guess is that such a pair consists of two electrons revolving about a line connecting the kernels of the adjacent atoms, whereas the electrons in the neon atom are revolving about eight positions located at the corners of a cube. We are thus led to a conception of the carbon atom which is practically identical with that of the organic chemist, namely : that the carbon atom exhibits four valence bonds arranged in space in a symmetrical way, corresponding to the corners of a tetrahedron."

According to the present theory, optical activity arises from a difference effect, and can be manifested only when there is lack of compensation amongst the electrons associated with the various parts of the molecule. If the chemical bond is to be attributed to a *pair* of electrons arranged side by side, it is easy to understand how such compensation can be brought about in the great majority of chemical compounds. In the case of a single asymmetric carbon atom, the symmetrical arrangement of each of the four electron pairs is disturbed by the presence of the adjacent groups, resulting in only partial compensation. Thus, in the compound $C\,a\,b\,c\,d$, the pair of electrons associated with group a is under the influence of the unlike groups c and d, and the condition of symmetry is absent. But if c and d are made alike, the whole molecule will have a plane of symmetry indicated by the broken line in the left half of fig. 3. Thus the molecule will be inactive through "internal compensation" with respect to the electrons which form the outer shell of the carbon atom.

This arrangement of the electron pair side by side gives readily an explanation of the fact that most chemical compounds show diamagnetic properties, for such a pair would produce a very weak external magnetic field, and this configuration has in fact been utilized by Oxley [*] to account for the diamagnetism of the hydrogen molecule.

* 'Oxley, 'Nature,' vol. cv. p. 327 (1920).

The evidence at present available does not justify a decisive verdict as between the two possible arrangements
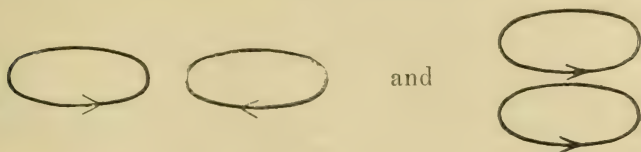
for the electron pair. It may be that *both* are possible, with corresponding differences in the optical and magnetic properties of the compound. On the basis of the latter configuration, a large number of isomerides may exist in accordance with the suggestion of Garner, referred to above. " The electrons rotating in pairs around the four carbon valencies may possess either clockwise or anti-clockwise rotation with respect to the central carbon atom. On the assumption that two of these pairs of electrons rotate in a clockwise and two in an anti-clockwise direction, it is possible to deduce that eight isomerides of cinnamic acid may exist." If the clockwise rotation of the electron gives a north-seeking character to the valency and the anti-clockwise rotation a south-seeking character, isomerides may exist which may be represented graphically as below
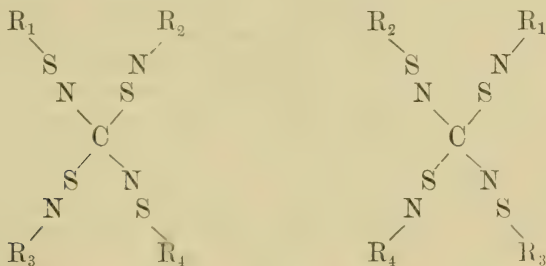
The existence of the isomeric compounds suggested by Garner depends upon the somewhat arbitrary assumption that two of the pairs of electrons are rotating in a clockwise sense, and the other two in an anti-clockwise sense as viewed from the carbon atom. In a three-dimensional model the four valencies may be supposed directed towards the corners of a regular tetrahedron. It will then be observed that Garner's assumption implies that the valency electrons in such a compound confer upon it paramagnetic properties, since the suggested arrangement of electrons would have

a resultant magnetic moment. It would, of course, be possible to overcome this difficulty by a further assumption that magnetic compensation arises from other parts of the molecule.

Optical Rotatory Power.

The theory of optical rotation for liquids and gases here proposed appears to be in good agreement with the experimental facts as summarized by Gray.

1. Any substance of which the molecules are truly asymmetrical causes rotation.
2. Antipodes, a molecule and its mirror image, rotate in opposite directions.
3. Symmetrical molecules are not active.
4. Absorption systems in an active substance cause anomalies in the rotary dispersion, although the origin of the band may lie in a part of the molecule distant from the central carbon atom.
5. The magnitude of the activity is profoundly influenced by the molecular structure, and is roughly dependent on the magnitude of the asymmetry of the molecule.
6. Activity varies with temperature and pressure, and with the concentration of active molecules.

From what has already been said it is obvious that the first three results are in accord with the theory. The fourth result follows alike from the electrostatic theories of Born and of Gray and from the electromagnetic theory here given. In the first case the rotation depends on a space derivative of the electric force, in the second on a space derivative of the magnetic force. The fifth result requires somewhat closer examination.

Guye [*] and Crum Brown [†] have discussed independently the relation of optical activity to the character of the radicles united to the asymmetric carbon atom. "It is obvious that the amount of optical activity of a given compound containing an asymmetric atom of carbon depends upon the amount of difference in character among the four radicles united to the asymmetric carbon atom, so that if two of them are very nearly equal we come very near to a compound of a symmetric carbon atom, in which the optical activity is zero. The question suggests itself, How are we to measure this difference of character?" Guye regarded

* Guye, *Compt. Rend.* vol. cx. p. 714 (1890) ; vol. cxvi. pp. 1378, 1451 (1893).

† Crum Brown, Proc. Roy. Soc. Edin. vol. xvii. p. 181 (1890).

the *mass* of each radicle and the distance of its centre of gravity from the centre of figure of the tetrahedron as all that need be considered—a view which could not be held at the present time ; but Crum Brown assumed merely " that there is a function, capable of numerical representation, derivable from the composition and constitution of the radicle and the temperature of the substance, and that it is the difference between the values of this function in the case of two radicles which gives us the difference of character referred to." According to the present theory, it would be the values of the magnetic and electric fields produced by the radicles which would determine the degree of asymmetry.

Amongst the papers read at the discussion on " Optical Rotatory Power," held before the Faraday Society in 1914, one of the most interesting from a theoretical standpoint was that by Leo Tschugaeff. He came to the conclusion that the electrons which are most active in producing rotation are attached to the asymmetric carbon atom itself, or are situated in the immediate neighbourhood of the centre of activity. As regards the other electrons which come into play in rotatory dispersion, we can assume that their activity is diminished with increasing distance from the asymmetric complex. Again, if it be admitted that the degree of asymmetry of the molecule depends upon the differences of four constants K_1, K_2, K_3, and K_4, corresponding with the four groups attached to the carbon atom, the value of the unknown function K must depend on the degree of saturation. " Thus, it would be expected that strongly unsaturated radicles containing free-movable electrons would exert a considerable influence on the electric field produced by the molecule, the differences $K_1 - K_2$ . . . being much larger if K_2 corresponds with a saturated group and K_1 to an unsaturated one than if both the groups are nearly equally saturated."

The present theory is in general agreement with the views just described, but the equation representing the views of Guye and Crum Brown would require some modification. Since the rotatory power as well as the dispersion is assumed to be equal to the sum of the effects produced by the several active electrons, as is expressed by the formula

$$\delta = \frac{k}{\lambda^2} \Sigma \frac{\theta f' N}{1 - \left(\frac{\tau_h}{\tau}\right)^2},$$

it is necessary to consider the contributions from the four *pairs* of electrons associated with the four attached groups.

If the arrangement represented in fig. 3 be adopted, the asymmetry of pair a is due to groups c and d, and the resulting contribution to the rotation will be equal to the algebraic sum of two terms of the type given above. In order to explain the absence of rotation in a symmetrical molecule, it is necessary to assume that the sign is positive for one electron and negative for the second electron of the pair. Let us further assume, at least as a first approximation, that the natural free period is the same for each electron, so that the denominator $1-\left(\dfrac{\tau_h}{\tau}\right)^2$ is the same. The contribution to the rotation made by the *pair* of electrons may then be written

$$\delta_a = \frac{k}{\lambda^2}\, \frac{\theta N}{1-\left(\dfrac{\tau_h}{\tau}\right)^2}\, (f'_{a_1}-f'_{a_2})$$

$$= A(f'_{a_1}-f'_{a_2}).$$

Hence the total result may be written

$$P = A(K_c-K_d)+B(K_d-K_c)+C(K_a-K_b)+D(K_b-K_a),$$

since the difference between f'_{a_1} and f'_{a_2} is due to the presence of the unlike groups c and d. It follows that

$$P=(A-B)(K_c-K_d)+(C-D)(K_a-K_b).$$

In the case in which the groups c and d become identical, $K_c=K_d$ and $C=D$, so that there is no resultant activity.

If, on the other hand, the alternative arrangement of coaxial rings be adopted, the resultant effect would have to be calculated by methods similar to those employed by Gray * in the case of purely electrostatic forces.

According to the principle of optical superposition formulated by van't Hoff, the total rotatory power in a compound containing several asymmetric carbon atoms is the algebraic sum of the various radicles taken separately. This rule seems to be valid at least to a first approximation †. The work of C. S. Hudson ‡ and his collaborators shows that the principle holds fairly closely in the case of certain amides. The approximate validity of the rule is to be expected on such a theory of optical rotation as that here put forward.

The variation of optical activity with temperature,

* *Loc. cit.*

† Tschugaeff, *loc. cit.*

‡ C. S. Hudson, Journ. Amer. Chem. Soc. vol. xli. pp. 1140, 1141 (1919).

pressure, and concentration presents difficulties whatever view may be adopted as to the origin of the rotation. The subject has been discussed by Livens [*], who has examined the effect of the presence of inactive substances, as in the case where a simple active substance is dissolved in an inactive liquid, and also by Gray [†]. Assuming that the atoms are vibrating about points of equilibrium inside the molecule, the average value of both the electrostatic and the magnetic field produced will change with the amplitude of the oscillations, and consequently the degree of asymmetry will be a function of the temperature.

Finally, it may be noted that the optical activity of compounds containing asymmetric atoms other than carbon atoms follows at once from the theory. Such active compounds are known in the case of nitrogen, phosphorus, sulphur, selenium, tin, silicon, cobalt, chromium, rhodium, and iron [‡]. It is perhaps not without significance that the three elements cobalt, rhodium, and iridium occupy a peculiar position in Langmuir's theory, as in each case there is an odd electron in the outer shell which is assumed to occupy a position at one end of the polar axis.

Summary and Conclusion.

In the present paper a theory of optical rotation has been advanced in which the electron, instead of being regarded as a point charge, is looked upon (as suggested by A. L. Parson) as an anchor ring of negative electricity rotating rapidly about its axis. Such a ring-electron vibrating in a linear path takes the place of an ordinary electron moving in a spiral path as postulated by Drude. It is shown that rotation of the plane of polarization of light will result, and an expression is found for the amount of rotation per unit length. Employing the theory of atomic structure due to Lewis and Langmuir, a graphical representation may be obtained for dextro- and lævo-rotatory forms of a compound. The experimental facts with regard to optical activity are in good agreement with the theory put forward, which may be applied not merely to carbon compounds, but to any compound containing an asymmetric atom.

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[*] Livens, Phil. Mag. vol. xxv. p. 817 (1913).

[†] *Loc. cit.*

[‡] A. W. Stewart, ‘Stereochemistry,’ chapter x. (1919).

XLIX. *The Effect of a Trace of Impurity on the Measurement of the Ionization Velocity for Electrons in Helium. By* FRANK HORTON, *Sc.D., Professor of Physics in the University of London, and* DORIS BAILEY, *M.Sc., Assistant Lecturer in Physics in the Royal Holloway College, Englefield Green*[*].

IT has been found by Horton and Davies[†] that radiation is produced when electrons having a velocity of 20·4 volts collide with helium atoms, and that this effect is not accompanied by any ionization of the gas. Ionization of helium was found to occur when the electron velocity was raised to 25·6 volts. An account of the experiments from which these results were obtained was given to Section A of the British Association at the meeting in Bournemouth in 1919, and in the discussion which followed, the view was expressed by some of the speakers that ionization of helium occurs at the lower critical velocity mentioned above. Dr. Goucher reported that experiments made by him with an improved form of his original apparatus for distinguishing between the photoelectric effect of radiation on the electrodes and the ionization of the gas by electron impacts, had resulted in the detection of some ionization as well as radiation at about 20 volts, and copious ionization at about 25·5 volts. He stated that the helium used by him was possibly not as pure as that used in the experiments of Horton and Davies. The evidence of other speakers was mainly to the effect that when helium was used in a thermionic valve the current-E.M.F. curves showed a rise at about 20 volts which could only be due to the production of ionization at that point.

The ionizing velocity for electrons in helium was first investigated by Franck and Hertz, who gave 20·5 volts as the critical value at which ionization occurs[‡]. It was pointed out by Bohr that the method used by these experimenters was not capable of distinguishing the effects of a production of radiation in the gas from those of ionization of the gas by electron collisions. From theoretical considerations Bohr had deduced the value 29 volts as the minimum ionization velocity of helium, and he suggested that the effect detected at 20·5 volts was not a genuine ionization of the helium, but a secondary effect due to the production of radiation in the gas. He pointed out that such a radiation

would not only act photoelectrically on the metal parts of the apparatus, but would also be able to ionize any impurities present in the gas*. It is clear that the presence of easily ionizable impurities would thus result in the detection of ionization at the radiation velocity, even when the experiment is performed in an apparatus such as that of Dr. Goucher. In the early experiments with helium-filled valves, which were made at the Royal Holloway College in 1915, evidence of ionization at about 20 volts was always obtained, and it was only during the course of the investigation referred to at the beginning of this paper, that the view that helium can be ionized by electron collisions with this velocity was finally abandoned. Franck and Knipping have also arrived at the conclusion that the earlier experiments of Franck and Hertz measured the minimum radiation velocity and not the minimum ionization velocity of the gas ; and in a recent paper † they have given values of these two critical velocities in good agreement with those obtained by Horton and Davies.

Several forms of apparatus were used in the present experiments ‡, some of these being thermionic valves of the cylindrical pattern, in which the filament was completely enclosed by the grid. In another form two parallel grids

Fig. 1.
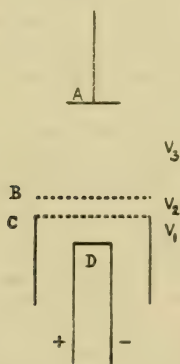
A, Anode ; B, C, Grids ; D, Filament.

were used, the filament being enclosed below the first, and the anode, a small platinum plate, being situated about 1·5 cm. beyond the second grid and parallel to it (see fig. 1).

With this form of apparatus, a magnetic field parallel to the axis of the tube was used to prevent the electron stream from spreading laterally. All the metal (except the tungsten filament) was platinum and had been boiled for several days in strong nitric acid before being used. In every case the complete apparatus was baked for many hours, and at the same time kept evacuated to a low pressure by means of a mercury-vapour pump; the filament was also heated to a high temperature to rid it of occluded gases. During this process mercury vapour from the pump was prevented from passing over by an intervening U-tube containing carbon cooled in solid carbon dioxide. In filling the experimental apparatus with helium, the purified gas was allowed to pass very slowly along a fine capillary tube and then through the charcoal tube which was cooled in liquid air.

The electric currents between the various electrodes were measured by sensitive moving-coil galvanometers, while the potential difference accelerating the primary electron stream was gradually increased. It was found that the current due to photoelectric action of the radiation on the electrodes was too small in comparison with the original electron current to be detected by the anode galvanometer, for when the apparatus contained perfectly pure helium there was no sudden rise in the current-E.M.F. curve until ionization of the gas occurred.

On account of the velocity of emission of the electrons from the filament and possibly of other causes, the measured potential difference does not give the velocity of the electrons passing through the gauze. In order to obtain the minimum ionization velocity it is necessary to determine the correction which must be added to the applied potential difference at which ionization is first detected. For this purpose the type of apparatus with two parallel grids has an advantage over the type with one grid only; for with the former type it is possible to obtain the correction to be added to the applied potential difference so as to give the velocity of the electrons which *actually produce* the effect measured by the anode galvanometer, whereas with the single grid the correction which is obtained gives the velocity of the swiftest electrons present under a given applied accelerating potential difference, irrespective of whether these swiftest electrons are sufficiently numerous to produce a measurable amount of ionization when their velocity reaches the critical value.

A special investigation made with the apparatus represented in fig. 1 showed that the minimum number of electrons which could be detected by the galvanometer could also produce a detectable ionization current when their velocity

was above the critical value, so that, using a galvanometer as the current-measuring instrument, the two "corrections" referred to above are identical. The experiments were made as follows:—A potential difference V_1 was applied between the filament and the first grid in such a direction as to oppose the emission of electrons from the filament. By the variation of this field the number of electrons passing through the gauze could be controlled. In order to determine for what value of the potential difference V_1 the minimum number of electrons capable of giving a current measurable with the anode galvanometer was obtained, the electrons after passing through the first gauze were accelerated by the fields V_2 and V_3, towards the collecting electrode, the sum of the potential differences V_2 and V_3 being less than the ionization potential difference. While V_2 and V_3 remained constant, V_1 was gradually reduced from a value too great to allow any electrons to pass through the first gauze, until the anode galvanometer gave the first indication of a current passing through it. The value of V_1 at which this first indication was obtained is the correction to be applied to give the velocity of the swiftest electrons present.

In the second part of the experiment, the field V_1 controlled the number of electrons employed, but the potential difference V_2 was made a little above the ionization value, so that the electrons which passed through the first gauze attained sufficient velocity between the first and second gauzes to be able to ionize helium atoms on collision with them in the space above the second gauze. The potential difference V_3 in this space opposed the electrons from the filament and was maintained sufficiently great to prevent any of them from reaching the collecting electrode. As the photoelectric effect of the radiation on the electrodes does not produce a measurable current, the only current measured by the anode galvanometer is that due to the positive ions produced in the space between the second gauze and the collecting electrode, by the impact of the electrons with helium atoms. Keeping the potential differences V_2 and V_3 constant, V_1 was adjusted to the limiting value at which a detectable ionization current was measured by the galvanometer. It was found that this limiting value of V_1 was the same as the value of V_1 obtained in the first part of the experiment. Thus it is safe to assume that when a single-grid valve was used, the ionization velocity deduced from the swiftest electrons detectable, was actually the velocity of those which first produce a measurable ionization.

In investigating the ionization velocity for electrons in

the gas, the currents to the anode were measured as the accelerating potential difference was gradually increased, and the currents were plotted against the corresponding values of the electron velocities, which were deduced by applying to the accelerating potential differences the corrections found in the manner just described. With perfectly pure helium in the apparatus, curves similar to I. of fig. 2 were obtained, indicating that the minimum ionization velocity of helium is 25·0 volts.

Fig. 2.
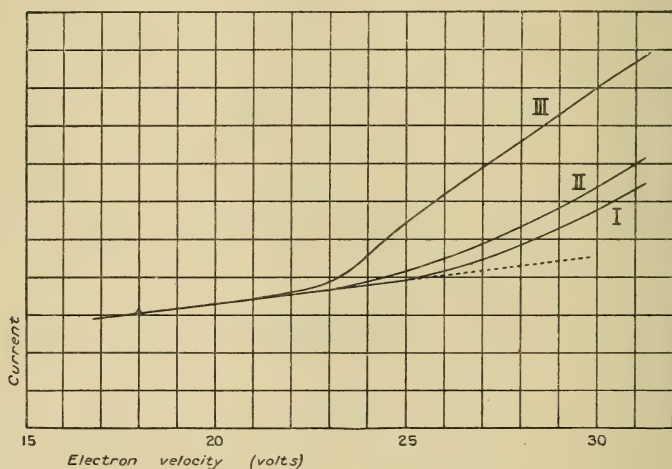
The figure also contains curves showing the effect of a small but gradually increasing quantity of impurity upon the electron velocity at which ionization was first detected. The observations from which these particular curves were plotted were taken with a valve in which the grid and anode were connected together and formed the positive electrode, the glowing filament being the negative electrode. The pressure of the helium was about 0·85 mm., and the distance of the filament from the grid—about 5 mm.—was several times the mean free path of an electron in the gas, so that when the ionization potential difference was reached, ionization would take place mainly in this space. When the observations plotted in curve I. had been made, a wide-bored tap, which separated the discharge chamber from the purifying charcoal tube, was closed, and after an interval of 5 minutes, during which the heating of the filament was continued, the characteristic curve was again taken. Curve II. of the figure represents the result obtained. It is seen that

this curve breaks away from the straight line at a lower value of the electron velocity than curve I. An hour later the observations were repeated, and, as will be observed from curve III., ionization was then detected at an electron velocity of about 21 volts. After these observations the gas was withdrawn from the apparatus and made to circulate repeatedly through carbon cooled in liquid air, the gas being thus re-purified ; on again testing, ionization did not occur until the electron velocity had been increased to 25 volts. These experiments show that the detection of ionization at electron velocities less than 25 volts is due to impurity, which can be removed from the helium by repeated circulation through carbon cooled in liquid air.

It will be noticed that in curves II. and III. of fig. 2 in which the indication of ionization occurs before 25 volts, there is no indication of additional ionization when 25 volts is reached. This shows that the direct ionization of the helium by 25 volt impacts does not result in the production of more ionization than the indirect ionization of the impurity by the helium radiation.

The amount of impurity collecting in the apparatus under the conditions indicated must have been very small in view of the long treatment to which the apparatus had been subjected before these observations were begun, and it might seem unlikely that so small an amount of impurity should cause so marked an effect in the current-E.M.F. curve. It must be observed, however, that when the helium is pure, ionization is caused only by electron collisions, and is therefore limited to that part of a column of gas in the path of the electron stream, in which the electrons collide with atoms with enough velocity to ionize them, while with the impure gas the impurity is ionized by the helium radiation, so that in the presence of sufficient radiation, ionization can take place throughout the whole volume of the gas in the apparatus, thus giving a considerable current through the galvanometer when only a very small percentage of impurity is present.

The same considerations also explain why the ionization of the impurity by the radiation from the helium atoms is marked when there is no indication of the direct ionization of the impurity by electron impacts, although the impurity must be ionizable by collisions with electrons having less than 20 volts velocity, since it is ionized by the helium radiation. If there were enough impurity present in the helium for an indication of its ionization by electron impacts to be given in the curves, it is probable that the extra

ionization produced by the helium radiation would not show in the marked way it does in fig. 2. In curves which were taken at various time intervals after the manner of those of fig. 2, the electron velocity at which ionization was first detected decreased gradually from 25 volts to about 21 volts, as the amount of impurity present increased, but the rise in the curve never occurred before about 21 volts, indicating that this is the minimum velocity at which radiation is produced from the helium atom. With a very small amount of impurity (such as that collecting in a few minutes heating with the tap closed) the current-E.M.F. curve rises at some value of the electron velocity intermediate between the ionization potential difference and the radiation potential difference. This is explained by the facts that the radiation is produced throughout a gradually increasing layer of gas as the accelerating potential difference is raised, and that with a very small amount of impurity a large amount of radiation is necessary to produce sufficient ionization to give an indication on the galvanometer.

Another instance of the marked effect of a small amount of impurity was obtained in the course of some experiments in which a speck of lime on a platinum strip was used as the source of electrons. To make the lime adhere to the platinum it had been mixed with a small proportion of powdered red sealing-wax. The filament had been raised to incandescence by an electric current, and the organic matter burnt up before the filament was sealed into the apparatus, and the heating of the filament had been continued for some days. It was, however, found that with this filament, ionization was always detected at an electron velocity of about 21 volts, even when the apparatus was in connexion with a carbon tube cooled in liquid air. By examining the spectrum of the luminosity which appeared in the gas at an electron velocity slightly higher than that necessary for ionization, it was found that the mercury green line $\lambda 5461$ was faintly visible. The small trace of mercury present in the otherwise spectroscopically pure helium must have come from the vermilion colouring matter in the sealing-wax used, for it was impossible for mercury vapour to have passed into the apparatus from the pump, as the connecting stopcock had never been open without the intervening U-tube being cooled in liquid air or in solid carbon dioxide. Moreover, with a tungsten filament, the mercury lines were never seen in the spectrum of the luminous discharge when the same precautions were taken to keep the helium pure.

Fig. 3 is an example of the curves obtained with a

single-grid valve having a lime-coated filament and containing helium contaminated with a trace of mercury vapour from the sealing-wax used in coating the platinum strip. In taking the observations recorded in this figure a constant difference

Fig. 3.
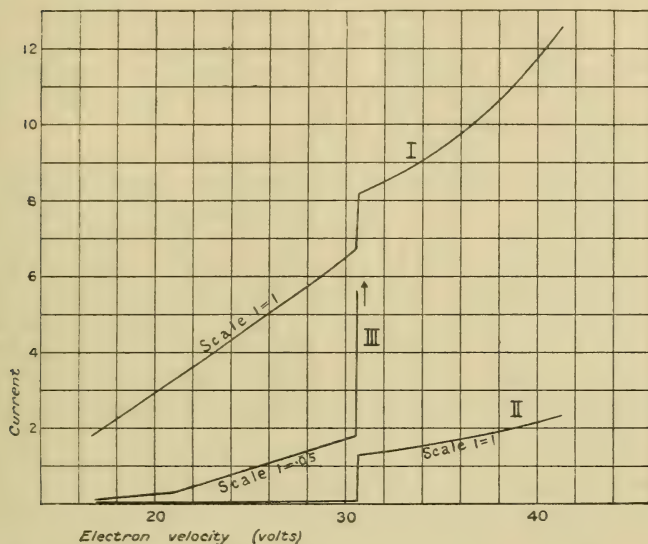
of potential of 8 volts was maintained between the anode and the grid and the difference of potential between the grid and the filament was gradually increased. The currents measured by the galvanometer connected directly to the filament are given (Curve I.), as well as those measured by the anode galvanometer (Curve II.), the latter being also plotted on a larger scale (Curve III.), so that the rise in the current at about 21 volts may be seen. The curves show that both the measured currents increased abruptly at an electron velocity a few volts above that at which ionization of the helium can occur. The current measured by the filament galvanometer is mainly that carried by the stream of electrons from the glowing lime, and the sudden rise in the curve must be due to an increased emission, which no doubt results from the neutralization of the space-charge near the filament by the positive ions travelling to it. It was found that the point at which the sudden large increase in the current occurs depends very much upon the electric fields used between the electrodes. It could be prevented by adjusting the fields so as to prevent the positive ions formed in the

anode space from travelling to the filament, and at the same time arranging so that no ionization could take place between the first gauze and the filament. In order to secure the sharp rise in the curve it is necessary for the electric fields to be arranged so that the neutralization of the space-charge occurs suddenly. If the neutralization occurs gradually, the increase of electron emission from the filament is also gradual and a sudden rise in the current does not occur. This condition is attained when the grids and anode are connected together to form one electrode, as in the experiments the results of which are shown in fig. 2.

The rise in curve III. of fig. 3 at about 21 volts is due to the ionization of the small trace of mercury vapour which the otherwise pure helium contained, although the ionization chamber opened into a purifying tube containing carbon which was cooled in liquid air. The impurity present in the apparatus during the experiments described earlier was probably gas evolved from the glass in spite of the long treatment to which it had been subjected. The spectrum of the luminous discharge in this case showed no trace of the mercury lines but a very faint indication of a band spectrum, probably due to oxides of carbon.

The view that the ionization which has been detected in helium when electron velocities of less than 25 volts are used, is due to the indirect ionization of traces of impurities by the helium radiation, is also supported by the results of some experiments in which the spectrum of the luminosity produced in helium by electron bombardment was investigated for different velocities of the electron stream. These experiments were performed with a single-grid apparatus, the metal parts of which were not all of platinum and had been contaminated by contact with mercury vapour while they were being used in another research. It was consequently found to be impossible to eliminate mercury vapour completely during the investigation, although the amount of this impurity present in the helium must have been very small, for the apparatus was in direct connexion with a charcoal tube cooled in liquid air throughout the experiments.

A series of photographs of the spectrum of the luminosity produced in the gas between the anode and the grid was taken by means of a Hilger direct wave-length reading spectroscope, for various values of the applied potential difference. The lines seen on the photographic plate in a typical case are given in the following table. With the three lower electron velocities, namely 21·4 volts, 23·7 volts,

and 25·8 volts, the time of exposure of the plate was from
4 to 5 hours. With an electron velocity of 50 volts a
bright luminosity was obtained and the exposure was only
about 1 hour.

Velocity of the electron stream.

21·4 volts.	23·7 volts.	25·8 volts.	50 volts.
		5048 (0·5)	5048 (5)
		5016 (2)	5016 (8)
		4922 (1)	4922 (6)
		4713 (5)	4713 (6)
		4472 (5)	4472 (10)
		4438 (0·5)	4438 (6)
		4388 (0·5)	4388 (6)
4359 very faint	*4359* (2)	*4359* (1)	*4359* (5)
	4348 (0·5)		*4348* (1)
			4337 (0·5)
			4169 (1)
			4144 (2)
			4121 (3)
			4026 (3)
			3868 (0·5)

The numbers in brackets indicate the relative intensities
of the lines on the photographic plate. The wave-lengths
printed in italics are due to mercury.

The lines 4359 and 4348 are due to mercury, and these
were the only lines obtained so long as the maximum velocity
of the electron stream was less than 25 volts. The line 4337,
which was faintly visible on the plate when an electron
velocity of 50 volts was used, is also due to mercury, but
all the other lines given in the table are due to helium. On
the view, now generally accepted, that the many-lined
spectrum of a gas can be produced when ionization has
occurred, these results indicate that ionization of helium
does not occur below 25 volts, but that ionization of mercury
was taking place between the resonance and ionization velo-
cities of helium. From the first column of the table it will
be observed that the only line seen on the photographic plate
when the electron velocity was 21·4 volts was the mercury
line λ 4359, and as this was extremely faint, it is evident that
there was very little ionization of the mercury vapour by
direct impact, even although the electron velocity was well
above the ionization value for mercury (10·4 volts). The
greatly increased intensity of this line when the voltage
was raised to 23·7 volts must therefore be due to the largely
increased amount of helium radiation then produced. These
two spectra thus indicate that the amount of ionization of
mercury vapour by direct electron impact is extremely small

compared with that produced by the helium radiation at the higher electron velocity, a result which is in agreement with that found by means of the current-E.M.F. curves.

The experiments described in this paper thus emphasize the importance of maintaining helium perfectly pure when attempting to investigate the ionization of the gas by electron collisions. The only satisfactory method when a glass apparatus is used is to have a slow circulation of freshly purified helium through the ionization chamber during the experiments. It is possible that if fused silica were substituted for glass, contamination of the gas would be less likely to occur.

The curves which have been given indicate that the minimum ionization velocity for electrons in helium is 25·0 volts, a rather lower value than that obtained by Horton and Davies. In their experiments the correction applied to the accelerating potential difference to give the critical velocity was that found from the swiftest electrons present, and, although a sensitive electrometer was used to detect ionization, it is possible that the swiftest electrons were not sufficiently numerous to produce a measurable ionization current. The results given in this paper also indicate that the minimum radiation velocity for electrons in helium is about 21 volts; but this value is no doubt too high, for the point at which ionization of the impurities by the helium radiation was detected depended on the amount of impurity present, and was probably always higher than the point at which radiation was first produced from the helium atoms.

L. *The Ignition of Gases at Reduced Pressures by Transient Arcs. By* W. M. Thornton, *Professor of Electrical Engineering in Armstrong College, Newcastle-on-Tyne**.

1. *Introduction.*

THE momentary arc formed at the point of break of a current-carrying circuit is an active source of ignition. It differs essentially in character from disruptive discharge, and consists mostly of a stream of charged particles passing from the negative to the positive pole. At the latter there is always a bright spot formed corresponding to the crater of

maintained arcs. This is more noticeable when the inductance of the circuit is low ; when it is high there is a flaming arc which, though it has a resistance low compared with that of the film of gas at the cathode, obscures the effect.

The ignition of gases by such noninductive transient arcs between platinum poles is remarkably uniform in type, differing in this from the more varied phenomena of impulsive spark ignition. It is in one sense simpler than the latter in that there is no preliminary ionization of the gas before the spark passes. The action is therefore confined to contact between the explosive mixture and hot metallic vapour in which there is intense electrification under the combined influence of high temperature and strong field. The mode of ignition is then a chemical combination of the gases started partly by high temperature collision, as in flame, aided by the direct electrification of the incandescent vapour with which the gases collide. At normal pressures heat alone may be more important ; at low pressures the temperature of the arc falls, but ionization by collision rises in value—the electric gradient being kept the same.

It was therefore to be expected that the limiting conditions of ignition would vary and show critical points or phases, characteristic respectively of heat and ionization, though not to the same extent as with impulsive discharge, and the results obtained show this to be the case.

2. *The nature of Transient Arcs.*

The voltage across the points of break of a circuit is the sum of the inductive voltage $L\dfrac{di}{dt}$ and of part of the circuit volts, the remainder being that absorbed in the resistance. In the present work the inductance was made as low as possible by the use of flat woven grid resistances. Oscillograms of break reveal no voltage overshoot, the circuit break sparks were therefore miniature arcs extinguished by air cooling.

The influence of gas pressure on the properties of such arcs is now being investigated. It has been found that as the pressure is lowered the length of the arc falls to a minimum, almost to zero, after which the discharge changes character, spreads into a luminous glow, lengthens and increases in duration. This change is always exceedingly sudden, and is possibly in the first place to be associated with the sudden drop in the number of ions emitted from a

hot surface when the temperature reaches a critical value[*].
The electronic state is set up at values X/p from ·2 to ·5,
where X is in volts per centimetre and p millimetres of
mercury. In order to have this at pressures of say 300
millimetres in air on arcs 5 mm. long X must be from 60 to
150, or the voltage on the arc 30 to 75. It is clear that this
will be passed through sometime during the break, for the
gap voltage starts at zero and ends at that of the circuit, in
this case 100.

3. *Results with Direct Current.*

The break was made electromagnetically between platinum
rods by drawing an iron plunger, to which they were
attached, into the core of a coil[†]. The curves obtained,
figs. 1 to 4, have for ordinates the currents broken, and for
abscissæ the pressures in atmospheres. They all approach a
lower limit at a little above 0·2 atmosphere, and pass through
an extraordinary fluctuation of inflammability from 0·4 to
0·5 atmosphere, after which they fall smoothly to a minimum
reached in most cases at about 1·5 atmospheres.

The most interesting feature of this set of curves is the
progressive change of the paraffins as the order rises.
Hydrogen is in a class by itself; the currents are much
smaller and the oscillation greater. Regarding the latter as
an indication of instability about a mean ordinate similar to
that of the curves of change of state, the following values of
the ordinates are taken to give equal areas above and below
the mean line :

Hydrogen	0·30	ampere.
Methane..............	1·20	,,
Ethane	1·12	,,
Propane	0·87	,,
Pentane	0·66	,,

For ethane, propane and pentane, these currents are
expressed by $i = 0·334 + \dfrac{23·5}{\text{mol weight}}$, that is, in the limit
the higher paraffins approach hydrogen in ease of ignition.

[*] J. J. Thomson : ‘The Conduction of Electricity in Gases,’
pp. 479–480.

[†] “The Influence of Pressure on the Ignition of Methane,” Brit.
Assoc. Newcastle ; ‘The Electrician,’ Sept. 8th, 1916.
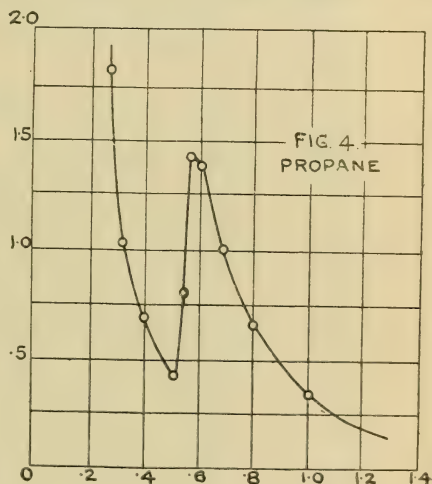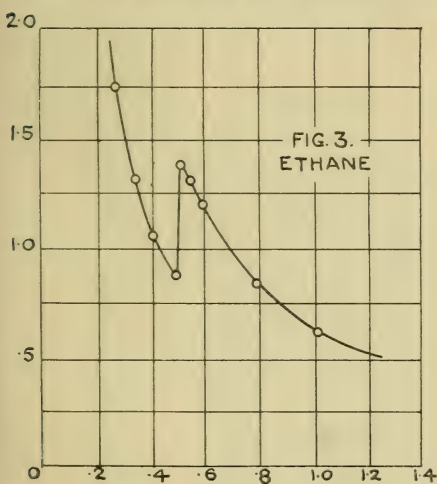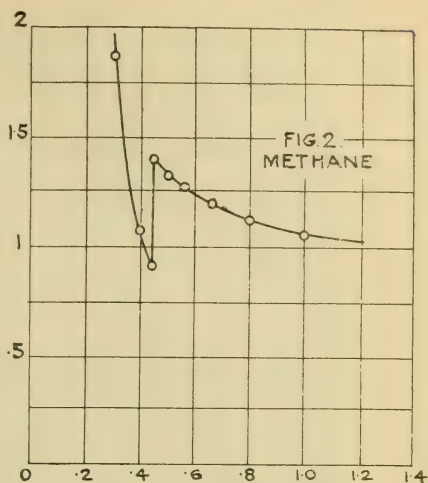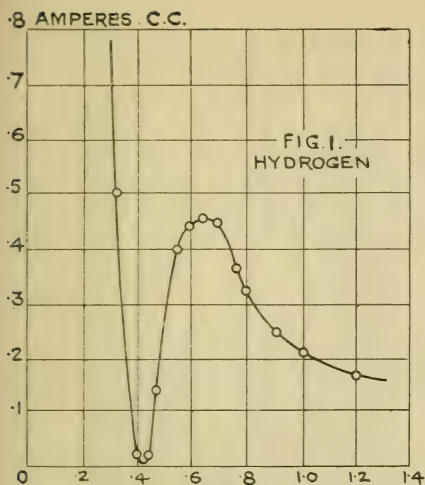
4. *Relative Influence of Carbon and Hydrogen Atoms on the Ignition of Paraffins.*

A curve similar to fig. 5 has been obtained for the same gases ignited by incandescent wires[*]. The presence of a carbon atom increases affinity for oxygen, methane having a stronger affinity than hydrogen for oxygen as shown by analysis of the products of combustion at high pressures.

[*] "The Ignition of Gases by Hot Wires," Phil. Mag. vol. xxxviii. November 1919, fig. 3.

It retards ignition either by arcs or hot wires. But if the readier ignition of the higher paraffins is to be regarded as caused by the hydrogen atoms their influence must follow a higher power than the first, or that of the carbon must remain constant. For the curve, fig. 5, may be taken as a straight line through the origin combined with an hyperbola. Writing $(i - i_0) = a n_C / (n_H)^2$, where n_C is the number of carbon atoms and n_H that of the hydrogen atoms in a molecule, and noting that $n_H = 2 n_C + 2$, then

$$(i - i_0) = a/4 \left(n_C + 2 + \frac{1}{n_C} \right).$$

When the value of the coefficient a, derived from the currents in fig. 5, is constant, it is evidence that the igniting current is proportional to the ratio $n_C / (n_H)^2$. From the figure $i_0 = \cdot 06$, or is negligibly small. For ethane $a = 20 \cdot 08$, propane $18 \cdot 55$, pentane $19 \cdot 0$. It is therefore probable that the relative influence of carbon and hydrogen atoms on the ignition of the higher paraffins is defined by $(i - i_0) = a n_C / (n_H)^2$, where a is constant.
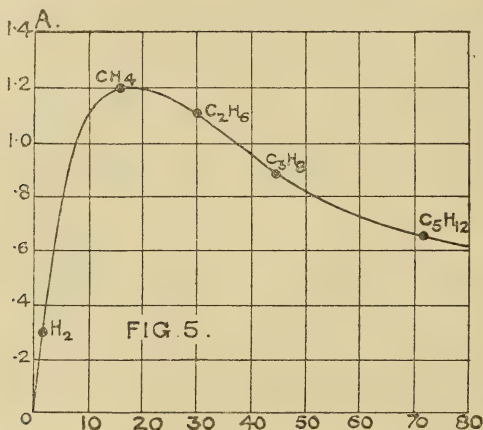
5. *The Form of the Curve of Inflammability.*

There is a close resemblance between fig. 1 and the curve of change of state. The shape of the ignition curve can be varied by the rate of break or by the use of alternating current. Change of frequency has an extraordinary influence on the current required for ignition[*].

The reciprocal of the time of duration T of an arc is the analogue of temperature, and the equation

$$\left(i+\frac{a}{p^2}\right)(p-b)=C/T$$

can be used to express fig. 1 in general form, where a is not the constant of § 4, but a function of T.

The simplest ignition by a break spark is that in which the energy of the spark necessary for ignition is inversely proportional to the number of molecules which come into contact with it in unit time. In that case pqV is constant, where p is the gas pressure, V the circuit voltage, and $q=iT$ the quantity passing while the spark lasts. V is constant and $piT=$ constant is the first equation of this kind of ignition, or $ip=C/T$. There is a lower limit of pressure b at which the flame cannot travel by conduction and $i(p-b)=C/T$ takes account of this. So far there is no action considered but the heat energy of the spark. The influence of calorific value per unit volume is included in the term p.

Any action other than thermal, such as that caused by a change in the number of ions emitted from the hot pole or produced in a second from any cause, must be expressed by a modification of the current. If such an effect occurs which retards ignition the current required will rise, if it accelerates ignition it will fall, more or less suddenly according as the action develops gradually or with critical sharpness.

The temperature of the arc without doubt falls with the pressure, its brightness is less. The volume of the arc, as shown by its photographic image, at first falls and then at low pressures rises. The one action that is definitely electrical which might increase the igniting power of a transient arc is a greater production or diffusion of ions in the gas in contact with it, that is, an increase in their velocity. Judging by the colour of a spark in gases with distinctive coloration, such as cyanogen, there is free penetration of the arc by the gas. The suggestion now made is that in ignition the "activation" agreed by chemists to be necessary for combination in gases and thought by physicists to be a blend of ionization and high temperature collision, becomes suddenly more intense. The oscillation of fig. 1 is found in ignition by disruptive discharge, where there is ionization by collision before a spark can pass. It is not found in the same mixtures when ignition is by hot wires*, where ionization by collision does not occur.

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* *Loc. cit.* fig. 8.

In an arc the gap is saturated with electrons from the circuit, and these have high temperature velocity apart from that given by the field. A lower voltage fall than 87 would then be sufficient to ionize a molecule by collision with an electron [*], and in flame the velocity of combination is such that ions are produced with no electric field.

In the case of normal ionization by collision change of gas pressure does not affect the total current passing between plates. The velocity and rate of diffusion are both increased. As shown by the influence of traces of moisture, ignition is started by internal combination of a few molecules rather than by general action. The variation of ignition, if influenced in any case by ionization, is not a function of the ionization current taken as a whole; but it is known that when the velocity of an electron reaches a certain value ionization by collision begins suddenly. The velocity $U = \dfrac{X}{m} \cdot e\dfrac{D}{p}$, where m is the mass of the ion carrying the current, and D a coefficient expressing the dimensions of this mass which varies with the field and pressure [†]. As $\dfrac{X}{p}$ increases m diminishes and $\dfrac{D}{m}$ rises in value. For small changes of pressure D/m may be taken as a first approximation proportional to $\dfrac{X}{p}$, and writing it $= k\dfrac{X}{p}$, $U = k\, e\left(\dfrac{X}{p}\right)^2$, and here k, e and X are constant. Thus as p falls U increases until, as a critical value is approached, ionization begins.

When ignition is made easier by such a strong ionization by an electric field in addition to that caused by the high temperature of the arc, a term of the form a/p^2 added to the circuit current expresses the influence of ionization by collision on the igniting current. This applies to ions moving in gases at relatively high pressures, such as half an atmosphere. When, however, X has values of the order of 1000 volts per cm. and $p = 1$ mm., U varies as $\sqrt{\dfrac{X}{p}}$ [‡], and "the whole character of the motion then changes."

Over the range of pressure within which ignition is possible D/m is in all probability a more complex function of

* E. Rutherford and R. K. McClung, Phil. Trans. A, 196. p. 25 (1901). See Townsend, 'Electricity in Gases,' p. 263.

† Townsend, *loc. cit.* p. 290.   ‡ Townsend, p. 312.

$\dfrac{X}{p}$ and of the time of duration of the arc. The velocity which an ion or a number of ions can acquire while the arc lasts depends on its duration, so that T enters directly and the term aT/p^2 expresses the fact that when the break is extremely rapid ignition becomes more an energy effect, dependent upon i alone, the ionization then being negligibly small. It is again shown by the relation between α/p and X/p for air[*] that ionization approaches an upper limit as X/p is raised, so that when p is very small the term does not become great. There is then a constant to be added to p, so that the final term is $aT/(p + p_0)^2$ and $\left\{ i + \dfrac{aT}{(p + p_0)^2} \right\} (p - b) = C/T$ expresses all the essential facts of break spark ignition. It may be remarked that this closely resembles Clausius' equation for the curve of change of state, though the present work is clearly in too early a stage for any equation to have more than general interest as collecting the facts for a typical case.

6. *Two phases of Ignition.*

Such an expression as that given above is only valid when the accelerating forces, molecular attraction in the change of state, activation in the case of ignition, are developed gradually. The action of spark ignition is too local for this to be generally applicable except in the case of a gas with high velocity of translation such as hydrogen. If in any other case the critical stage is reached suddenly, as might be expected, the term added to the current would come as suddenly into effect. The result would be that for a small change of pressure the igniting current should fall sharply, with almost discontinuity, as it does in methane, ethane, and propane. At pressures below this ignition proceeds with the ionization term fully active. There are as it were two distinct phases of ignition, and this is specially marked in ethane and propane. It is not in the facts of ionization alone or of the thermal changes in combustion that a sudden change in the conditions of ignition arises, but in their combination, having regard to the influence of the mean free time in allowing an ion to acquire sufficient velocity for collision to become decisive.

[*] *Loc. cit.* fig. 50.

7. *Ignition by Alternating Current Break Sparks.*

The curves of figs. 6 to 9 contain the results obtained by the use of alternating currents at a frequency of 36 and a voltage of 200. There is a general modification of the shapes of the curves of considerable interest in its bearing on the views advanced in the last two sections.
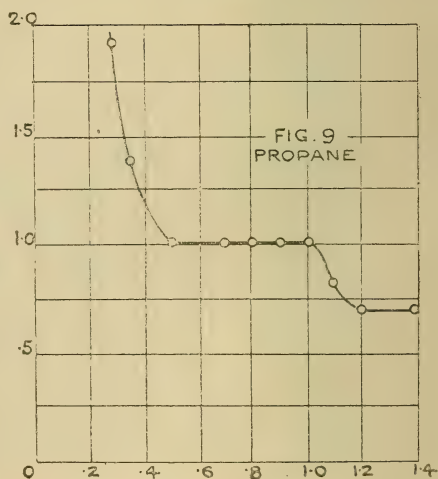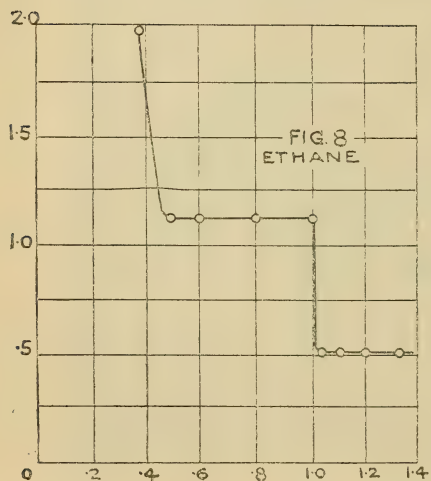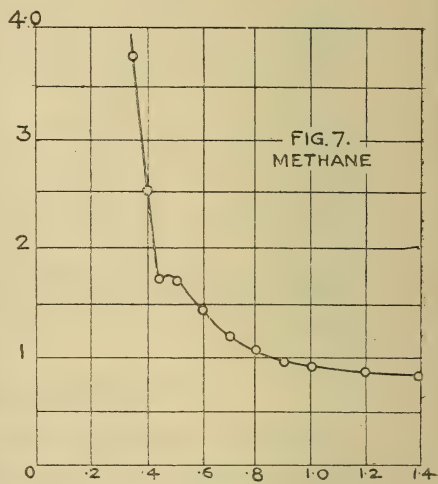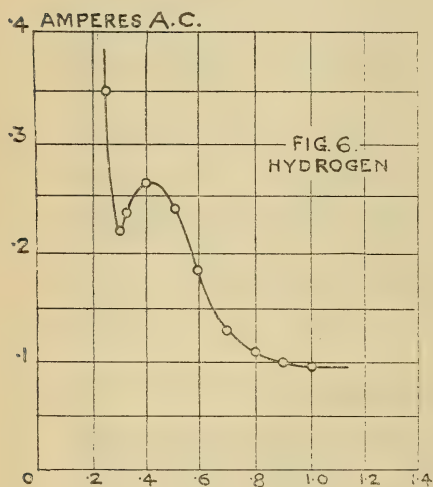
Hydrogen no longer has the extreme oscillation of fig. 1, and the extent to which it has been wiped out is an indication of the change in the relative values of the two phases, in which heat and ionization are respectively dominant. The

latter is losing influence, because presumably of the 'cup and
ball' action of an alternating field on ions from the arc.
Though the frequency is low it appears to be sufficiently high
to check the activity of the arc in promoting ignition. When
in the case of methane the current is continuous 0·5 of an
ampere at 200 volts will cause ignition, while a current
alternating at 100 periods a second requires 20 amperes to
be broken (with bright coruscations) before the gas explodes.
In the present case the change is not so great. Fig. 1 bears
to fig. 2 much the same resemblance as fig. 6 to fig. 7. The
position of the maximum at ·65 atmosphere in the first is at
·4 in fig. 6, and the minima have similarly moved. That is,
ionization now becomes critical at pressures lower than with
direct current.

Methane has changed only in magnitude of the oscillations.
There is little sign of the ionization term here, the curve is
almost hyperbolic. The interesting point is that so small a
change of ordinate is significant. If fig. 7 had been observed
first the kink in it would have been possibly regarded as an
experimental error, instead of being as it is an indication of
a process reaching its maximum in fig. 1.

The resemblance between the curve of change of state and
those of figs. 1 to 4 has been mentioned previously. Figs. 8
and 9 are illustrations of the flat stage corresponding to
liquefaction at constant pressure. All that is wanted to
complete the series is a curve having a point of inflexion
corresponding to a critical isothermal. This has been
observed with disruptive spark ignition*, and with break
sparks at a frequency of 60 when the gas is methane†.

The meaning of a flat stage between two phases is that as
the influence of one falls it is exactly compensated by the
increase of the other. The cause of the fall of the thermal
term is the smaller number of molecules in unit volume; the
rise of the ionization term is the increase in velocity due to
the longer free path. It is clear that when these are the two
chief factors such a compensation is not improbable.

8. *Coal Gas and Carbon Monoxide.*

The ignition of these by continuous currents is given in
figs. 10 and 11 and by alternating currents in figs. 12 and 13.
Fig. 10 is a fair average of figs. 1 and 2. The magnitudes
of the ordinates are those of hydrogen and this is again found
by a comparison of figs. 6 and 12. As might have been
expected hydrogen is the cause of the more sensitive ignition

* Proc. Roy. Soc. A, vol. xcii. 1915, figs. 6 and 7.
† Proc. Roy. Soc. A, vol. xc. 1914, fig. 9.

of coal gas. Carbon monoxide is not so readily ignited as
hydrogen by continuous current break sparks, but it is little
behind it at atmospheric pressure. On the other hand, it is
much more difficult to ignite by impulsive sparks. The

FIG. 10.— COAL-GAS

FIG. 11.— CARBON-MONOXIDE

FIG. 12— COAL-GAS

FIG. 13.— CARBON-MONOXIDE
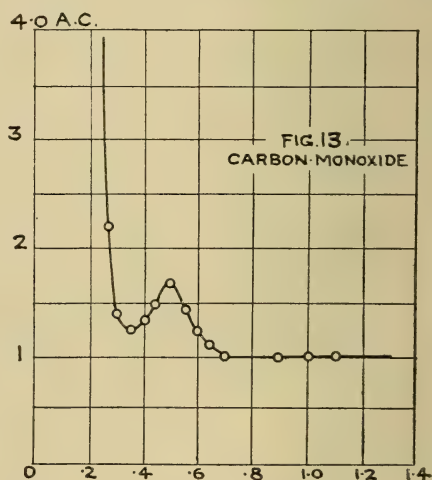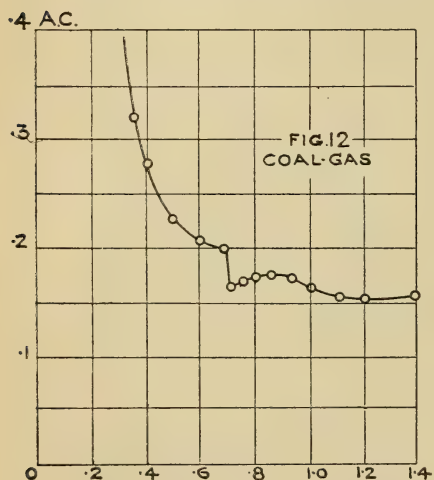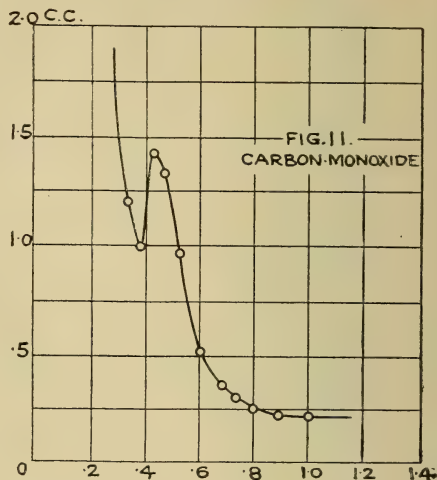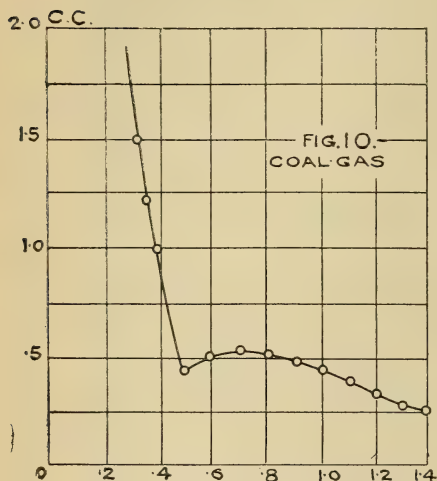
practice of using low tension break sparks for the ignition of
large slow speed blast-furnace gas-engines is here justified
by the sensitiveness of this gas, largely carbon monoxide, to
ignition by such sparks. There is a marked difference when
alternating currents are used, coal gas is then ten times
easier to ignite than carbon monoxide, on account, probably,
of the greater mobility of the hydrogen ions.

LI. *On the Velocity of Unimolecular Reactions. By* Eric
K. Rideal, *Professor of Physical Chemistry at the Uni-
versity of Illinois, U.S.A.**

IN a recent communication (Phil. Mag. vol. xxxix. p. 26,
1920) W. C. M. Lewis has drawn attention to the
anomalous results obtained in the calculation of the velocity
constant of a unimolecular chemical reaction, the decom-
position of phosphine, from the standpoint of the radiation
hypothesis.

This lack of agreement in a monomolecular reaction is
all the more serious, since if the correct solution could be
found the radiation hypothesis could be extended to the
vaporization of metals, thus permitting us to calculate
the so-called "chemical constants" of substances with the
aid of the Clausius-Clapeyron and Knudsen relationships, in
terms of the molecular diameters and the natural radiation
frequencies.

Drs. Dushman and Langmuir have recently indicated that
Trautz's values for x in the following general equation,

$$\frac{dn}{dt} = x e^{-\frac{Q}{RT}},$$

are proportional to Q.

This purely empyric relationship has, however, a theo-
retical basis, and in the light of the radiation theory leads to
remarkable conclusions.

In the general equation for a monomolecular reaction,
Q is replaced by the quantum relationship $Q = Nh\nu$.

Hence the rate of change per molecule per unit of time is

$$\frac{dn}{dt} = K e^{-\frac{h\nu}{kT}}.$$

In this expression K has the dimensions of t^{-1} and is the
reciprocal of the time necessary for the molecule to pass from
the inactive to the active condition, and is thus identical with
Perrin's molecular "sensibilité" (*Ann. de Phys.* ii. p. 21,
1919) and with the inverse of Maxwell's "time of molecular
relaxation."

An approximation to the values of K or the inverse of the
times of molecular relaxation may be obtained from thermal
conductivity data. A few of these are appended in the
following table, the calculations being performed according

to the method suggested by Langmuir (Phys. Rev. viii. p. 171, 1916) from the equation

$$K = \frac{h\sigma}{3k},$$

where h is the thermal conductivity in ergs per cm. per sec., σ the distance between adjacent atoms, or approximately the molecular diameters, and k the gas constant $= 1 \cdot 37 \cdot 10^{-16}$ erg per degree.

For comparison are appended the ultra-violet vibration frequencies of the elements, calculated with the aid of the Lindemann melting-point equation and Haber's relationship,

$$M\nu^2 \text{ red} = m\nu^2 \text{ violet},$$

where M and m are the atomic and electronic masses respectively.

Metal.	$K \cdot 10^{-14}$.	$\nu \cdot 10^{-14}$.
Cu	21·5	22·9
Ag	22·3	19·5
Na	9·5	10·8
K	9·4	6·9
Al	11·2	16·7
Cd	5·2	13·2
Zn	5·6	15·1
Mg	8·7	15·2
Au	11·6	20·4
Sn	3·7	10·5
Ni	4·1	21·5
Fe	4·0	26·7
Hg	0·51	13·2

In the case of the non-metals where the thermal conduction is molecular and not electronic in character, the reciprocal of the time of relaxation calculated in the above manner is equal to the period of the natural infra-red vibration, as in the case of sulphur :

	K.	ν.
S	$1 \cdot 9 \times 10^{-12}$	$2 \cdot 1 \times 10^{-12}$

It will be noted that, in spite of the errors introduced in the calculations of the ultra-violet vibration frequencies, the time of molecular relaxation is identical with, or a few times longer than, the natural period of vibration.

It is significant to note that the time of molecular relaxation increases with the valency of the element, indicating

that the relaxation is hindered by all the valency electrons. It seems probable, however, that in the gaseous state where we are concerned with the movement of one electron in a single molecule isolated from the others, the time of relaxation will, as in the case of solid silver and copper, be exactly equal to the period of vibration of the electron.

As a very close approximation we may therefore write $K = \nu$, or the rate of a monomolecular reaction

$$= \frac{dn}{dt} = \nu \cdot e^{-\frac{h\nu}{kT}}.$$

For the decomposition of phosphine according to Lewis $\nu = 8 . 10^{14}$ and $e^{-\frac{h\nu}{kT}} = 4\cdot37 . 10^{-18}$; hence the velocity constant $\frac{dn}{dt} = \nu . e^{-\frac{h\nu}{kT}} = 3\cdot5 . 10^{-3}$, while the observed value is $10\cdot2 . 10^{-3}$.

It may be noted that the natural vibration frequency of phosphorus ν violet $= 14\cdot9 . 10^{14}$, indicating that the mechanism of decomposition operates through an electron whose time period has not been sensibly affected by the presence of the hydrogen atoms.

The general expression for the velocity coefficient of a monomolecular reaction is thus in accordance with the observation of Dushman and Langmuir (who have recently computed the reaction velocity constants of a great number of physical and chemical reactions from this law), and is thus an indirect confirmation of the radiation hypothesis.

This, however, leads to the somewhat singular conclusion that one " light wave " contains one quantum of energy $h\nu$, for the molecule acquires this amount of energy in a time period $1/\nu$ which on the wave theory of light is identical with the time for light to make one undulation.

Assuming that the premises of the radiation theory of chemical action are correct, light appears to be corpuscular in nature, the energy varying inversely as the size of the corpuscular quantum. Sir J. J. Thomson's Faraday-tube hypothesis would lead to similar conclusions.

On the corpuscular assumptions, as W. C. M. Lewis has pointed out, it should be possible to calculate the velocity coefficient on the basis of a bimolecular reaction between phosphine molecules and quanta. The velocity coefficient is then equal to

$$\frac{dn}{dt} = \pi\sigma\lambda \sqrt{u_1^2 + u_2^2} \frac{u_\nu \delta\nu}{h\nu},$$

where $\lambda = \frac{c}{\nu}$ the quantum diameter, σ the effective diameter

of the phosphine molecule, u_1 the mean velocity of the molecules negligible in comparison with $u_2 = c$ the velocity of the light quanta, $\dfrac{u_\nu \delta\nu}{h\nu}$ = the number of quanta per unit volume $= \dfrac{8\pi\nu^2}{c^3} e^{-\frac{h\nu}{k\mathrm{T}}}$.

Hence the reaction velocity constant

$$= \frac{dn}{dt} = \frac{8\pi^2\sigma}{c} \nu \cdot e^{-\frac{h\nu}{k\mathrm{T}}} \delta\nu.$$

$$\frac{dn}{dt} = \frac{8\pi^2\sigma\nu^3}{c^2} \delta\lambda \, e^{-\frac{h\nu}{k\mathrm{T}}},$$

since

$$\nu = \frac{c}{\lambda} \quad \text{and} \quad -\delta\nu = \frac{c}{\lambda^2}\delta\lambda = \frac{\nu^2}{c}\delta\lambda.$$

Taking the value of $\delta\lambda$ equal to the actual molecular diameter σ', the velocity coefficient becomes equal to

$$\frac{dn}{dt} = \frac{8\pi^2\sigma\sigma'\nu^2}{c^2} \cdot \nu \, e^{-\frac{h\nu}{k\mathrm{T}}}.$$

The actual diameter of a phosphorus molecule σ' is ca. $2 \cdot 3 \cdot 10^{-8}$ cm., whilst the effective diameter in reaction with light quanta is the diameter of the orbit of the reacting valency electron. The diameter of the orbit in the case of the hydrogen atom is $5 \cdot 5 \cdot 10^{-9}$ cm., and since the atomic number of phosphorus is 15, the electron orbit diameter will be ca. $\dfrac{5 \cdot 5 \cdot 10^{-9}}{15} = 0 \cdot 37 \cdot 10^{-9}$; hence $\sigma' = 62\,\sigma$.

The velocity V of an electron circulating in the phosphorus atom in an orbit of effective diameter σ and with a frequency ν is $\pi\sigma\nu$; hence

$$\mathrm{V}^2 = \pi^2\sigma^2\nu^2,$$

or the velocity coefficient

$$\frac{dn}{dt} = \frac{62 \times 8 \cdot \mathrm{V}^2}{c^2} \cdot \nu \, e^{-\frac{h\nu}{k\mathrm{T}}} = \frac{496\,\mathrm{V}^2}{c^2} \cdot \nu e^{-\frac{h\nu}{k\mathrm{T}}}.$$

Bohr has calculated the velocity of the electron in the common orbit of the hydrogen molecule, and finds it equal to $3 \cdot 62 \cdot 10^7$ cm. per sec. In the phosphorus atom, of atomic number 15, this velocity is certainly higher. According to Sanford and Kunz (Phys. Rev. ix. p. 383, 1917, and xii. p. 60, 1918) the electron velocity is approximately proportional to the atomic number, which would assign a value

of $0 \cdot 54 \cdot 10^9$ cm. per sec. for the phosphorus electron. Hence the velocity coefficient will certainly not be less than

$$\frac{496\{0 \cdot 29 \cdot 10^{18}\}}{9 \cdot 10^{26}} \cdot \nu e^{-\frac{h\nu}{kT}}$$
$$= 0 \cdot 67 \cdot 10^{-3},$$

or one-tenth of the observed rate.

The agreement is only fair.

If the energy of the quantum is electrical in its nature, the electrostatic energy of a quantum of diameter λ will be $\frac{1}{2} \frac{E^2}{\lambda}$ in a medium of unit S.I.C. This energy can be equated to the light energy

$$\frac{1}{2} \frac{E^2}{\lambda} = h\nu = \frac{hc}{\lambda}$$

or $\quad E^2 = 2hc.$

This relationship is dimensionally correct: [by adopting with G. N. Lewis (Phys. Rev. iii. p. 101, 1914) as fundamental dimensions M mass and I an interval in space or time we find $E = M^{\frac{1}{2}} I^{\frac{3}{2}}$, $h = MI$, c has no dimensions in these units].

In ordinary units, however, E assumes very large values. G. N. Lewis has shown that

$$ch = 900 e^2 \text{ (approx.)},$$

where e is the electron charge. The above hypothetical charge would on the same basis be equal to $30\sqrt{2}\,e$. The energy can thus not be entirely electrostatic in its nature.

Summary.

The reaction velocity of a unimolecular reaction is given by the expression $\frac{dn}{dt} = \nu e^{-\frac{h\nu}{kT}}$, where ν the activating radiation frequency is identical with the time of molecular relaxation. On the basis of the radiation theory light would appear corpuscular, the size of a quantum being equal to a wavelength of light. If its energy be due to an electrostatic charge E, then $E^2 = 2hc$.

University of Illinois,
        Urbana, Ill., U.S.A.
    April 24th, 1920.

LII. *The Radium Content of the Rocks of the Loetschberg Tunnel.* *By* J. H. J. POOLE, *B.A.I.*[*]

THIS series of results was obtained some years ago, but its publication has been delayed owing to circumstancs arising out of the war. The fusion method of determining the radium content was employed in all cases. This method has been fully described by Prof. Joly in previous papers [†], but perhaps a brief recapitulation of the process employed is desirable.

The rock to be dealt with is first pulverized till it passes through a sieve of about 25 mesh to the centimetre. Six grammes of the powdered rock are weighed out and 18 grammes of an equal mixture of potassium and sodium carbonate are added. In the case of calcareous rocks about one gramme each of borax and boracic acid is also used in order to increase the evolution of CO_2. The resulting mixture is heated in a platinum boat in an electric tube furnace to about $1100°$ C., at which temperature the rock is completely decomposed. A large amount of CO_2 is evolved during this process, which is led through a soda-lime tube, where it is absorbed ; and the residual gases (for the most part air driven out from the furnace by thermal expansion) are stored in a strong rubber bladder. When the rock is completely decomposed (an hour is usually amply sufficient for this purpose), an exhausted electroscope is attached to the apparatus, and all the gases are swept into the electroscope, the arrangement being such that the gas in the rubber bladder is carried through the furnace and soda-lime tubes again before reaching the electroscope, thus ensuring a thorough wash-out of the system. Any excess of air necessary to fill the electroscope is drawn in through a mercury trap at the far end (from the electroscope) of the tube furnace ; this air also serving to ensure that the last traces of emanation are carried into the electroscope. All the air used, both for filling the electroscope and also for supplying the mercury trap connected to the furnace, was drawn in from outside the laboratory, as it was found that the natural leak of the electroscope did not vary so much from day to day when filled with air thus obtained.

The electroscope used was one which had previously been standardized by Prof. Joly. Its constant, when working in conjunction with the electric furnace, was $0·75$ scale-division per hour per billionth of a gramme of radium, and this constant was accordingly used. No direct sunlight was allowed to enter the room in which the electroscope was

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[*] Communicated by Prof. J. Joly, F.R.S.
[†] Joly, Phil. Mag. July 1911 and Oct. 1912.

kept, as it has been found that any strong light affects the insulating powers of the sulphur support of the gold leaf. It was found by taking these precautions that the natural leak of the electroscope remained fairly constant at about six scale divisions per hour, but this leak was, however, determined for each experiment separately.

The Loetschberg tunnel runs from Kandersteg to Goppenstein in the Bernese Oberland. As originally planned, the tunnel was to be straight and 13,744 m. in length, but owing to an incursion of water while passing under the Kander River, it was found necessary to deviate from the original design, with the result that the tunnel as completed follows a slightly sinuous path and is 14,536 m. long.

The rocks met with for the first 3965 m. from the north portal, near Kandersteg, consist nearly entirely of limestone of Jurassic age. After this point the tunnel enters the Gastern Granite, through which it runs for about 6400 m., and from here to the southern portal, a distance of 4170 m , crystalline schists of all classes are encountered. The specimens employed were not uniformly distributed over the whole length of the tunnel, most of them being from the schistose rocks at the southern end, but some specimens from the Gastern Granite and also from the Jurassic Limestone Zone were also dealt with.

Each rock was dealt with separately, as it was desired to ascertain if there was any large variation of radium content along the length of the tunnel. Unfortunately, however, there is a gap in the results from 3545 m. from the south end to 6415 m. from the north end—a distance of 4576 metres, most of which is in the Gastern Granite. No very striking variation in radium content was detected along the length of the tunnel, which agrees with the fact that apparently no abnormal variations were met with in the thermal gradient, as was the case in the St. Gothard Tunnel, in which the abnormally high-temperature gradient at the northern end of the tunnel was shown to coincide with rocks of a large radium content [*].

The result for each specimen of rock is given and its position in the tunnel in the following table. A table is also shown giving the mean result for each class of rock encountered. The radium content is given in billionths of a gramme of radium per gramme of rock—*i. e.*, the figure given in the column for radium content has to be multiplied by 10^{-12} in order to reduce the result to number of grammes of radium to one gramme of rock.

* Joly, Phil. Mag. Feb. 1912.

TABLE I.

Distance from South Portal in metres.	NATURE OF ROCK.	Radium Content.
34	Quartziferous Talc Schist	1·2
55	Talc Felspar Schist	2·6
69	Quartz Schist	1·5
95	Talc Schist	1·9
145	Quartz Schist	1·6
190	Felspar Biotite Tale Schist	2·2
194	Grey Schist	2·1
205	Quartz Schist	1·4
235	Felspathic Schist	3·2
249	Schist	2·8
265	Mica Schist	2·8
273	Quartz Schist	1·8
212	Schist	1·6
225	Mica Schist	1·5
305	Felspar Biotite Schist	2·6
345	Quartz Schist	1·9
355	Hornblende Schist	3·3
395	Talc Felspar Schist	6·5
427	Schist	1·0
470	Talc Schist	1·7
473	Quartz Schist	0·9
480	Talc Schist	0·8
546	Quartz Schist	2·2
580	Black Schist	3·3
610	Talc Schist	1·6
826	Quartz Schist	3·2
911	Ditto	3·0
917	Talc Schist	1·9
1000	Quartz Schist	2·2
1095	Talc Schist	1·3
1220	Schist	1·8
1230	Acid Hornblende Schist	3·0
1385	Talc Schist	1·4
1480	Quartz Schist	3·1
1505	Talc Schist	2·7
1522	Schist Lustré	2·8
1531	Ditto	4·1
1580	Talc Schist	1·2
1640	Ditto	0·9
1720	Quartz Schist	6·4
1735	Talc Schist	1·7
1800	Schist	2·5
1840	Ditto	5·9
1950	Talc Schist	1·3
2245	Schist	2·8
2280	Ditto	4·4
2464	Talc Schist	2·3
2620	Limestone	1·0
2717	Schist	2·2
2995	Ditto	2·45
3545	Ditto	1·3

TABLE I a.

Distance from North Portal in metres.	NATURE OF ROCK.	Radium Content.
6415	Granite	2·8
6120	Ditto	2·5
5715	Ditto	2·9
5160	Ditto	2·3
4345	Ditto	2·0
4235	Ditto	2·1
4200	Aplite	2·5
4180	Ditto	2 5
4010	Quartz Porphyry	2·5
3978	Granite	1·3
3965	Limestone	1·5
3945	Ditto	1·6
3938	Ditto	1·5
3935	Anhydrite	1·0
3885	Limestone	1·5
3870	Ditto	1·6
3850	Ditto	1·5
3810	Schist	2·9
3761	Anhydrite	1·2
3755	Limestone	1·1
3740	Ditto	2·0
3715	Black Schist	2·8
3640	Quartz Sandstone	4·3
3600	Black Schist	2·8
975	Limestone	1·1
760	Ditto	1·2
725	Ditto	0 9
640	Ditto	1·5
540	Ditto	2·9
175	Limestone	1·8
90	Ditto	1·0

It will be seen from Table I. that, as previously mentioned, there is no very striking variation in the radium content as we proceed along the tunnel. The northern end of the tunnel is the poorest in radium, and there is not much difference between the mean radium content for the central section through the Gastern Granite and the south end, where schists are mostly met with. We would naturally expect the northern end through the Jurassic Limestone to be the poorest, as all previous investigators have found that calcareous rocks contain, on the whole, the smallest quantity of radium.

TABLE II.

Rock.	Number of Specimens.	Mean Radium Content.
Granite	7	2·3
Limestone	16	1·5
Talc Schist	16	2·0
Quartz Schist	12	2·4
Mica Schist	2	2·1
Hornblende Schist	2	3·1
Schist Lustré	2	3·4
Felspathic Schist	3	2·7
Schist (Unclassified)	16	2·5
Aplite	2	2·5
Quartz Porphyry	1	2·5
Anhydrite	2	1·1
Quartz Sandstone	1	4·3

Mean Radium Content for all schists (53 Specimens)
$= 2\cdot4 \times 10^{-12}$ grm. per grm.

Mean Radium Content for all rocks (82 Specimens)
$= 2\cdot2 \times 10^{-12}$ grm. per grm.

With regard to the mean results given in Table II., it may be remarked that the radium content of the Gastern Granite appears to be rather low. Dr. Joly obtained a radium content of $2\cdot7 \times 10^{-12}$ grm. per grm. of rock from a composite rock powder in which 63 granites from various localities were represented. The discrepancy between this figure and that of $2\cdot3 \times 10^{-12}$ is, however, not so large as it appears, for if we neglect one abnormally low value of $1\cdot3 \times 10^{-12}$, which was obtained from a specimen just near the junction of the limestone and the granite, we obtain a mean for six specimens only of $2\cdot5 \times 10^{-12}$; a result which is not much below the mean radium content for granites previously quoted. It may be of interest to note in passing that there seems to be a certain indication in Table 1. that the centre of the Gastern Granite Massif is more radio-active than the edges; but there are not really enough specimens to be absolutely sure of this fact.

On the other hand, the mean radium content, both for the calcareous and schistose rocks, seems to be, on the whole, higher than the average value for calcareous rocks.

A. L. Fletcher, also employing the fusion method (Phil. Mag. Feb. 1912), found a mean of 0·8 for 24 calcareous and 1·1 for 9 schistose rocks, both considerably lower than the corresponding means found in this series of experiments. The mean value for the schists, however, is not so high as that obtained by Dr. Joly (Phil. Mag. Feb. 1912), also by the fusion method, for the schists of the St. Gothard Tunnel —namely, $2·8 \times 10^{-12}$ grm. per grm. It is rather unexpected that the schistose rocks should, on the whole, prove to be apparently slightly more radio-active than the Gastern Granite, but probably if more specimens from the centre of the granite zone had been obtained, this result would not have been confirmed. The mean obtained for the limestone is undoubtedly rather high, most previous investigators having obtained values ranging from about 0·5 to 1·0. Buchner (*Konink. Akad. van Wetensch. te Amsterdam, Proc.* Feb. 1911) obtained a mean for 11 calcareous rocks of 1·4, which agrees with my value of 1·5 for the Loetschberg limestone pretty closely. He employed the solution method of determining the radium, which usually seems to give slightly lower results than the fusion method; so there is really little reason to anticipate that there is any serious error in the value obtained for the limestones.

The general mean for all the rocks dealt with is also given. It is of interest to note that the value 2·2 obtained falls between the limits of 2·0 to 2·5, between which the mean radium content of the surface materials probably lies (Joly, Phil. Mag. Oct. 1912). We cannot attach too much importance to this point nevertheless, as the specimens used certainly could not be considered as really representative of the surface materials, containing, as they do, 53 schists, 7 granites, 16 limestones, and 6 miscellaneous rocks.

In conclusion, I wish to express my best thanks to Dr. Joly, under whose direction this research was carried out.

Iveagh Geological Laboratory,
    May 1920.

LIII. *Ionization in the Solar Chromosphere.* *By* Megh Nad
Saha, *D.Sc., Lecturer on Physics and Applied Mathematics,
Calcutta University* *.

IT has been known for a long time that the high-level
chromosphere is generally distinguished by those lines
which are relatively more strengthened in the spark than in
the arc, and which Lockyer originally styled as enhanced
lines. The following list taken from Mitchell's † list of
chromospheric lines, along with the respective intensities
of the line in the arc and the spark, illustrates the case :—

TABLE I.‡

Element	Wave-length of the line in A.U.'s.	Chromospheric level reached in Kms.	Intensity. Arc.	Spark.
Calcium	3968 (H) ⎱ 3933 (K) ⎰	14000	⎰ 300 ⎱ 500	500 L 1000 L
Strontium	4216 ⎱ 4078 ⎰	6000 6000	500 1000	500 L 1000 L
Barium	4994 ⎱ 4554 ⎰	750 1200	500 1000	1000 L 1000 L
Scandium	4247	6000	50	1000 L
Titanium	3685·4	6000	8	100
	3741·8	1500	3	10
	3759	6000	10	20 L
	3761	6000	6	10 L
	3900	1600	5	50 L
	3914	2000	5	20 L
	4290	1300	2	10 L
	4294	1200	3	8 L
	4300	1200	3	8 L
	4395	2500	10	10 L
	4444	1600	4	15 L
	4468	1500	4	15 L
	4501	1600	4	15 L
	4563	1200	3	10 L
	4572	1200	5	20 L

This table makes it quite clear that generally only those
lines occur in the highest levels which are relatively more
strengthened in the spark discharge spectrum. We can add
to the above table a list of the high-level iron and other
lines, but the conclusion would be the same.

* Communicated by the Author.
† Mitchell, 'The Astrophysical Journal,' vol. xxxviii, p. 424.
‡ L denotes "enhanced" according to Lockyer.

It appears that no satisfactory explanation of this fact, as well as of the extraordinary height reached by these lines, has yet been offered. It is intimately connected with the physical mechanism of the arc and the spark. In this connexion, it is well to recall Lockyer's original hypothesis, which, however, does not seem to have been, at any time, much in favour with the physicists. According to Lockyer, the passage from the arc to the spark means a great, though localised, increase of temperature, to which mainly the enhancement of the lines was to be ascribed. But, apart from its physical incompleteness, Lockyer's theory launches us amidst great difficulties as far as the interpretation of solar phenomena is concerned. It would lead us to the hypothesis that the outer chromosphere is at a substantially higher temperature than the photosphere, and the lower chromosphere ; and that the temperature of the sun increases as we pass radially outwards. This hypothesis is, however, quite untenable and is in flagrant contradiction to all accepted theories of physics.

A much more plausible explanation is that the lines in question are not due to radiations from the normal atom of the element, but from " an ionized atom, *i. e.*, one which has lost an electron." The high-level chromosphere is, according to this view, the seat of very intense ionization. Let us see briefly how this hypothesis has grown up.

Modern theories of atomic structure and radiation leave little doubt that the " enhanced lines " are due to the ionized atom of the element. As a concrete example, let us take the case of the calcium H, K, and g lines. The " H, K " lines are of the enhanced type, while " g " is of the normal type. The " H, K " are the leading members of the principal pair-series of the system of double lines of Calcium, while the " g-" line is the first member of the system of single lines of Calcium. Lorenser and Fowler [*] have shown that the series formula of the double lines is of the type

$$\nu = 4N \left[\frac{1}{\{f(m)\}^2} - \frac{1}{\{\phi(n)\}^2} \right],$$

while the series formula of the single lines is of the type

$$\nu = N \left[\frac{1}{\{f'(m)\}^2} - \frac{1}{\{\phi'(n)\}^2} \right],$$

where $f(m)$, $\phi(n)$ are functions of the form $m + \alpha$, according

[*] Fowler, Phil. Trans. vol. ccxiv.

to Rydberg, and $m + \alpha + \beta[t(m)]$, according to Ritz, $t(m)$ being a function of m which vanishes with increasing values of m.

In other words, in the series formula of the enhanced lines, the spectroscopic constant is 4N instead of the usual Rydberg number N. In the light of Bohr's theory, this is to be understood in the sense that, during the emission of the enhanced lines, the nucleus, and the system of electrons (excluding the vibrating one) taken together behave approximately as a double charge, so that the spectroscopic constant, $= \dfrac{2\pi^2 e^2 \mathrm{E}^2 m}{h^3}$, becomes 4N, as $\mathrm{E} = 2e$. This means that if the nuclear charge is n, the total number of electrons is $(n-1)$, and the system has been produced by the removal of one electron from the normal atom.

What has been said of the Calcium lines H and K is also true of the Strontium pair 4216 and 4078, and the Barium pair 4934 and 4554, *i. e.*, they are due to the ionized atom of these elements. The principal lines of the system of single lines of these elements also occur in the flash spectrum, but the following table shows that they reach a much lower level :—

<div align="center">TABLE II.</div>

Element.	Lines due to the Ionized Atom.	Chromospheric level.	Lines due to the Normal Atom.	Chromospheric level.
Ca	(H) 3968 (K) 3933 }	14000	(*g*) 4227	5000
Sr	4216 4078 }	6000	4607	350
Ba	4934 4554 }	750 1200 }	5536	400

N.B.—The lines chosen are the fundamental lines or the first lines of the principal series, having the symbolic formula $\nu = (1 . \mathrm{S}) - (2 . \mathrm{P})$.

No satisfactory series formula are known for the other high-level chromospheric elements, viz., Titanium, Scandium, Iron, and other elements. But the recent remarkable work of Kossel and Sommerfeld [*] makes it quite clear that the spark-lines of these elements are due to the ionized atom. The spark-lines of alkalies have not been much investigated and lie in the ultraviolet beyond 3000, so that, even if they

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[*] Kossel and Sommerfeld, *Ber. d. d. Phys. Gesellschaft*, Jahrgang 21, p. 240.

are present in the high-level chromosphere, we shall have no means of detecting them *.

As regards Hydrogen, ionized Hydrogen would mean simply the hydrogen core, and this probably by itself would be incapable of emitting any radiation. But as H_α and H_β lines occur high in the chromosphere, we have to admit that hydrogen probably is not much ionized in the chromosphere.

The case of helium is very interesting. It is well known that the Fraunhofer spectrum does not contain any helium lines, which are obtained only in the flash spectrum. But these lines are all due to normal helium, and the highest level reached by the second line of the so-called principal series is some 8500 kms.†, while the better-known D_3 reaches a level of 7500 kms. The lines due to ionized helium are represented by the general series formula

$$\nu = 4N \left[\frac{1}{m^2} - \frac{1}{n^2} \right],$$

and the best known of them, in the visible range, are the Rydberg line 4686 and the Pickering system

$$\nu = N \left[\frac{1}{2^2} - \frac{1}{(m + \frac{1}{2})^2} \right]$$

once ascribed to "cosmic hydrogen." Mitchell ‡ states that 4686 occurs in the flash spectrum, and reaches a level of 2000 kms. If the identification be all right, helium would present a seemingly anomalous case, for, whereas other elements are ionized in the upper strata, it is ionized in the lower strata of the chromosphere.

The above sketch embodies, in short, the problems before us. The alkaline earths and the heavier elements are ionized throughout the whole of the solar atmosphere, but the ionization is complete in the chromosphere, which seems to contain no normal atom at all. But hydrogen and helium are probably unionized throughout the whole chromosphere, and in the case of helium we have probably some slight ionization in the lower parts—a rather anomalous case.

The explanation of these problems, and some other associated problems of solar physics, will be attempted in this paper. The method is based upon a recent work of

* Kossel and Sommerfeld, *loc. cit.* p. 250.
† This line is masked by the strong hydrogen line H_ζ.
‡ Mitchell, *loc. cit.* pp. 490–491.

Eggert [*]—" On the State of Dissociation in the Inside of fixed Stars." In this problem, Eggert has shown that by applying Nernst's formula of " Reaction-isobar,"

$$K = \frac{p_M^{\nu_m} p_N^{\nu_n} \cdots}{p_A^{\nu_A} p_B^{\nu_B} \cdots},$$

to the problems of gaseous equilibrium in the inside of stars, it is possible to substantiate many of the assumptions made by Eddington [†] in his beautiful theory of the constitution of stars. These assumptions are that in the inside of stars the temperature is of the range of 10^5 to 10^6 degrees and the pressure is about 10^7 Atm., and the atoms are so highly ionized that the mean atomic weight is not much greater than 2. This method is directly applicable to the study of the problems sketched above. The equation of the Reaction-isobar is

$$\log K = \log \frac{p_M^{\nu_m} p_N^{\nu_N} \cdots}{p_A^{\nu_A} p_B^{\nu_B} \cdots} = -\frac{U}{4 \cdot 571\,T} + \frac{\Sigma \nu C_p}{R} + \Sigma \nu C, \quad (1)$$

where K = the Reaction-isobar,

U = heat of dissociation,

C_p = specific heat at constant pressure,

C = Nernst's Chemical constant,

and the summation is extended over all the reacting substances. The present case is treated as a sort of chemical reaction, in which we have to substitute ionization for chemical decomposition. The next section shows how U is to be calculated. The equation will be resumed in § 3.

§ 2.

We may regard the ionization of a calcium atom as taking place according to the following scheme, familiar in physical chemistry,

$$Ca \rightleftarrows Ca_+ + e - U. \quad \cdots \quad (2)$$
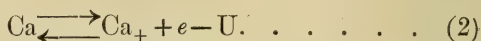
Where Ca is the normal atom of calcium (in the state of vapour) Ca_+ is an atom which has lost one electron, U is the

[*] Eggert, *Phys. Zeitschrift.* Dec. 1919.
[†] Eddington, M. N. R. A. S. vol. lxxvii. pp. 16 and 596.

quantity of energy liberated in the process. The quantity considered is 1 gm. atom.

The value of U in the case of alkaline earths, and many other elements, can easily be calculated from the value of the ionization potential of elements as determined by Franck and Hertz, MacLennan *, and others. Let V = ionization potential. Then, to detach one electron from the atomic system, we must add to each atom an amount of energy equivalent to that acquired by an electron falling through a potential difference V, where V (in volts) is given by the quantum relation,

$$\frac{e\mathrm{V}}{300} = h\nu_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

ν_0 being the convergence frequency of the principal series, *i. e.*, $(1, s)$ in Paschen's notation †. If this quantity be multiplied by the Avogadro number N, and expressed in calories, we obtain U.

Thus if V = 1 volt, we have

$$\mathrm{U} = \frac{e\mathrm{V} \cdot \mathrm{N}}{\mathrm{J} \cdot 300} = \frac{9645 \cdot 10^8}{4 \cdot 19 \times 10^7} = 2 \cdot 302 \cdot 10^4 \text{ calories.}$$

Table III. contains for future use the values of the ionization potentials ‡ as far as known, and the calculated

TABLE III.

Element.	Ionization Potential.	U in Calories.
Mg	7·65	$1 \cdot 761 \cdot 10^5$
Ca	6·12	1·409 ,,
Sr	5·7	1·313 ,,
Ba	5·12	1·178 ,,
Ra	?	?
Na	5·112	$1 \cdot 177 \times 10^5$
K	4·318	·994 ,,
Rb	4·155	·957 ,,
Cs	3·873	·892 ,,
Zn	9·4	$2 \cdot 164 \times 10^5$
Cd	9	2·072 ,,
Hg	10·45	2·406 ,,

* MacLennan, 'Proceedings of the Physical Society of London,' Dec. 1918.

† Paschen uses the symbol $(1 \cdot 5, s)$, but following Sommerfeld (*loc. cit.* p. 243), I have taken off ·5 and used $(1, s)$.

‡ MacLennan, *loc. cit.* p. 18.

value of U. Here I wish to remark that an element may have more than one ionization potential, depending upon the successive transfer of the outer electrons one by one to infinity, or the simultaneous existence of two more constitutions of the normal atom (e. g. helium and parhelium). The ionization potential given in the table corresponds to the case when only one electron is transferred to infinity leaving an excess of unit positive charge in the atom. We have made it clear in the introduction that the high-level alkaline earth-lines are due to the atoms with one plus charge in excess.

The cases of hydrogen and helium will be taken up later on.

§ 3. Equation of the Reaction-isobar for Ionization.

As mentioned in the introduction, the equation of gaseous equilibrium proceeds according to the equation,

$$\log K = -\frac{U}{4 \cdot 571\,T} + \frac{\Sigma\nu C_p}{R}\log T + \Sigma\nu C, \quad . \quad . \quad (1)$$

where the reaction proceeds according to the scheme,

$$\nu_a A + \nu_b B + \ldots\ldots = \nu_m M + \nu_n N + \ldots$$
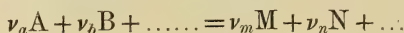
and K is the " Reaction-isobar,"

$$\frac{p_M^{\nu_m} p_N^{\nu_n} \ldots\ldots}{p_A^{\nu_a} p_B^{\nu_b} \ldots\ldots}$$

$p_M^{\nu_m}$, $p_N^{\nu_m}$... being the partial pressures of the reacting substances—M, N, etc.

In the present cases, viz., for a reaction of the type,

$$Ca \underset{\longleftarrow}{\overset{\longrightarrow}{}} Ca_+ + e - U, \quad . \quad . \quad . \quad . \quad (2)$$
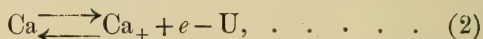
we have

$$\Sigma\nu C_p = (C_p)_{Ca+} + (C_p)_e - (C_p)_{Ca}.$$

We can take

$$(C_p)_{Ca} = (C_p)_{Ca+},$$

and $(C_p)_e = \frac{5}{2}R$, the electron being supposed to behave like a monatomic gas.

Eggert calculates the chemical constant from the Sackur-Tetrode-Stern relation,

$$C = \log \frac{(2\pi M)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} = -1\cdot 6 + \tfrac{3}{2} \log M, \quad . \quad . \quad (4)$$

where M = molecular weight, the pressure being expressed in atmospheres.

Now C has the same value for Ca and Ca_+. For the electron $M = 5\cdot 5 \times 10^{-5}$, and $C = -6\cdot 5$.

We have thus

$$\Sigma \nu C = -6\cdot 5. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

To calculate the "Reaction-isobar" K, let us assume that P is the total pressure, and a fraction x of the Ca-atoms is ionized.

Then we have

$$\log K = \log \frac{x^2}{1 - x^2} P = -\frac{U}{4\cdot 571\, T} + 2\cdot 5 \log T - 6\cdot 5. \quad (1')$$

This is the equation of the "reaction-isobar" which is throughout employed for calculating the "electron-affinity" of the ionized atom.

Ionization of Calcium, Barium, and Strontium.

With the aid of formula (1), the degree of ionization for any element, under any temperature and pressure, can be calculated when the ionization potential is known. As a concrete example, we may begin with Calcium, Strontium, and Barium.

A glance at equation (1') shows that pressure has a very great influence on the degree of ionization, which does not seem to have been anticipated. This is due to the occurrence of P in the first power in the expression for the "Reaction-isobar." A reduction in the value of P is attended with greatly enhanced ionization. This will become apparent from an inspection of the following tables, which show the ionization of Calcium, Strontium, and Barium under varying conditions of pressure and temperature.

Table IV.

Ionization of Calcium (in per cents.).
$U = 6 \cdot 12$ volts $= 1 \cdot 40 \cdot 10^5$ calories approximately.
Pressure in atmospheres—Temperature on the Absolute
Scale.

Pressure ...	10.	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-6}.	10^{-8}.
Temp.								
2000°					$5 \cdot 10^{-4}$	$1 \cdot 4 \cdot 10^{-3}$		
2500					$2 \cdot 10^{-2}$	$7 \cdot 10^{-2}$		
3000					$3 \cdot 10^{-1}$	1	9	
4000				2·8	9	26	93	
5000		2	6	20	55	90		
6000	2	8	26	64	93	99		
7000	7	23	68	91	99			
7500	11	34	75	96·5				
8000	16	46	84	98·5				
9000	29	70	95					
10000	46	85	98·5			Complete		
11000	63	93				Ionization.		
12000	76	96·5						
13000	84	98·5						
14000	90							

Table V.

Ionization of Strontium (in per cents.).
$U = 1 \cdot 3 \times 10^5$ calories.

Pressure ...	10.	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-6}.	10^{-8}.
Temp.								
2000°					$1 \cdot 2 \cdot 10^{-3}$	$4 \cdot 10^{-3}$		
2500					$6 \cdot 10^{-2}$	$2 \cdot 10^{-1}$		
3000			$7 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$7 \cdot 10^{-3}$	2·5		
4000			1·6	5	15	45	98·5	
5000	1	3·2	11	32	73	96		
6000	4	13	37	78	97			
7000	10	32	73	96				
7500	15	45	84	98·5				
8000	22	58	91	99				
9000	38	79	97·5			Complete		
10000	56	90	98·5			Ionization.		
11000	71	95						
12000	82	97·5						
13000	89	98·5						
14000	93							
15000	96							

TABLE VI.

Ionization of Barium (in per cents.).

$U = 1\cdot2 \cdot 10^5$ calories approximately.

Pressure ...	10.	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-6}.	10^{-8}.
Temp.								
2000°......					$6 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-1}$	
2500					$1\cdot8 \cdot 10^{-1}$	$7 \cdot 10^{-1}$	6	
3000					1·6	5	46	
4000		1	3	9	28	68	99	
5000	1·7	5·5	17	48	86	98		
6000	6·2	19	52	88	99			
7000	15	43	83	98				
7500	22	57	91					
8000	30	70	94		Complete			
9000	47	85			Ionization.			
10000	65	93						
11000	97							
12000	99							

We are not aware how the temperature and the pressure (partial pressure for a particular element) vary with height in the solar atmosphere. According to F. Biscoe *, the temperature of the photosphere is about 7500° K., while the pressure in the reversing layer varies, according to different investigators, from 10 to 1 atmospheres. If we suppose that the variation in temperature is entirely caused by radiation, the temperature of the upper layers should tend to the limit $\dfrac{7500}{2^{\frac{1}{4}}}$ †, or a little more than 6000° K. The partial pressure may be supposed to vary from 10 atmospheres in the reversing layer to 10^{-12} atmosphere in the outermost layers.

An examination of Tables IV., V., VI. shows that, under the above-mentioned assumptions, about 34 per cent. of the Ca-atoms are ionized on the photosphere. When the pressure falls to 10^{-4} atmosphere, almost all the atoms get ionized, so that up to this point in the solar atmosphere, we shall get combined emission of the H, K, and the g-line, but above this point, we shall have only the H, K lines. This is in very good agreement with observed facts.

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* F. Biscoe, 'The Astrophysical Journal,' vol. xlvi. p. 355.
† Schwarzschild, *Gott. Nachrichten*, p. 41 (1906).

In the case of strontium and barium, owing to their comparatively low ionization potential, ionization at 6000° is practically complete at 10^{-3} atmosphere, and the heights shown by the lines of the unionized atoms of these elements are still lower. Compare the Tables IV., V., VI.

The results of the flash-spectrum observations are thus seen to be very satisfactorily accounted for on the basis of our theory.

Laboratory experiments also, as far as they go, are in qualitative agreement with our theory. It is well known that in the flame, the flames due to the ionized atom either do not occur at all, or even if they do occur they are extremely faint compared with the lines of the unionized atom. As the temperature is increased, the "enhanced lines" begin to strengthen, until at the temperature of the arc they are comparable in intensity to the lines of the normal atom.

We give below the results of King [*] on the relative intensity of the "enhanced" and ordinary lines of the

Table VII.

Element.	Temp. Actual ... Approx.... Line.	1923 2000	2273 2500	2623 3000	Arc. 4000	Photosphere. 7500	Chromosphere. 6000
			Intensity.				
Ca	4227 (g) ...	300	500	1000	500	20	25
Ca+ ...	3968 (H)...	18	25	50	350	700	80
	3933 (K)...	20	30	60	400	1000	100
Proportion of ionized atoms in per cents.		$1 \cdot 4.10^{-3}$	7.10^{-2}	1	26	75 ($P=10^{-1}$)	93 ($P=10^{-3}$)
Sr	4607	300	400	600	600	1	2
Sr+ ...	4216 ... }	6	15	30	400	5	40
	4078 ... }	12	25	40	400	8	40
Proportion of Sr+ in per cents.		4.10^{-3}	2.10^{-1}	$2 \cdot 5$	45	84 ($P=10^{-1}$)	97 ($P=10^{-3}$)
Ba	5536	400	500	1000	1000	2	1
	4934 ... }	50	60	70	700	7	12
	4554 ... }	70	80	100	1000	8	20
Proportion of Ba+ in per cents.		2.10^{-2}	7.10^{-1}	5	68	91 ($P=10^{-1}$)	98 ($P=10^{-3}$)

N.B.--The intensity scale under the headings photosphere and chromosphere is different from the scale in King's furnace spectra.

* King, 'The Astrophysical Journal,' vol. xlviii. p. 13.

alkaline earths in vacuum-tube furnaces at varying temperature. Unfortunately, the pressure, which is a vital point, is not mentioned. The last line shows the percentage of the ionized atoms under a pressure of 10^{-4} atmosphere, or ·1 mm. of mercury.

The tables show that an increase of temperature causes an increase of ionization and the proportion of emission centres of the enhanced lines. The increasing intensities of the double lines are mainly to be ascribed to this fact. These become comparable in intensity to the principal lines of the normal atom only when the degree of ionization is rather large (comp. the figures at 4000°). Comparing the relative intensities of the corresponding lines of the calcium and barium group, we find that for the same temperature the enhanced lines of barium are relatively stronger than the calcium lines ; and this, according to our theory, is due to the comparatively lower ionization potential of barium.

The objection may be raised whether the proportion of ionized atoms at low temperatures, as given by the theory, is not rather too low. The tables show that at 2000° K., only 1 in 10^5 calcium atoms is ionized. Is this small number of ionized atoms capable of affecting the photographic plate by the emission of the H and the K lines?

No definite answer can be given to this point. We may, however, point out that, according to Ladenburg and Loria[*], when a hydrogen vacuum tube at a pressure of a few mms. of mercury is excited by a spark, only 1 atom in 50,000 is found to be radiant, *i. e.*, capable of emitting H_α and H_β. A very low proportion of radiant centres may therefore affect the photographic plate. It should also be remembered that at low temperatures the principal line of the normal atom is not only relatively more intense, but very broad and diffuse, when the enhanced lines are extremely narrow in addition to being faint.

A reduction in pressure will cause the relative intensity of the H–K line to increase, but not the absolute intensity, because the total available number of radiant particles will now decrease. I am not aware whether there is any laboratory experiment for testing this point.

§ 4. *Hydrogen in the Sun.*

It has been mentioned in the introduction that hydrogen is not appreciably ionized at even the highest levels of the

* Ladenburg and Loria, *Ber. d. D. Phys. Gesellschaft*, 1908.

solar chromosphere. We should add to this the fact that hydrogen exists in the Sun only in the atomic state, for, if there were molecular hydrogen in the Sun, we could have detected some at least of the lines of the secondary spectrum. But this is not the case; hydrogen enters into chemical combination with calcium and magnesium in the sun-spot, but does not probably form molecules of its own.

We shall consider in this section whether these facts are reconcilable with our theory. This requires a knowledge of the heat of molecular combination and the ionization potential of hydrogen.

These data already lie available in a recent paper by Franck * and others. They find evidences of the following chemical and electronic reactions:—

$$H_2 = H + H + 3\cdot5 \text{ volts } (= 84{,}000 \text{ calories}), \quad \text{(A)}$$

$$H_2 = (H_2)_+ + e + 10\cdot6 \text{ volts}, \quad \text{(B)}$$

$$H = H_+ + e + 13\cdot6 \text{ volts } (= 3\cdot2 \cdot 10^5 \text{ calories}), \quad \text{(C)}$$

$$H_2 = H_+ + H_+ + 2e + 30\cdot7 \text{ volts } (= 7\cdot2 \cdot 10^5). \quad \text{(D)}$$

The first is a purely chemical reaction, and the heat of molecular combination has been directly measured by Langmuir † and found to be 82,000 calories. The ionization voltage 13·6 in (C), can be calculated from the relation $V = \dfrac{h\nu_0}{e}$, taking $\nu_0 =$ convergence frequency of the Lyman series $\nu = N \left[\dfrac{1}{1^2} - \dfrac{1}{m^2} \right]$, *i. e.*, $\nu = N$. The actual occurrence of this process in the ionization of H_2 is indicated by a sudden increase of ionization at 17·1 volts (13·6 + 3·5 volts). The ionization voltage 30·7 in process (D) = 2 . 13·7 + 3·5, corresponding to the complete breaking up of the H_2-molecule into 2 atoms, and of these again into the core and the electron.

Let us first consider reaction (A)—dissociation of the molecule into atoms. Taking the equation of the reaction-isobar,

$$\log K = -\frac{U}{4\cdot571 \, T} + \frac{\Sigma\nu C_p}{R} \log T + \Sigma\nu C,$$

* Franck and others, *Ber. d. D. Phys. Gesellschaft*, vol. xxi.
† Langmuir, *Zeits. f. Elektrochemie*, vol. xxiii. p. 217 (1917) no. 20.

we have $$\Sigma\nu C_p = 2(C_p)_{\mathrm{H}} - (C_p)_{\mathrm{H}_2} = \frac{3R}{2},$$

$$C_{\mathrm{H}_2} = -3 \cdot 40 \ *, \quad C_{\mathrm{H}} = -1 \cdot 6, \quad \Sigma\nu C = \cdot 2,$$

$$U = 8 \cdot 2 \ . \ 10^4 \ \text{calories}.$$

$K = \dfrac{x^2}{1-x^2}P$, where $P =$ total pressure, and a fraction x has been dissociated. We have thus

$$\log \frac{x^2}{1-x^2}P = -\frac{8 \cdot 2 \ . \ 10^4}{4 \cdot 571 \ T} + 1 \cdot 5 \log T + \cdot 2.$$

Table VIII. shows the dissociation of hydrogen under different pressures and temperatures (in per cents.):—

TABLE VIII.

Dissociation of the H_2-molecule.

Pressure......	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.
Temp.					
2000°	1	3	9	29	70
2500	11	35	75	97	
3000	46	85	98·5		
3500	85	98·5			
4000	96·5		Complete Ionization.		
5000	100				

The table shows that under the conditions prevailing in the Sun the dissociation is complete. Even in the umbra of sun-spots, assuming that the temperature is 4000° K. and the pressure is of the order of 1 atmosphere, the dissociation is almost *complete* (96·5 per cent.).

Ionization of Hydrogen.

For a rigorous treatment of the case, we should start with the process (D). But since in the Sun the hydrogen is entirely in the atomic state, we may use the process (C). The results will be but approximate, for the equation which follows does not hold over the whole range of temperature.

The case is quite analogous to the ionization of calcium. We have only to put $U = 3 \cdot 2 \times 10^5$ calories (approximately)

* Reiche, *Ann. d. Physik*, vol. lviii. p. 657, and Leon Schames, *Phys. Zeits.* vol. xxi. p. 41.

corresponding to 13·6 volts.   We have then

$$\log \frac{x^2}{1-x^2} P = -\frac{3\cdot2 \cdot 10^5}{4\cdot571\,T} + \frac{5}{2}\log T - 6\cdot5$$

$$= \overline{6}\cdot020 \ \text{ for } \ T=7500 \Big\}$$
$$= \overline{9}\cdot279 \ \text{ for } \ T=6000 \Big\} .$$

These figures show that at a point where $T=6000°$, hydrogen can be completely ionized if $P=10^{-11}$ atmosphere.   Thus only at the highest points of the chromosphere, where the partial pressure falls to 10^{-11} atmosphere, can the ionization be complete, and the vanishing of the H-lines be expected.

Helium.

The previous work on the ionization of H atoms will have made it clear that the higher the ionization potential of an element is, the less will be its degree of ionization under a given thermal stimulus.   This is best exemplified in the case of helium, which has got the highest ionization potential of the elements so far investigated.

The experimental results, however, are rather discordant. According to Bohr, the ionization potential should be 29 volts, while most investigators have detected the commencement of a distinct ionization at 20·5 volts.   Some investigators have detected two distinct stages of ionization, one at 20·5 and another at 25 volts.   In addition to this last, Rau detected a rather strong ionization when the potential is raised by 54·6 volts, *i. e.*, to about 80 volts.

These processes probably take place according to the following schemes :—

$$\text{He} = \text{He}_+ + V_1 \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$
$$\text{Parhe} = \text{He}_+ + V_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$
$$\text{He} = \text{Parhe} + V_1 - V_2 \quad . \quad . \quad . \quad \text{(C)}$$
$$\text{He}_+ = \text{He}_{++} + e + V_3. \quad . \quad . \quad . \quad \text{(D)}$$
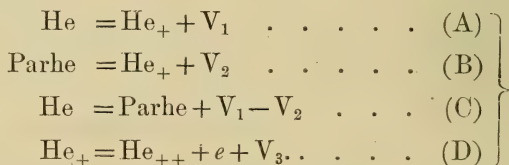
The distinction between He and the so-called parhelium is taken as one of relative configuration of the steady orbits of the two electrons [*]. V_2 may be identified with 20·5 volts, V_1 with 25 volts, and V_3 with $4 . 13\cdot6 = 54\cdot6$ volts [†].

[*] See a paper by Laude, *Ber. d. D. Phys. Gesellschaft*, 1919.
[†] It is not possible to deduce V from the quantum relation $eV = h(1, s)$, for the fundamental term $(1, s)$ is unknown both for helium and parhelium.   What are generally called the principal series of helium are really the series $\nu = (2, s) - (m, p)$ (the leading lines being 10380, for He and 20587 for parhelium).

Taking $V_2 = 20\cdot5$ volts, $U = 4\cdot8 \times 10^5$ calories approximately, we have the following table for the first step ionization of parhelium. If the ionization voltage be taken $= 25$ volts, the degree of dissociation will become still less :—

TABLE IX.

Ionization of Helium (in per cents.).

$U = 4\cdot8 \cdot 10^5$ calories (approximately).

Pressure ...	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-6}.
Temp.						
6000	5.10^{-6}	$1\cdot7.10^{-6}$	5.10^{-5}	$1\cdot7.10^{-4}$	5.10^{-4}	5.10^{-3}
7000	1.10^{-4}	$3\cdot6.10^{-4}$	1.10^{-3}	$3\cdot6.10^{-3}$	1.10^{-2}	1.10^{-1}
7500	4.10^{-4}	$1\cdot2.10^{-3}$	4.10^{-3}	$1\cdot2.10^{-2}$		
8000	$1\cdot2.10^{-3}$	$3\cdot7.10^{-3}$	$1\cdot2.10^{-2}$	$3\cdot7.10^{-2}$	$1\cdot2.10^{-1}$	$3\cdot7.10^{-1}$
9000	7.10^{-3}	$2\cdot3.10^{-2}$	7.10^{-2}	$2\cdot3.10^{-1}$	7.10^{-1}	7
10000	3.10^{-2}	1.10^{-1}	3.10^{-1}	1	3	31
11000	1.10^{-1}	$3\cdot4.10^{-1}$	1	$3\cdot4$	11	72
12000	$3\cdot10^{-1}$	1	3	10	28	93
13000	7.10^{-1}	2	7	22	58	
14000	$1\cdot5$	4	15	43	83	
15000	3	10	28	68	94	
16000	6	17	47	85		

The table shows clearly the ionization of helium is too slight under the conditions in the solar atmosphere, both in the reversing layer (T 7500, pressure = 1 atm.), as well as in the high-level chromosphere (T = 6000°, $p = 10^{-6}$ atmos.) But somewhere between the two (T 7000°, $p = 10^{-3}$ atm.), there may be some slight ionization (1 in 10,000) which may account for the occurrence of the line of ionized helium $\lambda = 4686$, which has been detected by Mitchell. The calculations are, of course, of the roughest nature.

The investigation also incidentally shows that the Pickering lines $\nu = N \left[\dfrac{1}{2^2} - \dfrac{1}{(m + \frac{1}{2})^2} \right]$ and the Rydberg line 4686 can occur as absorption-lines only in stars having the highest temperature, exceeding 16,000° K. This seems to be independently borne out by the investigations of Eddington and Russell.

The application of the method and the results obtained in the present paper to the problems of temperature radiation of elements and of the different spectral types of stars naturally suggest themselves, and will be taken up in a future communication.

Summary.

1. In the present paper it has been shown from a discussion of the high-level chromospheric spectrum that this region is chiefly composed of ionized atoms of Calcium, Barium, Strontium, Scandium, Titanium, and Iron. In the lower layers both ionized and neutral atoms occur.

2. An attempt has been made to account for these facts from the standpoint of Nernst's theorem of the " Reaction-isobar," by assuming that the ionization is a sort of reversible chemical process taking place according to the equation $Ca \rightleftharpoons Ca_+ + e - U$. The energy of ionization U can be calculated from the ionization-potential of elements as determined by Franck and Hertz, and MacLennan. For determining Nernst's chemical constant and the specific heat, the electron has been assumed to be a monatomic gas having the atomic weight of $\frac{1}{1836}$.

3. The equation shows the great influence of pressure on the relative degree of ionization attained. The almost complete ionization of Ca, Sr, and Ba atoms in the high-level chromosphere is due to the low pressure in these regions. The calculated values are in very good accord with observational data and the laboratory experiments of King.

4. Hydrogen has been shown to be completely dissociated into atoms at all points in the solar atmosphere.

5. It has also been shown that the greater the ionization potential of an element, the more difficult ionization will be for that element under a given thermal stimulus. Calculations have been made in the case of hydrogen ($V = 13.6$ volts) and helium ($V = 20.5$ volts), which show that these elements cannot get ionized anywhere in the Sun to an appreciable extent. Helium can have appreciable ionization only in stars having the highest temperature ($> 16,000°$ K.), which only are therefore capable of showing the Rydberg line 4686 and the Pickering lines $\nu = N \left[\frac{1}{2^2} - \frac{1}{(m + \frac{1}{2})^2} \right]$.

In conclusion, I beg to record my best thanks to my students for their valuable help in the calculations, and to my friend Dr. J. C. Ghosh for revising the proofs.

Calcutta, India,
        March 4, 1920.

LIV. *The Helium-Hydrogen Series Constants.*
By Herbert Bell [*].

A S is well known, Bohr proposed to modify the Balmer formula for these series by a term depending on the relativity-effect on the moving electron [†]. The formula for Helium thus becomes

$$\nu = 4\mathrm{N_{He}} \left(\frac{1}{p^2} - \frac{1}{m^2} \right) \left\{ 1 + \alpha^2 \left(\frac{1}{p^2} + \frac{1}{m^2} \right) \right\}, \quad . \quad (1)$$

where p and m are integers, $m > p$, $\mathrm{N_{He}} = \mathrm{R M_{He}}/(\mathrm{M_{He}} + \mu)$, R being Rydberg's constant $2\pi^2 e^4 \mu/ch^3$, $\mathrm{M_{He}}$ the mass of the helium atom and μ that of the electron, while $\alpha = 2\pi e^2/hc$.

The Helium lines, however, display a fine-structure under high resolving power, and Sommerfeld [‡] in explanation of this developed a theory of adjacent (elliptical) orbits with eccentricities depending on quantum considerations. He gives α a physical meaning as the ratio of angular momenta, and proposes to measure it from fine-structure observations. We know from other considerations that α^2 has approximately the value $5 \cdot 3 \times 10^{-5}$.

Paschen [§] tested this theory by an exhaustive set of measurements in the helium spectrum and substantial verification was apparently obtained. His value for α^2 from the line 4686 is $5 \cdot 315 \times 10^{-5}$.

According to Sommerfeld's theory the series (1) when $p = 3$, $m = 4, 5, \ldots$, which is the one most easily resolved, consists of a set of triplets having components I, II, III, in diminishing order of wave-length, their wave-number differences being constant. $\mathrm{III} - \mathrm{II} = 1 \cdot 73$ cm.$^{-1}$, $\mathrm{II} - \mathrm{I} = \cdot 58$ cm.$^{-1}$. Further, each component is bordered towards the red by a set of fainter lines rapidly closing in on them as higher terms of the series are reached.

Formula (1) is to apply only to I, and can therefore be accurately tested. Paschen of course did this, implicitly, but the new table from the Bureau of Standards [||] for the refractive index of air slightly alters his derived constants. His measurements are given in Table I., along with the new additive correction to reduce to vacuum, the figures in italics referring to the series $p = 4$, $m = -, 6, 7, \ldots$, the others to $p = 3$, $m = 4, 5, \ldots$.

Re-writing (1) in the form

$$
\begin{aligned}
N_{He} &= \frac{p^2 m^2}{4(m^2 - p^2)}\, \nu \left\{ 1 - \alpha^2 \left(\frac{1}{p^2} + \frac{1}{m^2} \right) \right\} \\
&= \frac{p^2 m^2}{4(m^2 - p^2)}\, \nu - N_{He}\, \alpha^2 \left(\frac{1}{p^2} + \frac{1}{m^2} \right),
\end{aligned} \quad \Bigg\} \quad . \quad . \quad (2)
$$

we see that if the formula is to hold the second or relativity term must be just large enough at each value to reduce the corresponding first one to a constant. Both terms are given in the table, and their difference is under N_{He}.

For the series $p = 3$ a constant value is reached, average 109722·31 ; but such is not the case for the unresolved series $p = 4$. Now this series is according to the theory one of quadruplets I, II, III, IV, each bordered towards the red by fainter lines as before ; but I, II, III were not resolved, and it is most likely that Paschen's readings apply to some kind of a mean among them, and consequently the wave-numbers are all too high for I to which the formula applies. Theoretically, $IV - III = ·730$ cm.$^{-1}$, $III - II = ·243$ cm^{-1}, $II - I = ·123$ cm.$^{-1}$.

If we assume the wave-numbers to be all too high by $\delta\nu$, then by (2) we need to apply a correction :

$$
\frac{p^2 m^2}{4(m^2 - p^2)}\, \delta\nu = \frac{p^4}{4}\, \delta\nu \left(\frac{1}{p^2} + \frac{1}{m^2} + \frac{p^2}{m^4} \right).
$$

It is rather surprising [*] that this should so exactly, as far as present accuracy in measurements goes, be the relativity correction. To equal it we require $\delta\nu = N\alpha^2 4/p^4 = ·091$ cm.$^{-1}$. However, it is readily seen that we cannot correct these terms by subtracting a suitable multiple of the relativity correction, for although a multiple 4 or 5 would do away with the diminishing trend the resultant N_{He} would be much lower than that from the other series. It will be seen from the following that this difficulty is due to systematic error among unresolved lines.

The components III of the triplet series and IV of the quadruplets stand farthest out, differing from I by 2·31 cm.$^{-1}$ and 1·09 cm.$^{-1}$ respectively. Their corresponding N values have therefore to be corrected by these differences multiplied

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[*] If the differences in wave-number among the standard iron lines are all counted correctly (by interference methods) but the reference Cadmium line is in error by $\delta\nu$, we should have a spurious relativity effect $\delta\lambda = -\lambda^2 \delta\nu$ throughout the spectrum. This error ·09 cm.$^{-1}$ would, however, represent a miscount by about one part in 200,000 for a red line. An accuracy of one part in ten million is claimed.

by $\dfrac{p^2m^2}{4(m^2-p^2)}$ in each case. Paschen was able to record
these lines in some cases, as shown in Table II. It will
be seen that the tendency to lower values in the higher
terms has disappeared in the series $p=4$. The results are
not very consistent among themselves, but this is readily
explained if we assume that in some cases only the bordering
satellites were observed. The errors are all on the same
side of the determined N_{He}. Paschen's estimates of possible
error of observation are also given, reduced to our scale.

Turning now to the Hydrogen (Balmer) series, we have
the formula

$$N_H = \frac{4m^2\nu}{m^2-4} - N_H \frac{\alpha^2}{4}\left(\frac{1}{4}+\frac{1}{m^2}\right), \quad m = 3, 4, \ldots \quad (3)$$

N_H being $RM/(M+\mu)$, M mass of hydrogen nucleus. The
careful measurements of Curtis [*] and Paschen (*loc. cit.*) are
given in Table III. Unfortunately they exhibit a small
systematic drift—Curtis's values increasing relatively to
Paschen's roughly linearly in terms of wave-lengths.
The first line H_α is easily resolved into a doublet, *e. g.*
by Paschen in the third-order spectrum $\delta\lambda = \cdot124$ A.U.
$\delta\nu = \cdot289$ cm.$^{-1}$. The second line has also been resolved.
In Sommerfeld's theory the series is a set of doublets I, II,
of constant wave-number difference $II - I = \cdot365$ cm.$^{-1}$, the
stronger component I being towards the red, but both
components being bordered on the long-wave side by fainter
lines rapidly converging in the higher terms. Paschen's
measurements are for "centres of gravity," while Curtis
endeavoured to record the centres of the diffuse lines (they
were not resolved). Now for the fainter lines component II
would probably vanish first, and the diffuse mean of the
photographic plate would tend towards I—that is, longer
wave-lengths. This may partly explain the minute drift.
Again, Curtis used Burns's secondary iron lines, while
Paschen used a variety—Fabry and Buisson, Neon lines by
Meissner, &c.

The values of $4m^2\nu/(m^2-4)$ for the two observers are
given under C. and P., and in each case we find that a
minimum seems to have been reached for Paschen at H_γ,
Curtis at H_ϵ. Now the stock corrections to the Balmer
formula all have the property of steadily decreasing, *i. e.*
no maximum or minimum, as for example the relativity
correction given in the table. Such a correction could

[*] Proc. Roy. Soc. vol. xc. (1914) and vol. xcvi. (1919).

TABLE I.—Helium Lines (Paschen).

$m.$	λ (air).	Corr.	$\dfrac{p^2m^2}{4(m^2-p^2)\lambda}$	Rel.	$N_{He}.$	p.e. cm.$^{-1}$
6	6560·130	1·8092	109723·67	·53	3·14	·12
7	5411·551	1·5003	·51	·48	3·03	·09
8	4859·342	1·3666	·39	·46	2·93	·06
4	4685·808	1·3093	·29	1·01	2·28	u
9	4541·630	1·2691	·13	·44	2·69	
10	4338·709	1·2164	·21	·42	2·79	
11	4199·857	1·1792	(·50)			
12	4100·049	1·1530	(·93)			
5	3203·165	·9225	·13	·88	2·25	·06
6	2733·345	·8007	·21	·81	2·40	·12
7	2511·249	·7561	·11	·77	2·34	·18
8	2385·440	·7280	·03	·74	2·29	·18
9	2306·215	·7110	(·93)			

$$N_{He} = 109722\cdot31$$

TABLE II.—Helium Lines (Paschen).

$m.$	λ (air).	$\dfrac{p^2m^2}{4(m^2-p^2)\lambda}$	Rel.	$N'_{He}.$	Corr.	$N_{He}.$	p.e. cm.$^{-1}$
6	....						
7	5411·290	109728·89	·48	28·41	−6·47	109721·94	·20
8	4850·135	28·23	·45	27·17	5·81	1·96	·14
4	4685·307₂	35·01	1·01	34·00	11·35	2·12	·04

m							
9	*4541·436*	*28·17*	*27·73*	*·44*	*5·43*	*2·30*	·24
10	*4538·586*	*27·57*	*27·15*	*·42*	*5·19*	*1·96*	·18
11	......	*27·57*	*27·19*	·38	4·91	*2·28*	·06 u
12	*4099·913*	*30·42*	*29·54*	·88	8·12	1·42	·12
5	*3202·952*	*29·73*	*28·92*	·81	6·93	1·99	
6	*2733·189*						·18
8	*2385·326*	......	......	·74	6·05	1·73	
9	......	*28·52*	*27·78*				

TABLE III.—Hydrogen Lines.

m.	λ (air). Curtis.	Paschen.	$\frac{4m^2}{(m^2-4)\lambda}$ P. C. 10967·+	Rel.	$\frac{1}{3}$(II—I).	$\frac{1}{4}$(I).	N_H C. 109677·+ P.	N'_H C. 109677·+ P.
3	6562·793	*2·797*	2·155 *2·083*	·526	·878	+·036	·817 *·745*	1·037 *0·965*
4	4861·326	*1·326*	1·896 *1·896*	·455	·650	·009	·800 *·800*	·963 *·963*
5	4340·467	*0·465*	1·776 *1·824*	·423	·581	·003	·775 *·823*	·920 *·968*
6	4101·738	*1·735*	1·748 *1·829*	·405	·549	·001	·795 *·876*	·932 *1·013*
7	3970·075		1·738	·395	·531		·812	·935
8	3889·051		1·750	·388	·521		·841	·971
							·807 *·811*	·960 *·977*

never remove the turning value, although it might displace its incidence. Curtis found the Ritz formula $\nu = N(\frac{1}{4} - 1/(m+\mu)^2)$, $\mu = 7\cdot4 \times 10^{-6}$, to best fit his observations, but a simple rearrangement throws this into the form

$$N = \frac{4m^2\nu}{m^2 - 4} - N\frac{2\mu}{m^3}\left(\frac{1}{4} + \frac{1}{m^2}\right),$$

whence we see that the correction is a good deal smaller than the relativity one and vanishes so rapidly as not to affect the terms where the difficulty occurs. The fainter unresolved lines in both Helium series, as shown in Table I., had to be discarded for the same reason.

These wave-lengths being presumably between I and II are too small, and we have an additional quasi-relativity correction to subtract from N. Paschen estimates the correction at $\frac{1}{3}(II-I) = \cdot122$ cm.$^{-1}$. Furthermore, the bordering lines on the long-wave side shift the observations that way. Paschen adds on a correction of $\frac{1}{4}$ of the "spread" of the first component I. Both corrections are tabulated in our scale. The resultant values of N after the three corrections are not constant. Paschen's values would seem to have been over-corrected. Taking $\frac{1}{4}(II-I)$ instead of $\frac{1}{3}$, we get the last N'_{He} columns, where his first three N's have become constant. It seems safe to adopt

$$N_{He} = 109677\cdot9.$$

Paschen gave (older value for refraction) $109677\cdot691 \pm 0\cdot6$. Curtis gives as a mean of the various formulæ tried $109678\cdot3$.

It is evident that we need interferometer measurements on the earlier hydrogen lines.

London, May 1920.

LV. *The Internal Energy of the Lorentz Electron.* By S. R. MILNER, *D.Sc.*[*]

THE Lorentz electron, as has long been recognized, is not a purely electromagnetic system. In order to make it a system amenable to the laws of mechanics it is necessary to ascribe to it a certain amount of energy in addition to that which is accounted for by the electric and magnetic forces of the field. This energy, apparently non-electromagnetic in character, is assumed to be located in

what may be called the "nucleus" of the electron (to distinguish it from the surrounding electronic field), and for an electron of charge e and major semi-axis a, moving with velocity $v = \beta c$, is of the amount

$$\frac{1}{6} \frac{e^2}{a} (1-\beta^2)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

While the physical character of this internal energy is largely a matter of conjecture, the postulation of its presence is essential for two separate reasons. In the first place, if we consider the electron to be a system capable of being set in motion by a mechanical force we must have simultaneously satisfied two mechanical conditions : (1) that the force is measured by the rate of increase of the momentum of the system, and (2) its activity by the rate of increase of the total energy. But this fundamental law of mechanics is not satisfied unless to the energy of the electronic field the internal energy (1) is added *. In the second place, the presence of the same internal energy is required to make the electron fit into a relativistic scheme, viz., to make its total energy at any speed equal to c^2 times its mass.

The object of this note is to point out that there is another reason for postulating the existence of this internal energy, and it is one which has a more clearly defined electromagnetic character than either of the above. It comes from a consideration of the Poynting flux of energy in the field of a uniformly moving electron.

At a point whose polar coordinates are r, θ with reference to the centre of the electron, the electric and magnetic forces are

$$\mathrm{E} = \frac{e}{r^2} \frac{1-\beta^2}{(1-\beta^2 \sin^2 \theta)^{\frac{3}{2}}} \quad . \quad . \quad . \quad . \quad (2)$$

radially, and

$$\mathrm{H} = \beta \sin \theta \cdot \mathrm{E} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

along the circles of latitude (calling the line of motion of the centre of the nucleus the polar axis). The energy density is

$$w = \frac{1}{8\pi} (\mathrm{E}^2 + \mathrm{H}^2), \quad . \quad . \quad . \quad . \quad (4)$$

and the vector flux of energy through a plane fixed in space is

$$\mathrm{P} = \frac{c}{4\pi} [\mathrm{EH}]. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* Lorentz, 'Theory of Electrons,' p. 213 (1909 edition).

The net effect of the flux must of necessity be exactly such as will transfer uniformly forward, along with the nucleus, the electromagnetic energy associated with the moving electronic field. In fact, at any point ahead of the equatorial plane the convergence of the flux will express the rate of increase there of the density of the energy, which is continually increasing as the nucleus of the electron gets nearer to the point. But the actual Poynting flux is not equivalent simply to a bodily transference of the energy of the field in the direction of motion of the electron. At the point r, θ the flux is directed along the instantaneous meridian of longitude, and, except in the equatorial plane, it has a component perpendicular to the axis. Poynting's theorem, although, of course, it does not require that electromagnetic energy should be a material thing which moves bodily from one place to another of the field, does demonstrate that the local variations of energy are mathematically the same as if this were the case. The flux can therefore be expressed as the product of the energy density of the field and the velocity with which it is (virtually) moving. From this point of view the total flux (along the meridian of longitude) must be decomposable into two—one $w\mathbf{v}$ which transfers the energy bodily forward in the direction, and with the velocity v, of the electron's motion, and the other $w\mathbf{u}$ such that

$$w\mathbf{u} = \mathbf{P} - w\mathbf{v}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since

$$\operatorname{div} w\mathbf{v} = -\frac{dw}{dt} = \operatorname{div} \mathbf{P},$$

the $w\mathbf{u}$ flux has no divergence anywhere; from the symmetry of the field it must pass through the nucleus of the electron. Poynting's theorem thus requires that the electromagnetic energy of the field, in addition to taking part in the forward motion of the whole system, is also travelling round and round through the field, passing on each journey into the nucleus at one face and out of it at the other.

The magnitude and direction of the circuital flux $w\mathbf{u}$ is easily determined by substituting in the vector equation (6) the values of w and $\mathbf{P}$ given in (4) and (5). The lines of flow are portions of ellipses of eccentricity β which have their major axes in the equatorial plane, and all pass through the centre of the nucleus. They are illustrated in the accompanying figure, in which O is the centre and BAC the upper half of the surface of the nucleus, moving in the

direction X. (The figure is drawn for $(1-\beta^2)^{\frac{1}{2}} = \frac{4}{5}$, and $\frac{1}{6}$ of the total flux lies between successive lines.) The velocity u with which the energy travels is given by

$$u = v\left\{1 - \left(\frac{2\beta\sin^2\theta}{1+\beta^2\sin^2\theta}\right)^2\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (7)$$

u is the velocity relative to the moving nucleus. When β is small, $u = v$ practically, and the ellipses become circles.
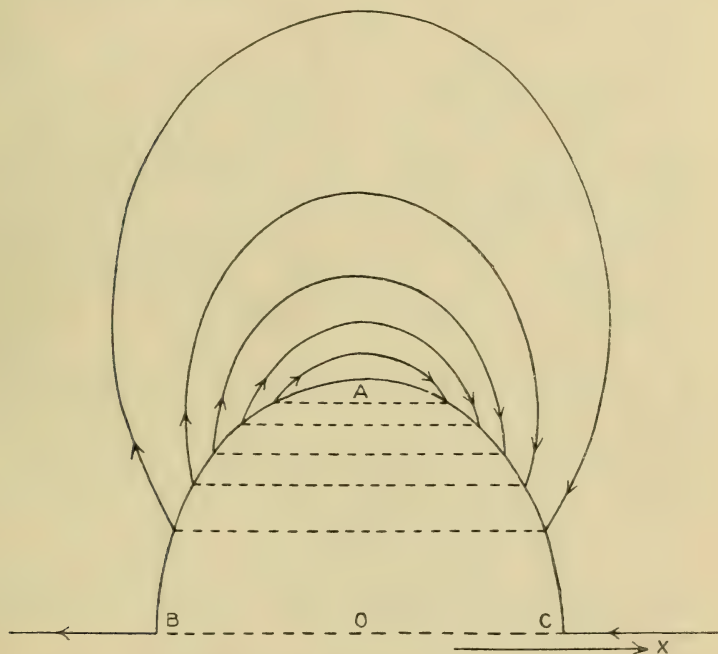
Thus at small velocities the energy of the field, viewed from the nucleus, goes round in circular paths with a uniform velocity equal to that of the forward motion of the system. The actual velocity in space (or relative to the observer) is the resultant of u and v; this is $2v$ in the equatorial plane and diminishes gradually to zero as the axis is approached. It is the same as if the (completed) ellipses rolled forward on the axis without changing their shape as the nucleus advanced.

Consideration of what happens in the space occupied by the nucleus presents the pure electromagnetic theory of the

electron with a dilemma, in that the idea of a continuous flux of energy is inconsistent with the view that the energy of the field is everywhere electromagnetic (*i. e.*, is of the form $\frac{E^2 + H^2}{8\pi}$). For, unless denial is made of the continuity through space of the flux, the circuit must be imagined to be closed through the nucleus, *e. g.*, as indicated by the dotted lines. We can exclude, as practically identical with that of the discontinuity of the flux, the supposition that it traverses the nucleus with an infinite velocity; consequently there must be a finite energy density in the nucleus, in spite of the fact that E and H are zero there. Thus accepting the continuity of the Poynting flux it is necessary to postulate the presence of non-electromagnetic energy in the nucleus. The equations (4) and (5) of an electromagnetic field are in this respect inconsistent with each other inside the nucleus, and one of them must be supplemented or modified. There is, however, no advantage to be gained by sacrificing both. If we make the supposition that Poynting's expression forms a valid measure of the energy flux in every part of an electromagnetic field, we not only retain as much of the original theory as is possible, but we can deduce a value of the internal energy of the electron which is in complete accord with that necessitated by the mechanical theory. The supposition implies that in the interior of the nucleus, since P vanishes along with E and H, the energy present (whatever its nature) is in a condition of zero flux through a plane fixed in space—or, in other words, is (virtually) at rest *.

It is evident from the figure that the whole *wu* flux which passes through the moving equatorial section of the nucleus must be equal and opposite to the whole flux through the moving equatorial plane of the external field, or to

$$\int_a^\infty (wu)_{\theta = \frac{\pi}{2}} \cdot 2\pi r \, dr,$$

which reduces to $v \cdot \frac{e^2}{8a^2}$ on inserting the values of w and u from (4) and (7). If this flux is produced by the equatorial section of the nucleus moving with velocity v past energy

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* This view agrees with the attribution of the energy to the Poincaré internal stress, for the activity of the stress in the moving nucleus will give an energy current of $-Tv$, which will just counteract the convective current $+Tv$, where T is the stress or the (equal) energy density.

momentarily stationary in space, the average energy density which is required for this is $\dfrac{e^2}{8\pi a^4}$; the total stationary energy thus present in the spheroidal nucleus at any moment is given by multiplying this expression by the volume $\frac{4}{3}\pi a^3 (1-\beta^2)^{\frac{1}{2}}$, and it is precisely the same in amount as that (1) which is required to satisfy the mechanical and also the relativity theory.

The University, Sheffield.
8th June, 1920.

LVI. *On the Orbit of a Planet.* By Prof. A. ANDERSON [*].

IF we equate the space-time interval ds in a central gravitational field to $(\gamma - \alpha\, dr^2 - \beta\, d\theta^2)^{\frac{1}{2}}$, where γ, α, β are any functions of r that, when m, the astronomical mass of the body to which the field is due, is zero, become, respectively, 1, 1, and r^2, we have

$$\frac{ds}{dt} = (\gamma - \alpha \dot{r}^2 - \beta \dot{\theta}^2)^{\frac{1}{2}}$$

and

$$s = \int_{t_0}^{t_1} (\gamma - \alpha \dot{r}^2 - \beta \dot{\theta}^2)^{\frac{1}{2}}\, dt.$$

Making the variation of this integral between two fixed points zero, the time limits being given, we have

$$\frac{d^2u}{d\theta^2} + \left(\frac{du}{d\theta}\right)^2 \left[\frac{1}{2\gamma}\cdot\frac{d\gamma}{du} + \frac{1}{2\alpha}\cdot\frac{d\alpha}{du} - \frac{1}{\beta}\frac{d\beta}{du} - \frac{2}{u}\right] + \frac{u^4}{2\alpha}\left[\frac{\beta^2}{h^2\gamma}\left(1+\frac{h^2}{\beta}\right)\frac{d\gamma}{du} - \frac{d\beta}{du}\right] = 0,$$

where $h = \beta\dot{\theta}\Big/\dfrac{ds}{dt} = \text{constant}$, and $u = 1/r$.

To make the coefficient of $\left(\dfrac{du}{d\theta}\right)^2$ vanish, we must have

$$\frac{\alpha\gamma}{\beta^2 u^4} = \text{constant} = 1,$$

and then the equation becomes

$$\frac{d^2u}{d\theta^2} + \frac{1}{2}\left(\frac{1}{h^2}\frac{d\gamma}{du} + \frac{d}{du}\left(\frac{\gamma}{\beta}\right)\right) = 0.$$

[*] Communicated by the Author.

That this equation may reduce to

$$\frac{d^2u}{d\theta^2} + u - \frac{m}{h^2} = 0,$$

the ordinary differential equation for elliptic motion, we must have

$$\gamma = 1 - 2mu,$$

and

$$\beta = \frac{1 - 2mu}{u^2},$$

and, therefore,

$$\alpha = 1 - 2mu;$$

and we have

$$ds^2 = \left(1 - \frac{2m}{r}\right)dt^2 - \left(1 - \frac{2m}{r}\right)dr^2 - \left(1 - \frac{2m}{r}\right)r^2 \, d\theta^2,$$

which makes the velocity of light constant and equal to unity.

But the gravitation potentials thus introduced do not satisfy Einstein's contracted-tensor equations. They must be rejected, if these equations are valid.

If now we wish to explain the unexplained part of the advance of the perihelion of Mercury, the simplest form of the differential equation of planetary motion for that purpose is

$$\frac{d^2u}{d\theta^2} + u - \frac{m}{h^2} - 3mu^2 = 0;$$

and, again, we have

$$\gamma = 1 - 2mu,$$

also,

$$\frac{d}{du}\left(\frac{\gamma}{\beta}\right) = 2u - 6mu^2.$$

Hence,

$$\frac{\gamma}{\beta} = u^2 - 2mu^3,$$

or

$$\beta = \frac{1}{u^2},$$

and, since $\alpha\gamma = \beta^2 u^4$,

$$\alpha = \frac{1}{1 - 2mu}.$$

Thus, in this case,

$$ds^2 = \left(1 - \frac{2m}{r}\right)dt^2 - \frac{dr^2}{1 - \frac{2m}{r}} - r^2 \, d\theta^2.$$

These gravitation potentials satisfy Einstein's equations; and, in fact, if $\gamma = 1 - \dfrac{2m}{r}$, which appears to be a natural assumption to make for approximately elliptic motion, α must be $\dfrac{1}{1 - \dfrac{2m}{r}}$ and $\beta = \dfrac{1}{u^2}$ if these equations are to be satisfied.

It may be worth mentioning that the above method of finding the path of a particle in a central gravitational field is the same as the application of Hamilton's Principle if $\dfrac{ds}{dt}$ multiplied by any constant is substituted for $T + U$, where T is the kinetic energy and U the force function.

Thus, reverting to ordinary units, we may write

$$T + U = - Mc^2 \left[1 - \frac{2m}{rc^2} - \frac{\dot{r}^2}{c^2 \left(1 - \dfrac{2m}{rc^2} \right)} - \frac{r^2 \dot{\theta}^2}{c^2} \right]^{\frac{1}{2}},$$

or, neglecting small quantities,

$$= \tfrac{1}{2} M \left(r^2 \dot{\theta}^2 + \dot{r}^2 \right) - M \left(c^2 - \frac{m}{r} \right),$$

c being the velocity of light.

LVII. *The Specific Heat of Saturated Vapours and the Entropy-Temperature Diagrams of certain Fluids.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN thanking Dr. A. W. Porter for his comments (p. 211) on my paper in the June number of the Philosophical Magazine (vol. xxxix. p. 633), and for his reference to the interesting work of Mathias on Sulphurous Acid, which I had overlooked, I should like to explain one point which was put too briefly in my paper. The entropy of the liquid, ϕ_w, is of course $\displaystyle \int \frac{K_w d\phi_w}{T}$, as follows from one of the relations there mentioned, namely, $K_w = \dfrac{T d\phi_w}{dT}$. But we have in general no direct experimental knowledge of K_w, whereas in certain fluids we know (approximately and through a

limited range) the specific heat at constant pressure, C_p. If we suppose the liquid to be initially at temperature $0°$ and at a pressure P_t equal to the saturation pressure for temperature t, the increase of entropy while the liquid is heated to its saturation temperature under that pressure is $\int_0^t \frac{C_p dT}{T}$. Using this expression we may apply known values of C_p to calculate the increase of entropy in the process of heating the liquid. This integral gives the quantity $\phi_w - [\phi_w]_0$ where $[\phi_w]_0$ is the entropy of the liquid at temperature $0°$ and pressure P_t. For the purpose indicated in the paper, namely, that of obtaining a "first approximation to the entropy-temperature diagram," the small quantity $[\phi_w]_0$ was ignored. Each constant-pressure line in the diagram, along which the heating of the liquid was supposed to take place, was treated as practically coinciding with the liquid boundary curve : it actually lies slightly to the left of that curve until the saturation temperature is reached.

<div style="text-align: right">

Yours faithfully,
J. A. EWING.

</div>

P.S. There is apparently a clerical error in the second expression for K_w as printed on p. 212. It should read

$$K_w = C_v + T\left(\frac{\partial p}{\partial T}\right)_v \frac{ds}{dT}.$$

LVIII. *On the Thermal Conductivity of some Solid Insulators.* By J. R. CLARKE, *M.Sc. (Sheffield)* [*].

IN a paper in the Philosophical Magazine for December 1919, Professor W. M. Thornton remarks that from an inspection of the recorded values of the physical constants of some heat insulators, it was observed that the thermal conductivity of a substance is equal to the product of the coefficient of elasticity and the density of the substance. The agreement between this product and the thermal conductivity was so pronounced, except in the case of some complex organic bodies, that it invited further investigation.

Among the substances which showed this agreement were various kinds of glass. The data used, however, were obtained from tables of physical constants, and it is not certain, nor even probable, that the sample of " flint glass,"

* Communicated by the Author.

the thermal conductivity of which is given by Landolt and
Börnstein, was of the same composition as the " flint glass "
whose density is recorded by Kaye and Laby. The same
applies to the other substances mentioned. It is desirable,
therefore, to ascertain if the relation observed holds good if
the constants concerned are measured using the same glass.

The composition of an ordinary glass is liable to be
different with each melt, and it may even vary throughout
the same melt. In the case of optical glass, however,
homogeneity throughout the melt is essential, and in order
that the glass may possess definite optical properties, pre-
cautions are taken to ensure that the composition is always
the same. Optical glasses are thus very suitable for testing
the validity of the relationship $k = \mathrm{E}\rho$.

The physical constants of a large number of these glasses
made in the Jena Optical Works have been determined by
various observers, and these results have been used to
compile the following table. The figures are taken from
Hovestadt's " Jena Glass," but the original papers are re-
ferred to :—

No. of Glass.	Density ρ*.	Elasticity $\times 10^5$.		Thermal Conductivity $k \times 10^3$ §.	$\mathrm{E}_1\rho$ $\times 10^9$.	$\mathrm{E}_2\rho$ $\times 10^9$.	$k/\mathrm{E}_1\rho$ $\times 10^{12}$.	$k/\mathrm{E}_2\rho$ $\times 10^{12}$.
		E_1 †.	E_2 ‡.					
19	2·370	7296	7563	2·712	1·729	1·793	1·569	1·513
20	5·944	5088	—	1·595	3·025	—	0·527	—
21	2·758	5474	5468	2·103	1·510	1·508	1·393	1·394
22	2·243	4699	4906	1·927	1·054	1·100	1·828	1·752
23	3·532	7952	7972	2·041	2·808	2·822	0·727	0·701
24	3·578	5389	—	2·044	1·929	—	1·059	—
25	2·572	6498	6766	2·458	1·670	1·740	1·471	1·413
26	3·879	5467	5461	2·003	2·120	2·118	0·944	0·945
27	2·588	6780	—	1·974	1·755	—	1·126	—
28	2·580	6626	6599	2·269	1·710	1·702	1·327	1·332
29	2·629	6514	6638	2·407	1·713	1·745	1·405	1·379
30	2·518	—	6014	2·128	—	1·515	—	1·405
31	3·070	6296	6373	1·819	1·933	1·956	0·920	0·909
32	2·668	5862	5843	2·016	1·564	1·559	1·289	1·293
33	4·731	5512	5477	1·715	2·608	2·592	0·657	0·662
38	2·585	—	7465	2·442	—	1·930	—	1·267

* Winkelmann & Schott, *Ann. d. Phys.* 1894, li. p. 730.
† *Loc. cit.* p. 697.
‡ Winkelmann, *loc. cit.* 1897, lxi. p. 119.
§ Focke, *loc. cit.* 1899, lxvii. p. 132.

The two values of the elasticity given were obtained by
Winkelmann at different times. He notes, in explanation
of the differences, that glasses 19 and 22 were from different
meltings, and glass 38 contained bubbles. The error in the

thermal conductivity also may be great. Paalhorn [*] made
measurements with several glasses, including numbers 5, 23,
and 27, and obtained for these three the values 2·267, 1·610,
and 1·409 respectively. These are much lower than Focke's
values, and the reason for the variation is discussed by
Winkelmann [†], who does not, however, decide which values
are the more trustworthy. Focke's coefficients are employed
because he used the glasses of which the elasticities are also
known. It does not matter which values of k and E are
selected, the relation $k = E\rho$ is not even approximately valid.
The complexity of the substance cannot be adduced as the
explanation of the discrepancy, as a very simple glass,
number 20, the composition of which is 20 per cent. SiO_2,
80 per cent. PbO, shows the largest deviation from the
empirical relation. It will be observed that $k/E\rho$ is small
for the heavy glasses—for example, numbers 20 and 33; but
it has not been found possible to postulate a value of n such
that $k = E\rho^n$. A survey of the other physical constants of
these glasses, such as the coefficient of expansion and the
specific heat, has been made in the hope that some empirical
relation might be discovered as suggested by Prof. Thornton.
The employment of the volume elasticity, calculated from
the given values of Young's modulus and the values of
Poisson's ratio obtained by Straubel, makes the deviations
from the equation $k = E\rho$ even more pronounced ; and no
other connexion between the constants could be observed.
Also, it does not seem probable that the variation of $k/E\rho$ is
due to any particular constituent oxide, except that the
presence of lead tends to make this quotient small, numbers
20, 24, 26, and 33 all containing large quantities of lead and
being the only glasses in the list to do so. It may be that
P_2O_5 has a similar effect, as numbers 27 and 31 both contain
more than 50 per cent. of this oxide, and in both cases the
value of the quotient is below the average. In general,
however, the compositions are so varied that it is not possible
to attribute an abnormal influence to any particular oxide.

It may be added that, although the empirical relation
suggested by Prof. Thornton does not hold good, the state-
ment that the thermal conductivity increases with the elasticity
and with the density seems to be approximately correct,
except for the heavy glasses, and may be of use as a rough
guide when seeking for a heat insulator or for a good con-
ducting glass.

Manchester,
   12th June, 1920.

* Paalhorn, Dissertation, Jena, 1894.
† Winkelmann, *Ann. d. Phys.* 1899, lxvii. p. 794.

LIX. *The Collisions of Electrons with Molecules of a Gas. By* J. S. TOWNSEND, *F.R.S., Wykeham Professor of Physics, Oxford* [*].

IN a paper on Ionization by Collision P. O. Pedersen [†] gives a method of calculating ionization potentials from the currents obtained through a gas between parallel plates at various distances apart, when electrons are set free from the negative electrode. In these calculations it is assumed that each collision with a molecule of air has the effect of reducing the velocity of the electron to zero, and the following formula is obtained by Pedersen for the total number n_a of electrons arriving at the positive electrode when n_0 electrons start from the negative electrode,

$$n_a = n_0 \epsilon^{\gamma a(a - l_0)},$$

the additional ions being generated by collisions in which the velocity of the electrons exceeds a certain critical value.

This formula is applied to the following numbers, which were published several years ago as an example of the experiments on which the theory of ionization by collision was founded [‡], a being the distance between the plates in centimetres, and q the currents in arbitrary units. The experiments were some of those made with air at a pressure of one millimetre, when electrons are set free from the negative electrode by the action of ultra-violet light, the force being 350 volts per centimetre:—

a	·2	·4	·6	·8	1·0	1·1
q	2·86	8·3	24·2	81	373	2250

The shortest distance between the plates at which a measurement of current was made was ·2 centimetre, as it was necessary to allow the electrons starting from the negative electrode to traverse a certain distance in the gas in order that they should attain the final average velocity corresponding to the electric force. The currents at the shorter distances ·2, ·4, and ·6 centimetre between the plates are in geometrical proportion, and may be represented by the simple formula $n_a = n_0 \epsilon^{aa}$ given at the time the experiments were first published, and the only quantity which can be deduced from the ratio of these currents is α the coefficient

[*] Communicated by the Author.
[†] P. O. Pedersen, Phil. Mag. July 1920, p. 129.
[‡] J. S. Townsend, Phil. Mag. (6) vol. vi. p. 598, Nov. 1903.

of a in the exponential term. Admitting that the ionization due to positive ions produces appreciable effects at the larger distances, the currents at the distances ·8, 1·0, and 1·1 centimetre between the plates cannot be represented by a formula of this type.

Thus in the notation adopted by Pedersen the only quantity which can be determined directly from these experiments is the product $\gamma\alpha$, and by means of a theoretical investigation the ionizing potential in volts is found to be 16. But it appears from other experiments that no reliable estimate of the velocity of an electron required to ionize a molecule can be obtained from the value of $\gamma\alpha$ by a calculation founded on the supposition that a large proportion of the kinetic energy of an electron is lost at each collision. I have already pointed this out in various publications, but it may be of interest to refer to a series of experiments which show how the velocities of electrons are distributed when moving under an electric force in a gas, and afford a more reliable means of estimating the velocities required to generate ions by collisions.

2. In the first * of this series of investigations of the motion of electrons in gases, experiments were made on the diffusion of electrons moving in air under forces much smaller than those required to generate ions by collisions. It was found that in an electric field the electrons moved freely and acquired a mean velocity of agitation which is much larger than the normal value corresponding to thermal equilibrium with the molecules of the gas. This shows that when an electron collides with a molecule of air it retains to a remarkable extent a large proportion of the kinetic energy acquired under the electric force. A similar result was obtained in oxygen, hydrogen, and carbonic acid. For a given force Z, the maximum pressure of the gas at which the electrons move freely, varies in different gases; this pressure is greater in hydrogen than in air, and in carbonic acid it is less than in air. Subsequently Franck and Hertz† found by another method that electrons after colliding with molecules of helium or hydrogen retained a large proportion of the energy acquired under an electric force, and the collisions were described as being of an elastic type. Reference has been made so frequently to this result that the phenomenon is generally supposed to be peculiar to monatomic gases or hydrogen.

    * J. S. Townsend, Proc. Roy. Soc. lxxxi. p. 464 (1908). ,
    † J. Franck & G. Hertz, *Verh. d. D. Phys. Ges.* xv. 9. p. 373, May 1913.

3. When considering the velocities of electrons in air under an electric force, both the motion of agitation and the motion in the direction of the electric force must be taken into consideration; for even when the forces are sufficiently large to produce appreciable numbers of additional electrons by collisions, the mean velocity of agitation may be greater than the mean velocity in the direction of the electric force. Let W be the mean final velocity of a stream of electrons in the direction of the electric force Z in a gas at pressure p, u the mean final velocity of agitation. The velocities W and u have been found for air over large ranges of forces and pressures, and the values obtained are in good agreement with the general kinetic theory. Thus the quantities W and u have been found to depend on the ratio Z/p, and since u increases with the force the velocity W is not proportional to the force. The experiments are comparatively simple as they only involve the determination of the distribution of electrons in a stream moving under an electric force, and the deflexion of the stream by a magnetic force of small intensity. If the motion of agitation were in thermal equilibrium with the molecules of the gas the lateral diffusion of the stream of electrons would follow certain simple laws, but in practice the lateral diffusion is found to be abnormally large owing to the increased velocity of agitation, and the factor k by which the energy of agitation exceeds the normal value corresponding to thermal equilibrium is easily obtained from the experiments. The normal mean velocity of agitation u_0 of electrons in equilibrium with molecules of a gas at 15° C. is approximately 1.14×10^7 cm. per second, so that the actual mean velocity of agitation when the electrons are moving in an electric field is $1.14 \times 10^7 \times \sqrt{k}$. The following table[*] gives the values of $W \times 10^{-6}$ and $u \times 10^{-6}/1.14 = 10\sqrt{k}$ for electrons moving in dry air, obtained from experiments in which the forces ranged from 2 to 20 volts per centimetre, and the pressures from ·25 to 18·5 millimetres.

Z/p	·2	·5	1	2	5	10	20	50	100
$W \times 10^{-6}$	·5	·9	1·25	1·75	3·0	5·2	9·0	17·3	27
$\dfrac{u \times 10^{-6}}{1·14}$	16	24	34	47	62	67	75	101	127
$\dfrac{e}{m} \times 10^{-17}$ calculated.	5·1	5·8	5·8	5·4	4·4	3·9	3·6	3·9	3·8

* J. S. Townsend & H. T. Tizard, Proc. Roy. Soc. lxxxviii. p. 336 (1913).

4. In order to draw conclusions from these results by representing the motion of the electrons as taking place in a series of free paths between collisions with molecules, it is necessary to specify the distance between an electron and the centre of a molecule when a collision may be considered to take place. This distance most probably depends on the velocity of the electron, but with the velocities which are here considered, the values of k and W as found experimentally are in fair agreement with calculations made on the hypothesis that collisions occur with molecules when the distance between the electron and the centre of a molecule is equal to the diameter of the molecule as determined in the kinetic theory of gases. This is seen by means of the formula given by Langevin * for the velocity W in terms of molecular quantities. In the case of electrons where the mass m of an electron is small compared with the mass of a molecule of the gas the formula becomes

$$\mathrm{W} = \frac{\mathrm{Z}e}{m} \times \frac{l}{u} \times \cdot 815,$$

l being the mean free path, and $u = u_0 \sqrt{k}$ the velocity of agitation of the electron. The formula may be applied to test the numbers given in the above table for the smaller values of Z/p where u is large compared with W. The mean free path l is taken as $1/\pi\sigma^2\nu$, where σ is the radius of a molecule of air, ν the number of molecules per cubic centimetre at a millimetre pressure. The value of l thus obtained is $3\cdot2 \times 10^{-2}$ cm.

When the above equation is written in the form

$$\mathrm{W}^2 = \frac{\mathrm{Z}^2 e}{m} \times \frac{\nu e}{m\nu u_0^2 k} \times l^2 \times \cdot 664,$$

and the known values of νe and $m\nu u_0^2$ are substituted, it reduces to

$$\frac{e}{m} = \left[\frac{\mathrm{W}p}{\mathrm{Z}} \right]^2 \times \frac{k}{2\cdot8} \, ;$$

so that the ratio of e/m may be calculated from the values of W and k. The values of $e/m \times 10^{-17}$ thus obtained are given in the fourth row of the above table, and those corresponding to the smaller forces are in good agreement with the known value $e/m \times 10^{-17} = 5\cdot3$. This result confirms the conclusion already arrived at as to the free movement of the electrons.

5. With forces from 50 to 100 volts per centimetre, the number of ions generated by collisions with molecules of air

* P. Langevin, *Ann. de Chim. et de Phys.* (8) v. p. 245 (1905).

at a millimetre pressure will depend on the distribution of the velocity of agitation, which is much greater than the velocity in the direction of the electric force. When an electron travels a distance of one centimetre in the direction of the electric force the total length of its trajectory is u/W approximately, and the total number of collisions it makes with molecules is $u/\mathrm{W}l$, where l is the mean free path of the electron. If α be the number of molecules ionized by an electron in moving a distance of one centimetre in the direction of the force, the ratio of the number of collisions in which ionization takes place to the total number of collisions is $(\alpha \mathrm{W}l)/u$.

In order to find an average value of the velocity V' of the electron required to ionize a molecule the quantity $(\alpha \mathrm{W}l)/u$ may be equated to the ratio of the number of collisions in which the velocity exceeds V' to the total number of collisions. Assuming the velocities of the electrons to be distributed according to Maxwell's law it is easy to show [*] that the latter ratio is

$$\epsilon^{-\frac{3\mathrm{V}'^2}{2ku_0^2}}\left(1 + \frac{3\mathrm{V}'^2}{2ku_0^2}\right).$$

It is convenient to represent the velocity V' in terms of the potential P in volts required to give this velocity to a particle with an atomic charge. The value of P in terms of V' is given by the relation $\dfrac{\mathrm{V}'^2}{u_0^2} = 27 \times \mathrm{P}$, and the equation to determine P becomes

$$\frac{\alpha \mathrm{W}l}{u} = \epsilon^{-\frac{81 \times \mathrm{P}}{2k}}\left(1 + \frac{81 \times \mathrm{P}}{2k}\right).$$

The values of P thus obtained are 23·7, 26, 28, 29 volts from the experiments with the smaller forces in which the values of Z/p were 40, 50, 70, 90 respectively.

It might seem that this method of finding the potential P would be inaccurate, as the errors of several experimental determinations would be involved. But the values of P as given by the above formula are only slightly affected by large errors in the values of α, l, and W, and the quantity k is the only factor which need be known accurately. The principal error in the calculation is probably due to taking Maxwell's law as giving the distribution of the velocities of electrons acted on by an electric force. It should be remembered that the potentials P thus found are average values, and with the definition of a collision that has

* Phil. Mag. (6) vol. xxvii. p. 269 (1914).

been adopted it is most improbable that ionization takes place in all collisions in which the velocity exceeds the value corresponding to the voltage P, or that ionization does not take place in a collision in which the velocity is less than the value.

The potentials P do not therefore represent a critical potential, and the minimum potential required to ionize a molecule when the collision occurs under the most favourable conditions should be less than the above values. In air, the minimum ionizing potential as found by Lenard * by a different method is 11 volts; but it may be concluded that ionization is produced in a comparatively small number of cases when electrons collide with a velocity corresponding to this voltage. In air at one millimetre pressure the observed increase of conductivity due to the motion of electrons would be accounted for if ionization took place in about 2 per cent. of all the collisions in which the velocity was greater than that corresponding to 11 volts, when Z is 100 volts per centimetre, and in about ·4 per cent of these collisions when Z is 50 volts per centimetre.

6. The numbers obtained for the velocities W and the factor k provide a simple means of measuring the proportion of the energy of an electron which is lost on colliding with a molecule. Thus with air at a pressure of one millimetre, and a force of 20 volts per centimetre, the value of k is 56·3, so that the mean final velocity of agitation corresponds to a potential of 2·1 volts, and in passing through a distance of one centimetre in the direction of the force the electron makes 290 collisions with molecules. Thus in the final steady state of motion the energy corresponding to a potential fall of 20 volts is dissipated in 290 collisions, so that the average loss of energy at each collision is 1/14·5 volt. Thus about 3 per cent. of the energy is lost on each collision, or about 1·5 per cent. of the velocity, when collisions take place with velocities of $8·5 \times 10^7$ centimetre per second.

The exact value of the elasticity has been found by Pidduck † taking into consideration the distribution of the velocities. If the collisions are perfectly elastic the following relation is obtained between the values of W and k :

$$k - 1 = \frac{W^2}{\Omega^2},$$

Ω being the mean velocity of agitation of the molecules of the gas.

    * P. Lenard, *Ann. der Phys.* (4) viii. p. 194 (1902).
    † F. B. Pidduck, Proc. Roy. Soc. A. lxxxviii. p. 296 (1913).

If ϵ be the coefficient of restitution, and $f = \frac{1}{2}(1 + \epsilon)$, f is unity when the collisions are perfectly elastic, but a very small reduction in f below this value has the effect of making a large reduction in the velocity of agitation. The following are the values of f found by Pidduck corresponding to the observed value of k:—

z/p	·2	2	20	150
$k-1$ observed...	1·8	20	55	210
f	·9993	·9988	·99	·96

Thus as the velocity of the electrons increases, the elasticity tends to diminish, but with the smaller velocities the molecules may be considered to be perfectly elastic.

LX. *On the Pressure on the Poles of an Electric Arc.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN his latest publication under the above title Prof. Duffield (Proc. Roy. Soc. June 1920), discussing his results, tries to show that the motion of ions within an electric arc and the electric wind could not be expected to produce a pressure upon the poles of the arc. Having myself contributed to your Magazine a few papers on the electric wind, will you once more give me your hospitality in order to clear up some points in connexion with this question?

I am very much indebted to Sir J. J. Thomson for having shown to me some time ago (in a way similar to that used by Prof. Duffield) that ions moving under an electric force *towards* an electrode (evidently of opposite sign) cannot produce a pressure upon it, the pull on this electrode during the motion of the ions being balanced by the impact of the ions on the electrode. Prof. Duffield, however, has entirely overlooked the fact that ions moving *from* an electrode (of the same sign) produce a reaction upon this electrode which is not compensated by any other force. Consequently, a strong pressure upon the poles of an electric arc is to be expected as a result of the motion of the ions within the arc. Moreover, when the experiments are carried out not in a vacuum (as in the case of Prof. Duffield's experiments), the energy of the ions is partly transferred by collision to the neutral gaseous molecules, which results in the formation of a stream of the surrounding atmosphere in the direction of the electric field —a phenomenon known as the electric wind. Experiments show that only a small part of the momentum of this stream

is imparted to the electrode, the stream expanding under ordinary experimental conditions over a large volume. It is therefore easy to see in view of the above considerations that in this case ions will produce a reaction also on the poles of opposite sign.

Whatever the theoretical considerations may be, the experiments carried out by Chattock and his pupils, Zeleny and myself, undoubtedly show that such a reaction does exist in reality. The pressure of the electric wind upon a sensitive vane may be detected when the ionization current passing through the gas is as small as 10^{-10} amp. (Phil. Mag. November 1916), and it appears to be proportional to the current. When the current through the gas is of the order of 10^{-5} amp. the pressure of the electric wind may impart large deviations to a vane suspended by a rigid brass wire ·1 mm. in diameter, and is at the lowest estimate as large as 25 dynes per cm.² In an electric arc, where several amperes pass through the gas, the expected pressure should be sufficiently strong to smash at once the carbon poles of the arc.

I have noticed, however, long ago the remarkable effect, that the pressure of the electric wind increases with the current only to a certain limit, and then tends to diminish. Thus, in a discharge-tube the wind pressure appears to be disproportionately small when a current of one milliampere passes through the tube and disappears completely when this current is increased to ·5 ampere. Now it appears from Prof. Duffield's experiments that also in an electric arc the electric wind for some reasons does not arise, since, supposing even the whole pressure effect observed by him to be due to the electric wind, it is negligibly small compared with the effect to be expected.

These results are very striking, since the electric wind originates solely in collisions between the ions and neutral molecules in gases and can only increase with the density of the current. There seems to be no other alternative to explain it than to suppose that when the current density is large, the carriers of electricity do not collide with the gaseous molecules—an assumption which seems incredible.

I believe that further investigation of this phenomenon may throw fresh light on the nature of discharge of electricity through gases.

<div style="text-align:center">I am, Gentlemen,
Yours faithfully,</div>

The Physical Laboratory,   S. Ratner.
   Owens College.
Manchester, July 12th, 1920.

LXI. *On a Method of Finding a Parabolic Equation of the rth Degree for any Graphically Faired Curve.* By T. C. Tobin, *M.A.*

IF a mean curve be drawn through a series of points plotted with respect to a set of rectangular axes, then an approximate equation to the curve may be found in the form

$$y = a_0 + a_1 x + \ldots + a_r x^r$$

by the following method, which lends itself readily to arithmetical computation.

Take "n" equidistant abscissæ, such that

$$x = 1, 2, 3 \ldots n \qquad \text{correspond to}$$
$$y = y_1, y_2, y_3 \ldots y_n \quad \text{as measured from the curve.}$$

Then the equations of condition to determine the constants a_0, a_1, a_2, &c., are

$$y_1 = a_0 + \quad a_1 + \quad a_2 + \ldots + \quad a_r,$$
$$y_2 = a_0 + 2 \cdot a_1 + 2^2 \cdot a_2 + \ldots + 2^r \cdot a_r,$$
$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots$$
$$y_n = a_0 + n \cdot a_1 + n^2 \cdot a_2 + \ldots + n^r \cdot a_r.$$

These give

$$1 - {_n}C_1 y_1 + {_n}C_2 y_2 \ldots (-)^n y_n$$
$$= 1 - a_0 \big[\quad {_n}C_1 - \quad {_n}C_2 + \ldots (-)^{n-1}{_n}C_n \big]$$
$$- a_1 \big[1 \cdot {_n}C_1 - 2 \cdot {_n}C_2 + \ldots (-)^{n-1} n \quad \big]$$
$$- a_2 \big[1^2 \cdot {_n}C_1 - 2^2 \cdot {_n}C_2 + \ldots (-)^{n-1} \cdot n^2 \big]$$
$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots$$
$$- a_r \big[1^r \cdot {_n}C_1 - 2_r \cdot {_n}C_2 + \ldots (-)^{n-1} n^r \big]$$

that is, $\quad 1 - {_n}C_1 y_1 + {_n}C_2 y_2 \ldots (-)^n y_n = 1 - a_0,$ . . . (1)

since $n^r - {_n}C_1 (n-1)^r + \ldots (-)^{n-1} 1^r {_n}C_1 = 0$ so long as $n > r$.

This latter relation may be easily verified by considering the identity

$$\frac{1}{y} \cdot \frac{1}{y+1} \cdot \frac{1}{y+2} \cdots \frac{1}{y+n} = \frac{1}{n!} \sum_{s=0}^{s=n} (-) \frac{{_n}C_s}{y+s},$$

which may be written

$$\frac{n!}{y^n} \left(1 + \frac{1}{y} \right)^{-1} \left(1 + \frac{2}{y} \right)^{-1} \ldots \left(1 + \frac{n}{y} \right)^{-1}$$
$$= \sum_{s=0}^{s=n} (-)^s {_n}C_s \left[1 + \Sigma (-)^r \left(\frac{s}{y} \right)^r \right].$$

Since there is no power of $\dfrac{1}{y}$ on the left-hand side less

* Communicated by the Author.

than the nth, the coefficient of $\dfrac{1}{y^r}$ on the right-hand side will be zero if $n > r$, and this coefficient is

$$n^r - {}_nC_1(n-1)^r + \ldots (-)^{n-1}1^r \cdot {}_nC_1.$$

Hence, instead of equation (1), we may write

$$1 - a_0 = 1 - {}_{r+1}C_1 y_1 + {}_{r+1}C_2 y_2 \ldots (-)^{r+1} y_{r+1}. \quad . \quad (2)$$

Having thus determined a_0, the original equation for the curve may be written

$$\eta = \frac{y - a_0}{x} = a_1 + a_2 x + \ldots + a_r x^{r-1};$$

and from this we obtain, in a similar manner to the above,

$$1 - a_1 = 1 - {}_rC_1 \cdot \eta_1 + {}_rC_2 \cdot \eta_2 \ldots (-)^r \eta_r. \quad . \quad . \quad (3)$$

Proceeding as before, we may now write the equation for the curve in the form

$$\eta' = \frac{\eta - a_1}{x} = a_2 + a_3 x + \ldots + a_r \cdot x^{r-2},$$

and obtain

$$1 - a_2 = 1 - {}_{r-1}C_1 \cdot \eta_1' + \ldots (-)^{r-1} \cdot \eta'_{r-1}, \quad . \quad (4)$$

and so on.

If the curve cuts the axis of y so that $y_0 = a_0$ is known, then a_1 may be determined as before from

$$\eta = \frac{y - a_0}{x} = a_1 + a_2 x + \ldots + a_r \cdot x^{r-1}.$$

To illustrate the arithmetical convenience of the method, let the observed "y" values corresponding to equidistant abscissæ be as follows:—

$$\left. \begin{array}{l} y_0 = 1\cdot00 = a_0 \\ y_1 = 1\cdot14 \\ y_2 = 1\cdot36 \\ y_3 = 1\cdot70 \\ y_4 = 2\cdot11 \end{array} \right\},$$

the assumed equation of the curve being

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4.$$

The calculation of the coefficients can be arranged in tabular form (p. 515).

The method may, of course, be used to obtain an approximate equation to any arc of a continuous curve of one signed curvature whose ordinates can be measured at equidistant abscissæ values.

x.									.	
—	η.		η'.	η'.			η''.			η'''.
1	·1400	+4	·3600	·0055	+3	·0165	·0246	+2	·0492	·0037
2	·1800	−6	−1·0800	·0228	−3	−·0684	·0209	−1	−·0209	
3	·2330	+4	·0320	·0328	+1	·0328				
4	·2775	−1	·2775							
			$a_1 =$ ·1345			$a_2 = -·0191$			$a_3 = +·0283$	·0037 $= -a_4$

Column 1 gives the abscissæ values.

2 gives the values of $\dfrac{y - a_0}{x}$.

5 is derived from Col. 2 by subtracting a_1 from each term; and similarly Col. 8 from Col. 5; and Col. 11 from Col. 8.

Columns 3, 6, 9 give the Binomial multipliers with appropriate sign as occurring in Equations (2), (3), (4) ...

Columns 4, 7, 10 are derived from Cols. 2, 5, 8 by using the corresponding multipliers in Cols. 3, 6, and 9.

The coefficient "a_1" is the algebraical sum of the terms in Col. 4, and a_2, a_3, a_4 evolve successively as shown, and the equation becomes

$$y = 1 + ·1345\,x - ·0191\,x^2 + ·0283\,x^3 - ·0037\,x^4.$$

LXII. *On the Dimensions of Atoms.* By A. O. RANKINE, *D.Sc., Professor of Physics in the Imperial College of Science and Technology* *.

1. IN the August number of this Magazine W. L. Bragg† has placed on record estimates of the sizes of the domains occupied in crystals by the atoms of various elements. He has also examined these data, which cover about half the known elements, in terms of Langmuir's‡ theory of atomic structure, and has shown in a convincing manner that definite values may be assigned to the diameters of the atoms in a limited number of cases. By the diameter of an atom in this connexion is meant the diameter of the outer shell of electrons as defined by Langmuir. It is interesting to compare these values with those derived from the well-known and quite different method based on the kinetic theory of gases. It will be seen that the data obtained by calculations from viscosity afford general support to the conclusions which W. L. Bragg has arrived at in the paper referred to. The number of elements to which this procedure can be applied is small, being limited to cases where the element is in the gaseous state at temperatures sufficiently low for the convenient measurement of its viscosity. But it happens, fortunately, that the elements in question are just those for which Bragg does interpret the atomic domain as being nearly coincident with the outer electron shell. It is thus possible to make comparisons for nine elements, including four inert gases, three halogen gases, and oxygen and nitrogen.

2. *The inert gases.*—According to Langmuir's theory these elements constitute the most stable arrangements of electrons round positively charged nuclei. They are monatomic and do not enter into chemical combination. A definite physical significance can thus readily be attributed to what is often vaguely called the atomic diameter by regarding it as the diameter of the outer shell of electrons. It is true that no direct calculation of these diameters can be made from crystal measurements, since the inert gases form no compounds, and have not yet been obtained themselves in crystalline form. For reasons which appear to be adequate§, however, Bragg has been able to assign probable values, and these are reproduced in column 2 of Table I. The numbers in column 4 of the same table have been calculated from

the author's measurements of the viscosities previously recorded in various papers[*], and represent the distances of nearest approach of the centres of two atoms during a collision, the Sutherland correction having been applied. These distances it has been customary hitherto to call the diameters of the atoms. In order to facilitate comparison the increments of diameter in passing from one element to the next have been placed in columns 3 and 5. All the dimensions are given in Ångström units ($\text{Å} = 10^{-8}$ cm.).

TABLE I.

Element.	From Crystal measurements.		From Viscosity measurements.	
	Atomic diameter.	Increment.	Atomic diameter.	Increment.
Neon	1·30		2·02	
		0·75		0·54
Argon	2·05		2·56	
		0·30		0·20
Krypton	2·35		2·76	
		0·35		0·30
Xenon	2·70		3·06	

With regard to these figures, it should be borne in mind that whereas those in the second column represent the actual diameter of the outer electron shell, those in the fourth cannot be regarded as such. It is quite improbable that even in a direct collision between thermally agitated atoms, the approach is so close that the electrons of the atoms intermingle. The mean distance between atomic centres during collisions may therefore be expected to be in excess of the diameter of the outer electron shell of each participating atom.

The above figures support this view, all the numbers in column 4 being in excess of the corresponding numbers in column 2, although the order of magnitude is the same. Moreover, although there is no evidence of strict proportionality, which, quite possibly, we are not entitled to expect, there is general accordance between the increments of diameter in passing from one electron shell to the next. Thus, according to both estimates, there is a comparatively large increment in passing from neon to argon, followed by one less than half as large in the step between argon and krypton, and, finally, a somewhat larger one between krypton and xenon. This is fairly good agreement, considering the wide difference between the methods of estimation.

3. *The halogen gases.*—In these cases the comparison

* A. O. Rankine, Phil. Mag. vol. xxii. p. 45, and vol. xxix. p. 552.

contemplated is complicated by the fact that in the gaseous state the atoms combine into pairs forming molecules, so that we are no longer able to regard the molecules as spheres, and apply the kinetic theory with the confidence permissible in the consideration of monatomic gases. According to Langmuir's theory we should picture a chlorine atom as identical with the argon arrangement except that the nuclear charge is 17 instead of 18 and that there is one less electron in the outer shell. In other words, we should expect the diameters of the outer shells of chlorine and argon atoms to be practically the same. In the gaseous state, however, the unstable arrangement of the chlorine atom is avoided by the junction of the atoms in pairs, so that each pair shares two electrons, and thus forms a stable molecule. The fact that two electrons are shared implies intimate contact between the outer electron shells, and, as far as dimensions are concerned, therefore, a chlorine molecule is almost identical with two argon atoms in contact. Similarly, a bromine molecule has the size and shape of two krypton atoms in contact, and an iodine molecule is similarly related to two xenon atoms. According to this view, the molecules of chlorine, bromine, and iodine have, respectively, twice the volumes of the atoms of argon, krypton, and xenon. This is in complete agreement with the conclusion arrived at by the author [*] in 1915, from deductions from the viscosities of the gases in question. The procedure by which this result was obtained was, of course, only approximate, for it was based on the assumption of spherical molecules, according to the usual statement of kinetic theory. To extend this theory so as to include diatomic molecules of the shape which Langmuir's views lead us to infer, would be a very complicated matter. But in so far as it is justifiable to treat such molecules as colliding with the same frequency as they would, were they spheres of the same volume and mass, the diameter of each atom can be calculated for comparison with the values obtained by W. L. Bragg. The results are shown in Table II., the arrangement of which is the same as for Table I.

It will be seen that here again the " viscosity " estimate of the diameter is in excess of the " crystal " estimate, and that the increments are general accordance. A comparison between the 4th columns of the two tables will show how nearly the diameters of the atoms of argon, krypton, and xenon are equal respectively to those of chlorine, bromine, and iodine.

TABLE II.

Element.	From Crystal measurements.		From Viscosity measurements.	
	Atomic diameter.	Increment.	Atomic diameter.	Increment.
Chlorine......	2·10		2·54	
		0·28		0·17
Bromine......	2·38		2·71	
		0·42		0·27
Iodine	2·80		2·98	

4. *Oxygen and Nitrogen.*—It is well known that the kinetic theory has indicated that the molecules of these two gases are of approximately the same dimensions. The actual figures are somewhat uncertain, owing to inconsistencies in the values of the viscosities obtained by different observers. Approximate calculation based on the assumptions indicated in the last paragraph indicate that the molecules of both nitrogen and oxygen resemble dimensionally two atoms of neon in contact. This agrees with W. L. Bragg's measurements, and affords additional justification for his assumption that the diameter of the outer electron shell of neon is practically identical with those of the incomplete outer shells of nitrogen and oxygen.

LXIII. *A Double Solenoid for the Production of Uniform Magnetic Fields. By* S. J. BARNETT [*].

THE universal use and great importance of the solenoid in magnetic research have led me to believe that a brief account of a method of construction devised here will be useful. So far as my knowledge goes, it is the first description of a precise method of winding a solenoid of more than one layer, and at the same time eliminating the troublesome effects of leads and interconnexions.

Probably the best way in which a single-layer coil can be constructed with great precision is by winding uniform round wire in a spiral groove accurately cut in a circular cylinder, as first suggested by Viriamu Jones and as exemplified in the work of the National Physical Laboratory. If the cylinder is conducting and long, as in the case of a solenoid, the effect of the leads may be practically eliminated, as they often are, by connecting one end of the coil to the cylinder and using the other end as one terminal; but such a coil cannot be used satisfactorily with alternating currents.

* Communicated by the Author.

In order to produce fields of moderate intensity in ordinary circumstances, a solenoid must have at least several layers. Such a coil may be constructed with precision, as Bestelmeyer [*] has pointed out, by winding one layer as described above, and with pitch considerably less than twice the diameter of the wire, winding a second layer in the same direction in the depressions between the first, and so on.   A serious defect of this arrangement, however, is due to the long conductors necessary to connect the far end of each coil with the near end of the next, which may interfere greatly with the direction and uniformity of the field due to the spiral windings.

All the advantages of precise winding may be obtained, and at the same time the (small) effect of spirality on the uniformity of the field may be largely eliminated and the trouble due to connectors and leads avoided, as follows. Two solenoids are constructed with the same pitch and number of layers, and with practically the same length, but with somewhat different diameters, so that one may be placed inside the other.   One coil is wound in left-handed spirals, the other in right-handed spirals, and the two are mounted coaxially and concentrically.   The construction necessitates that the successive layers in each solenoid start from points 180° apart.   When each coil has two or more layers it is probably best to wind all layers of one coil with the same integral number of turns, and all layers of the other coil with this same number of turns plus or minus one half-turn.

It is then clearly possible to join successive layers of the two solenoids systematically in series by very short connectors at the ends, in such a way that the current goes alternately up a layer of one solenoid and down a layer of the other, and that the small effects of each pair of short connectors are practically cancelled near the centre of the field.   Difficulties are encountered in making the windings precise close to the ends, but slight irregularities there are of little consequence.

The same general method of construction, of course, applies to solenoids of all dimensions.   In a large double solenoid constructed in this laboratory the coils are wound on tubes of bakelite-dilecto, which is known to have excellent magnetic and mechanical properties, and to insulate so well that any kind of current may be used.   It can be worked readily with a diamond tool.

Department of Terrestrial Magnetism,
    Carnegie Institution of Washington.

LXIV. *The Torsion of Closed and Open Tubes.* By JOHN
PRESCOTT, *M.A., D.Sc., Lecturer in Mathematics in the
Manchester College of Technology* [*].

THE object of the present paper is to deduce, from St.
Venant's theory of torsion, approximate formulæ for
the torsion of closed tubes, and of rods whose sections are
long thin strips, such, for example, as split tubes. Although
the results are only approximate the percentage errors they
contain approach zero as the ratio of the length to the
breadth of the section approaches infinity. The results have
thus the same sort of limitations as the ordinary beam theory,
which applies accurately only to rods whose lengths are
infinitely greater than their lateral dimensions.

Axes of x and y are taken in the plane of one normal
section of the rod, and the z-axis along the untwisted axis.
The displacements of a particle parallel to the three axes
are u, v, w; the three shear stresses are S_1, S_2, S_3; the first
of these acts on xy planes and zx planes, the second on
yz planes and xy planes, the third on zx planes and yz planes.
Fig. 1 shows the relation of S_1 and S_2 to the axes of x and y.
The usual assumption in St. Venant's theory is that the
section at z is twisted through τz, so that τ is the angle
of twist per unit length. This gives, as the component

displacements parallel to the axes of x and y of the particle originally at (x, y, z),

$$u = -\tau z y \atop v = \tau z x \Bigg\} . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Fig. 1.
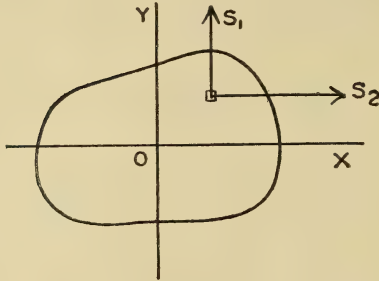
The displacement w is unknown but is assumed to be a function of x and y only. This assumption means only that each similar element of rod has the same strains.

If n is the modulus of rigidity the shear strains are

$$S_1 = n\left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}\right)$$

$$= n\left(\frac{\partial w}{\partial y} + \tau x\right). \quad . \quad . \quad . \quad . \quad (2)$$

$$S_2 = n\left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z}\right)$$

$$= n\left(\frac{\partial w}{\partial x} - \tau y\right). \quad . \quad . \quad . \quad . \quad (3)$$

It is next shown that there is a function ψ of x and y such that

$$\frac{\partial \psi}{\partial y} = \frac{\partial w}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\frac{\partial \psi}{\partial x} = -\frac{\partial w}{\partial y}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

whence $$S_1 = -n\left(\frac{\partial \psi}{\partial x} - \tau x\right), \quad . \quad . \quad . \quad . \quad (6)$$

$$S_2 = n\left(\frac{\partial \psi}{\partial y} - \tau y\right). \quad . \quad . \quad . \quad . \quad (7)$$

The condition that there should be no stress at the surface of the rod is now, in terms of ψ,

$$\psi - \tfrac{1}{2}\tau(x^2 + y^2) = \text{constant}, \quad \ldots \quad (8)$$

this equation being true all along a boundary of the section. If the rod is a tube, so that the boundary of the section consists of two closed curves, the constant in (8) is a different constant along each closed curve.

The equations of internal equilibrium give

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = 0, \quad \ldots \quad (9)$$

and equations (4) and (5) give also

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = 0. \quad \ldots \quad (10)$$

It follows from (4) and (5), which depend upon (9), that

$$w + i\psi = f(x + iy), \quad \ldots \quad (11)$$

where i denotes $\sqrt{-1}$.

It is convenient to introduce a function ξ such that

$$\xi = \psi - \tfrac{1}{2}\tau(x^2 + y^2), \quad \ldots \quad (12)$$

so that the boundary condition makes

$$\xi = \text{constant} \quad \ldots \quad (13)$$

along each closed boundary of a section.

The torque on a section is

$$Q = \iint (xS_1 - yS_2)\,dx\,dy, \quad \ldots \quad (14)$$

the double integral extending over the whole area of the section.

Now

$$S_1 = -n\left(\frac{\partial \psi}{\partial x} - \tau x\right)$$

$$= -n\frac{\partial \xi}{\partial x}. \quad \ldots \quad (15)$$

$$S_2 = n\left(\frac{\partial \psi}{\partial y} - \tau y\right)$$

$$= n\frac{\partial \xi}{\partial y}. \quad \ldots \quad (16)$$

Therefore

$$Q = -n\iint\left(x\frac{\partial \xi}{\partial x} + y\frac{\partial \xi}{\partial y}\right)dx\,dy. \quad \ldots \quad (17)$$

2 M 2

Now let
$$x = r \cos \theta \brace y = r \sin \theta, \qquad \qquad \qquad (18)$$

and let us regard ξ as a function of r and θ. Then

$$d\xi = \frac{\partial \xi}{\partial x} dx + \frac{\partial \xi}{\partial y} dy$$

$$= \frac{\partial \xi}{\partial x}(\cos \theta \, dr - r \sin \theta \, d\theta) + \frac{\partial \xi}{\partial y}(\sin \theta \, dr + r \cos \theta \, d\theta).$$

Therefore, keeping θ constant and varying r, we get

$$\left(\frac{\partial \xi}{\partial r}\right)_\theta = \frac{\partial \xi}{\partial x}\cos \theta + \frac{\partial \xi}{\partial y}\sin \theta$$

$$= \frac{x}{r}\frac{\partial \xi}{\partial x} + \frac{y}{r}\frac{\partial \xi}{\partial y}, \qquad \cdot \quad \cdot \quad \cdot \quad (19)$$

whence
$$Q = -n \iint r \frac{\partial \xi}{\partial r} dx \, dy. \qquad \cdot \quad \cdot \quad \cdot \quad (20)$$

The element of area suitable for polar co-ordinates is the element between two radii and two circles and its magnitude is $r \, d\theta \, dr$, and this takes the place of $dx \, dy$ in (21). Therefore

$$Q = -n \iint r \frac{\partial \xi}{\partial r} r \, d\theta \, dr$$

$$= -n \iint r^2 \frac{\partial \xi}{\partial r} dr \, d\theta. \qquad \cdot \quad \cdot \quad \cdot \quad (21)$$

The limits for r and θ in (21) must be such as to include the whole area of the section. Suppose we are dealing with a tubular section as shown in fig. 2. Then the limits for r

Fig. 2.
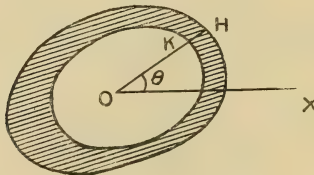
are OK and OH, which we may denote by r_0 and r_1. Now let the values of ξ along the outer and inner boundaries of the section be 0 and C. We are at liberty to choose the value of ξ at any point, since ξ is indeterminate to the extent of an added constant. The differences of ξ are, however

fixed by the equations of equilibrium. We are therefore justified in choosing 0 for ξ over one of the boundaries where ξ is constant.

Now integrating by parts we get

$$\int_{r_0}^{r_1} r^2 \frac{\partial \xi}{\partial r} dr = \left[r^2 \xi \right]_{r_0}^{r_1} - \int_{r_0}^{r_1} 2r\xi dr$$
$$= 0 - r_0^2 C - \int_{r_0}^{r_1} 2r\xi dr.$$

Therefore

$$Q = nC \int_0^{2\pi} r_0^2 d\theta + 2n \int_{r_0}^{r_1} \int_0^{2\pi} \xi r dr d\theta$$
$$= 2nCA_0 + 2n \iint \xi dx dy, \quad . \quad . \quad . \quad . \quad (22)$$

where A_0 denotes the area enclosed by the inner boundary of the section, and the double integral extends over the area of the section of the material.

If we had taken ξ to be zero over the inner boundary and $-C$ over the outer boundary, thus keeping the same difference as before over the two boundaries, we should have got

$$Q = 2nCA_1 + 2n \iint \xi dx dy, \quad . \quad . \quad . \quad (23)$$

where now A_1 denotes the area enclosed by the outer boundary of the section. The double integral has not, of course, the same value in (22) and (23) because, in the first equation, ξ varies from C to 0 in passing from the inner to the outer boundary, while in the second equation ξ varies from 0 to $-C$.

There is a slightly better form for Q than either the one in (22) or that in (23). Since ξ varies continuously from one boundary to the other there must clearly be some closed curve, between the two boundary curves, along which ξ is constant, and such that, if we make this constant zero, the values of ξ along the inner and outer boundaries are $\frac{1}{2}C$ and $-\frac{1}{2}C$ respectively. If A denotes the area enclosed by this midway curve, then the torque is

$$Q = 2nCA + 2n \iint \xi dx dy. \quad . \quad . \quad . \quad (24)$$

Equation (24) could have been obtained by adding corresponding sides of equations (22) and (23) and then dividing by 2. It follows from this that A is the arithmetic mean of A_0 and A_1.

If we apply (24) to a thin tube the double integral must

be very small, since ξ varies from $-\frac{1}{2}C$ to $\frac{1}{2}C$ from one boundary to the other.   For such a tube then

$$Q = 2nCA \quad . \quad . \quad . \quad . \quad . \quad (25)$$

approximately.   It will make no appreciable difference whether we regard A as the arithmetic mean of the areas enclosed by the two boundaries or as the area enclosed by the curve which runs midway between the two boundaries.

Equation (25) would give an approximate value of the torque in a thin tube if the constant C were known.   We shall now look at the problem of the torsion of a thin tube from another point of view and return to the question of the value of C afterwards.

Shear Lines.—Since the x-axis may have any direction we choose in the plane of a section, it follows from the equation for S_1, namely,

$$S_1 = -n\frac{\partial \xi}{\partial x},$$

that the component shear stress across any element of length ds drawn in a section is S given by

$$S = -n\frac{\partial \xi}{\partial s}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

the relative directions of S and ds being such that S makes a positive right angle with ds, just as S_1 makes a positive right angle with dx (see fig. 3).

Fig. 3.
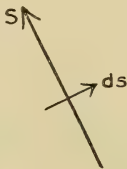
Now along the closed boundaries of the section the function ξ is constant so that, if ds is measured along one of these boundaries,

$$\frac{\partial \xi}{\partial s} = 0,$$

which shows that there is no component shear stress perpendicular to the boundary.   Moreover, there are other closed curves inside the boundaries along which ξ is constant,

and each one of these curves has the same property as a boundary, namely, the property that there is no component shear stress perpendicular to the curve. At every point of one of these curves then the resultant shear stress is along the curve itself. That is, the curve

$$\xi = k$$

is a curve whose direction at every point is the direction of the resultant shear stress at that point. Each of these curves, obtained by giving different values to k within the range of variation of ξ inside the section, is called a *Shear Line*. The shear lines form a system of closed curves inside the section, and, in the case of a tube, each of these closed curves encloses the inner boundary and is enclosed by the outer boundary. In the case of a thin tube whose two boundaries are nearly parallel curves, it is quite clear from continuity that all the shear lines are also nearly parallel curves.

Suppose now that we are dealing with a thin tube such that the normal to one boundary is approximately normal to the other boundary also. Let t denote the thickness of the tube at any point; that is, t is the length, intercepted between the boundaries, of the normal to one of the boundaries, say the inner boundary for definiteness. Let ds now represent an element of length perpendicular to t at its mid-point. Then, since the shear stress must be approximately constant across the thickness, the mean shear stress across t will be, by (26),

$$S = + n\frac{\delta\xi}{t}, \quad \ldots \ldots (27)$$

where $\delta\xi$ is the excess of ξ at the inner, over that at the outer, boundary, and this shear stress is approximately the resultant shear stress at the middle of t.

Fig. 4.
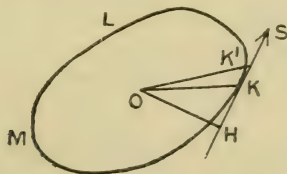
The Torque.—Let the curve KLM (fig. 4) be the locus of the mid-points of the thickness t, and let OH be the perpendicular from the axis of twist on the tangent to this

curve at K. Then, if ds represents the element of length KK', the shear force on the element of area between the two boundaries and the two normals at the ends of ds is

$$S t \, ds = + n \, \delta \xi \, ds.$$

The moment of this about O is

$$\begin{aligned} d\mathrm{Q} &= n \times \mathrm{OH} \times ds \, \delta \xi \\ &= n \times \mathrm{OH} \times \mathrm{KK'} \times d\xi \\ &= 2 n \, d\mathrm{A} \, \delta \xi, \quad \ldots \ldots \quad (28) \end{aligned}$$

where $d\mathrm{A}$ represents the area of the triangle OKK'.

Then the total torque in the tube is

$$\begin{aligned} \mathrm{Q} &= 2 n \, \delta \xi \int d\mathrm{A} \\ &= 2 n \, \mathrm{A} \, \delta \xi, \quad \ldots \ldots \quad (29) \end{aligned}$$

which is the same equation as (25) since $\delta \xi$ and C represent the same thing.

The result in (29) is merely the torque due to the stresses between two shear lines whose ξ's differ by $\delta \xi$, the outer curve having the smaller ξ. Then the equation applies equally well to the torque due to the shear between any two shear lines which are infinitely near together, whether these two shear lines are the boundary curves of a section or not. If the lines are infinitely near together we may take A as the area enclosed by the inner shear line. Then the total torque on any section whatever is

$$\mathrm{Q} = 2 n \int \mathrm{A} \, d\xi. \quad \ldots \ldots \quad (30)$$

By eliminating $\delta \xi$ from (27) and (29) we get the torque in a thin tube in terms of the stress and thickness at any point of the tube. Thus

$$\mathrm{Q} = 2 \mathrm{A} \mathrm{S} t, \quad \ldots \ldots \quad (31)$$

whence

$$\mathrm{S} = \frac{\mathrm{Q}}{2 \mathrm{A} t}. \quad \ldots \ldots \quad (32)$$

At different points of the tube Q and A are constant while S and t may be variable and such that their product is constant. The mean shear stress across the thickness of the tube at any point varies therefore inversely as the thickness, whence it follows that the shear stress in a tube of variable thickness is greatest where the thickness is least. Moreover, in any section whatever, the intensity of the shear stress at any point of any one shear line is indicated by the closeness of the next line.

Let us take the x-axis parallel to the tangent at K to the middle line of a thin tube, as indicated in fig. 5. The stress

Fig. 5.
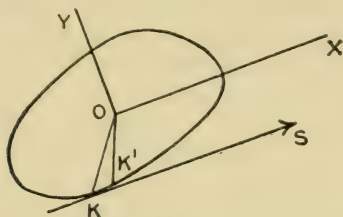
at K is
$$S = S_2$$
$$= n\left(\frac{\partial w}{\partial x} - \tau y\right),$$

whence
$$n\frac{\partial w}{\partial x} = S + n\tau y.$$

Let us now write ds for the element of length KK', which is approximately the same as dx. Then

$$n\frac{\partial w}{\partial s} = S + n\tau y.$$

This equation is true at any point of the shear line, but $-y$ must be regarded as the perpendicular from O on to the line of the shear stress S. Writing $-p$ for y,

$$n\frac{\partial w}{\partial s} = S - n\tau p, \quad . \quad . \quad . \quad . \quad (33)$$

and now we no longer need the axes.

Now w must return to the same value if we travel once round the shear line. Then, integrating once round the shear line from K back again to K, we get

$$n\int\frac{\partial w}{\partial s}ds = \int S ds - n\tau\int p ds,$$

that is,

$$0 = \frac{Q}{2A}\int\frac{ds}{t} - n\tau\int p ds.$$

But $p ds$ is twice the area of the triangle OKK'. Writing dA for this, we get

$$0 = \frac{Q}{2A}\int\frac{ds}{t} - n\tau\int 2 dA$$
$$= \frac{Q}{2A}\int\frac{ds}{t} - 2n\tau A.$$

Therefore

$$Q \int \frac{ds}{t} = 4n\tau A^2. \quad . \quad . \quad . \quad . \quad (34)$$

The integral involved in this last equation can be obtained either analytically or graphically when the shapes of the boundary curves are known. If t is constant and l is the arithmetic mean of the lengths of the two boundary curves, the torque is given approximately by

$$Q = \frac{4n\tau A^2 t}{l} \quad . \quad . \quad . \quad . \quad (35)$$

Equation (34) gives the torque in a thin tube in the general case, and (35) gives the special form when t is constant. It is necessary to recall that A does not mean the area of the section, but means the total area enclosed by the curve passing midway between the two boundaries.

There is a certain indeterminateness concerning the actual curve which encloses A and along which ds is measured. For a thin tube this indeterminateness does not much matter. If we took the inner boundary instead of the mean curve, equation (34) would give a value for Q below the true value, while if we took the outer boundary that equation would give a result too great. This gives some idea of the error in the formula.

A Uniform Circular Tube.

St. Venant's accurate method applied to a circular tube whose inner and outer radii are $(r - \frac{1}{2}t)$ and $(r + \frac{1}{2}t)$ gives

$$Q = \frac{1}{2}n\tau\pi\{(r + \frac{1}{2}t)^4 - (r - \frac{1}{2}t)^4\}$$
$$= 2\pi n\tau r t(r^2 + \frac{1}{4}t^2). \quad . \quad . \quad . \quad . \quad (36)$$

Equation (35) above gives

$$Q = \frac{4n\tau t}{2\pi r} \times (\pi r^2)^2$$
$$= 2\pi n\tau r^3 t \quad . \quad . \quad . \quad . \quad . \quad (37)$$

The proportional error in our result in this case is thus $\frac{t^2}{4r^2}$. If t is as much as a quarter of the mean radius this proportional error is only 1·5 per cent.

A Tube whose boundaries are similar Ellipses.

If we apply equation (34) to the tube whose section is bounded by the similar ellipses

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

and

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 + 2k, \quad . \quad . \quad . \quad . \quad (39)$$

k being very small compared with a or b, we find, neglecting all powers of k above the first, that

$$ds = d\theta(a^2 \sin^2\theta + b^2 \cos^2\theta)^{\frac{1}{2}} \quad . \quad . \quad . \quad (40)$$

$$t = kab(a^2 \sin^2\theta + b^2 \cos^2\theta)^{-\frac{1}{2}}. \quad . \quad . \quad (41)$$

θ being the eccentric angle.

Hence

$$\int_0^{2\pi} \frac{ds}{t} = \frac{\pi(a^2 + b^2)}{kab}. \quad . \quad . \quad . \quad (42)$$

Now equation (34) gives

$$Q = \frac{kab}{\pi(a^2 + b^2)} \times 4n\tau(\pi ab)^2$$

$$= \frac{4\pi nk\tau a^3 b^3}{a^2 + b^2}. \quad . \quad . \quad . \quad . \quad . \quad (43)$$

The precise value of the torque can be obtained by taking the difference of the torques on the complete ellipses. This method of differences is justified because the shear lines in an elliptic section are similar ellipses. Thus, since the torque on an elliptic section is

$$Q = \pi n\tau \frac{a^3 b^3}{a^2 + b^2}, \quad . \quad . \quad . \quad . \quad (44)$$

it follows that the torque in the tube is

$$Q = \pi n\tau \left\{ \frac{a^3(1+k)^3 b^3(1+k)^3}{(a^2 + b^2)(1+k)^2} - \frac{a^3 b^3}{a^2 + b^2} \right\}$$

$$= \pi n\tau \frac{a^3 b^3}{a^2 + b^2} \{(1+k)^4 - 1\}, \quad . \quad . \quad . \quad (45)$$

which becomes, when powers of k above the first are neglected,

$$Q = \pi n\tau \frac{4a^3 b^3 k}{a^2 + b^2}, \quad . \quad . \quad . \quad (46)$$

exactly as by the approximate equation (34).

The stress is greatest at the ends of the minor axis, and its value at these points is, by (32),

$$S = \frac{Q}{2At}$$
$$= \frac{Q}{2\pi ab \cdot kb}$$
$$= \frac{2n\tau a^2 b}{a^2 + b^2}. \quad \cdots \quad (47)$$

The two particular examples we have worked out show that equation (34) gives, in every case, the value of the torque obtained on the assumption that t is so small compared with the greatest dimension of the section of the tube (or with the perimeter of the section) that powers of t beyond the first may be neglected.

Torsion of thin unclosed Tubes.

The approximate results that we have obtained for closed tubes fail altogether when we come to deal with unclosed or split tubes. For a split tube there is only one boundary to the section and ξ has one constant value over the whole of this boundary. Thus, in fig. 6, ξ has the same value at P as

Fig. 6.
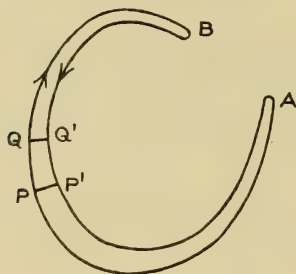
at P′, whereas if the tube were closed by fastening A and B together there would be a continuous increase or decrease of ξ from P to P′. Any shear line that crosses PP′ in fig. 6 crosses that line twice since it has the form of a closed curve lying entirely within the boundary of the section. If, however, the tube were closed each shear line would only cross PP′ once, since it could close up by encircling the inner boundary. Then across approximately one half of PP′ there are shear lines going in one direction, and over the remainder the shear lines cross in the opposite direction, and there are the same number of lines crossing each way

since the return lines are merely the outward lines continued. The boundary itself is one shear line, and the stresses at P and P′ act in opposite directions. From the preceding argument it is easy to convince oneself that a piece such as PP′Q′Q is stressed in much the same way as a piece of a long rectangle. Let us then find the stresses in an infinitely long rectangle. Let the y-axis be taken parallel to the dimension which has an infinite length and along the middle of the strip. Then the shear lines are, except near the ends of the rectangle, parallel to the y-axis. Therefore

$$0 = S_2 = n\left(\frac{\partial \psi}{\partial y} - \tau y\right).$$

Integrating this and dividing by n, we get

$$\psi - \tfrac{1}{2}\tau y^2 = f(x),$$

$f(x)$ being any function of x. In consequence of the equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = 0$$

$f(x)$ must satisfy the equation

$$\frac{d^2 f(x)}{dx^2} + \tau = 0,$$

whence we get

$$f(x) = -\tfrac{1}{2}\tau x^2 + Mx + N.$$

Therefore

$$\psi = \tfrac{1}{2}\tau(y^2 - x^2) + Mx + N.$$

If t is the width of the rectangle the boundary conditions along the two sides are

$$\psi - \tfrac{1}{2}\tau\{y^2 + (\tfrac{1}{2}t)^2\} = C,$$
$$\psi - \tfrac{1}{2}\tau\{y^2 + (-\tfrac{1}{2}t)^2\} = C,$$

which makes ψ the same along the two boundaries. This shows that the constant M is zero. Then

$$\psi = \tfrac{1}{2}\tau(y^2 - x^2) + N. \quad . \quad . \quad . \quad . \quad . \quad (48)$$

Thus the resultant shear stress is

$$S = S_1 = n\left(\tau x - \frac{\partial \psi}{\partial x}\right)$$
$$= 2n\tau x. \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

This gives the shear stress at any point of a long thin rectangle not too near the ends.

If we imagine the section to contain two rectangular pieces of different widths equation (49) gives S in either portion at a considerable distance from the ends and from the junction of the two parts. If shear lines are drawn for equal increments of ξ it is clear that there must be some

Fig. 7.
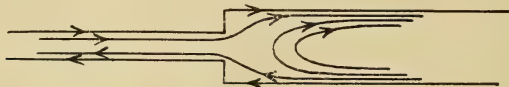
shear lines in the wider portion which do not run in the narrower portion, as is shown in fig. 7. The boundary itself is one shear line and the extra lines in the wider part are found inside the lines coming from the narrower part. What happens in this extreme case must happen wherever the section broadens. That is, new lines come into existence where the section broadens and some of the lines close up again where the section narrows.

The statement was made above that the distribution of shear stress and shear lines is approximately the same in the portion PP′Q′Q as in a long thin rectangle, and now we have found that the shear stress at distance x from the central line of a long thin rectangle, at points not near the ends, is $2n\tau x$. As the result for the torque obtained on this assumption is rather unexpected, we shall make quite sure that the shear stress is the same in a thin curved strip. For this purpose we shall find the shear stress in a thin circular split tube at points not near the open ends.

Let the mean radius of the thin split tube be a and its thickness t, so that the radii of the boundaries are $a \pm \frac{1}{2}t$. Now the general solution for ψ is contained in the equation

$$w + i\psi = f(x + iy)$$
$$= f(re^{i\theta}), \quad . \quad . \quad . \quad . \quad . \quad (50)$$

r and θ being polar coordinates, with the pole at the origin of the xy axes. Let this origin be taken at the common centre of the boundary circles. Now, since the shear lines are circles except near the open ends, ξ must be a function of r alone. But, since

$$\psi = \xi + \frac{1}{2}\tau r^2,$$

it follows that ψ is a function of r when ξ is a function of r. Then we have to find a form of the function f in equation (50) which makes ψ a function of r and not of θ. The only

function satisfying this is the log function. That is,

$$w + i\psi = i\mathrm{H} \log_e (re^{i\theta}) + \mathrm{M} + i\mathrm{N}$$
$$= i\mathrm{H} \log_e r - \mathrm{H}\theta + \mathrm{M} + i\mathrm{N},$$

whence

$$\psi = \mathrm{H} \log_e r + \mathrm{N}.$$

Therefore

$$\xi = \mathrm{H} \log_e r - \tfrac{1}{2}\tau r^2 + \mathrm{N}.$$

Now ξ has the same constant value over each boundary circle. Thus

$$\mathrm{H} \log (a + \tfrac{1}{2}t) - \tfrac{1}{2}\tau(a + \tfrac{1}{2}t)^2 + \mathrm{N} = \mathrm{C},$$
$$\mathrm{H} \log (a - \tfrac{1}{2}t) - \tfrac{1}{2}\tau(a - \tfrac{1}{2}t)^2 + \mathrm{N} = \mathrm{C},$$

whence, by subtraction,

$$\mathrm{H} \log \frac{a + \tfrac{1}{2}t}{a - \tfrac{1}{2}t} = \tau a t$$

or

$$\mathrm{H} = \frac{\tau a t}{\log \dfrac{a + \tfrac{1}{2}t}{a - \tfrac{1}{2}t}}.$$

Since we are only aiming to get an approximate solution we may as well neglect powers of t beyond the first at once. Then, expanding the logarithm in powers of $\dfrac{t}{a}$, we get

$$\mathrm{H} = \frac{\tau a t}{\dfrac{t}{a}} = \tau a^2.$$

Therefore

$$\xi = \tau a^2 \log_e r - \tfrac{1}{2}\tau r^2 + \mathrm{N}. \quad . \quad . \quad . \quad (51)$$

The resultant shear stress, which acts perpendicular to r, is

$$\mathrm{S} = -n \frac{\partial \xi}{\partial r}$$
$$= n\left(-\frac{\tau a^2}{r} + \tau r\right). \quad . \quad . \quad . \quad (52)$$

If we write $(a + x)$ for r in this, x being thus measured radially from the mean circle of the section, we get

$$\mathrm{S} = n\tau \left\{ -a\left(1 + \frac{x}{a}\right)^{-1} + a + x \right\}$$
$$= n\tau \left\{ 2x - \frac{x^2}{a} + \dots \right\},$$

which becomes, on neglecting powers of x beyond the first,

$$\mathrm{S} = 2n\tau x, \quad . \quad . \quad . \quad . \quad (53)$$

exactly as along a straight strip.

We have now shown that, wherever the shear lines are nearly parallel either in a thin straight strip, or in a thin curved strip where the width is small compared with the radius of curvature, the shear stress is approximately proportional to the distance from the middle line of the strip and is in contrary directions on the two sides of the middle line.

Torque in a Long Thin Section.

Any particular shear line in a long thin section such as a long thin rectangle, or an unclosed tube, or a long narrow ellipse, is a closed curve which crosses the width of the strip at any point at distance x from the centre on one side and $-x$ on the other side. Then the area enclosed by this shear line is

$$A = \int 2x\,ds, \quad \ldots \ldots \quad (54)$$

ds being an element of the middle line.

This integral extends between the two points where the line bends round and turns back. In the integral for the area x must be regarded as a function of s, since the length x increases as the section broadens out and decreases as it narrows again.

Now, by equation (30),

$$\begin{aligned}
Q &= 2n\int A\,d\xi \\
&= 2n\iint 2x\,ds\,d\xi \\
&= 4\iint x\,ds \cdot S\,dx \\
&= 4\iint x\,ds \cdot 2n\tau x\,dx \\
&= 8n\tau \iint x^2\,dx\,ds. \quad \ldots \ldots \quad (55)
\end{aligned}$$

The limits for x in this integral are 0 to $\frac{1}{2}t$, not $-\frac{1}{2}t$ to $\frac{1}{2}t$, since the shear lines enclosing the area A expand from the centre outwards. Therefore

$$\begin{aligned}
Q &= 8n\tau \int \tfrac{1}{3}(\tfrac{1}{2}t)^3\,ds \\
&= \tfrac{1}{3}n\tau \int t^3\,ds. \quad \ldots \ldots \quad (56)
\end{aligned}$$

We have thus expressed the torque by means of an integral of t^3 (which must be regarded as a function of s) with respect to s, the length measured along the middle curve of the section. The result in (56) is accurate for a strip in which the shear lines are parallel curves running in a strip whose width is everywhere infinitesimal in comparison with the radius of curvature of the central line. For the application of this equation it is important that the two parts of

the boundary of the strip should be approximately parallel over nearly the whole length of the strip. The formula will fail to apply, for example, to a strip, however thin, made of a number of small circles strung together by thin strips whose widths are infinitesimal compared with the diameters of the circles, such a section, in fact, as would be obtained by cutting through a string of spherical beads, the circles being supposed to be complete.

If the central line of the strip is straight equation (56) gives

$$Q = 4n\tau I_y, \quad . \quad . \quad . \quad . \quad . \quad (57)$$

I_y being the moment of inertia of the strip about the central line. It should be noticed that our results show that the torque is the same for the same twist whether the central line is straight or not. For example, a circular tube split longitudinally has the same strength under torsion whether it is left in its circular shape or flattened out into a plane sheet.

We can verify equation (57) by means of some accurate results worked out by St. Venant's analysis. Thus, for a rectangle of length a and width b, when $a > 3b$, the torque is approximately

$$Q = \tfrac{1}{3}n\tau b^3 a \left(1 - 0{\cdot}630\frac{b}{a}\right)$$

$$= 4n\tau I_y \left(1 - 0{\cdot}630\frac{b}{a}\right). \quad . \quad . \quad . \quad (58)$$

If the width b is so great as one-third of the length, the formula (57) is wrong by a little over 20 per cent. But if b is one-tenth of a then the result is wrong by just over 6 per cent.

If the rectangular section were bent into any curved shape, the lines of shear stress would be distributed in the section in almost precisely the same way as when the section was rectangular. Consequently there would be just about the same proportional error in equation (57) for a curved section as for a straight section, always assuming that the thickness is small compared with the radius of curvature.

To take another example. The accurate torque in an elliptic section with semi-axes a and b is

$$Q = \pi n\tau \frac{a^3 b^3}{a^2 + b^2}. \quad . \quad . \quad . \quad . \quad (59)$$

Suppose b is small compared with a. Then we get

$$Q = \pi n \tau b^3 a \left(1 + \frac{b^2}{a^2} \right)^{-1}$$

$$= 4 n \tau I_y \left(1 - \frac{b^2}{a^2} + \dots \right), \quad . \quad . \quad . \quad (60)$$

I_y being the moment of inertia about the major axis. The proportional error in equation (57), when applied to this section, is therefore approximately $\dfrac{b^2}{a^2}$. Thus there is an error of about 10 per cent. when $a = 3b$, and about 1 per cent. when $a = 10b$. For this section then our formula gives more accurate results than for the rectangular section. We may expect in general that (57) will give better results for a strip with tapered and rounded ends than for one with rectangular ends.

Uniform Circular Tube split Longitudinally.

If r is the mean radius of the tube and t the uniform thickness, equation (56) gives

$$Q = \tfrac{1}{3} n \tau \int_0^{2\pi r} t^3 ds$$

$$= \tfrac{1}{3} n \tau t^3 \times 2\pi r. \quad . \quad . \quad . \quad . \quad (61)$$

The ratio of the torque in the split tube to that in the complete tube is $\dfrac{1}{3}\dfrac{t^2}{r^2}$ for the same angle of twist. But this is not a fair comparison because the maximum shear stresses are not the same in the two cases. The maximum shear stresses are, for the split tube $n\tau t$, and for the complete tube $n\tau(r + \tfrac{1}{2}t)$. If we make these shear stresses equal by giving different values to τ in the two cases, then the ratio of the torque in the split tube to that in the complete tube is

$$\frac{1}{3} \frac{t(r + \tfrac{1}{2}t)}{r^2} = \frac{1}{3} \frac{t}{r} \text{ nearly.} \quad . \quad . \quad . \quad (62)$$

The split tube is therefore much weaker than the complete tube under torsion, and very much less rigid.

It is interesting to find the relative axial displacement of the open ends of the split tube. For this purpose we may use equation (33) and regard S in that equation (which is the *mean* shear stress across the section) as zero for the split tube. Then

$$w = -\tau \int p \, ds$$

$$= -2\tau \int dA$$

$$= -2\tau A, \quad . \quad . \quad . \quad . \quad . \quad (63)$$

A being the area enclosed by the central line of the section. For the split circle we get

$$w = -4\pi\tau r^2. \quad . \quad . \quad . \quad . \quad . \quad (64)$$

Equation (63) could be applied to any split tube of variable or constant thickness. If it is applied to a section whose open ends do not come close together, then A is the area enclosed between the curve of the central line of the section and the radii drawn from the axis of twist to the two ends of that line. For example, if it were applied to a section with a straight central line which is intersected by the axis of twist the area A would be zero, and therefore w would be zero.

The difference in the behaviour of a split and a complete tube is due to the freedom of the open ends of the section of the split tube to move axially relatively to each other. If this freedom is constrained in any way the split tube does not differ from the complete tube. If, for instance, a short split tube is gripped at the ends so that no relative motion of the particles in the end planes is possible, then the tube behaves almost exactly like a closed tube. The rules for the split tube apply to a tube twisted in such a way that the end sections have perfect axial freedom, or to sections in a long tube at great distances from the ends. In actual practice a split tube welded into brackets at its ends would behave very nearly like a complete tube because the axial displacement represented by (63) would be so great that the effect of preventing all this displacement at the ends would be considerable even at the middle of the rod.

The rules that we have given for split tubes will apply with fair accuracy to any thin portion of a section of a twisted rod where the shear lines must all go forward and return across the same normal. For example, the I-section shown in fig. 8 may be treated as if the two end-pieces and

Fig. 8.

the backbone were put end to end to form a continuous strip with open ends. That is, if the two ends be supposed to be cut off along the dotted lines, then the torque in any

one of the three strips is

$$Q = \tfrac{1}{3} n\tau \int t^3 ds$$

and the total torque is the sum of the torques due to the three strips separately.

Again consider the box section with projecting pieces shown in fig. 9. The shear lines in the projecting pieces

Fig. 9.
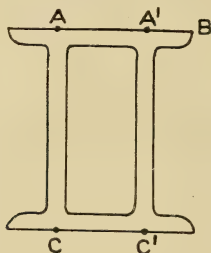
go and return along the same strip, whereas all the lines that run along $A'A$ also run along AC. Thus the torque in the part $ACC'A'$ may be obtained from the rules for a closed tube, whereas the torque in the projecting pieces must be obtained from the rules for open tubes. Suppose the width of the strip is constant everywhere and has the value t, and suppose $AA'=a$, $AC=c+t$, $A'B=b$, and let all the other projecting pieces have a length b. Then the torque in the closed tube is, by (35),

$$Q_1 = \frac{4n\tau a^2 c^2 t}{2(a+c)}, \quad . \quad . \quad . \quad . \quad . \quad (65)$$

and the torque in the four projections is

$$Q_2 = \tfrac{4}{3} n\tau t^3 b. \quad . \quad . \quad . \quad . \quad . \quad (66)$$

The total torque is therefore

$$Q = Q_1 + Q_2$$
$$= \frac{2n\tau a^2 c^2 t}{a+c} + \tfrac{4}{3} n\tau t^3 b. \quad . \quad . \quad . \quad (67)$$

It is obvious that the torque due to the projections is negligible compared with that due to the tube. In fact Q_2 is itself of the same order as quantities neglected in

finding Q_1 by our approximate theory. Then, to our order of approximation,

$$Q = \frac{2n\tau a^2 c^2 t}{a + c}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (68)$$

It is usual to make box sections by rivetting plates together. Such rivetted girders may be treated as if they were solid for the purpose of torsion provided the rivets are near enough and strong enough. There may be, of course, considerable shear on the rivets.

The formulæ obtained in this paper are suitable only for long thin sections in which the shear lines are nearly parallel curves over practically the whole of their length. A rod whose section is a complete circle could not reasonably come under either the rule for a closed tube or the rule for a long thin unclosed section. Nevertheless we shall, just for the sake of noting to what extent the formulæ fail, treat the complete circle

- (1) as a closed tube with no central hole,
- (2) as a long thin section whose central line is a diameter.

In the first case the central line is a circle of half the radius of the section. If r denotes the radius of the section then equation (35) applied to this section gives

$$Q = \frac{4n\tau(\tfrac{1}{4}\pi r^2)^2 r}{\pi r} = \tfrac{1}{4}\pi n\tau r^4. \quad \cdot \quad \cdot \quad \cdot \quad (69)$$

Again treating the section by the second method, equation (57) gives

$$Q = 4n\tau(\tfrac{1}{4}\pi r^4) = \pi n\tau r^4. \quad \cdot \quad \cdot \quad \cdot \quad (70)$$

The correct result for this section is

$$Q = \tfrac{1}{2}\pi n\tau r^4. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (71)$$

Of the two results in (69) and (70) one is half the correct result and the other is twice the correct result. It is not intended that the formulæ shall be used for such extreme cases, and they are given here only to indicate that fair accuracy can be expected from the formulæ for all reasonable cases.

LXV. *On the Variation of Thermal Conductivity during the Fusion of Metals.* By Seibei Konno [*].

§ 1. *Introduction.*

ACCORDING to the electron theory the ratio of the thermal and electric conductivities of metals is independent of the nature of the materials and proportional to the absolute temperature. The experimental investigations [†] of different steels and iron alloys—such as carbon steels, iron-nickel, iron-cobalt, and iron-manganese alloys—at ordinary temperature shows that the said ratio is roughly the same for these steels and alloys, notwithstanding a large divergence in the respective values of the two conductivities. That is, the variation of the thermal conductivity of iron along with the concentration of the other components is similar to that of the electric conductivity, so that we can approximately expect the magnitude of one variation from the other. It was also found that in the case of carbon steels the above relation holds good for different high temperatures up to 900° C., and also that the proportionality between the said ratio and the absolute temperature is fairly well satisfied. It has been shown by E. F. Northrup [‡] and H. Tsutsumi [§] that the electric conductivity of different metals makes a conspicuous abrupt decrease during melting, with the exception of bismuth and antimony, in the case of which an abrupt increase of conductivity is observed. It was therefore thought very desirable to see, whether up to a temperature beyond the melting-point, a similar relation exists between the two conductivities. The present investigation was carried out on the one hand to test this relation, and, on the other hand, formed a preliminary experiment for studying the conductivity of molten steel, which has a very great importance in connexion with the metallurgy of iron.

As to the change of thermal conductivity of different substances during melting, a few experiments have been made. Barus [‖] first made an experiment with Thymol, and found that the thermal conductivity of the substance

abruptly decreases by about 13 per cent. during the melting (at 13° C.). The same experiments on $Na_2HPO_4 + 12H_2O$, Paratoluidine, Naphthylamine, and $CaCl_2 + 6H_2O$ were also made by C. H. Lees *; but there was no apparent break in the regularity of the change of thermal conductivity at the melting-point in the case of the first three substances, and a decrease of about 20 per cent. in the case of $CaCl_2 + 6H_2O$. A. W. Porter and F. Simeon † made a similar experiment with mercury and sodium, and showed that the abrupt change in the thermal conductivity during melting is of the same order of magnitude as the corresponding change in the electrical conductivity—that is, the ratio of the thermal conductivity for the solid state to that for the liquid is 3·91 for mercury and 1·31 for sodium. The only experiment at high temperatures was that of E. F. Northrup and F. R. Pratt ‡ for two typical metals— tin and bismuth, for each of which the conductivity changes in the opposite direction during melting, but their result is rather of a qualitative nature. They concluded that the characteristic change of thermal conductivity for tin and bismuth during melting is substantially the same as the corresponding change for the electrical conductivity, and that Wiedemann-Franz's law holds good, at least qualitatively, through the change of state of these metals.

So far, the literature regarding the abrupt change of the conductivity during melting has been very meagre. Hence, to determine as accurately as possible the thermal conductivity of different metals at temperatures both below and above their melting-points was a very important work, and, therefore, I began—as a preliminary experiment—with some fusible metals. The following pages contain the method and the result of the present experiment.

§ 2. *Description of the Apparatus.*

The method used in the present experiment is to measure the conductivity of metals at different high temperatures relative to the values at room-temperature. A vertical section of the main part of the apparatus is shown in fig. 1. A, B, D are short cylindrical pieces made of a very low carbon steel, and C is the specimen to be tested. The iron cylinders A and B are each 2·5 cm. in height and 2·2 cm. in diameter; between these two pieces there is a flat

* Phil. Trans. Roy. Soc. A. cxci. p. 399 (1898).
† Proc. Phys. Soc. xxvii. p. 307 (1915).
‡ Jour. Frank. Inst. clxxxiv. p. 675 (1917).

cylindrical cavity 5 mm. high and 20 mm. wide, in which
a small, flat heating-coil is placed. On each side of the
cavity two narrow holes a, b and c, d, each 1 mm. wide
and 11 mm. deep, are radially bored at a distance of one
centimetre to receive the two junctions of a differential
thermocouple, which measures the temperature-gradient
along the axis of the cylinder. The two thermocouples
consist of iron and nickel wires in the case of the investi-
gation of the metals having relatively low melting-points ;
but in the case of aluminium and antimony, iron wire is
replaced by a platinum wire to avoid the disturbance caused
by an abnormal change of thermoelectromotive force due

Fig. 1.
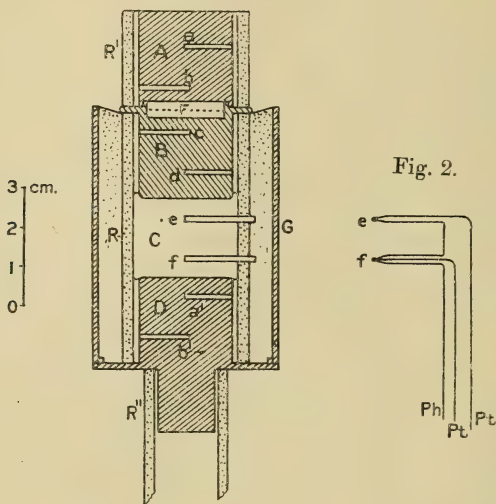
Fig. 2.

to the A_2 transformation of iron. e, f is a duplex thermo-
couple, consisting of platinum and platinum-rhodium wires,
by which the temperature-gradient in the specimen C, and
at the same time that of the specimen at point f, can be
measured. Its connexion is shown in fig. 2. The two
junctions e, f are coated with thin asbestos paper in such
a way that the insulation between the junctions and the
specimen, both in the solid and liquid states, is perfect, the
horizontal portions of the wires being protected by thin
porcelain tubes. Its cold junction is placed in a water-
bath, whose temperature is read by a thermometer. R is
a thick porcelain tube, and the interspace between the tube
and the steel pieces B and D is tightly packed with caolin
kit. The two junctions e, f go out through the wall of the
tube, and are so firmly fixed to it that the distance between

e and *f* does not change in any appreciable degree during the melting and solidification of the specimen. R' and R'' are also similar porcelain tubes protecting iron cylinders A and D. Two narrow holes *a'*, *b'* are also radially bored to receive the two junctions of a differential thermocouple, as in the iron piece A. G is a thick iron tube, which serves as an equaliser of temperature, and the interspace between the tube and the porcelain tube R is packed with caolin powder in order to avoid the lateral loss of heat as much as possible.

The small heating-coil in the cavity between the iron cylinders A and B consists of a nichrome wire 0·5 mm.

Fig. 3.
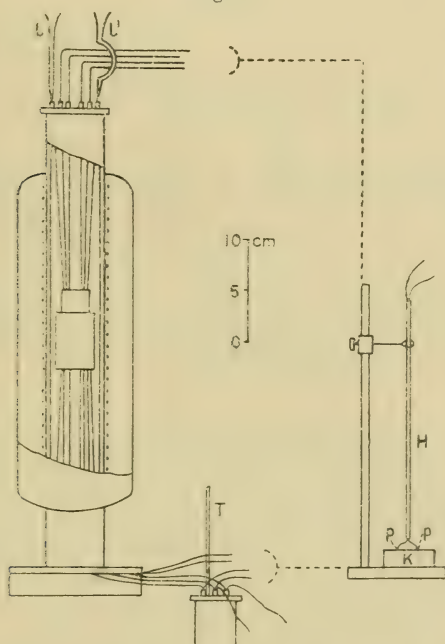
thick and about 30 cm. long, wound in a spiral form and well insulated with caolin kit. To the terminals of the coil are fused thick copper leads *l*, *l'*, which are used as the current and potential leads. The terminal volt and the current passing through the heating-coil are measured by a voltmeter and an ammeter (made by Siemens & Halske); the heat generated in the cavity per unit of time can thus be evaluated.

The whole arrangement is vertically supported by a porcelain tube R'', so as to lie in the middle portion of a

vertical electric furnace. To avoid the convection-current in the furnace as much as possible, the free space in the furnace is loosely filled with asbestos fibre. The furnace consists of a porcelain tube 5·5 cm. wide and 45 cm. long, a nichrome wire being uniformly wound round it and the exterior thickly covered with asbestos paper. The whole arrangement is shown in fig. 3.

The terminals of four sets of the thermocouples ab, cd, ef, $a'b'$ are dipped in the eight mercury cups on a paraffin block, as shown in fig. 4. Two copper wires connected to

Fig. 4.
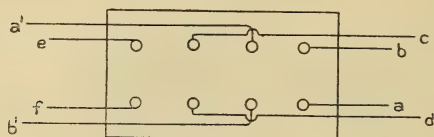
a wall-galvanometer (made by Leed & Northrup), is led into a glass tube H and fixed by paraffin, the two terminals pp protruding from the lower end of the tube. The terminals can be put in any pair of the mercury cups by holding the glass tube in the hand. In this way the difference in the temperatures between two junctions in any pair of the four thermocouples can successively be observed with the single galvanometer.

§ 3. *Method of Observation.*

Let Q be the quantity of heat generated per unit of time in the heating-coil, and let q, t, and K be the quantities of heat flowing per unit of time, the temperature differences per unit of length and the thermal conductivities respectively, subscripts 1, 2, 3 and 4 referring to the iron pieces A, B, C, and D respectively. When the stationary state is attained, the lateral loss of heat is always very small in comparison with q, and we have

$$q = K_1 S_1 t_1, \quad q_2 = K_2 S_2 t_2, \quad q_3 = K_3 S_3 t_3, \quad q_4 = K_4 S_4 t_4,$$

where S is the sectional area of the iron pieces. Since A, B, D are made of the same material, we have

$$K_1 = K_2 = K_4 = K', \quad \text{and} \quad K_3 = K.$$

Under the supposition that the lateral loss of heat is negligibly small, we have

$$Q = q_1 + q_2 = K'S(t_1 + t_2);$$

$$q_2 = Q\frac{t_2}{t_1 + t_2}, \quad q_4 = Q\frac{t_4}{t_1 + t_2}.$$

In an actual case, q_3 is slightly less than q_2, and q_4 less than q_3 by nearly the same amount; hence we may put as the first approximation

$$q_3 = KSt_3 = \tfrac{1}{2}(q_2 + q_4) = \tfrac{1}{2}Q\frac{t_2 + t_4}{t_1 + t_2},$$

or

$$K = \tfrac{1}{2}\frac{Q}{St_3}\frac{t_2 + t_4}{t_1 + t_2}.$$

Since the distances between two junctions of each of the three differential thermocouples ab, cd, $a'b'$ are equal to each other, t_1, t_2, and t_4 in the above relation may be replaced by the corresponding deflexions of the galvanometer δ_1, δ_2, and δ_4 respectively. Moreover, if the distance between two junctions of the differential thermocouple ef and its difference of temperature be respectively denoted by s and Δt, we have

$$t_3 = \frac{\Delta t}{s},$$

and therefore

$$K = \frac{1}{2}\frac{Qs(\delta_2 + \delta_4)}{S\Delta t(\delta_1 + \delta_2)}.$$

In the above relation the determination of the quantity Q is somewhat uncertain. For the heat generated per unit of time in the heating-coil F is accurately known, but a part of it is lost by lateral conduction before flowing into the specimen. It is very difficult to ascertain exactly how much of the heat is thus lost. Hence the absolute values of thermal conductivity obtained by the present method may be somewhat uncertain; but if we assume that for all temperatures, the above loss is always the same fraction of the total heat generated, the relative values of the conductivity are perfectly correct. Hence in the present investigation only the relative measurements were made.

The observation was conducted in the following way :—
A constant electric current of about 2·7 amperes was passed through the heating-coil. After an interval of about one hour, when an approximate stationary state was attained, the temperature of the specimen was first observed, then the readings of the galvanometer corresponding to the junctions

cd, *ef*, *a'b'*, and *ab* were taken; and again the same obser-
vations were repeated by reversing the poles of the
galvanometer leads *pp*, by turning the glass tube H, the
disturbing effect of the thermoelectric current in the circuit
leading to the galvanometer being thus eliminated. The
difference between each pair of these readings corresponds
to 2δ in the above formula. The heat generated in the
cavity F per unit of time was then measured by observing
the current passing through the heating-coil and its terminal
volt. Finally, the temperature of the specimen and its
gradient were re-determined for confirmation. Next, the
current in the heating-coil was broken, and a current passed
through the furnace. When the temperature of the furnace
was raised by a certain amount, another current was passed
through the heating-coil F; after the temperatures had
become stationary, the observations were repeated as above.
In this way the observations at gradually increasing tem-
peratures were made step by step. It was found that the
interval required for the approximate stationary state
gradually decreases with the rise of temperature, the
smallest, however, being 30 minutes.

§ 4. *Results of Experiments.*

In order to see how much of the heat generated in the
coil is lost before entering the iron piece D, the specimen C
was removed and the pieces B and D were brought in direct
contact, and the temperature-gradients in the two junctions
cd and *a'b'* were observed. The gradient in the second
junction was about 30 per cent. less than that of the first
junction. With the specimen C in its proper position, this
difference was not in any case greater than 40 per cent.;
hence the portion of the loss due to the lateral conduction
through the specimen is of the order of magnitude of
10 per cent. It is, however, a merit of the present method
that a fairly correct value for the conductivity is always
obtained. In order to show this, the absolute determination
of the thermal conductivity of a carbon steel containing
0·35 per cent. of carbon was measured. As the results of
the experiment we obtained the following values : 0·095
at 128° C., 0·088 at 305° C., 0·072 at 473° C. These values
agree very satisfactorily with those obtained by Prof. Honda
and Mr. Shimizu[*]. In the actual case the determination of
the conductivity was made relative to the conductivity at
room temperature.

[*] Sci. Rep. vi. p. 219 (1917).

The values of the latter quantity for different metals were taken from Landolt and Börnstein's table.

The results obtained are given in the following tables and in figs. 5 and 6. In these tables, t is the mean temperature of the specimen. K_s and K_l are respectively the thermal conductivities in solid and liquid states of different metals, expressed relatively to the known values at ordinary temperature.

1. Tin.		2. Lead.		3. Bismuth.	
Temp.	K_s.	Temp.	K_s.	Temp.	K_s.
18	0·157 (1)	18	0·083 (2)	18	0·0194 (3)
108	0·151	108	0·080	89	0·0181
125	0·149	222	0·077	160	0·0170
209	0·143	298	0·074	222	0·0177
		326	0·069	233	0·0177
				256	0·0183
Temp.	K_l.	Temp.	K_l.	Temp.	K_l.
292	0·081	355	0·039	298	0·0418
417	0·079	447	0·038	286	0·0400
498	0·078	531	0·037	376	0·0378
		601	0·037	484	0·0372
				584	0·0369

In (1), (2) Lees' values for K_s at 18° C. were assumed.
In (3) Jaeger & Diesselhorst's value at 18° C. was assumed.

4. Zinc.		5. Aluminium.		6. Antimony.	
Temp.	K_s.	Temp.	K_s.	Temp.	K_s.
18	0·268 (1)	18	0·504 (2)	0	0·0442 (3)
97	0·263	116	0·490	113	0·0401
129	0·262	273	0·471	182	0·0386
242	0·250	324	0·434	344	0·0414
280	0·246	430	0·425	469	0·0456
313	0·241	470	0·394	557	0·0510
362	0·233	605	0·360	610	0·0575
400	0·220				
Temp.	K_l.	Temp.	K_l.	Temp.	K_l.
460	0·140	675	0·223	692	0·0503
537	0·138	800	0·214		
578	0·137				

In (1), (2) Lees' values for K_s at 18° C. were assumed.
In (3) Lorenz's value for K_s at 0° C. was assumed.

Thus the thermal conductivity of tin, lead, zinc, and aluminium rapidly decreases with the rise of temperature. At the melting-points a discontinuous decrease of the conductivity is observed, after which they diminish slightly.

Fig. 5.
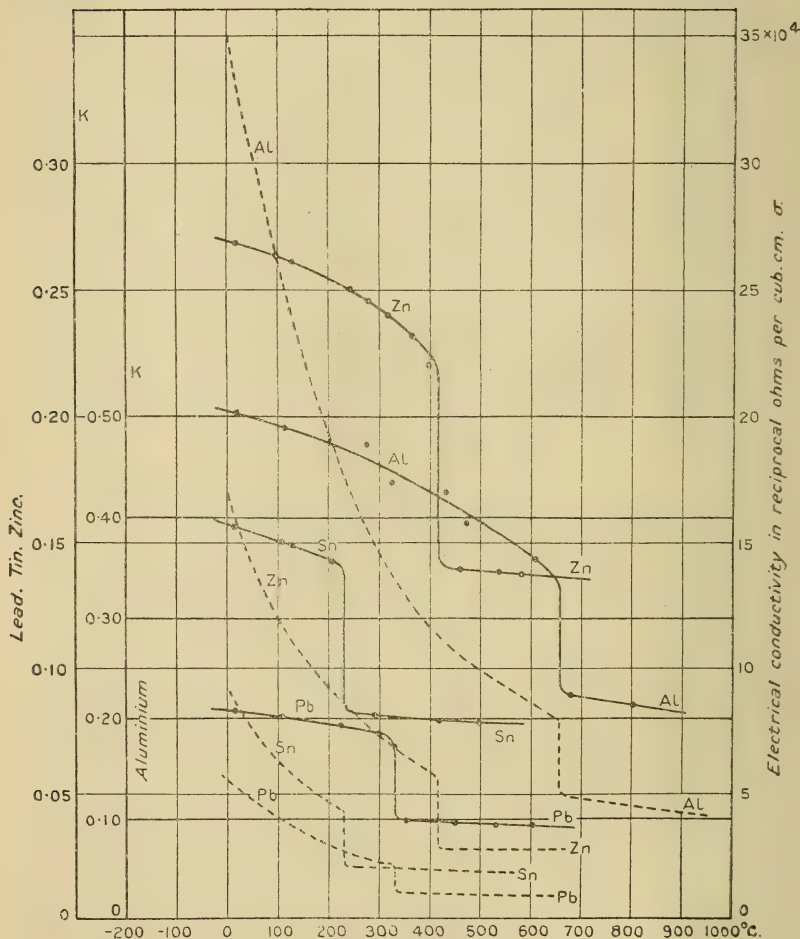
These changes of conductivity are similar to those of the electric conductivity, as observed by Mr. H. Tsutsumi. For the sake of comparison, his results are reproduced in figs. 5 and 6 with dotted curves. In order to see whether

Lorenz's law—that is, that the ratio of the thermal and electric conductivities is proportional to the absolute temperature—is valid, the calculation was made by combining

Fig. 6.
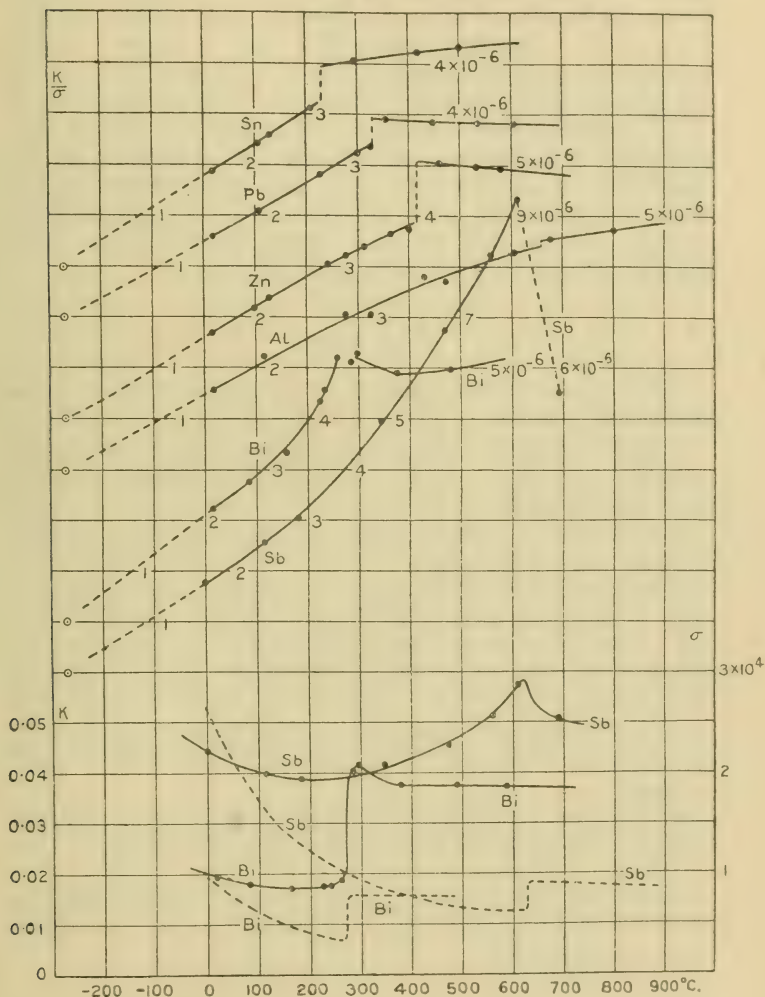
my result with that of Mr. Tsutsumi, and the ratio thus found graphically given in fig. 6. Below the melting-points the law is fairly well satisfied, but in the liquid state of these metals the applicability of the law completely fails.

The electrical conductivity of bismuth and antimony shows an abnormal change during melting—that is, the conductivity increases by melting. It is therefore very interesting to see whether the thermal conductivity of these metals, unlike other metals, increases during melting. From fig. 6 we see that the thermal conductivity of bismuth at first slightly decreases and then increases : during melting the conductivity considerably increases in the same way as the electric conductivity does. The conductivity of liquid bismuth slightly decreases along with the rise of temperature. In the case of antimony the variation of the conductivity is similar to that of the conductivity for bismuth, but there is some difference in the quantitative respect. In the case of these metals Lorenz's law holds good only below 100°, as seen from fig. 6.

Summary.

The results of the present investigation may be summarized as follows :—

1. The thermal conductivity of tin, lead, zinc, and aluminium decreases with the rise of temperature up to their melting-point.

2. The thermal conductivity of these metals decreases abruptly during melting.

3. The thermal conductivity of bismuth and antimony slightly decreases at first, and then increases a little.

4. During melting the conductivity of bismuth considerably increases, and that of antimony seems to increase only slightly.

5. The thermal conductivity of all liquid metals here investigated decreases but slightly with the rise of temperature.

6. The above changes of thermal conductivity are similar to those of electric conductivity for the same metals.

LXVI. *Ionization and Production of Radiation by Electron Impacts in Helium investigated by a New Method. By* K. T. COMPTON, *Ph.D., Professor of Physics in Princeton University* [*].

Introduction.

THE recent studies of the ionization of metallic vapours and the excitation of their spectra by electron impacts[†] have established relations between the absorption spectra of the unexcited vapours and their resonance and ionization potentials which are in accord with a theory of radiation and atomic structure such as that proposed by Bohr. Briefly stated, the results are as follows :—The atoms gain no internal energy as a result of electron impacts unless the kinetic energy of the electrons exceeds the amount $h\nu_r$, where ν_r is the frequency of the first (longest wave-length) member of the absorption series of the vapour. If the energy exceeds $h\nu_r$ the atom may absorb this amount of energy, which it subsequently re-emits as radiant energy of this frequency. If the energy of the impinging electron exceeds $h\nu_i$, where ν_i is the convergence frequency of the absorption series of which ν_r is the frequency of the first line, the atom may be ionized. The potential differences V_r and V_i through which an electron must fall to acquire the energies $h\nu_r$ and $h\nu_i$ respectively, are termed the Resonance and Ionization Potentials, and are given by the quantum relation $eV = h\nu$. There is evidence[‡] that there may be two resonance potentials, corresponding to two different absorption series which have the same convergence frequency, but no one has yet proved the existence of additional resonance potentials corresponding to intermediate members of a given absorption series.

These phenomena, together with phenomena of dispersion of excited and unexcited gases, seem to prove the existence within the atom of series of related states or orbits in which electrons may exist in more or less stable equilibrium. Energy derived from absorbed radiation or from impact by

an electron may displace an electron from a more to a less stable state; whereas, if an electron falls directly from a less to a more stable state, it emits radiation whose frequency equals the difference of energy in the two states divided by h. Bohr's theory of atomic structure is based on these considerations, and, together with its modifications by Debye and Sommerfeldt, has been remarkably successful in accounting quantitatively for the spectra of systems constituted of a single electron and nucleus. The theory has not been developed to account quantitatively for the spectra of more complicated systems, although, if certain assumptions are made, the convergence frequencies may be calculated in some cases. It is obviously of the greatest importance to secure definite information regarding the spectra and energies of formation of those atoms (other than atoms with a single electron) for which the theoretical assumptions may be most easily put into quantitative form. Of these cases, the simplest is the normal helium atom, with its single nucleus and two outer electrons.

In Bohr's model of the normal helium atom the two electrons are symmetrically located in the same orbit, and their combined energy is equal to $e \times 83$ volts/300. If one electron is removed, and the remaining electron takes its most stable position, the energy equals $e \times 54·3$ volts/300. The difference gives 28·7 volts as the ionizing potential; and the corresponding frequency gives 430 Å as the convergence wavelength of the fundamental series. The frequencies of the other lines in the series cannot be calculated without a knowledge of the behaviour of one electron while the other is being displaced from orbit to orbit. Analogy with hydrogen would suggest that 3/4 of 28·7, or 21·5 volts should be the resonance potential of helium. There is no reason, however, for believing that hydrogen and helium should have homologously spaced series. Evidently quite different results from those obtained by Bohr might be obtained by assuming a different configuration of electrons in the normal atom*.

Early experimental determinations of the minimum ionizing potential of helium † indicated a value between 20 and 21 volts. Recent discoveries, stimulated by applications of Bohr's theory, suggest that this is really a resonance potential, the effects previously attributed to ionization being accounted

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* Landé, *Phys. Zeit.* xx. p. 228 (1919).

† Franck and Hertz, *Verh. d. D. Phys. Ges.* xv. p. 34 (1913); Pawlow, Roy. Soc. Proc. A. xc. p. 398 (1914); Bazzoni, Phil. Mag. xxxii. p. 566 (1916).

for by the photoelectric effect on the electrodes produced by the resonance radiation. This has been confirmed independently by Horton and Miss Davies* and by Franck and Knipping†. These investigators used the well-known method of Davies and Goucher ‡ for distinguishing between the effects of ionization and of resonance radiation, while Franck and Knipping also used the total and partial current method of Tate and Foote§. Both sets of investigators found the true ionization potential to be at about 25·5 volts, the actual values published being 25·7 and 25·3 volts respectively. Horton and Miss Davies further concluded that the effect at 20·4 volts is one of *pure* radiation—*i. e.*, there is no accompanying ionization.

On the other hand, Franck and Hertz‖ have pointed out that the successive maxima and minima observed by them at multiples of 20·4 volts cannot be adequately explained by a photoelectric effect of the radiation on the electrodes, but prove an actual production of ions in the gas in the region where the collisions become inelastic. Furthermore, Rentschler¶ has obtained results which cannot reasonably be accounted for by a photoelectric effect setting in when the accelerating potential exceeds 20·4 volts, but indicate an actual ionization at this voltage. Rentschler attributed this ionization to ionization from the surface of his gauze electrode, rather than to a true ionization of the gas, and concluded that helium exhibits no resonance at 20 volts, but only ionization at 25·5 volts. Finally, the experiments made by Benade and Compton **, and especially by Bazzoni††, in which the electron current between two electrodes was found to increase abruptly as the accelerating potential reached multiples of 20 volts, can only be accounted for on the assumption of actual ionization of the gas at 20 volts, since the effects observed were entirely too large to be accounted for as a photoelectric effect by that portion of the resonance radiation which could have fallen on the emitting cathode.

The present research was undertaken to investigate the resonance and ionization potentials of helium by a method

* Roy. Soc. Proc. A. xcv. p. 408 (1919).
† *Phys. Zeit.* xx. p. 481 (1919).
‡ *Loc. cit.*
§ Phys. Rev. vii. p. 696 (1916) ; x. p. 77 (1917).
‖ *Phys. Zeit.* xxx. p. 132 (1919).
¶ Phys. Rev. xiv. p. 504 (1919).
** Phys. Rev. xi. p. 184 (1918).
†† *Loc. cit.*

different from any hitherto proposed, and was in progress when the papers of Horton and Miss Davies and of Franck and Knipping were published. The results corroborate the work of these investigators, and, in addition, explain the apparent discrepancies in conclusions which have been drawn from the various experiments on the effect at 20 volts. It appears that an atom may be ionized by first absorbing a quantum of energy of the resonance radiation from neighbouring atoms, and then being struck by an electron whose kinetic energy might be insufficient to ionize an atom in the normal state. In other words, the energy of ionization is supplied partly as radiant energy and partly as energy of impact. Ionization at 20 volts is therefore a secondary effect, which may or may not be important, depending on conditions.

The possibility of ionization by this process is obviously suggested by Bohr's theory. It appears to have been first pointed out by Richardson and Bazzoni[*]. The proof of its existence in the present experiments is due to the use of an apparatus which permits not only the differentiation of effects due to ionization and to radiation, but also the estimation of the proportion of the effect due to either when both are present.

Apparatus and Method.

The ionization chamber (fig. 1) is similar in principle to that used by Franck and Hertz. A tungsten filament F of 0·8 cm. length and 0·08 mm. diameter serves as a source of electrons. These are drawn toward the platinum gauze G by an accelerating difference of potential V_a. Those which pass through the openings in the gauze encounter a retarding difference of potential V_r, which is enough larger than V_a to prevent any of the electrons from reaching the electrode E. This electrode is connected with a quadrant electrometer, and it may gain a positive charge either from positive ions produced by ionization of the gas or as a result of electrons emitted photoelectrically from E by ultra-violet radiation set up by impacts of the electrons. The distance between F and G is 3·5 mm., and that between G and E is 7 mm.

In order to distinguish between these two causes of electrometer deflexions, the electrode E is constructed so that the area presented to the radiation may be varied without altering the geometrical relations " over all." This is done by closing

one end of a hollow copper cylinder, shaped like a napkin-ring, with platinum foil f and covering the other end with platinum gauze g. The cylinder is suspended by a platinum wire ending in a swivel, so that it can be rotated about its

Fig. 1.
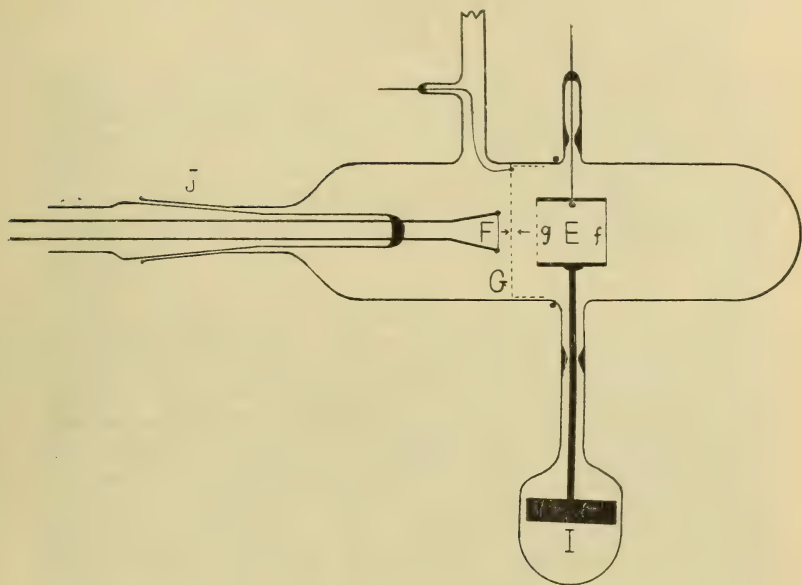
vertical axis by the aid of a horseshoe magnet acting on a soft-iron block I, which is rigidly attached to the cylinder by a light brass rod. Evidently it is a matter of indifference, as regards the receiving of positive ions, whether the foil end f or the gauze end g of the electrode E is turned to face the filament. But the two ends are differently affected by ultra-violet radiation; for, when the gauze side is exposed, a large part of the radiation passes through into the cylinder, and does not result in the loss of electrons from the cylinder. Thus the ratio $R = E_f/E_g$ of the electrometer deflexion with the foil end exposed, and the deflexion with the gauze end exposed, determines the proportion of the total observed effect which is due to true ionization or to ultra-violet radiation.

The calculation of this proportion is made very easily as follows:—Let i and r be the rates at which the electrode E gains a charge due to ionization and to photoelectric effect

respectively, and let c be the ratio of closed area to total area of the gauze end.

Then

$$R = \frac{E_f}{E_g} = \frac{i+r}{i+cr},$$

whence

$$\frac{i}{r} = \frac{1-cr}{R-1}.$$

The ratio c is a constant of the apparatus, and the ratio R is found by comparing the electrometer deflexions obtained with the foil and gauze ends respectively of the cylinder turned to face the filament. For pure radiation R should equal $1/c$, while for pure ionization R should equal unity. Any change in the type of the effect due to the electron impacts should be indicated by a change in the value of R.

The value of the ratio c was found to be 0·495 when calculated from geometrical considerations. This value is subject to small corrections because some electrons, photoelectrically excited on the inside of the cylinder, may escape through the gauze; because also the platinum surfaces of the foil and gauze may be intrinsically different in photoelectric sensitivity owing to different modes of manufacture; and because the surface in one case is curved and in the other case flat. Therefore, an independent experimental determination of c was made as follows :—The ground-glass cone J which supported the filament was removed and a quartz window sealed over the end. After thorough evacuation of the apparatus, a quartz-mercury arc was placed before the window and the photoelectric currents from E were measured with a field between E and G of the same general magnitude as in the ionization experiments. The ratio of these currents for the two positions of E gave $R = 1/c = 1·82$, whence $c = 0·55$. This value agrees as well as could be expected with the calculated value.

The remaining features of the apparatus require little explanation. A large tube of coconut charcoal is attached directly to the ionization tube. The helium is stored in a reservoir, from which it can be pumped into or out of the ionization tube through two U-tubes. The U-tube nearest the ionization chamber contains coconut charcoal, while the other serves as a mercury trap, into which the mercury vapour can be condensed by applying liquid air before the liquid air

is applied to the charcoal tubes. The pump and the copper-oxide spiral for removing traces of hydrogen have been previously described[*]. The spectrum, when excited by a discharge between incandescent tungsten electrodes, showed no impurities in the helium except a trace of neon, whose strong lines appeared faintly when an intense arc was set up between the electrodes. These neon lines, three in number, were of about the same intensity as the individual lines into which the band-spectrum of the helium could be resolved, and were therefore extremely faint. This, in connexion with the well-known effect of helium in accentuating the spectra of any impurities which may be mixed with it, shows that the helium was very pure. Its spectrum excited by a Geissler-tube discharge in a baked-out tube showed no lines except those of helium. A two-stage diffusion pump, with an oil-pump backer, is used for the initial exhaustion of the apparatus.

The electrometer arrangement is so satisfactory as to warrant particular mention. The electrometer sensitiveness may be varied quickly from zero to 10,000 mm. per volt by varying the potential of the needle. The electrometer key is designed either to insulate the quadrants and electrode E, to earth them directly, or to earth them through india-ink resistances of $3 \cdot 15 \, (10^8)$ ohms, $3 \cdot 75 \, (10^9)$ ohms, or $2 \cdot 37 \, (10)^{10}$ ohms as desired. It is therefore possible to pass instantly from one sensitivity to another, and to measure all currents by the steady deflexion method. The india-ink resistances are found to be constant and to show no polarization. A galvanometer is introduced in the connexion to the gauze G in order to measure the total electronic current I.

In preliminary experiments large ionization currents setting in at about 11 volts, and more strongly at about 15 volts, masked the effects due to helium. These were caused by water-vapour, which was slowly given off by the glass. This disturbing effect was eliminated by surrounding the ionization tube and the two charcoal tubes in electric heaters and maintaining them at 300° to 350° C. for about a week with the vacuum-pump in operation. The ground joint J was sealed with Khotinsky cement and was water-cooled during the "baking-out" treatment. During the later stages of heating, the filament was kept at a white heat to drive off occluded gases. Liquid air was placed around the mercury trap before these heaters were removed, and was kept there continuously throughout the course of the experiments.

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[*] Benade and Compton, *loc. cit.*

Experimental Results.

Figs. 2–5 show the results of several typical series of measurements of the rate of charging of the electrode E as a function of the accelerating difference of potential V_a at various pressures p and for various thermionic currents I.

Fig. 2. $p = 0.0005$ mm.; $I_{20} = 1.75 (10)^{-6}$ amp.
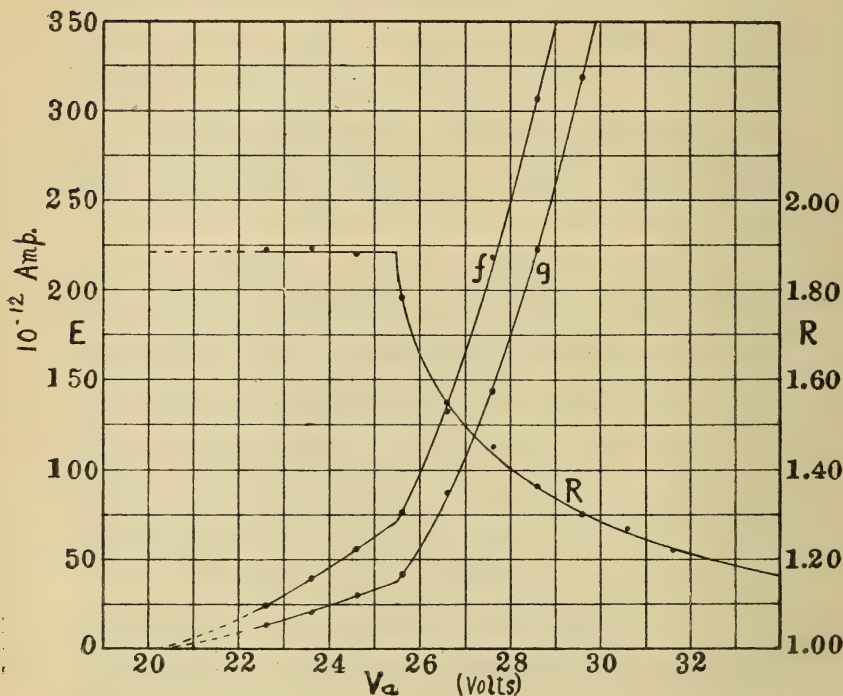
These thermionic currents I were determined by the filament temperature, and are specified by I_{20}, the total current to the gauze G with an accelerating field of 20 volts. To the applied value of V_a there is to be added a small correction due to initial velocity of emission, to contact difference of potential between electrodes, and to the aggregate loss of energy of the electrons due to the translatory motion imparted to the helium atoms at the many elastic collisions*. The correction due to the first two causes was not more than a fraction of a volt, except when the tungsten was heated near

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* Benade and Compton, *loc. cit.*

its melting-point, while that due to the third cause was not important except at the two higher pressures. Although the corrections were actually measured in some cases, it was found much easier and just as satisfactory to simply assume that the correct value of V_a for the first break is 20·2 volts [*], and to adjust every curve to this point.

Fig. 3. $p = 0.05$ mm.; $I_{20} = 1.5 (10)^{-6}$ amp.
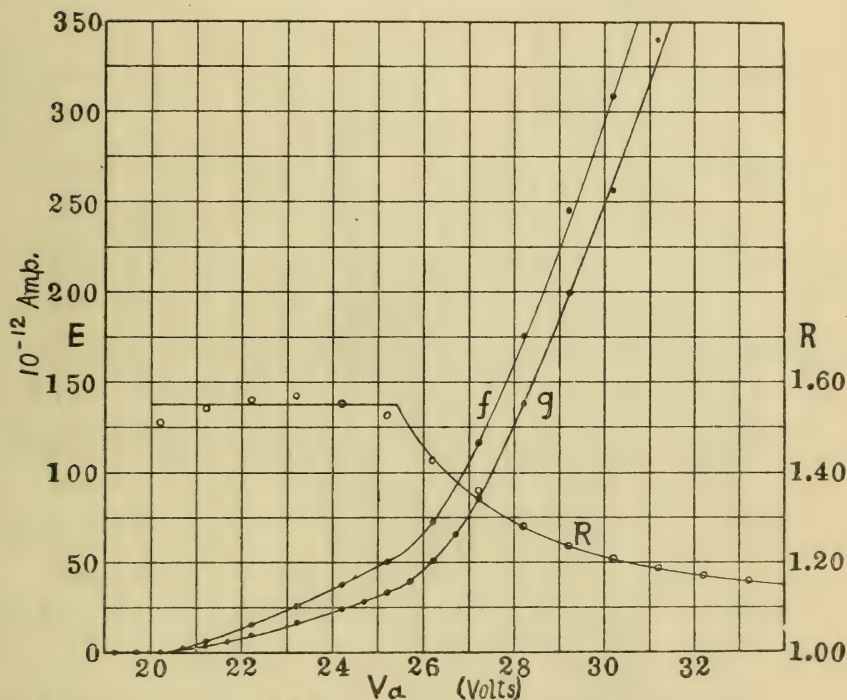
Figs. 2, 3. and 4 show that there are two "break" points in the $E-V_a$ curves, indicating two critical potentials or energies. The values of these critical potentials are 20·2 volts and 25·5 volts respectively. The $R-V_a$ curves show that between 20·2 volts and 25·5 volts the effect is due largely to radiation, whereas the effect at 25·5 volts marks the setting in of intense ionization. These results are, therefore, in entire

[*] This value is chosen as a mean between the values given by successive "breaks" in two electrode tubes, and by the corrected first "break" in tubes with three or more electrodes.

confirmation of the recent work of Horton and Miss Davies and of Franck and Knipping.

Even with intense ionization, there still remains an appreciable photoelectric effect on the electrode, evidenced by the fact that the ratio $R = E_f/E_g$ approaches a value not far from 1·06 instead of unity as V_a is indefinitely increased. This is exactly, as would be expected, due to the continued presence of 20-volt radiation and other radiation which may accompany recombination.

Fig. 4. $p = 0.17$ mm.; $I_{20} = 0.6 (10)^{-6}$ amp.
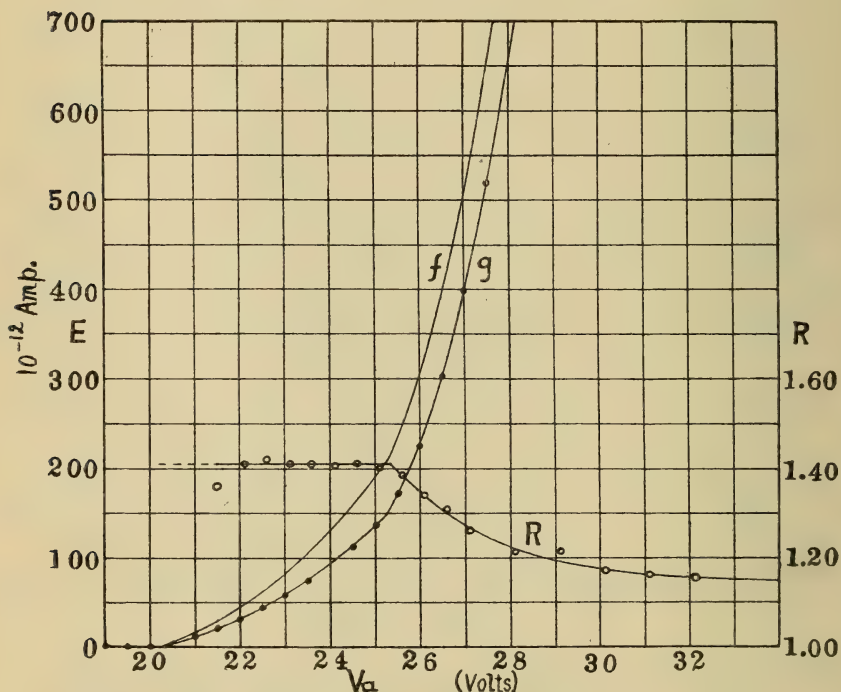
Between 20·2 and 25·5 volts it is seen that the ratio R decreases from 1·9 to about 1·08 as the gas-pressure is decreased from 0·0005 to 8 mm. This means that, as the pressure increases, the proportion of ionization increases, as shown by Table I. Here i/r is the ratio of the effect due to ionization to that due to radiation. The exact values of i/r are of no particular significance, since they will vary according to the construction of the apparatus, but the variation of i/r with p is important.

Fig. 5. $p = 8 \cdot 0$ mm.; $I_{20} = 0 \cdot 85 \,(10)^{-6}$ amp.
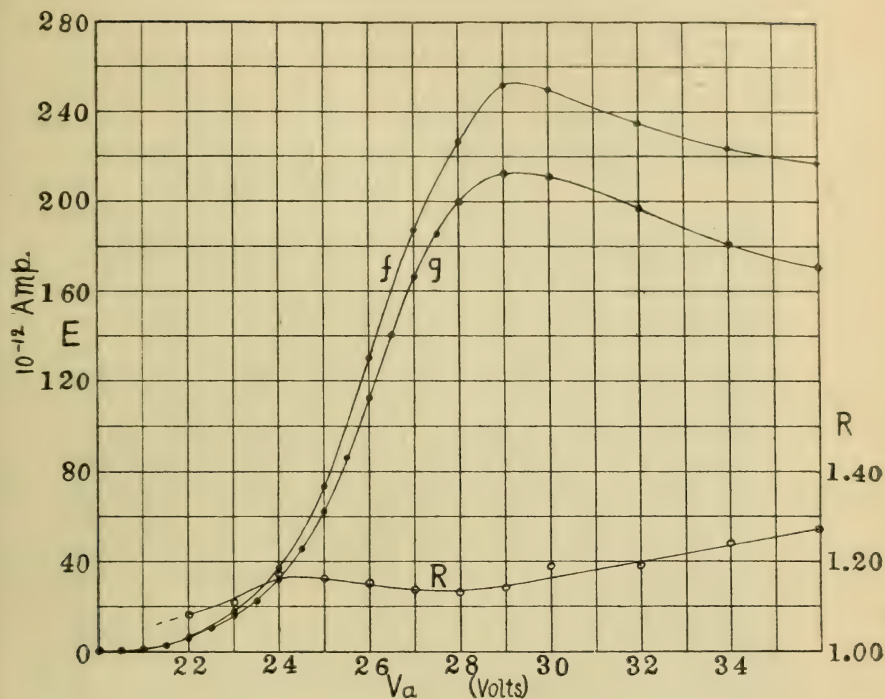
Table I.

$c = 0 \cdot 50.$

p (mm.).	R.	i/r.
0·0005	1·90	0·055
0·001	1·81	0·116
0·003	1·74	0·176
0·012	1·60	0·333
0·015	1·57	0·378
0·044	1·55	0·410
0·17	1·40	0·75
1·00	1·19	2·22
8·00	1·07	6·3
25·00	1·04	11·4

The effect between 20·2 and 25·5 volts apparently approaches one of pure radiation as the pressure is reduced. It seems obvious, therefore, that this effect must be one of pure radiation at any pressure. For in an atomic catastrophe so intimately related to the inner structure of the atom it is

inconceivable that other atoms at the large relative distances involved in these pressures could change the entire nature of the effect of an electron impact. The observed ionization must therefore be a secondary effect due, at least in part, to the radiation, or it must be due to electron impacts against atoms in such rapid succession that the energies of the impacts are additive in their effect. The latter possibility may be discarded, owing to the extremely long time during which an atom would have to retain energy from an impact in order to account for the observed results at these low pressures and current densities*. No secondary effect of the radiation which has been suggested, such as ionization by electrons photoelectrically emitted from the filament or the electrode E, seems at all adequate to account for the ionization and the variation of the proportion of ionization and radiation with pressure, except that which ascribes the ionization to electron impacts against atoms which, at the instant, are in a relatively unstable condition because they have absorbed radiant energy coming from neighbouring atoms which have been previously struck. In fact, some such phenomenon must occur, since the energy radiated is strongly absorbed and re-emitted as resonance radiation, and is thus passed on from atom to atom.

At the higher pressure it is obvious that no appreciable ionization *can* occur as a result of single impacts, since the electrons, however and wherever emitted, would collide so frequently while gaining the energy between 20·2 and 25·5 volts that they would certainly collide inelastically and produce 20·2-volt radiation before acquiring the 25·5-volt energy necessary for ionization. Thus practically all ionization observed at higher pressures, whatever be the applied voltage (unless this is so large as to give a potential drop of the order of magnitude of a volt in a mean free path), must be due to a secondary effect involving combined action of radiant energy and direct impact.

This point is well illustrated by fig. 5, for which the pressure was 8 mm. Here neither curve shows any indication of a break at 25·5 volts, while the $R-V_a$ curve shows that the effect from 20·2 volts up is very largely due to ionization. Thus this entire curve, in which the actual ionization currents were very large indeed, seems due to 20·2 volt impacts. The shapes of these curves differ from those for lower pressures. The maximum and succeeding decrease in the $E-V_a$ curve is due to the fact that, as V_a increases, more and more of the ionization occurs on the

* K. T. Compton, Phys. Rev. (in print).

filament side of the gauze, and the ions do not reach the electrode E. The rise in the $R-V_a$ curve as V_a increases is due to the fact that, whereas fewer and fewer ions reach the electrode E, the radiation from impacts and recombination still strikes it. This rise in R is therefore due to a peculiarity of the apparatus, and does not indicate a real increase in the actual proportion of radiation. If the curves were extended to higher values of V_a, the successive maxima at 20-volt intervals would be shown.

The question of the effect of radiation or ionization produced by impacts against the gauze has frequently been raised. Horton and Miss Davies[*] concluded that the platinum gauze emits positive ions, this emission beginning at about 13 volts and increasing as V_a is increased. This point was tested by thoroughly baking out and evacuating the apparatus, and making tests similar to those made in the presence of helium. Since the effects were exceedingly small, the thermionic current was increased to the limit of safety for the filament. The results, after correcting V_a for emission velocities, are shown in fig. 6. There is a very

Fig. 6. $p = 0.0$ mm.; $I_{20} = 205 (10)^{-6}$ amp.
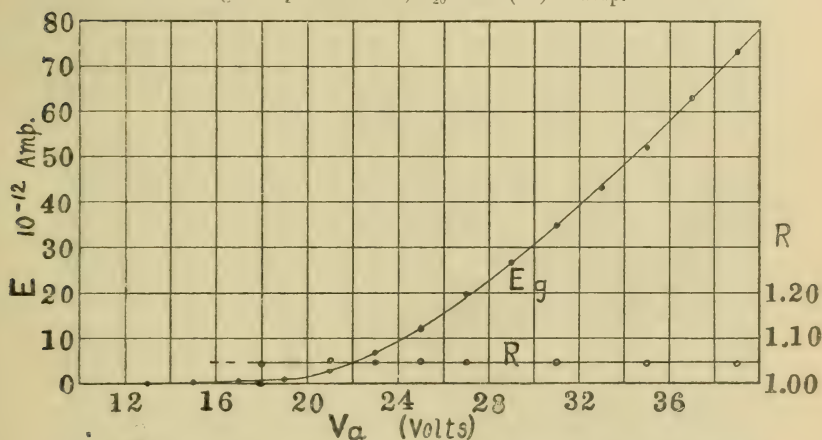
small effect beginning at about 15 volts and increasing considerably beyond 20 volts. The effect is seen to be almost entirely one of ionization. These ionization currents are so small in comparison with those observed with helium in the apparatus that they are entirely negligible except in the work at 0·0005 mm. and 0·001 mm. pressure. In these cases corrections to the observed values of E were made by

* Roy. Soc. Proc. A. xcvii. p. 23 (1920).

subtracting the corresponding values of E for zero pressure, allowance being made for the difference in total currents I in the respective cases.

If ionization between 20·2 and 25·5 volts is to be ascribed to the combined effect of radiant energy and energy of impacts, it is to be expected that, as the thermionic current I is increased, the amount of ionization should increase relatively more rapidly than the amount of radiation. That this is true is shown by fig. 7. The rate of variation of R with I, however, is not as great as might be expected.

Fig. 7. $p = 0.15$ mm.; Curve 1, $I_{20} = 0.15 (10)^{-6}$ amp.; Curve 2, $I_{20} = 1.5 (10)^{-6}$ amp.
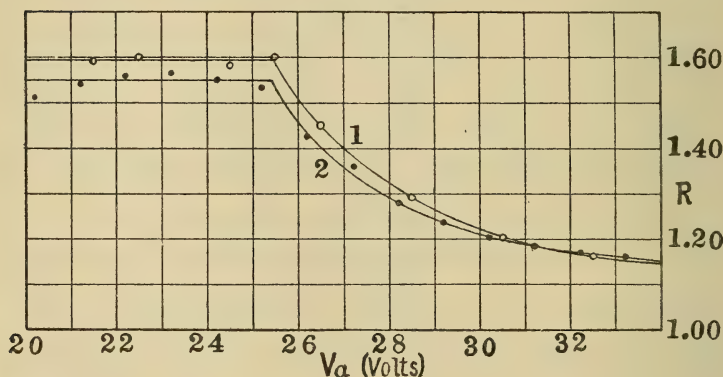
The curves of figs. 2, 3, 4, and 7 show a fairly constant value of R between 20·2 and 25·5 volts. This is not generally the case, however. Owing to the increasing values of I as V_a is increased, the value of R tends to diminish. On the other hand, owing to the increased proportion of the effective collisions which occur on the filament side of the gauze G as V_a is increased, the proportion of ionization (as measured by E) tends to decrease, and consequently the value of R to increase. Neither of these variations is very large, and it was always possible to find a value of I at which they practically neutralized each other. Table I. is based on values of R taken from such cases where R remained practically uniform within the specified range.

An attempt was made to express analytically the proportion i/r to be expected on the theoretical grounds outlined above, but there are too many uncertain factors to make a satisfactory analysis possible. There are involved the coefficient of absorption of the resonance radiation in the gas, the time during which radiant energy of impact is retained by an atom, the probability of ionization or inelastic impact at

collisions of various speeds, etc. It is probable that the low-voltage arc in helium, which is now being studied, offers a better opportunity to put the theory in suitable form for tests of a more quantitative nature than can be applied to the experiments of the present paper.

Can the Observed Ionization between 20·2 *and* 25·5 *volts be due to Impurities in the Helium?*

Franck and Hertz have accounted for ionization between the resonance and ionization potentials by a photoelectric effect of the 20-volt radiation on gaseous impurities. The only impurity detected in these experiments was a slight trace of neon, except for the possible presence of minute quantities of water-vapour, which were shown to be too small to affect the results. Neon is the only substance which could complicate the results without its effect being easily separable from that due to helium, since its ionization potential, 19·5 volts, is so near the resonance potential of helium that the two effects may merge into one another. Unfortunately, neon is that impurity most difficult to remove from helium. The helium used in this experiment was originally supposed to be very pure. It was subsequently, in the course of this and other researches, purified by several hundred fractionations from coconut charcoal in liquid air. No neon lines could be observed in its spectrum except with a very intense arc maintained by a thermionic current from a tungsten electrode.

There are three considerations which seem to disprove the appreciable influence of neon in the above experiments :—
(1) There is no evidence of radiation or of inelastic impacts due to collisions with neon atoms at velocities below 20 volts. If neon were present in sufficient quantity to account for the observed ionization, we should expect to detect its presence by the effect of inelastic collisions at its resonance potential below 20 volts, especially at higher gas-pressures where the chances of collisions with neon atoms are greatly enhanced by the enormously increased paths of the electrons resulting from the elastic impact with helium. (2) Since the ionizing potential of neon is a little less than the resonance potential of helium, we should expect the first effects detected as V_a is increased to be due entirely to ionization of neon, and therefore to find the value of R near to unity for the first measurable currents, increasing when V_a passes the resonance potential of helium. Such a variation of R has not been observed. (3) No variation in the gas-pressure should alter the proportion of the effect due to ionization of neon in comparison with that due to radiation from helium so long

as the electronic mean free path is greater than the distance between electrodes, or even if it is considerably smaller. It is only when an electron is likely to collide while its velocity increases by an amount equivalent to the difference between 19·5 and 20·2 volts that the influence of the neon should increase in proportion to that of the helium as the pressure increases. In the actual case, however, the ratio i/r changed more than tenfold with pressure—at pressures where the difference in probability of collision at 19·5 volts and at 20·2 volts is absolutely negligible. Furthermore, Richardson and Bazzoni have shown that the amount of ionization at multiples of 20 volts is about what would be expected if every electron, colliding against a helium atom with energy greater than 20 volts, should directly or indirectly liberate an additional electron. This amount of ionization could not, therefore, be attributed to collisions with atoms of an impurity present in small quantity. The first two objections above apply equally well to disprove a direct photoelectric action of the helium-resonance radiation on neon atoms in sufficient amount to explain the results. Richardson's and Bazzoni's work, together with the observed passage of resonance radiation through the gas to produce a photographic effect on the electrodes, also proves the inadequacy of an explanation based on a photoelectric emission from neon.

Note added to proof.—More recent experiments have been made in helium so pure as to show no trace of impurities under any conditions of exciting the spectrum. These experiments differ in no way from those described above.

Summary.

1. An experimental method is described for distinguishing between ionization and radiation and of estimating the proportion of either when both are present.

2. Resonance radiation sets in at 20·2 volts and ionization at 25·5 volts.

3. Ionization is observed between 20·2 and 25·5 volts, in proportions increasing with tne gas-pressure and with the bombarding current density. Evidence is presented to show that this ionization is a secondary effect, due to impacts against electrons which contain absorbed radiant energy of the resonance radiation from neighbouring atoms. This method of ionization appears to be very important at high gas-pressures.

Princeton, N. J., U.S.A.
    April 1, 1920.

LXVII. *The Rate of Chemical Action in the Crystalline State.*
By C. N. HINSHELWOOD *and* E. J. BOWEN, *Balliol College,*
Oxford*.

WITH regard to the study of reactions in the solid state,
a number of interesting observations on chemical
changes produced by the action of light have been recorded,
e.g., Lobry de Bruyn, *Rec. Trav.* xxii. 298, and Padoa, *Atti*
R. Accad. Lincei, 1919 (v.) ii. 372, but these do not lend
themselves to exact measurement, and, moreover, the intensity
of the active light falls off rapidly in the interior of the
crystal. Apart from these investigations little is known
as to the mechanism of chemical reactions in the solid
state.

Some previous experiments (Trans. Chem. Soc. 1920,
cxvii. 156) on the rate of decomposition of malonic acid in
the solid and supercooled liquid state, showed that the
decomposition was much more rapid in the supercooled liquid
than in the solid at the same temperature, and that it was
found difficult to obtain a definite value for the rate of
reaction in the solid state, large divergences being found
among specimens of apparently equal purity. As these
discrepancies might have been connected with the presence
of small quantities of liquid, the subject has been investigated
further by studying the decomposition of various crystalline
substances which do not melt, or at temperatures far below
their melting points. Irreversible reactions were naturally
chosen.

The method of measurement used consisted in the determi-
nation of either the volume or the pressure of the gaseous
products. The substances were enclosed in bulbs connected
with gas-measuring apparatus and heated at constant tem-
perature in vapour baths.

1. *Evolution of Oxygen from Potassium Permanganate.*

The curves given in figures 1 and 3 show that the initial
rate of reaction is determined by the state of subdivision of
the potassium permanganate, being greater the finer the state
of subdivision. In the case of the large crystals the curve
shows a marked acceleration owing to the disintegration of

* Communicated by the Authors.

the crystal and consequent increase of surface as the reaction proceeds. Clearly, then, the reaction is a heterogenous one and takes place only in a zone near the surface. The final retardation is of the nature of a discontinuity due to the exhaustion of the reserve of material ; but is rounded off owing to the earlier extinction of the smaller particles. Experiments VIII. and IX. show that manganese dioxide exerts no catalytic action to account for the acceleration, which must be due entirely to the physical cause.

Fig. 1.
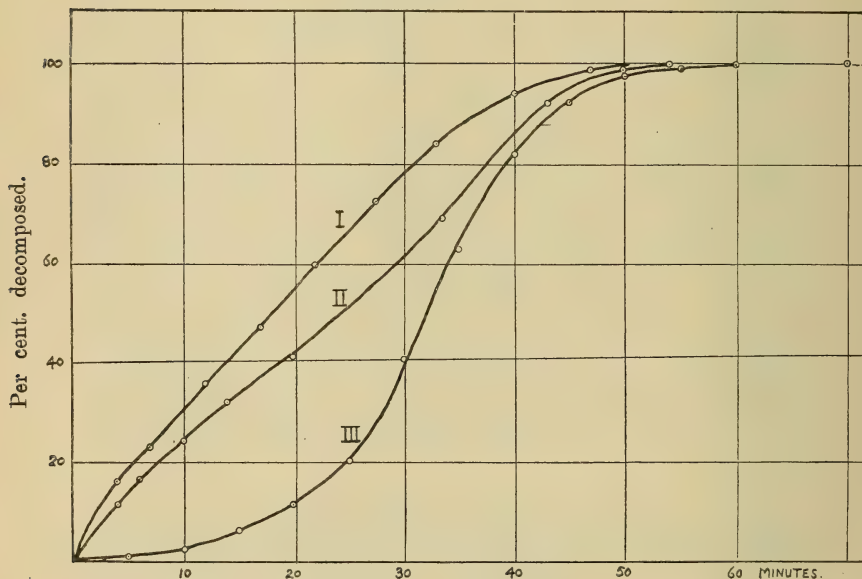
I. Finely ground $KMnO_4$ (agate mortar) at 240° C.
II. Finely ground $KMnO_4$ (porcelain mortar) at 240° C.
III. Large crystals $KMnO_4$ at 240° C.

2. *Evolution of Oxygen from Solid Solutions of Potassium Permanganate in Potassium Perchlorate.*

When potassium permanganate is dissolved in solid potassium perchlorate the rate of reaction is lowered. Figure 2 shows the results obtained with mixed crystals containing 82 per cent. and 26·8 per cent. of potassium

permanganate respectively. Crystals containing only 6·7 per cent. of potassium permanganate gave no measurable evolution of oxygen under the same conditions. The solid solution crystals were in each case fine and of uniform grain.

Fig. 2.
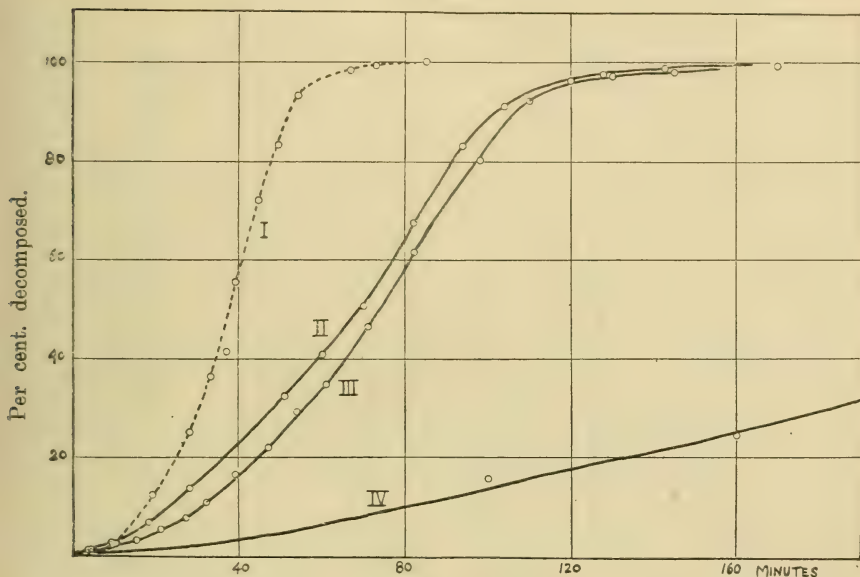
    I. Large crystals KMnO$_4$ at 239° C.
    II. { Solid solution of KMnO$_4$ and KClO$_4$
  III. {   (82% KMnO$_4$). Small crystals at 239° C.
   IV. Solid solution of KMnO$_4$ and KClO$_4$
       (26·8% KMnO$_4$). Small crystals at 239° C.

3. *Decomposition of Ammonium Bichromate.*

Figure 4 shows the type of curve obtained with finely ground ammonium bichromate at 219° C. In connexion with ammonium bichromate a further point of interest was noticed. When a large crystal was heated at 212° C. it did not disintegrate, but the chromium oxide formed remained as a coherent film, and when the whole surface was covered the reaction ceased or became very slow indeed. The interior of the crystal was unchanged. (*Cf.* an observation of Ball, Trans. Chem. Soc. 1909, xcv. 87.)

Fig. 3.
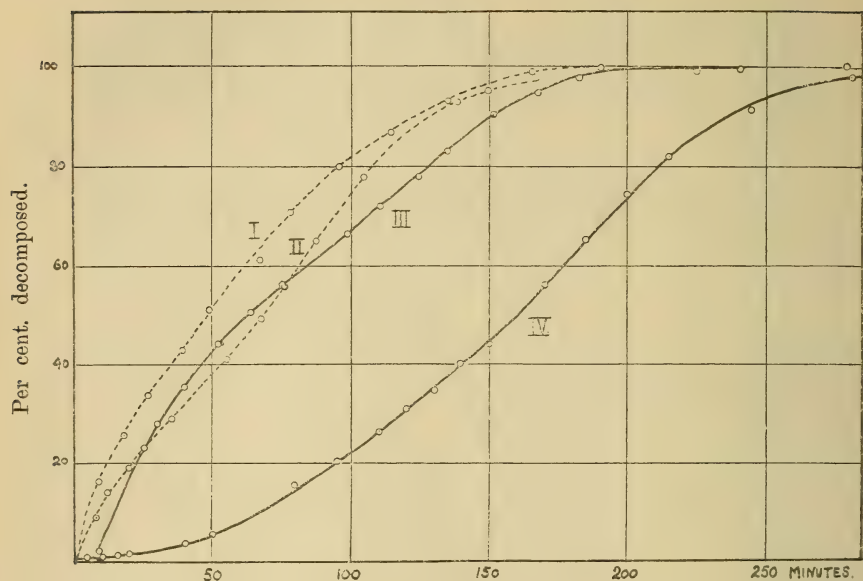
I. |
II. | Finely ground $KMnO_4$ + MnO_2 at 220° C.
III.   Finely ground $KMnO_4$ at 220°·5 C.
IV.   Large crystals $KMnO_4$ at 217° C.

Fig. 4.
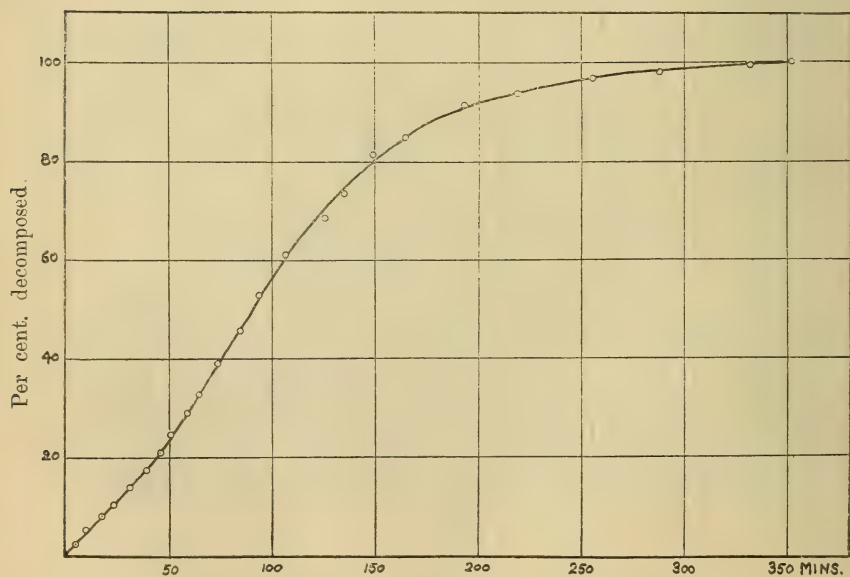
Ammonium Bichromate at 219° C.

4. *Decomposition of Tetranitroaniline.*

The similarity of the curves in figure 5 to those previously given is apparent. Experiment XIV. (Curve II.), the most fortunate of several trials, was sufficiently precise to allow not only a t, x, curve to be drawn, but also an accurate

Fig. 5.
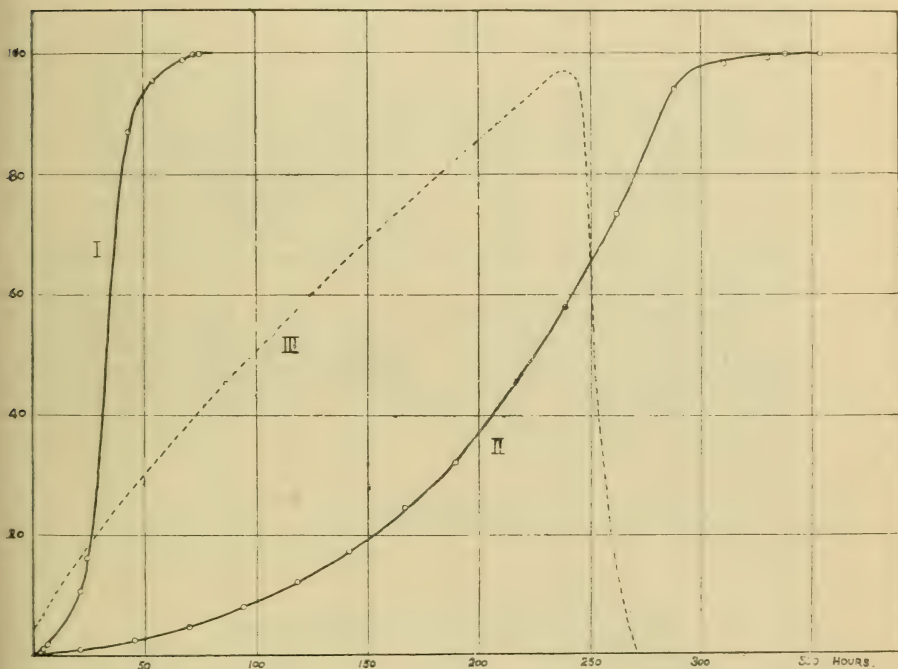
I. Tetranitroaniline at 140° C.   } Small crystals.
II. Tetranitroaniline at 120°·0 C. {

III. Derived curve from II.   Ordinates $\frac{dx}{dt}$
(different scale).

Abscissæ x.

derived velocity curve, since the lower temperature, 120°·0 C., was more easily controlled, and in this particular experiment did not vary by more than $\frac{1}{10}$° C. In the figure the derived curve $\left(\frac{dx}{dt}, x\right)$ is plotted on a different scale from the other two curves. It will be observed that the velocity increases steadily almost throughout, falling away sharply near the end

of the reaction.   This illustrates the point mentioned above that the final retardation is virtually the result of a discontinuity due to the exhaustion of the material.

The Form of the Curves.

The equation of the change may be expressed thus :

$$\frac{dx}{dt} = k \; \{a + f(x)\}.$$

$a + f(x)$ represents the magnitude of the zone in the crystal where decomposition takes place.   It will depend presumably on such factors as the nature of the space lattice and the closeness of packing. k is a factor representing the probability of a molecule in that zone acquiring sufficient energy to break up.   The expression differs from the usual type in containing no term $(c - x)$ to represent the decrease in active mass with time.

The actual form of the function $f(x)$ cannot be arrived at theoretically.   Nevertheless by putting $f(x) = bx^n$, we may determine how n varies with x and thus form an idea of the law of acceleration.   Empirically it is found that n is frequently almost constant.

If

$$\frac{dx}{dt} = A + Bx^n$$

then

$$\log \left\{ \frac{dx}{dt} - \left(\frac{dx}{dt}\right)_0 \right\} = n \log x + \log B.$$

Plotting the values of $\log x$ and $\log \left\{ \frac{dx}{dt} - \left(\frac{dx}{dt}\right)_0 \right\}$, from the derived curve for tetranitroaniline a straight line was obtained, the slope of which gave $n = 0.85$, so that $\frac{dx}{dt} = A + Bx^{0.85}$.

A few other cases were tested.   The derived curve was not actually drawn, but an empirical equation was fitted to the accelerating parts of the t, x, curves, the tangents at various points were calculated and then the same procedure

followed as above. From experiments V. and VI. the values of n for the 82 per cent. solid solution were 0·62 and 0·64. The large crystals of potassium permanganate give values of n which vary considerably with x, n being greater than unity for small values of x and diminishing as x increases.

Influence of Temperature.

The influence of temperature is complex since both k and $a + f'(x)$ vary. The variation of k is the true temperature coefficient in the ordinary sense of the term. If for the same substance in the same state of subdivision $a + f(x)$ could be assumed not to vary with temperature, k could be directly determined. In this case the curves for two temperatures should be similar. But the figures given below show that this is not so.

<table>
<tr><td colspan="4">Potassium Permanganate.</td><td colspan="4">Tetranitroaniline.</td></tr>
<tr><td>x.</td><td>t_{240}.</td><td>t_{217}.</td><td>Ratio $\dfrac{t_{217}}{t_{240}}$.</td><td>x.</td><td>t_{140}.</td><td>t_{120}.</td><td>Ratio $\dfrac{t_{120}}{t_{140}}$.</td></tr>
<tr><td>5·45</td><td>14</td><td>50</td><td>3·6</td><td>7·9</td><td>19·1</td><td>94</td><td>4·9</td></tr>
<tr><td>15·4</td><td>20·3</td><td>79</td><td>3·9</td><td>12·1</td><td>22·2</td><td>118</td><td>5·3</td></tr>
<tr><td>26·2</td><td>26·7</td><td>110</td><td>4·1</td><td>24·4</td><td>27</td><td>167</td><td>6·2</td></tr>
<tr><td>40·0</td><td>30</td><td>140</td><td>4·9</td><td>43·5</td><td>32</td><td>214</td><td>6·7</td></tr>
<tr><td>56·0</td><td>33·5</td><td>170</td><td>5·1</td><td>57·8</td><td>35·5</td><td>239</td><td>6·7</td></tr>
<tr><td>65·0</td><td>35·5</td><td>185</td><td>5·2</td><td>73·3</td><td>39·5</td><td>262</td><td>6·6</td></tr>
<tr><td>85·0</td><td>41·2</td><td>230</td><td>5·6</td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="4">Extrapolated to $x=0$ 3·4</td><td colspan="4">Extrapolated to $x=0$ 4·4</td></tr>
</table>

If we could assume that a were constant, then the above ratios extrapolated to $x=0$ would serve to measure the true temperature effect.

Conclusion and Summary.

When reactions take place in the crystalline state the change appears to be confined to those molecules in the neighbourhood of the surface. Where a progressive disintegration of the crystal structure takes place the change is strongly accelerated. Solution in another solid causes a reduction in the rate of reaction.

It is clear that the molecules in the interior are under some kind of restraint. This may be connected with the fact that in the interior the molecules are bound by valency forces on all sides, or it may be referred to the internal pressure. The two points of view are probably equivalent.

We have pleasure in thanking Brig.-Gen. H. Hartley for the interest he has taken in these experiments.

A. *Potassium Permanganate at* 240°.

I. Very finely ground in agate mortar. Temperature 240°.		II. Ground. Temperature 240°.		III. Large crystals. 240°.	
Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.
4	16·1	4	11·5	5	1·0
7	23·0	6	16·6	10	2·4
12	35·6	10	24·4	15	6·3
17	47·2	14	32·0	20	11·6
22	59·8	20	41·5	25	20·2
27·5	72·5	27	54·2	30	40·9
33·0	83·9	33·5	69·2	35	63·0
40	94·1	43	92·0	40	81·8
47	98·9	50	99·0	45	92·4
				50	98
				55	99
See Fig. 1, Curve I.		Fig. 1, Curve II.		Fig. 1, Curve III.	

B. *Solid Solutions of Potassium Permanganate in Potassium Perchlorate at* 239°.

IV. Large crystals of $KMnO_4$ (for comparison).		V. Solid solution with 82% $KMnO_4$.	
Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.
10·5	5·0	9	2·6
19	12·2	18	6·8
28	25·0	28	13·5
33	36·4	51	32·8
37	49·6	60	40·9
39	55·2	70	52·2
44·5	71·8	82	68·9
49·5	83·0	94	83·0
54	93·0	104	91·0
60	96·8	128	97·7
73	99·3	160	99·5
Fig. 2, Curve I.		Fig. 2, Curve II.	

VI. Solid solution with 82% $KMnO_4$.		VII. Solid solution with 26·8% $KMnO_4$.	
Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.
9	2·2	100	9·5
21	5·1	160	14·7
32	11·0	210	20·6
39	16·6	250	25·2
47	22·0	300	32·1
61	34·9	360	37·4
71	46·6	700	87·3
82	61·5		
98	80·0		
110	92·0		
130	97·0		
145	98·0		
Fig. 2, Curve III.		Fig. 2, Curve IV.	

C. *Experiments at lower temperature.*

VIII. Potassium permanganate finely ground with MnO_2 (220°).		IX. Similar to VIII.	
Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.
4	8·9	7	8·6
9	16·6	19	19·4
17	25·5	35	29·0
27	33·6	45	35·5
39	42·9	55	41·2
52	51·2	67	49·4
67	61·4	75	55·9
82	71·1	87	65·0
95	78·4	105	78·2
115	86·9	135	93·3
138	93·0	150	95·0
166	97·7		

Fig. 3, Curve I.   Fig. 3, Curve II.

X. Finely ground $KMnO_4$ (220°·5).		XI. Large crystals of $KMnO_4$ (217°).	
Time in minutes. t.	Per cent. decomposed. x.	Time in minutes. t.	Per cent. decomposed. x.
11	18·1	15	1·4
30	28·2	40	3·5
40	35·2	50	5·5
52	44·3	79	15·4
63	50·5	95	20·3
75	56·3	110	26·2
98	66·6	130	34·8
111	72·0	140	40·0
125	78·1	150	44·0
152	90·2	170	56·0
182	96·3	185	65·0
225	99·0	200	74·3
		230	85·4
		243	91·6
		295	99·6

Fig. 3, Curve III.   Fig. 3, Curve IV.

D. *Ammonium Bichromate at* 219° C.

XII.				
Time in minutes. t.	Per cent. decomposed. x.		Time in minutes. t.	Per cent. decomposed. x.
5	2·4		127	67·2
12	5·2		136	72·0
18	8·0		149	79·7
24	9·9		164	82·7
32·5	13·5		194	89·5
40	17·2		219	91·7
46	20·5		257	94·6
52	24·2		307	96·1
59	28·2		332	97·9
65	32·0		352	98·5
75	38·0			
85	44·4			
95	50·3			
807	59·9		Fig. 4.	

E. *Tetranitroaniline.*

XIII. At 140°.		XIV. At 120·0°.		XV. Derived curve from XIV.	
Time in hours. *t.*	Per cent. decomposed. *x.*	Time in hours. *t.*	Per cent. decomposed. *x.*	*x.*	$\dfrac{dx}{dt}$.
3	1·0	21	0·93		
5	1·5	45	2·29	·5	·044
21	10·5	70	4·56	1·6	·057
24	16·0	94	7·89	3·4	·091
28·5	29·5	118	12·12	6·2	·139
43	87·0	142	17·27	10·0	·176
49	95·5	167	24·40	13·9	·214
67	99·0	189	32·08	20·8	·286
72·5	100	214	43·47	28·2	·349
75	100	239	57·76	37·8	·456
		262	73·29	50·6	·572
		287·5	94·3	65·5	·672
		310·5	98·4	83·6	·824
		330·5	99·1	96·4	·179
		337	100	99·6	·04
		354·5	100	100	0
Fig. 5, Curve		Fig. 5, Curve II.		Fig. 5, Curve III.	

LXVIII. *The Precipitation of Colloids.* By HUMPHREY D. MURRAY, *Exhibitioner of Christ Church, Oxford* [*].

THE author has recently attempted to obtain a general expression for the precipitating effect of ions on colloids. Whilst the attempt has not at present been successful in discovering a general relationship, a special case has been found for which the expression reduces to a simple equation. This, as derived, is applicable only to the effect of univalent cations with the same anion upon the same colloid under equal conditions of temperature and concentration, the colloid carrying a negative charge. It relates the concentration of the cation in gm. atoms required to precipitate the whole of the colloid in a given time, with the atomic number of the cation, and is of the form

$$C = K \cdot N^n,$$

where C represents the concentration of the cation,

N represents the atomic number of the cation,

n is constant for the colloid at that particular concentration,

K is a constant depending upon the nature of the colloid and the anion.

In order to test the validity of the equation it was necessary to plot values of log N against values of log C.

It was difficult to find a series of concentration values of sufficient length to make an experimental verification possible. Failing an independent determination of a series of values for which the author had not sufficient time, an attempt was made with some results of Oden's, given below, on the precipitation of colloidal sulphur, the latter being negatively charged. The left-hand column shows the minimal concentration of cation in gm. atoms per litre required to effect precipitation in a given time. The anion in every case is Cl' :—

TABLE I.

Colloid :—Sulphur 18°–20° C.

Cation.	Minimal concentration with Cl' anion.	Log_{10}. Minimal concentration.	Minimal concentration with NO_3' anion.	Atomic number.	Log_{10}. Atomic number.
$H^{\cdot}$	6·0	0·778	—	1	0
$Li^{\cdot}$	·913	$\bar{1}$·960	—	3	·477
$Na^{\cdot}$	·153	$\bar{1}$·185	·163	11	1·041
$Al^{\cdots}$	·0044	$\bar{3}$·643	—	13	1·114
$K^{\cdot}$	·021	$\bar{2}$·322	·022	19	1·279
$Ca^{\cdot\cdot}$	·0041	$\bar{3}$·613	—	20	1·301
$Cu^{\cdot\cdot}$	·008	$\bar{3}$·903	—	29	1·462
$Rb^{\cdot}$	·016	$\bar{2}$·204	·0175	37	1·568
$Cs^{\cdot}$	·009	$\bar{3}$·954	·0096	55	1·740
$Ba^{\cdot\cdot}$	·0021	$\bar{3}$·322	—	56	1·748

On plotting the values of log minimal concentration of the cations associated with Cl' anions (C) against log atomic number (N), it will be seen that the values of the univalent ions, with the exception of that of potassium, lie approximately upon a straight line to which the equation is

$$C_1 = 5 \cdot 9 \ N^{-1 \cdot 64}.$$

In the case of the divalent ions the values are too few to be of any use in deducing a relation. If, however, we assume that the equations will be of the same form, *i. e.* that the expression $N^{-1 \cdot 64}$ is constant for sulphur, and that barium

and aluminium are typical divalent and trivalent ions, we obtain the equations

$$C_2 = 1 \cdot 46 \, N^{-1 \cdot 64},$$
$$C_3 = \cdot 33 \, N^{-1 \cdot 64},$$

where C_2 and C_3 are the minimal concentrations of divalent and trivalent ions respectively. We shall return to these

Fig. 1.
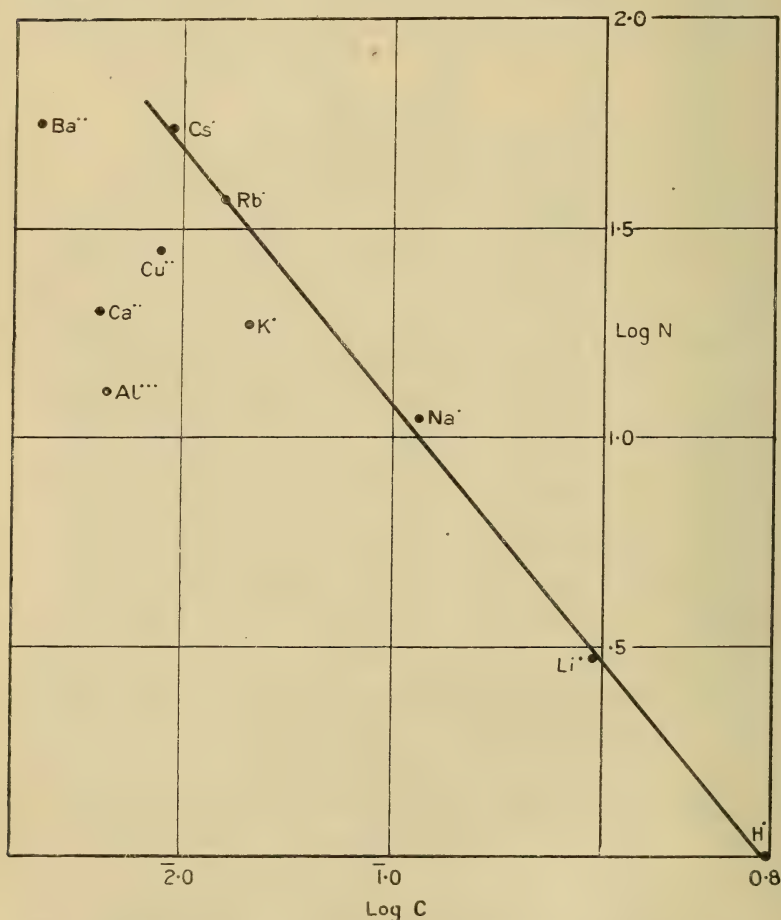
results later. The concentrations of cations with NO_3' anions are given in some cases to show that they follow approximately the same rule.

The next series of concentration values were taken from some data by Freundlich, corrected for dissociation, so that, as before, the minimal concentration of cations per litre is shown required to precipitate colloidal As_2S_3, at a concentration of ·007539 mols. per litre. The anion in every case is Cl′. The colloid is negatively charged.

TABLE II.

Cation.	Minimal concentration.	Log_{10}. Minimal concentration.	Atomic number.	Log_{10}. Atomic number.
H·	·029	$\bar{2}$·462	1	0
Li·	·0513	$\bar{2}$·710	3	·477
Na·	·045	$\bar{2}$·653	11	1·041
Mg··	·000717	$\bar{4}$·855	12	1·079
Al···	·000093	$\bar{5}$·968	13	1·114
K·	·044	$\bar{2}$·643	19	1·279
Ca··	·00065	$\bar{4}$·813	20	1·301
Zn··	·000685	$\bar{4}$·836	30	1·477
Sr··	·000635	$\bar{4}$·803	38	1·580
Ba··	·00069	$\bar{4}$·839	56	1·748

Here again we find the univalent ions lie approximately upon a straight line, to which the equation is

$$C_1 = 0·55\,N^{-0·09}.$$

The number of values for divalent ions is larger in this case but they do not give a very concordant result. We can, however, draw a line parallel to the first passing through the plotted results, to which the equation is

$$C_2 = ·0008184\,N^{-0·09}.$$

It is to be expected that secondary effects in dissociation will be more evident the higher the valence of the cation.

The question now arises as to the way in which we are to reconcile these results, if real, with Whetham's law. This states that the minimal concentrations of any univalent, divalent, and trivalent ion for the same colloid are in the ratio

$$K^3 : K^2 : K,$$
$$\text{or} \qquad K^2 : K \ : 1,$$

where K is a constant. Suppose that in the precipitation of sulphur, we have univalent, divalent, and trivalent cations

Fig. 2.
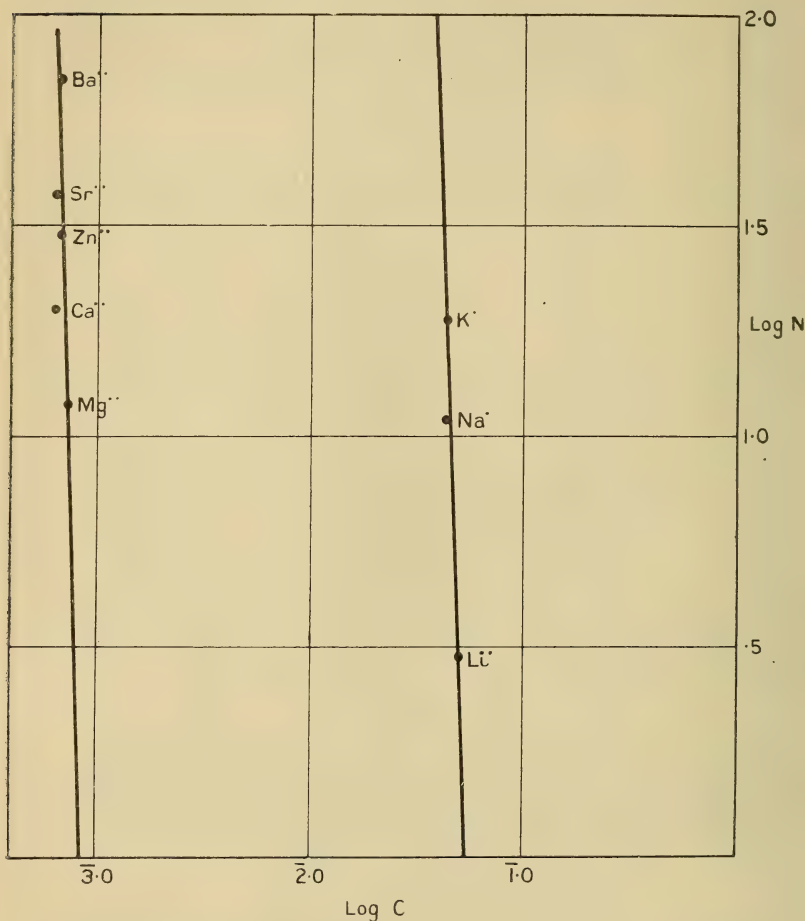
whose atomic numbers, or rather, the values of N^n, are approximately equal, then we may write,

$$C_1 : C_2 : C_3 = 5\cdot9\,N^{-1\cdot64} : 1\cdot46\,N^{-1\cdot64} : 0\cdot33\,N^{-1\cdot64},$$
$$= 5\cdot9 \qquad : 1\cdot46 \qquad : 0\cdot33$$
$$= 17\cdot7 \qquad : 4\cdot4 \qquad : 1$$
$$= (4\cdot2)^2 \qquad : 4\cdot4 \qquad : 1,$$

a result in accordance with Whetham's law. It seems probable, therefore, that the latter is only applicable to ions

for which the values of N'' are nearly equal. This result, however, requires confirmation. Freundlich gives one value for a trivalent ion in the precipitation of As_2S_3, namely, aluminium, which if we take N'' constant, gives the result

$$C_3 = \cdot 0001096 \, N^{-0.09}.$$

This, combined with the two equations above, gives for the minimal concentration of cations with approximately equal values of $N^{-0.09}$,

$$C_1 : C_2 : C_3 = 0.55 \, N^{-0.09} : 0.0008184 \, N^{-0.09} : 0.0001096 \, N^{-0.09}.$$
$$= 5018 \qquad : 7.47 : 1$$
$$= (70.8)^2 \qquad : 7.47 : 1,$$

a bad result from the point of view of the above hypothesis, but which, it may be pointed out, rests only on one result, and that the measurement of a small quantity, the concentration of the aluminium ion being $\cdot 000093$ gm. atoms per litre.

It is of interest now to see whether precipitation by anions follows a similar rule. In investigating this matter, we are met with the difficulty of not knowing what value to assign to N in the case of a complex ion, which is the most usual type of anion. We can, however, take three values from some data by Freundlich on the precipitation of colloidal $Fe(OH)_3$. The left-hand column shows the minimal concentration of the anion of potassium salts. The $Fe(OH)_3$ was positively charged and at a concentration of $\cdot 00163$ mols. per litre.

TABLE III.

Colloid :—$Fe(OH)_3$ $\cdot 00163$ mols. per litre.

Anion.	Minimal concentration.	Log_{10}. Minimal concentration.	Atomic number.	Log_{10}. Atomic number.
Cl'	·00848	$\bar{3}$·928	17	1·230
Br'	·0120	$\bar{2}$·079	35	1·544
I'	·0145	$\bar{2}$·161	53	1·724

The result, it will be seen, is satisfactory as far as it goes. We obtain the equation

$$C = \cdot 00215 \, N^{0.45},$$

in which it will be noticed that the value of n is positive.

It thus seems probable that the minimal concentration of anions is given by an equation of similar form to that for cations.

Fig. 3.
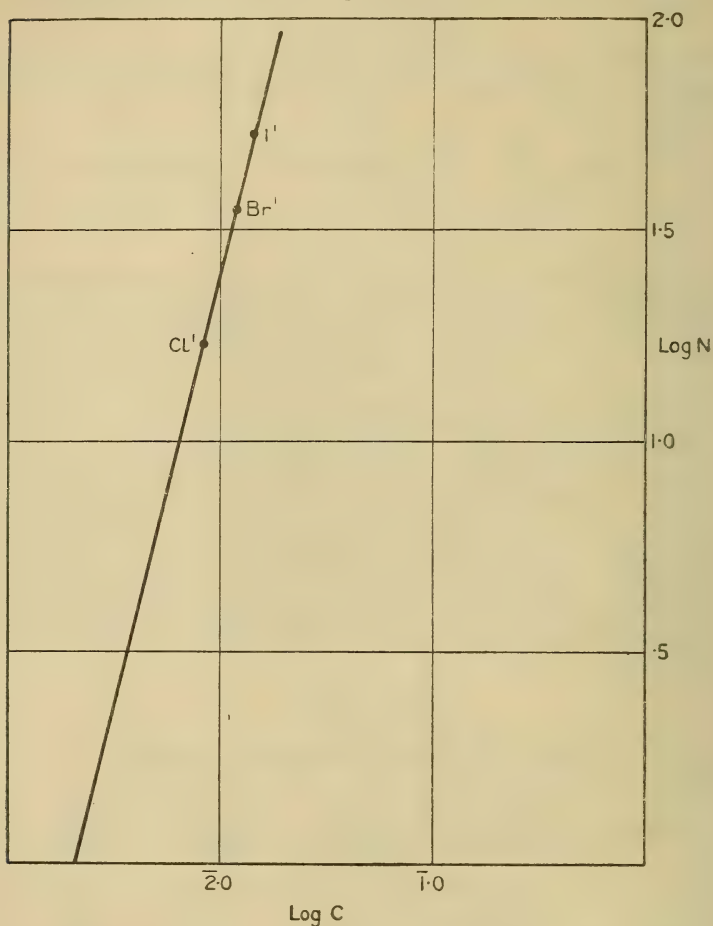
To summarize the results obtained :—

(1) The minimal concentration of univalent cations required to precipitate a negatively charged colloid under similar conditions of concentration and temperature in a given time varies with the atomic number of the cation and, in general, is given by an equation of the form

$$C = K \cdot N^n.$$

(2) The relation can probably be extended to the precipitation of positively and negatively charged colloids by anions and cations respectively of any valence.

(3) If the above is true, it follows that Whetham's law requires modification, probably by comparing the precipitating power of only those ions for which the values of N^n, as given above, are approximately equal.

Christ Church, Oxford.
April, 1920.

LXIX. *The Disappearance of Gas in the Electric Discharge.* *By* The Research Staff of the General Electric Company, Ltd., London [*]. (*Work conducted by* N. R. Campbell *and* J. W. H. Ryde.)

Introduction.

1. WHEN an electric discharge is passed through a gas at low pressure, the pressure often decreases and the gas seems to disappear. In spite of the considerable investigation to which the matter has been subjected, a complete understanding of it has not been reached. It is not known precisely what is the relation between the disappearance and the electrical conditions of the discharge, and it is not known precisely what becomes of the gas that has disappeared. The following pages describe some experiments designed to elucidate further the fundamental principles concerned in the process. It is not certain, of course, that there are any fundamental principles; there may be many totally distinct actions possible, each of which happens to have as one of its consequences the disappearance of gas; any attempt to explain them all by the same theory would then be misleading. Accordingly it may be well to state at the outset that no attempt will be made to cover the whole field, either in experiment or in theory. We shall merely point out certain features of the process which can be traced in certain cases, and must not be left out of consideration in the elaboration of any theory that is proposed to account for it.

2. First some of the main results established by earlier work may be recalled. It seems that by the passage of a current at a sufficiently low pressure, as in an X-ray tube of the old type, any gas whatever, including the inactive

gases, may be made to disappear, although some gases— *e. g.*, hydrogen and nitrogen—disappear more readily than others—*e. g.*, helium. Again, the material of the walls and the electrodes affects somewhat the rate of disappearance * ; but whatever the material, some disappearance will occur. On the other hand, there are instances in which the disappearance is determined directly by the chemical nature of the gases and the electrodes. Thus, a cathode of one of the alkali metals will produce a disappearance of most gases in circumstances in which a cathode of a less active metal would not ; but it has no effect on the inactive gases. Again, it is well known that the introduction of the vapour of phosphorus accelerates very greatly the disappearance of all active gases. The conclusion is therefore generally drawn that chemical action may play a part in the disappearance of gas, probably by the formation of chemical compounds of the elements of the gas and of the electrodes which have no appreciable vapour-pressure ; but that in some cases there must be at work agencies that are not chemical †. There is much evidence that the gas can be caused by the discharge to adhere to the solid parts of the discharge-tube in some manner which still remains obscure, and that it can be liberated again from them by a rise in temperature.

Concerning the electrical conditions which determine the rate of disappearance of the gas, the most definite evidence seems to be given by the experiments of Vegard ‡ and of Brodetsky and Hodgson §. These workers have shown that the disappearance of gas is closely connected with the cathode fall of potential in the discharge ; it is therefore connected with the cathodic sputtering, which also increases

* For the action of the glass walls of the vessel, see G. E. Hill, Phys. Soc. Proc. xxv. p. 35 (1912), and R. S. Willows and H. T. George, *ibid.* xxviii. p. 124 (1916). No experiments seem to have been made without glass or silica.

† The term " chemical " has been used by some writers to include so much that it may be well to state precisely what is here meant by the term. An action is not considered chemical unless it results in the formation of new combinations which follow the law of " constant proportions," which can be separated to some extent from the original combinations, and which can be shown to differ from them in physical characteristics—boiling and melting points, and so on. Of course, there may be reason for believing that an action is chemical in this sense without a definite proof that the law of constant proportions is obeyed ; but unless there is reason for such a belief, the action will not be termed chemical.

‡ L. Vegard, *Ann de Phys.* 1. p. 769 (1916).

§ S. Brodetsky and B. Hodgson, Phil. Mag. xxxi. p. 478 (1916).

with the cathode fall of potential. The connexion, though interesting and suggestive, does not seem a sufficient basis for any theory of the process, although the workers named argue that it proves that the absorption of gas cannot be due to chemical action between the gas and the anode or the glass walls.

However, the connexion between absorption and cathode fall cannot be universal, for the cathode fall cannot be abolished by causing the thermionic emission of electrons from the cathode ; and yet gas will undoubtedly disappear when the discharge passes from an incandescent cathode under a potential much less than the minimum spark potential which would be required to send a discharge through the gas if the electrode were cold. Indeed, it is the disappearance of gas in the presence of a hot cathode that has the greatest technical importance in connexion with lamp and valve manufacture, and has led in recent years to an increased interest in the matter.

But it must be noticed that the introduction of an incandescent cathode may effect the disappearance of gas otherwise than by altering the electrical conditions in the discharge ; in the absence of the discharge there may be some direct interaction between the hot metal and the gas which does not take place when the metal is cold. These two influences of the incandescent cathode are closely associated in all experiments, and may even be hard to distinguish ; for since the cathode, usually in the form of wire or strip, is almost always heated electrically, there will be a potential difference between its ends, and this potential difference may be great enough to cause a discharge between the ends, one of which acts as cathode and the other as anode. However, some observations described below, the results of which are confirmed by other work, seem to show that the two influences can be separated ; for, if the potential difference between the ends of the wire is sufficiently small, then, though it must cause some electric discharge through the gas, the discharge which it causes is not of a nature to influence the disappearance of gas. Accordingly, if the filaments are so stout or so short that the difference of potential between their ends when they are incandescent does not exceed this limit (which is apparently always greater than 20 volts), any action which the filament may have when it is heated must be due purely to its temperature and not to the electric field surrounding it.

This purely thermal influence of an incandescent filament

2 Q 2

(especially of a tungsten filament) has been studied with great care and with much success by Langmuir *. He finds that if tungsten is heated to a temperature of 2800° K. in gas at any pressure, so that evaporation of the metal is rapid, all traces of all gases, except the inactive group, can be removed completely and a very high vacuum obtained. He has also shown that in oxygen, nitrogen, and carbon monoxide definite chemical compounds are formed, sometimes by the interaction of the gas with the solid metal, but more often with its vapour. Some of the gases can be removed by the tungsten at a much lower temperature ; hydrogen, the extreme case, is removed at a temperature as low as 1300° K. But the removal of hydrogen is a more complex matter. Langmuir interprets the results of his very complex observations as proving that the hot metal converts the hydrogen into an " active " modification, probably with monatomic molecules, which is able to adhere tenaciously to the glass walls or interact chemically in the cold with oxygen and other elements.

These actions appear to be purely thermal and determined only by the temperature of the tungsten. When the electric field surrounding the filament is sufficiently great, a discharge occurs which affects the process, usually by causing the disappearance of gas and the progress of chemical reactions which would not take place under the influence of the hot filament alone. Thus in the discharge, nitrogen can be made to combine with tungsten to form the nitride WN_2 with the filament at a temperature much lower than that required to cause the combination in the absence of the discharge. But, in the main, Langmuir's observations on the effect of the discharge have been incidental, and his attention is directed rather to the thermal action. Nevertheless, his conclusions are extremely suggestive for any study of the effect of the discharge, and will be referred to frequently in the subsequent discussion. It appears to be his opinion in general that the nature of the changes which cause the disappearance under the discharge is the same as that of those which cause the disappearance under purely thermal action, and that in both cases the gas disappears because it enters into new chemical relations ; the only

* I. Langmuir, Journ. Amer. Chem. Soc. xxxiv. p. 1310 (1912) ; xxxv. pp. 105, 931 (1913) ; xxxvii. p. 1139 (1915). It is not always stated in these papers what was the potential difference between the ends of the filament, but since Langmuir recognizes that, if it exceeds 40 volts, an electric discharge which affects the disappearance of gas may occur, it may be assumed that the limit was never exceeded.

difference lies in the manner in which the chemical changes are brought about. If this view is accepted, the study of the thermal actions may well provide the clue to the explanation of the electrical actions.

3. It is the purpose of the experiments described in this paper to extend to the electrical actions the investigation which Langmuir has made of the thermal actions. There appears to be much evidence for believing that there is an electrical action which is as independent of the thermal action as the thermal action is of the electrical. In studying this action the incandescent cathode is a great experimental convenience, because it permits the electrical discharge to take place under potential differences too low to cause the discharge to pass between cold electrodes in the same gas; it gives much greater control over the electrical conditions. Further, it is the discharge with an incandescent cathode that is of primary technical importance. For these reasons all the experiments have been made with such a cathode. But it must be remembered that the conditions sought are those in which the incandescent cathode has no direct action on the gas causing it to disappear, but acts only by abolishing the cathode fall of potential and allowing the discharge to pass under small potential differences. If these conditions can be obtained, they will be much nearer to those of the older experiments, in which the discharge was passed between cold electrodes by high-potential differences, than to those of most of Langmuir's experiments, where the high temperature of the filament is the main agent in determining the disappearance of the gas.

Apparatus.

4. The apparatus employed is shown diagrammatically in fig. 1. L is the vessel in which the discharge took place; it is drawn approximately to scale and will be termed for brevity the lamp. It is connected through the liquid-air trap T, which served to exclude vapours, (1) to the McLeod gauge, (2) through the mercury cut-off C_1 to the pump, (3) to the gas-filling apparatus. The pump was a mercury diffusion pump backed by a rotary oil-pump, and gave pressures too low to measure. The gas was introduced from a generator or reservoir through the porous plug P, which could be covered by a mercury column; it then passed into the liquid-air trap T_2 to remove condensable gases, and could be admitted to the lamp by lowering the mercury cut-off C_2. The quantity admitted could be regulated roughly by the time for which the porous plug was uncovered.

The lamp contained the straight tungsten filament F, capable of carrying in a vacuum a current of 1·4 amp. with a voltage of 10 volts. The heating current was derived from the battery B, regulated as usual by a rheostat and ammeter

Fig. 1.
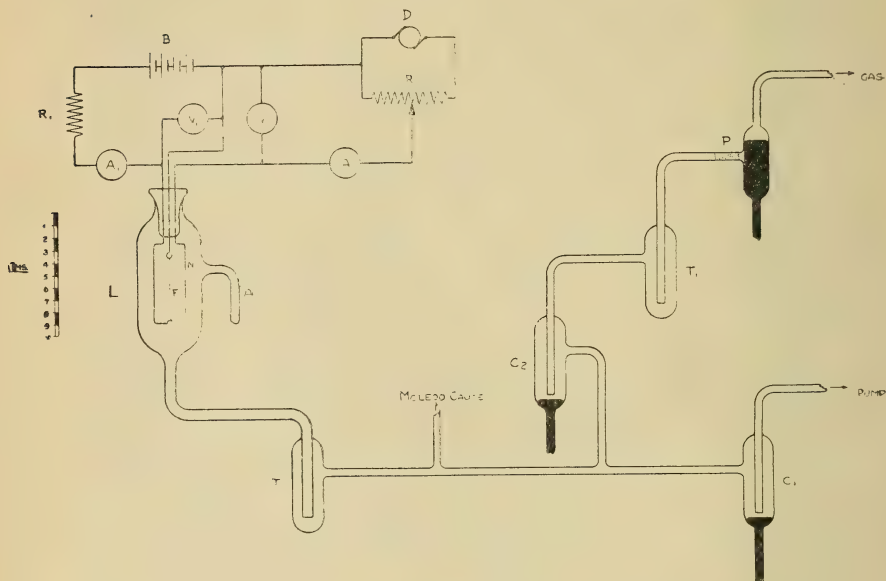
and voltmeter. The supports of the filament were of nickel wire 0·6 mm. in diameter. A similar piece of wire served as the anode. Any desired potential difference between the filament and the anode could be established by means of the 600-volt dynamo D acting through a potential divider R with a fine adjustment. The potential between the anode and the negative end of the filament (V) was measured by the voltmeter V reading to 0·1 volt; the current (i) flowing between the electrodes by the shunted microammeter A.

Physical Characteristics of the Discharge.

The Glow Potential.

5. If the vessel is very highly evacuated, then, as is well-known, i is independent within wide limits of the temperature and thermionic emission of the filament, and, so long as V is below a certain limit, varies simply as $V^{\frac{3}{2}}$: the current is limited by the space-charge. If V is increased sufficiently,

the current becomes saturated, and reaches a value (i_0) determined wholly by the thermionic emission and not by V. The relation between i and V in this condition is shown by curve I. in fig. 2, where $i^{\frac{2}{3}}$ is plotted against V. The curves

Fig. 2.

Relation between current (i) & potential (v) at different pressures
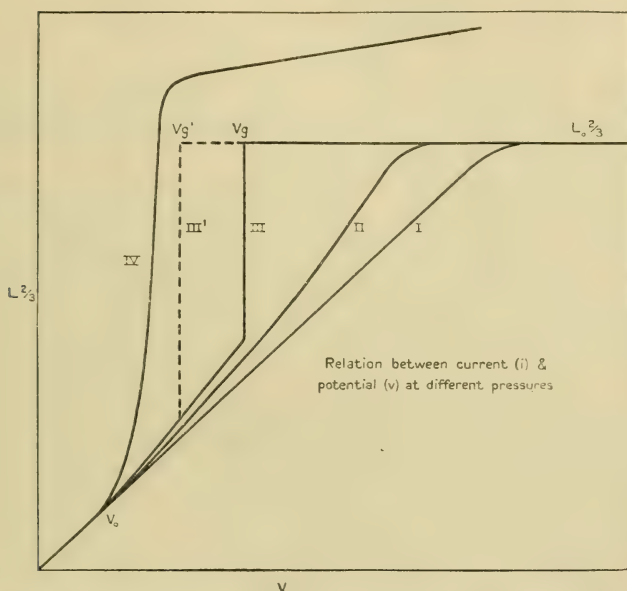
in this figure are not drawn accurately, but merely represent qualitatively the charges that occur.

If a little gas is present, curve II. is obtained. It leaves curve I. at the ionization potential of the gas (V_0), and attains the saturation current at a value of V less than before. But the saturation current reached is the same, because the current conveyed by the ions formed from the gas is an inappreciable fraction of that conveyed by the thermionic electrons. No luminosity appears in the discharge-tube before the saturation current is attained : if it appears at all, it is at potentials such as are used with a hard X-ray tube, which are much higher than the highest used in these experiments (600 volts). The pressure at this stage will be less than ·001 mm.

If the pressure is raised to (say) ·002 mm., a new feature appears (curve III.). Above the ionization potential, the current increases still more rapidly with the potential, but before the saturation current is attained, a potential is

reached at which there is a very sudden increase in the
current. The change in the current at this point is discon-
tinuous ; i increases from a value which is a small fraction
of the saturation current immediately to the saturation
current. At the same time, luminosity appears in the
discharge-tube. The potential at which this discontinuous
change occurs, accompanied by the development of the
glow, will be termed the glow potential, V_g. Such discon-
tinuous changes are obtained when the pressure is still so
low that the ionization is an inappreciable fraction of the
thermionic current and the saturation current is practically
the same as in the highest vacuum.

It has been said that the change is discontinuous. The best
proof of this statement is that, on reversing the changes of
potential, the changes of current are not reversed. If,
after the potential has been raised above V_g and the glow
started, the potential is reduced, the glow does not cease
immediately, nor does the current fall below saturation. The
dotted curve III.' is followed. When V has been reduced to
a lower value V_g', the discontinuous change is reversed, and
the current falls once more sharply to the value which it had
at the same value of V when the potentials were increased.
When it is necessary to make a distinction in words between
V_g and V_g', they will be called the rising and falling glow
potentials.

If the pressure is increased once more to ·05 mm., curve
IV. is obtained. It now appears at first sight as if the
current rose continuously with the potential, until a value
greater than the vacuum saturation current was obtained ; it
then continues to rise yet further, but more slowly. The
rise of the current above the saturation value in a vacuum
is, of course, due to the occurrence of ionization producing a
number of electrons comparable with those emitted from the
filament. At some point before the final slower rise sets in,
a glow appears in the lamp, which is usually fainter and
much more difficult to see than that characteristic of curve III.
It was thought at first that this glow entered without any
discontinuity in the curve, but later observations indicate that
here also there is a point of definite discontinuity, and that it
is at this point that the glow enters. In any case, the glow
appears at that part of the curve where the rate of increase
of i with V is greatest; the potential at which it appears can
be determined with somewhat less accuracy than in curve III.;
it will be denoted again by V_g. When there is no appearance
of discontinuity in the curve, there is also no difference
between V_g and V_g' ; if the potential is reduced, the curve

appears to coincide with that obtained when it is increased. But once more there are indications that V_g and V_g' are not precisely the same, but that it is merely very difficult to detect the difference between them. As the pressure is decreased, the curves of type IV. shade continuously into those of type III.

Observations on the Glow Potential.

6. Many of the facts just described are well known. Several observers have noted that the glow enters suddenly at a definite potential accompanied by a large increase of current. In particular, Horton and Davies [*] have described the phenomenon in a recent paper. But it was found that the glow potential was so intimately connected with the disappearance of gas under the discharge that a large number of observations on it were made in various circumstances. A full account of the results and the conclusions to be based on them is reserved for a later paper; here only the facts that are immediately relevant to our main purpose will be recorded.

A few remarks may be made on the method of determining the glow potential. It has been said that the appearance of the glow and the sudden increase of the current occur at the same potential, and all experiments indicate that this statement is accurately true. But it is usually very much easier to observe the increase of current than the occurrence of luminosity, for (especially in hydrogen) the glow is often so faint that without special optical arrangements it is difficult to see it in the neighbourhood of the incandescent filament; moreover, there is always the chance that the glow may occur in a region of the spectrum which does not affect the eye. Accordingly in all observations it is the increase of current and not the luminosity that has been observed when accurate measurements are taken. At low pressures, corresponding to curve III., there is no difficulty in observing this increase in the form of a "kick" of the microammeter A, but there is an even more convenient method of determining V_g. Since V was supplied through a potential divider of high resistance, the rapid increase of current causes a fall of potential across the electrodes, and, owing to the difference between V_g and V_g', this fall does not cause the glow to cease. Accordingly the method adopted was to increase V regularly and to watch the voltmeter; the pointer rises to a definite value and then drops back; the

* F. Horton and A. C. Davies, Proc. Roy. Soc. A, March 1920.

maximum value attained is V *. Similarly, V_g' can be determined by decreasing the voltage regularly and noting the minimum reading recorded. If the pressure of the gas remained constant during the observations (a condition by no means always fulfilled), V_g could be determined as accurately as the voltmeter could be read. The determination of V_g' was somewhat less accurate and consistent.

When the pressure is higher and the condition is that represented by curve IV., the determination of V_g is more difficult; the increase of current associated with the glow is much less. If the glow is visible it is best to watch for it; if it is not, rough measurements of i have to be taken in the neighbourhood of V_g. It is not possible in these circumstances to determine V_g to less than $\frac{1}{2}$ volt, and it is rather surprising that the consistency of the result shows that even this accuracy can actually be obtained.

It should be pointed out that the values of V_g given are always those between the anode and the negative end of the filament when the glow appears. The remainder of the filament differs less in potential from the anode; and the true value of V_g, or that which would be found if the filament were all at the same potential, may be slightly less. But the difference must be a small fraction of a volt; for the true V_g will be the potential difference between the anode and that part of the filament, hot enough to give a thermionic emission which falls within the range where V_g is independent of that emission, which is nearest to the negative end. Accordingly the observed values have only to be corrected for the potential drop along the portion of the filament which is cooled by the leads. The whole drop along the filament was usually 8·4 volts, and since it never varied by more than $\frac{1}{2}$ volt, the values obtained must be accurate within the error of observation, which was never less than 0·1 volt.

The first observations proved that the glow potential is independent of the temperature of the filament and of the thermionic emission from it within wide limits. If there is no thermionic emission, the glow does not appear, of course, until the spark potential of the gas is reached, but the change from this condition to that in which the glow occurs at the very much lower potential obtained with a hot cathode is so rapid that it could not be determined certainly whether the change was continuous or discontinuous. Once the lower

* V_g determined in this manner is doubtless not exactly the same as that determined from the " kick " of the current, unless the resistance in series is practically infinite. But the resistance was sufficiently great to make any difference between the two values inappreciable to experiment.

value is obtained, no further change occurs even if the thermionic emission is increased 100-fold. There is no evidence that the glow potential depends at all on the thermionic emission, so long as it is great enough to give at all a glow potential distinct from the spark potential.

On the other hand, the glow potential depends greatly on the pressure, as has been indicated already, and on the nature of the gas. Fig. 3 shows the variation of V_g and $V_{g'}$ with

Fig. 3.
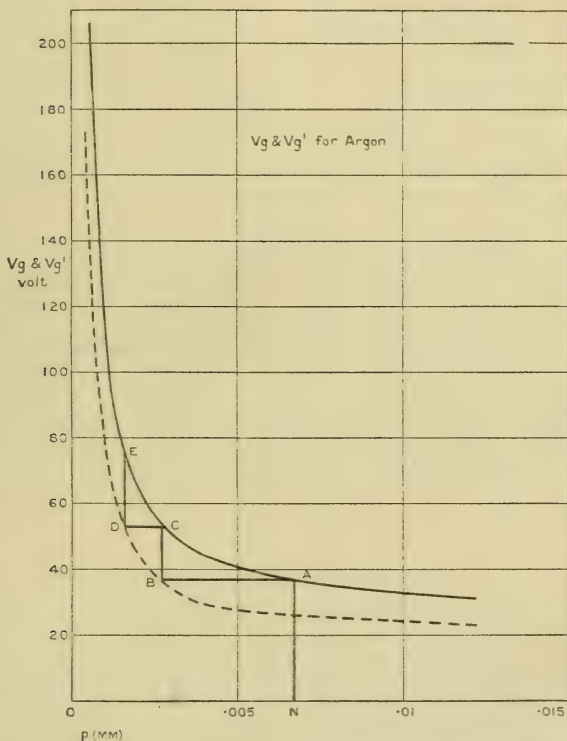
the pressure in argon, containing about 5 per cent. of nitrogen. (This gas is chosen because the difference between the rising and falling glow potentials is here measurable even at the highest pressures investigated. In the other gases it becomes inappreciable at pressure above 0·02 mm.) It will be seen that V_g, $V_{g'}$, and the difference between them all increase rapidly with decrease of pressure at the lowest pressures; at the higher they vary but little with the pressure. It is better, therefore, to plot

the glow potentials against the reciprocal of the pressure (which is proportional to the mean free path) ; this method is adopted in fig. 4, which shows V_g for various gases. It is to be observed that the glow potentials of hydrogen are much greater than those of nitrogen, carbon monoxide, or argon, and that the order of the glow potentials is roughly the inverse of the order of the molecular weights ; if the glow potential were determined only by the molecular weight, nitrogen would have the same glow potential as carbon monoxide ; actually the glow potentials are not very different. At the lower pressures all the curves seem to become straight lines, and at the higher all appear to tend towards nearly the same limit. The observations shown on one curve indicate the accuracy obtainable in the best conditions; the irregularities appear to be due to errors in the measurement of the pressure rather than to errors in V_g; if the pressure was constant, the determination of V_g could be repeated to a few tenths of a volt.

Lastly, the glow potential depends on the form of the electrodes and of the vessel. A full consideration of this influence is reserved for later discussion ; but it may be recorded here that the phenomena are changed completely if there is substituted for the wire anode a cylinder surrounding the filament, and that—contrary to what might have been expected—the glow potential at the lower pressures is apparently independent within wide limits of the size of the vessel, whereas at high pressures it depends upon that size.

Effect of Impurities.

7. If the gases are not pure very different results may be obtained. The " pure " hydrogen was prepared by allowing the vapour of water (that had been boiled to one-tenth of its volume in a vacuum) to act on metallic sodium in a vacuum ; the measurements were made after all possible precautions had been taken to free the apparatus from residual gas. " Hydrogen 99 per cent." refers to gas taken from a cylinder; it had been prepared from water-gas, and contained about 1 per cent. of impurity, chiefly methane, carbon monoxide, and nitrogen ; the remaining curve to the pure gas in the presence of the vapour of special " vacuum " wax.

It is clear that the glow potential of hydrogen is very greatly affected by the presence of small traces of other gases. On the other hand, no change in the glow potentials

of carbon monoxide or nitrogen could be made by special
efforts at purification; atmospheric and chemical nitrogen
agreed perfectly. The argon used contained about 5 per cent.
of nitrogen; pure argon has not been examined.

The effect of mercury vapour, which was absent from all
the gases of fig. 4, is especially remarkable. If the lamp is

Fig. 4.
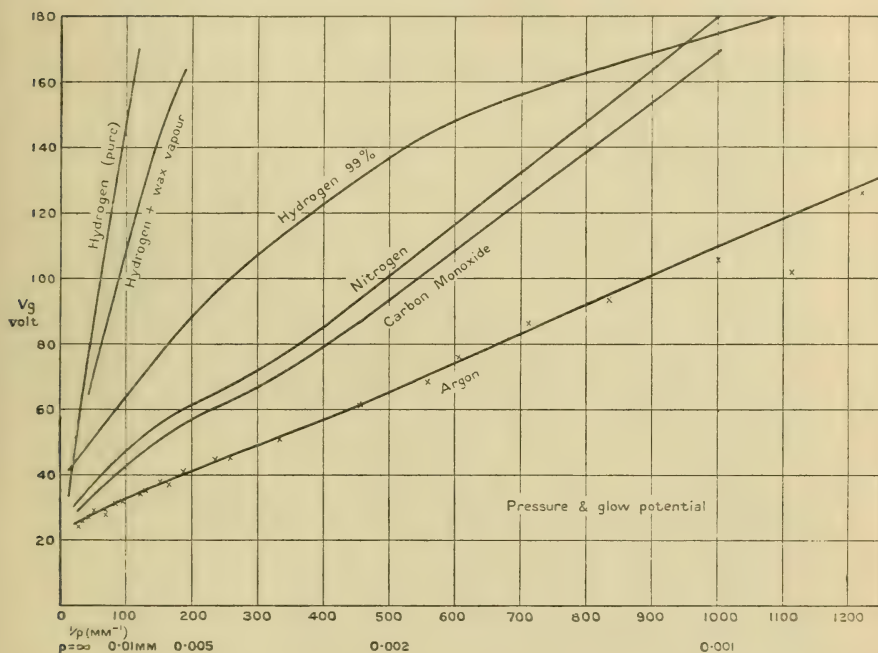
completely evacuated of all permanent gases while mercury
vapour is allowed to remain, the glow potential is found to
be 32·5 volts. The pressure of this vapour is known to be
about 0·002 mm.; so that the glow potential of mercury is
very much lower than that of the other gases at the same
pressure—a difference to be expected from its greater
molecular weight. If, now, one of the permanent gases is
admitted, there is no change in the glow potential; so long
as mercury vapour has access to the lamp, the glow potential
is always 32·5 volts, whatever the nature of pressure of the
gas with which it is mixed. Such a result might be antici-
pated. Since the glow potential decreases with an increase
of pressure, it is not to be expected that the addition of any

gas would raise the glow potential above that which would be obtained if the gas were not added. But it is important to notice that an impurity consisting of a gas or vapour, which is characterised by a low glow potential throughout the curve, may reduce the glow potential of a gas with which it is mixed far below that which the impurity would have in the absence of the gas ; the glow potential of a mixture may be lower than that of either of the constituents. Thus, if all the hydrogen were removed from the impure hydrogen from the cylinder, the residual gas, which would have a pressure only 1 per cent. of that of the original hydrogen, would have a glow potential a great deal higher than that of the mixture. Again, if mercury vapour in contact with frozen mercury ($234°$ K.), and not with mercury at room temperature, is allowed access to the lamp, the glow potential, when all permanent gases are evacuated, is greater than 300 volts. Nevertheless, this same quantity of mercury vapour, when mixed with nitrogen at a pressure of 0·01 mm. having a glow potential of about 45 volts, causes a notable diminution of its glow potential ; it makes the glow potential of the nitrogen almost identical with that of carbon monoxide (see fig. 4). Even when the temperature of the mercury was reduced to 200°K., its effect could still be detected in a slight but consistent diminution of the glow potential of nitrogen at low pressures. It may be added that the wax vapour which has so marked an effect on the glow potential of hydrogen had a glow potential greater than 600 volts in the absence of other gas.

Since, as we shall see, the glow potential is a very important factor in determining the disappearance of the gas, these observations, proving the large effect of very minute traces of impurity, are of great importance. The impurities that are important are those which, like mercury, are characterized by low glow potentials at all pressures; and the effect of the impurities is greatest in gases which, like hydrogen, have a high glow potential. The glow potential of hydrogen is probably one of the most delicate methods for detecting any common impurities, which are usually characterized by low glow potentials. It is not certain, of course, that the hydrogen of fig. 4 is absolutely pure ; all that can be said is that two samples agreed in giving the same glow potentials, and that these are higher than those of any other sample examined.

The reduction of the glow potential by impurities is associated with the development of the spectrum of the impurities in the glow ; such an association is natural, for the

low glow potential obviously indicates that the discharge is passing through the impurity as well as, or rather than, through the gas. Thus it is well known that the presence of mercury vapour is apt to mask the presence of all other gases, and that hydrogen is often concealed by CO. The spectroscopic observations in these experiments have been made so far with no instrument more effective than a small direct-vision prism pointed at the main body of the lamp ; but the great changes in the spectrum are visible to the unaided eye. Thus the glow in the purest hydrogen is almost invisible, much fainter than in any of the other gases examined. The minutest trace of impurity at once brightens the glow, and at the same time the spectrum of the impurity (mercury or carbon monoxide) appears. The spectrum of carbon monoxide is not easily suppressed ; it is clear even when mercury at room temperature is present, though the mercury lines are also bright. On the other hand such mercury entirely suppresses the nitrogen spectrum, so far as could be seen ; and the mercury lines could be seen in the nitrogen spectrum even when the mercury was at $200°\mathrm{K}$. As the mercury is allowed to warm up, the sudden cessation of the red nitrogen glow and its replacement by the mercury glow, much fainter (to the eye), are very striking.

The Glow and Ionization.

8. The facts that have been stated do not provide a complete theory of the physical meaning of the glow potential, but a few obvious conclusions may be noted.

There is no doubt that the appearance of the glow is accompanied by an increase of the ionization of the gas, but it should be remarked that the sudden increase of current, at the pressures of which curve III. is characteristic, does not represent merely the addition of current carried by ions from the gas. By far the greater part of this increase is due to the neutralization of the space-charge and to the passage between the electrodes of a greatly increased proportion of the electrons liberated by the thermionic emission of the cathode.

That the glow is closely connected with the neutralization of the space-charge is indicated also by the relation between the molecular weight of a gas and its glow potential at a given pressure. A given number of ions will be the more effective in neutralizing the space-charge the less is their velocity : their velocity with a given potential will be the less the greater is their molecular weight. It is doubtless

for this reason that the gases of greater molecular weight have the smaller glow potentials, for the smaller potential doubtless corresponds to the smaller number of ions. But as yet no simple numerical relation has been found between the molecular weight and the glow potential at a given pressure: doubtless the mean free path and the ionization potential of the gas are also effective in determining that relation.

However, though it is not permissible to conclude that, if the current increases 10- or 100-fold at the moment the glow starts, the ionization increases in the same proportion, the ionization when there is a glow must be greater than when there is not. For the neutralization of the space-charge implies the emergence of more electrons from the cathode ; and, unless the number of ions produced by each electron decreases very greatly, the greater number of electrons must produce a greater number of ions. Such considerations are of importance if it is asked whether the appearance of the glow is merely an indication of a great increase of ionization or whether it represents the entry of some new form of ionization. If the first alternative is adopted, it must be concluded that there is a glow even at potentials lower than the glow potential although it is too faint to be seen ; for at such potentials there is certainly some ionization. The matter can only be decided definitely by determining how great is the increase of ionization, and whether it is great enough to account for a change from a state in which the glow cannot be seen with the most elaborate precautions to one in which it can be seen in bright daylight. The fact that the increase of current is not a measure of the increase of ionization shows that much more inquiry must be made before the matter can be decided ; but all the evidence that has been accumulated so far tends to show that the appearance of the glow is not merely due to an increase in the number of ions produced.

On the other hand it is clear that the glow potential is not, like the ionization potential, a direct property of the individual atoms of the gas ; it must also be a function of their mode of reaction with each other or with the walls of the vessel ; for the glow potential is not, like the ionization potential, independent of the pressure. There is no evidence, therefore, that the glow represents a new form of ionization of the individual atoms.

Some Consequences of the Observations of the Glow Potential.

9. Before observations of a different nature are described it will be well to point out in what manner the glow potential, and in particular the difference between the rising and falling glow potentials, may affect the changes that are the main subject of investigation.

It will be seen later that there are circumstances in which gas disappears in the discharge if V is greater than V_g and the glow is developed, but not if there is no glow. Suppose, then, that in these circumstances we are raising V so slowly that the gas has time to disappear under the discharge. If the initial pressure is represented by A (fig. 3) and V is raised from zero along the line NA, then, when A is reached, the glow starts. The gas begins to disappear and the pressure to fall; but the glow will not cease immediately. It will continue, while the pressure falls along the line AB, until B is reached and the potential is no longer able to maintain the discharge. If the potential is raised once more along BC, the glow will not start again until C is reached, and till C is reached there will be no disappearance of gas. But when C is reached the gas disappears once more, and the pressure falls along CD until the glow ceases at D. It will not start again till V rises to E, and so on.

In suitable circumstances this process can be easily traced experimentally. As the potential is raised slowly, the glow in the lamp flickers in a way familiar to all who have watched the " cleaning-up" of a lamp; and by measuring the pressure every time the glow ceases, it can be established that the points lie as they should on the full and dotted curves of fig. 3. The flicker also appears when the potential is kept constant, if gas is slowly leaking into the lamp from the walls or along a narrow connecting tube. The glow appears when the pressure rises to the point at which V is equal to V_g; it falls until V is equal to V_g', and the glow does not start again till the pressure has risen once more.

A further consequence of the difference between V_g and V_g' should be noted. The potential available for causing the discharge which produces the disappearance of the gas may be limited—for example, in an ordinary lamp it is limited to that which can be applied to the ends of the filament without burning it out. If the maximum potential is C (fig. 3), then so long as the initial pressure in the lamp is greater than that corresponding to C, the lamp can be

" cleaned-up " by the discharge so completely that no further discharge will occur until the much greater potential E is applied. On the other hand, if the initial pressure is slightly less than C, the available potential will not start the discharge, and no " clean-up " can be obtained ; if at any subsequent time the potential is raised slightly above C the discharge will occur. It may easily happen that too low an initial pressure in the lamp is prejudicial to the obtaining of a complete " clean-up," and that the clean-up is more complete if initially a little extra gas is introduced.

Chemical Effects of the Discharge.

The Disappearance of Carbon Monoxide.

10. The changes just described will not occur unless the circumstances are such that the gas disappears only when the glow discharge passes, and not when the potential between the electrodes is insufficient to produce the glow. They would not occur if the gas disappeared when there was no potential between the electrodes, or when the potential, though sufficient to produce some ionization, was less than V_g. There undoubtedly are such circumstances ; there are conditions well known in technical practice in which the " clean-up " of the lamp is accompanied by, and inseparable from, a marked glow, and the experiments of Langmuir give clear evidence of their existence ; for he shows that in some gases—notably nitrogen and carbon monoxide—when the temperature of the filament is below that at which notable vaporization occurs, the gas disappears only " electrically " and in consequence of the passage of a discharge. It should be observed that in all his experiments there must have been some " discharge," for there was a difference of potential between the ends of his filament ; and if that potential exceeded (as it often did) the ionization potential of the gas, it must have been accompanied by some ionization of the gas, and cannot have been a pure electron current. The fact, therefore, that he distinguishes between conditions in which there was a discharge and those in which there was not, shows that it is only some special form of discharge that is effective : the experiments described here, in conjunction with his observations, leave little doubt that this form was the glow.

The matter has been studied more closely in the case of carbon monoxide, nitrogen, and hydrogen, both in the presence and in the absence of phosphorus vapour. It will

be well to consider first carbon monoxide in the absence of phosphorus, for here the most definite and illuminating results have been obtained.

The carbon monoxide was prepared from sulphuric and formic acids and stored over water ; it probably, therefore, contained a trace of air, but other likely impurities would be removed by the liquid-air trap T_1. When the apparatus was arranged as in fig. 1, it was found that practically no change of pressure occurred when the filament was heated to 2000° K. so long as V was less than V_g. But as soon as V_g was exceeded and the glow appeared, the pressure began to decrease, if it lay initially between 0·1 and 0·001 mm., and the gas disappeared. A large number of observations were taken on the relation between the rate of decrease of pressure and the values of V and i ; but, for a reason which will appear presently, it is not proposed at present to consider them in detail. In general, it may be said that the rate of decrease increased, as might be expected, when i was increased, either by increasing V or by increasing the temperature and thermionic emission of the filament. Further, an increase in V in general increased the rate of disappearance even if i was unchanged, though there were some exceptions to this rule ; sometimes there was an optimum value of V at which the rate of decrease was a maximum. With the very crude spectroscopic arrangements employed, no lines except those of the ordinary carbon monoxide spectrum could be detected.

The disappearance of gas continued in all cases until the pressure became so low that the potential applied could no longer maintain the discharge. V did not usually exceed 300 volts, and with this potential the glow ceased at about 0·0008 mm. If the potential were maintained after this limit was reached, a further slight decrease to 0·0006 mm. occurred, the ultimate limit depending on the potential ; the lowest limit was reached when V was about 200 volts, slightly higher limiting pressures being reached with either higher or lower potentials. Since some of the gas which disappears is undoubtedly contained on the walls of the lamp, it is thought that this limiting pressure represents a balance between the disappearance of gas and its evolution from the walls by the action of the discharge.

By admitting fresh gas to replace that which had disappeared, the process could be continued apparently without end and without any marked change in the rate of disappearance. A slight wastage of the filament occurred and the walls became slightly blackened, but no simple relation

between the wastage of the filament and the disappearance
of the gas could be traced. A fraction of the gas could be
liberated again by baking the lamp, but the amount thus
liberated appeared all to be absorbed in the early stages of
the disappearance, and did not increase greatly with the
quantity of gas that had disappeared. It may be observed
that there was no evidence of the accumulation of gas which
would not disappear, and accordingly any impurities that
the gas may have contained must have disappeared with the
carbon monoxide.

If after a quantity of gas had been caused to disappear in
the discharge the liquid air were removed from the trap T
and the trap warmed to room temperature, a marked increase
of pressure occurred, and much of the gas that had disappeared
seemed to reappear. Experiments showed that the gas thus
reappearing was about half of that which had disappeared.
The following table gives some of the results :—

TABLE I.

Decrease of pressure under discharge.	Increase on warming.	Ratio.
·0197 mm.	·0116 mm.	0·59
·1258 ,,	·0597 ,,	0·47
·0323 ,,	·0168 ,,	0·52
·0780 ,,	·0330 ,,	0·42
·0445 ,,	·0265 ,,	0·57
·0325 ,,	·0200 ,,	0·62
·1020 ,,	·0560 ,,	0·55
0·4348 mm.	0·2236 mm.	0·515

The first column gives the total pressure which would have
been exerted by the gas that had disappeared if it had been
present in the lamp at the same time—that is to say, it is
the sum of the decreases of pressure produced by the
discharge when several doses of gas were admitted succes-
sively ; the second column gives the increase of pressure
that occurred on warming the trap T (or the side tube A
—see fig. 1) ; the third column gives the ratio of the second
to the first. It is not certain whether the variations in this
ratio represent experimental error or indicate real variations,
but they justify the statement that about half the gas
reappears.

If the trap was cooled once more, the gas that had re-
appeared disappeared once more completely. Accordingly
it is clear that by the action of the discharge the carbon
monoxide had been converted into some gas that condenses

at liquid-air temperature. Carbon dioxide was naturally suspected. Accordingly the apparatus was rearranged so that the cooled tube in which the gas condensed could be sealed off from the rest of the apparatus. Gas to the total pressure of 1·02 mm. was then caused to disappear in the discharge, representing a volume at N.T.P. of 1·34 c.c. The sealed-off tube was opened under mercury and 0·74 c.c. of gas found to be present in it. All but a few per cent. of this gas was proved to be carbon dioxide by letting up a solution of barium hydroxide and showing by chemical tests that the white precipitate formed when the gas was absorbed was indeed barium carbonate.

The result was surprising. If a tungsten filament is heated in carbon dioxide, it is well-known that it absorbs oxygen and reduces the gas to the monoxide ; it could hardly have been expected that in the presence of so powerful a reducing agent as incandescent tungsten this action would be reversed. If oxygen had been present, the formation of some dioxide by combustion of the monoxide might have been anticipated ; but there was no free oxygen present in sufficient quantity, and the ratio of dioxide to monoxide indicates that the change is effected, not by the addition of oxygen, but by the abstraction of carbon : it appears to occur according to the equation $2nCO = nC + nCO_2$ *. The destination of the carbon abstracted has not been traced completely. It is almost certainly not taken up by the tungsten, for the filament showed none of the known characteristics of a carbonized filament. It may be deposited on the walls and give rise to some of the blackening, but it is suspected that it passes to the nickel of the anode; for the anode was found to be blackened and the surface layer undoubtedly contained carbon, detected by burning it. Unfortunately, however, it was found later that the metal itself contained some carbon ; and the examination was not sufficiently accurate to determine whether the carbon found was in excess of that contained in the original metal. The loss of weight of the filament during the disappearance of the quantity of carbon monoxide mentioned was 0·45 mgm. ; it is thought that this loss is merely due to the bombardment of the filament by the positive ions, or, in other words, merely represents cathodic spluttering ; as has been said, it

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* It is not easy to explain the occurrence of numbers greater than half in the third column of Table I. ; those less than half may be due to gas absorbed on the glass. But it is not yet certain that the deviations from half are real.

did not seem to bear any simple relation to the carbon monoxide absorbed.

An attempt was made to cause the gas to disappear without the trap T cooled, but it was found that in these circumstances the discharge caused little or no decrease of the pressure, except perhaps when the pressure was less than 0·002 mm. But if the trap is not cooled, mercury vapour has access to the lamp, the glow potential is depressed, and the spectrum of mercury is well developed: as was said on p. 599, it appears that the glow is carried rather by the mercury than by the carbon monoxide, so that the absence of action on that gas is intelligible. Steps were therefore taken to exclude mercury vapour otherwise than by the cooled trap, but it was not easy to attain that condition. Gold-foil placed in the tube between the lamp and T was quite ineffective in excluding mercury vapour *. Cooling the trap to some temperature above that necessary to condense CO_2 was an obvious course, but the experiments on nitrogen to be described later make it doubtful whether even at $200°$ K. the vapour-pressure of mercury is inappreciable for the present purpose. Moreover, it was decided to avoid having any part of the apparatus appreciably colder than the rest. Some kind of stop-cock seemed necessary, although it would involve the presence of wax or grease vapour. A pinch-cock of rubber tube with walls 1 cm. thick was actually used between the lamp and T ; but it was necessary to cement the ends of the tubing with wax, which must have introduced some vapour. This vapour (see p. 598) was sufficient to change somewhat the glow potential of hydrogen, but it made no measurable difference to the glow potential of CO. Moreover, it is known that the discharge through wax vapour always produces CO, so that it is less likely on this account that the vapour had any prejudicial effect on the observations.

When the absence of mercury vapour was thus secured without giving the gas access to liquid air, it was found that under the glow discharge, carbon monoxide would still disappear (though less rapidly than before) at the higher pressures. But when a pressure between 0·008 and 0·009 mm. was reached, the decrease of pressure ceased although the glow was continued. If fresh gas was admitted

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* It seems that gold-foil excludes mercury only when the gas is at considerable pressure. Probably the mercury molecules stick to the gold when they strike it, but they also tend to evaporate again. The high pressure reduces the evaporation. It is not asserted that the gold did not reduce the vapour-pressure somewhat, but only that it did not reduce it enough for the present purpose.

without pumping out the residue of the previous charge, the same limit was reached once more.

The side tube A of the lamp was now cooled in liquid air in the expectation that CO_2 would have been formed and that much of the gas would condense. But it was found that there was no decrease of pressure due to the cooling, or rather none that would not follow from the mere temperature change of incondensible gas. Though the carbon monoxide had disappeared under the discharge it had not now been converted in any appreciable quantity into the dioxide. With A still cooled, the discharge was started once more, and now, as before, the pressure fell rapidly to 0·0008 mm., when the glow ceased. If the liquid air was now removed from A and the tube allowed to warm up, some of the gas was restored and could be condensed again by cooling A once more. But at the first trial the restored gas was found to be markedly greater than half that which had been removed in the presence of the cooled tube. The decrease in pressure during the discharge was 0·007 mm., the increase on warming the tube 0·006 mm. Further investigation showed that the quantity restored on warming A depended on the time that the discharge was continued while A was cooled, and that in suitable circumstances the gas restored might be as great as half the total that had disappeared both with and without the side tube cooled. That is to say, if we start with gas at a pressure of p_1, and, by passing the discharge with A warm, reduce this pressure to p_2; further, with A cooled, reduce the pressure to p_3; then the gas restored on warming A again may be as great as $\frac{1}{2}(p_1-p_3)$ and not merely $\frac{1}{2}(p_2-p_3)$ as would be expected. The discharge can convert into carbon dioxide, so long as the tube A is cooled, not only the gas that disappeared while the tube was cool, but also the gas that disappeared while it was warm, although the discharge while A was warm did not at the time convert the gas into dioxide.

Explanation of the Observations.

11. A very simple and, to our minds, plausible theory will explain these facts. We have only to suppose that the effect of the discharge is to cause several *reversible* chemical actions to take place between the gas and the other materials in the lamp. Of these actions, one consists of the abstraction of carbon from the monoxide, resulting in its transformation into dioxide, together with its reverse, the combination of the dioxide with carbon to form monoxide. Another of

these actions results in the production of some compounds of the carbon and oxygen, which are solid and are deposited on the walls or electrodes ; it may be the formation of carbides and oxides of the metals of the electrodes, or it may be the formation of the compound WCO which Langmuir has detected. And this action again is accompanied by its reverse. The ultimate result of this complex of reversible reactions will depend, according to the accepted doctrines of chemical theory, upon which of the products of the reaction is being removed from the scene of action. If CO_2 is continually being removed by access to a cooled tube, then the action in which CO_2 is involved will proceed to completion in one direction, and all the carbon monoxide will ultimately be converted into CO_2. If it is not removed, then, since the equilibrium concentration of CO_2 is very small, no appreciable amount of the monoxide is converted into the dioxide. On the other hand, the equilibrium concentration of the solid products is greater, and much of the gas is converted into them ; but since they are not effectively removed from the scene of action, but remain on the walls and electrodes, where they are still influenced by the discharge, the production of these products does not proceed beyond the equilibrium concentration ; and if the removal of CO_2 is resumed, these products are decomposed once more and the ultimate complete conversion into CO_2 is again attained.

Nor is there anything extravagant in supposing that such reversible reactions are proceeding concurrently ; for the evidence of positive ray analysis has shown that, when a molecule is ionized, there are usually or always produced free atoms of all the elements contained in it, bearing electrical charges of both signs. Accordingly in an ionized gas there are always present positively and negatively charged atoms of all the elements on the scene of action. In these circumstances it is only reasonable to suppose that there will be formed in some quantity any chemical compound that can be formed from any grouping of those elements ; some of the compounds may be formed in very small amount, and all of them, like the original compounds, will be broken up again after a short life. But this is precisely what is asserted when it is said that several reversible reactions are proceeding in the gas. If the discharge, when accompanied by any appreciable ionization of the gas, produces any chemical changes whatever, the changes that are produced would be expected to be precisely of the nature that is necessary to explain the observations which have been described.

The only objection to this view that can be suggested is that if ionization is all that is necessary to cause these actions to proceed, the gas should disappear before the glow discharge starts ; for, as has been insisted already, there is ionization before the glow. But the difference may be merely one of degree * ; the actions may proceed before the glow, but so slowly that they are inappreciable. For, in order that the compounds may be formed, the charged atoms, which are a small fraction of the ionized molecules, have to meet. If n of them have to meet to form the compound, the rate of the reaction will vary as the nth power of the concentration of the ions. The greater concentration of the ions in the glow discharge would account for the far greater rate of chemical combination. Indeed, in order that the view offered should explain the facts, it is necessary to suppose that the actions do proceed to some extent even when there is no glow ; for the conversion into carbon dioxide of the gas originally disappearing, when the tube A was warm, is effected by the continuance of the discharge at a pressure too low for the applied voltage to cause the glow. We must suppose that this discharge, in which the thermionic current is very much greater than the ionization current, is capable of causing the reaction to proceed, and of maintaining the change whereby the solid products are converted reversibly into CO_2, which is condensed in the liquid air. The reaction proceeds at an appreciable rate because a high potential can be applied ; at higher pressures it is not possible to apply so high a potential without causing the glow.

Two further observations may be quoted in support of the view that the chemical actions involved are essentially reversible :—First, if, after the gas has been rest red to the lamp in the form of CO_2 by warming the previously cooled tube A, the discharge is passed (of course, with A warm), its first effect is to increase and not decrease the pressure ; it is only after the discharge has lasted some time that the pressure begins to decrease again. The increase of pressure doubtless represents the conversion of the CO_2 back into CO and the tendency towards the equilibrium concentration. Second, the rate at which the gas disappears in the presence

* If (the hypothesis is not thought probable) the glow represents the incoming of some new form of ionization, it is just possible that it is only this form of ionization which is effective in inducing chemical changes. But the idea is not plausible, for many lines of argument—especially that based on work on " delta rays "—show that the ionization of a molecule is of the same nature by whatever agent it is effected.

of a cooled tube depends very greatly on the ease of access to that tube. If A is cooled, the rate of disappearance in given electrical conditions is much greater than if T is cooled (actually T was separated from the lamp by about 40 cm. of tubing); and if the tube between the lamp and T is constricted, then (with A warm) the rate of disappearance is very much decreased. The rate of resultant reaction depends on the rate of removal of the product. It is because the rate of disappearance depends so intimately on the ease of access to liquid air that it is difficult to interpret at present the observations on the relation of that rate to the electrical conditions and that it is useless to give them in detail. In order to study this relation, conditions must be found in which this complicating factor is not present.

Summary.

1. The research is an attempt to determine the nature and cause of the disappearance of gas under the electric discharge at low pressure.

2. A brief summary of previous knowledge is given. It is not yet known what parts are played by absorption on the walls and by true chemical combination; nor is it known precisely what electrical conditions are most favourable to the disappearance.

3. Though an incandescent tungsten filament forms part of the discharge vessel, the changes investigated are not those studied with great care by Langmuir.

4. The apparatus is described.

5. Preliminary observations showed that the disappearance of gas was closely connected with the appearance of the glow in the vessel. The electrical conditions in which the glow appears are described briefly. In any given state of the discharge vessel it appears sharply at a definite potential difference between the electrodes, called the glow potential.

6. Observations are described on the relation between the glow potential and (1) the thermionic emission, (2) the pressure of the gas, (3) nature of the gas, (4) the form of electrodes.

7. Small amounts of impurities change very greatly the glow potential, especially in hydrogen.

8. The theory of the glow is deferred for later discussion; but the general connexion between the appearance of the glow and the increase of ionization in the gas is considered.

9. The great importance of the glow potential for interpreting the rate of disappearance of gas is pointed out.

10. Experiments on the disappearance of carbon monoxide in the glow discharge are described.

11. The results are discussed and explained by supposing that the glow causes a chemical change in the gas, which is reversible. The recognition of this reversibility seems necessary to explain the phenomena. The disappearance of other gases, illustrating other types of action, will be discussed in the sequel.

Research Laboratories of the General Electric Co., Ltd.,
      Hammersmith.
  April 16, 1920.

LXX. *Triple Pendulums with Mutual Interaction and the Analogous Electrical Circuits.*—I. *By* Prof. E. H. Barton, *F.R.S., and* H. M. Browning, *M.Sc.*[*]

[Plates XI.–XIII.]

I. Introduction.

MECHANICAL analogies to two circuits coupled together have been used to show the type of vibrations set up by the latter. (See " Coupled Vibrations," Phil. Mag. Oct. 1917, Jan. 1918 and July 1918.)

The mathematical theory of these circuits is comparatively simple, but the visual results of the mechanical analogy tend to elucidate and interpret the theory.

In the case of three circuits or three pendulums which are arranged to act on one another, the theory is more complicated, although in certain cases it can be resolved into a somewhat simpler form.

The experiments were carried out with a modified form of the apparatus shown in figs. 1 and 2 of " Vibrations under Variable Couplings " (Phil. Mag. Oct. 1917), and fig. 13, Plate V. " Coupled Vibrations " (Phil. Mag. July 1918). An extra bridle and pendulum were added, and three connectors substituted for the single one, each of the three connecting two of the pendulums. Later it was thought that two connectors were sufficient, and the apparatus was modified to obtain a result which might be more amenable to analytical treatment.

From the mathematical theory of three circuits coupled each to the other two, it was expected that the mechanical arrangement would give for each pendulum three superposed

vibrations. The periods of these vibrations were expected to be the same for each pendulum. The phases and amplitudes might, however, differ for each pendulum, thus giving very different resultant vibrations.

The results obtained with the first form of apparatus were even more complicated than was expected from three superposed vibrations, and on reflection this was seen to be due to the special arrangement in use. So it is proposed in this paper to describe this apparatus and give the figures obtained without dealing with its mechanical theory.

Results obtained with a modified apparatus will be dealt with later.

II. Theory of Three Mutually-interacting Electric Circuits.

The electric circuits are supposed to have self and mutual inductances, and capacities with resistances negligible.

Let L_1, L_2, L_3 be the self-inductances of the separate circuits, S_1, S_2, S_3 their capacities, and M_1, M_2, M_3 the mutual inductances between the second and third, the third and first, and the first and second circuits respectively. Then the simultaneous equations of motion may be written as follows:—

$$L_1 \frac{d^2x}{dt^2} + \frac{x}{S_1} = M_3 \frac{d^2y}{dt^2} + M_2 \frac{d^2z}{dt^2}, \quad . \quad . \quad . \quad (1)$$

$$L_2 \frac{d^2y}{dt^2} + \frac{y}{S_2} = M_1 \frac{d^2z}{dt^2} + M_3 \frac{d^2x}{dt^2}, \quad . \quad . \quad . \quad (2)$$

$$L_3 \frac{d^2z}{dt^2} + \frac{z}{S_3} = M_2 \frac{d^2x}{dt^2} + M_1 \frac{d^2y}{dt^2}, \quad . \quad . \quad . \quad (3)$$

where x, y, and z are the charges on the respective condensers.

The three couplings are given by

$$\begin{aligned}
\text{coupling } y \text{ to } z, \quad & \alpha^2 = \frac{M_1^2}{L_2 L_3}, \\
\text{,,} \quad z \text{ to } x, \quad & \beta^2 = \frac{M_2^2}{L_3 L_1}, \\
\text{,,} \quad x \text{ to } y, \quad & \gamma^2 = \frac{M_3^2}{L_1 L_2},
\end{aligned} \right\} \quad . \quad . \quad (4)$$

Suppose as solution that

$$\left. \begin{aligned}
x &= A e^{pit}, \\
y &= B e^{pit}, \\
z &= C e^{pit}.
\end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substituting these in (1), (2), and (3), we obtain

$$\left(\frac{1}{S_1} - L_1 p^2\right)x + p^2 M_3 y + p^2 M_2 z = 0,$$
$$p^2 M_3 x + \left(\frac{1}{S_2} - L_2 p^2\right)y + p^2 M_1 z = 0, \quad \Bigg\} \quad . \quad . \quad (6)$$
$$p^2 M_2 x + p^2 M_1 y + \left(\frac{1}{S_3} - L_3 p^2\right)z = 0.$$

Eliminating x, y, and z from (6) by the method of determinants, we have

$$\begin{vmatrix} \left(\dfrac{1}{S_1} - L_1 p^2\right), & p^2 M_3, & p^2 M_2, \\[2mm] p^2 M_3, & \left(\dfrac{1}{S_2} - L_2 p^2\right), & p^2 M_1, \\[2mm] p^2 M_2, & p^2 M_1, & \left(\dfrac{1}{S_3} - L_3 p^2\right). \end{vmatrix} = 0. \quad . \quad . (7)$$

This gives an equation of the sixth degree in p, viz.:—

$$p^6 \left[2 M_1 M_2 M_3 - L_1 L_2 L_3 + L_1 M_1^2 + L_2 M_2^2 + L_3 M_3^2\right]$$
$$+ p^4 \left[\frac{L_2 L_3 - M_1^2}{S_1} + \frac{L_3 L_1 - M_2^2}{S_2} + \frac{L_1 L_2 - M_3^2}{S_3}\right]$$
$$- p^2 \left[\frac{L_1}{S_2 S_3} + \frac{L_2}{S_3 S_1} + \frac{L_3}{S_1 S_2}\right] + \frac{1}{S_1 S_2 S_3} = 0. \quad . \quad . \quad (8)$$

This is a cubic equation in p^2, of which the roots may be written, $p^2 = p_1^2,\ p_2^2,\ p_3^2$.

Then $p = \pm p_1, \qquad \pm p_2, \qquad \pm p_3$;

but the negative signs may be disregarded as they introduce nothing new.

Hence vibrations of three periods are set up.

Thus the general solution of the equations may be written

$$x = E_1 \sin(p_1 t + \epsilon_1) + F_1 \sin(p_2 t + \phi_1) + G_1 \sin(p_3 t + \chi_1), \quad (9)$$

and similar equations for y and z.

If the circuits were vibrating each isolated from the others, then their vibrations would be proportional to

$$\sin lt, \qquad \sin mt, \quad \text{and} \quad \sin nt, \quad . \quad . \quad (10)$$

where

$$l^2 = \frac{1}{L_1 S_1},$$
$$m^2 = \frac{1}{L_2 S_2}, \quad \Bigg\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$
$$n^2 = \frac{1}{L_3 S_3},$$

Then using equations (4) and (11), equation (8) may be written

$$p^6(1-\alpha^2-\beta^2-\gamma^2-2\alpha\beta\gamma)-p^4[l^2(1-\alpha^2)+m^2(1-\beta^2)$$
$$+n^2(1-\gamma^2)]+p^2(l^2m^2+m^2n^2+n^2l^2)-l^2m^2n^2=0.. \quad (12)$$

Thus it is seen that in general the vibrations after coupling the circuits differ from the free vibrations of the separate systems.

The less the coupling the more nearly do the superposed vibrations approximate to those of the systems when free.

III. ARRANGEMENT OF THREE CONNECTED PENDULUMS.

The apparatus shown in fig. 13, Plate V. " Coupled Vibrations " (Phil. Mag. July 1918) was adapted for the tripled pendulums. Figs. 1 and 2 give the side and end elevations

Fig. 1.—Side elevation.
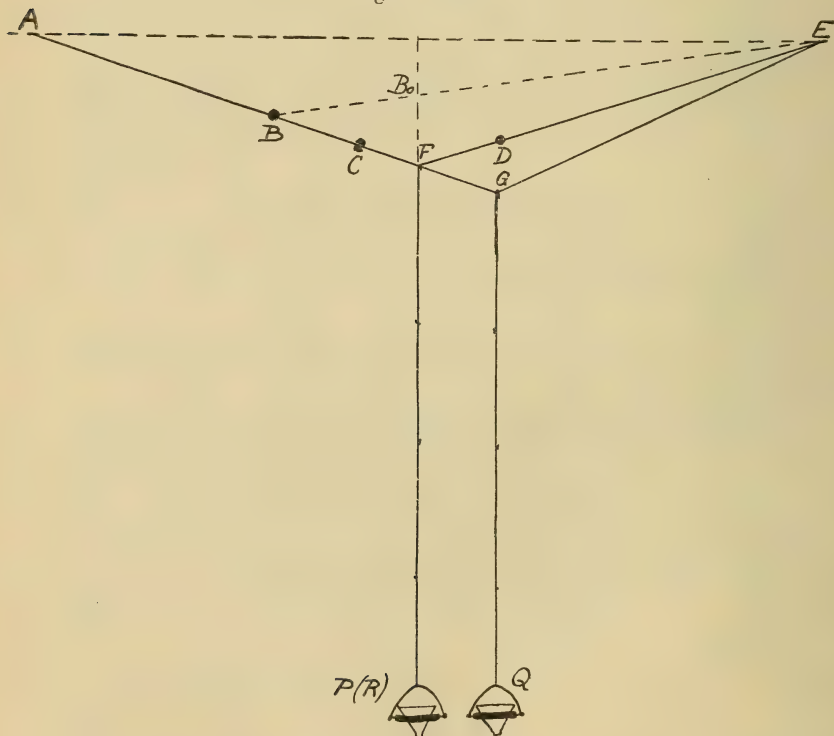
of the actual arrangement used. The masses are confined as far as possible to the bobs P, Q, and R, which are heavy carriers with funnels containing sand.

In fig. 1 only two pendulums are visible, the third is hidden by FP. The positions of the bridles are determined by the three light connectors BB', CC', and DD'.

The normal oscillations occur in the plane of fig. 2, and are recorded by sand traces on a black-board drawn perpendicular to the direction of vibration.

Fig. 2.—End elevation.
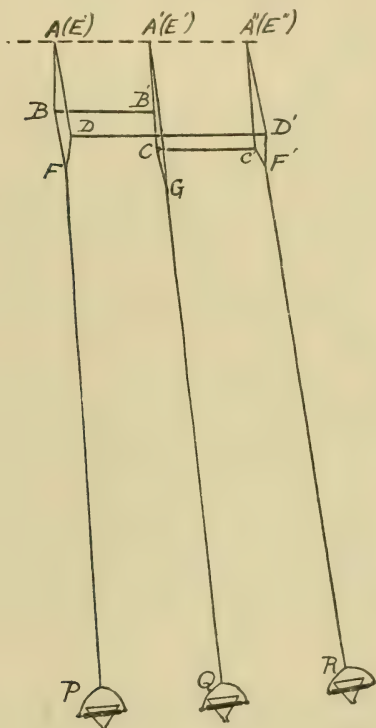
The trace from Q is received on a narrow black-board. The pendulums are started when all the bobs are just above the boards, and afterwards the board containing the trace from Q is moved until the three initial motions, shown by the traces, are in the same straight line.

If the advantages and disadvantages of this arrangement are considered, it is seen :—

(1) That although the three connectors make for generality, yet if DD' is eliminated, the action of the pendulum-bob

P may still be transmitted through the connectors BB′ and CC′ to the pendulum-bob R. Further, the connector DD′ may tend to force in extra vibrations, so that four, or more vibrations may be felt by each bob.

(2) That the bridle droop being different for one pendulum may also complicate matters.

The bridle droops do not enter into these experiments in exactly the same way as in those of the Double-Cord Pendulums, " Coupled Vibrations " (Phil. Mag. Oct. 1917); for in that the bridle droop directly determined the length of the oscillating pendulums.

Suppose the pendulum P is considered, and the one connector at BB′. Then the two oscillations possible to this pendulum, if others are not forced upon it, are :—

(*a*) One about AE ;

(*b*) One about BE if B is held stationary. Now if the bridle AFE is altered, but the connector B is so adjusted that BE makes the same angle with the horizontal, then the period of the oscillation of the pendulum about this position is unaffected. For small oscillations, the effective length would be found by producing PF upwards until it met the line joining BE in B_0.

For this arrangement it is not easy to write down definite values for the couplings. However, from general considerations, it is seen that, if BB′ and CC′ are near AA″, and DD′ to EE″, the couplings will all be small. The coupling between two only will be large if those are connected near F, and the others near A or E.

The early experiments were done with the apparatus as described. Later the connector CC′ was removed, and results obtained for certain couplings were found to be similar to those obtained when using three connectors.

IV. Photographic Records of Vibrations.

Nine photographs of traces were taken with the three connectors in use (Pls. XI. & XII.). Six others with only the two connectors BB′ and CC′, but otherwise the same arrangement (Pl. XIII.)

For details of the lengths mentioned in the table reference must be made to figures 1 and 2. The masses of the bobs in these experiments were all the same and equal to 660 gms. In all the experiments the total depth of the bobs below AE was kept constant and equal to 140 cms. The distance between AE was 180 cms. The positions of B, C, D, F, and G will now determine the whole of the system.

Table of Experimental Details.

	Photograph Letter.	Length AB.	Length A'C.	Length AF.	Length A'G.	Length FE.	Length DE.
		cm.	cm.	cm.	cm.	cm.	cm.
Using Three Connectors.	A	52	71	84	100	98	81
	B and B₂...	52	71	84	100	98	45
	C	18	71	84	100	98	92
	D and E ...	18	71	86	100	106	68
	F, G, and H	18	71	86	100	106	30
Using Two Connectors.	I	18	71	86	100	106	
	J	32	75	86	100	106	
	K and L...	31	31	86	100	106	
	M and N...	41	41	86	100	106	

The table indicates that for photograph A (Pl. XI.), the coupling due to the bridle droop is small, but, for this droop, that due to the connectors is large. The vibrations were produced by drawing aside the pendulum P at the point F. The traces from the three bobs P, Q, and R all show that there are more than two simple harmonic motions combining to produce the curves.

For the photographs B and B_2 the coupling is still less between the pendulums P and R. This is shown both in the table and in the traces. For photograph B the pendulums were started by drawing Q aside at G, and for B_2 by drawing P aside at F. The trace of P in photograph B does not indicate more than two simple harmonic vibrations, nor are the traces in photograph B_2 very striking.

For photograph C, the coupling between the pendulums P and R was considerably increased, but that between P and Q was decreased. The resultant effect was to materially increase all the couplings as P acted on Q by means of the connectors DD' and CC', which were both tightly coupled. All these traces can be seen to contain more than two simple harmonic motions.

For the photographs D to H inclusive the droop of the bridle was increased. For traces shown on photographs D and E, the couplings between all the pendulums due to the position of the connectors were decreased, but this was compensated by the increased droop. With P pulled aside (see D), the traces from P and Q only appear to be the resultant of two simple harmonic vibrations, but the beats in R are slower on reaching their maximum than in falling to their minimum. All the traces with Q pushed aside (see E) show more complicated curves. These could be obtained by compounding three simple harmonic vibrations of the proper phase and amplitude.

For F, G, and H (Pl. XII.), the coupling between pendulums P and R was decreased by moving the connector DD′ nearer to E. The curves are very similar, F was obtained with Q pushed aside, and G with R pushed aside. From the photographs it is seen that the couplings are small between P and each of the other pendulums, but that between Q and R is very much larger. The interaction between the pendulums Q and R does not seem to be communicated to P at all, although the reaction of the slow waxing and waning of the amplitude of P is clearly seen in the traces of both the other pendulums.

Photograph H was obtained with an arrangement of pendulums like those used for F and G. R was started and after three complete cycles of change was held stationary; the pendulum then settled quickly to a state showing two superposed simple harmonic vibrations, as in coupled pendulums.

At this point it was thought probable that the two connectors B and C would be sufficient. D was removed. Everything else was kept the same. The photograph I (Pl. XIII.) shows traces with the couplings between P and each of the other pendulums considerably reduced, but other things much the same.

The connectors were then lowered considerably, and curve J was obtained by drawing aside R. This was found to be almost identical with G, which shows that connector D was superfluous.

Photographs K and L were obtained with the two connectors at the same position on the cords. The photographs show which bobs were drawn aside, and the resultant effect was that of a light bob driving one heavy bob which is composed of the other two. There is little to indicate more than two harmonic vibrations in the curves.

M and N were obtained with the connectors together on the cords, but with the coupling increased. Studying the four last photographs carefully, it is seen that the two pendulums which are the driven ones to begin with do not give exactly identical curves, the distance between the nodes is gradually increasing. This points to the fact that there are more than two simple harmonic vibrations involved.

Other experiments have already been carried out with a simpler arrangement of three interconnected pendulums, but these are reserved for a separate paper.

Nottingham, July 14, 1920.

LXXI. *On the Deduction of Rydberg's Law from the Quantum Theory of Spectral Emission. By* Satyendra Nath Basu, *M.Sc., University Lecturer in Physics, University College of Science, Calcutta* *.

IT is well known that Rutherford's model of the atom has been fruitful in explaining many facts connected with atomic radiation. In the simplest case of hydrogen, with a nucleus consisting of a single positive charge, and an electron, Dr. Bohr † has successfully applied the quantum theory to explain the Balmer series of hydrogen spectra. The mathematical problem of finding the spectral series for any atomic system has since been clearly formulated by Sommerfeld ‡, and the quanta condition has been generalized in a form suitable for systems with any number of degrees of freedom. If q_1, q_2, q_3, ... q_n are co-ordinates to fix the position of the electron responsible for emission, and p_1, p_2, p_3, ... p_n are the corresponding generalized momenta, any statical path, according to Sommerfeld, is characterized by the conditions $\int p_1 dq_1 = n_1 h$, $\int p_2 dq_2 = n_2 h$, $\int p_n dq_n = n_r h$, where n's are whole numbers and h is Planck's constant, the integral being extended generally over the complete orbit. The radiation is supposed to take place when the electron jumps from one statical path to another. The difference in energy, at the same time, flows away in the form of a homogeneous radiation of frequency ν, which can be calculated from the Bohr's equation $h\nu = W_1 - W_2$. Sommerfeld has successfully applied this conception in explaining the fine structure of hydrogen lines. It is clear, however, that the problem of theoretically calculating the spectrum of any atom other than hydrogen is beset with difficulties of a formidable nature. It is exactly analogous to the dynamical problem of " n " bodies, where only in favourable cases we are able to find approximate solutions. Nevertheless, from a purely experimental standpoint, we know that the visible radiation from any element can be classified in definite series. The frequency of any line in the series can be expressed as a difference of two terms, each of which has the form $\dfrac{N}{\left(m + \alpha + \dfrac{\beta}{m^2}\right)^2}$, where m is a whole number and α and β are two constants

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depending upon the element and the nature of the series. So that if we are to explain the formation of the series from theoretical considerations following Bohr and Sommerfeld, we must look upon each member multiplied by "h" as giving the energy of the atomic system when the radiating electron moves in a definite statical path. The complexity of the inner atomic field under which the radiating electron moves is to be looked upon as bringing in the terms involving α and β. So it seems interesting to see what will be the corresponding expression for energy in a system by which the complex nature of the internal field may be approximately represented. In the case of any atom we have, in general, a condensed nuclear charge of $+ne$ (where n is the atomic number) surrounded by rings of electron at different distances. The number of electrons in total must be also equal to n in order to secure that the atom is electrically neutral in the ordinary state.

In X-ray emission the electron displaced comes from the inner rings; in the case of visible radiation, however, we have reasons to think that the displaced electron responsible for radiation comes from the outermost ring—the valency electrons, as they have been designated by Sommerfeld. When excited for radiation, we can suppose that the electron in the outermost ring is removed to a greater distance from the centre than the others, so that the force acting upon it may be regarded as the resultant of the various forces exerted by the central charge and the remaining electrons. The potential at any point can be regarded as given by $-\dfrac{ne^2}{r}+e^2 \sum\limits_{s=n-1} \dfrac{1}{r_s}$, where r is the distance from the centre and r_s is the distance from the s-th electron. If we neglect the influence of the moving electron upon the arrangement of the others surrounding the nucleus, it is clear that the potential can be approximately represented as $-\dfrac{e^2}{r} + \dfrac{\mathrm{L}\cos\theta}{r^2}$. The resultant field might be looked upon as due to a single positive charge, together with a doublet of strength L in a certain fixed direction, which we take as our Z-axis. If we neglect the disturbing effect of the outer electron, L may be taken to be approximately fixed in direction and in magnitude in the small interval of time during which the active emission takes place.

We may, therefore, take as our model a system consisting of a positive charge and a doublet of strength L. We proceed to calculate the energy in a statical path on the above simplified hypothesis.

The kinetic energy of the moving electron is obviously

$$T = \tfrac{1}{2}[m\dot{r}^2 + mr^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2];$$

the potential energy

$$V = -\frac{e^2}{r} + \frac{eL\cos\theta}{r^2}.$$

Two integrals can be at once written down :

$$mr^2\sin^2\theta\dot{\phi} = c_1,$$

$$m[\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2] - \frac{2e^2}{r} + \frac{2Le\cos\theta}{r^2} = -W.$$

To get another integral, we write

$$\frac{d}{dt}(mr^2\dot{\theta}) - mr^2\sin\theta\cos\theta\dot{\phi}^2 = \frac{eL\sin\theta}{r^2},$$

or

$$mr^3\dot{\theta}\frac{d}{d\theta}(mr^2\dot{\theta}) - \frac{c_1^2\cos\theta}{\sin^3\theta} - meL\sin\theta = 0.$$

Integrated, it gives

$$(mr^2\dot{\theta})^2 + \frac{c_1^2}{\sin^2\theta} + 2meL\cos\theta = c_2.$$

The expressions for three impulses $m\dot{r}$, $mr^2\dot{\theta}$, and $mr^2\sin^2\theta\dot{\phi}$ can now be written down : in terms of the constants of integration we have

$$mr^2\sin^2\theta\dot{\phi} = c_1,$$

$$mr^2\dot{\theta} = \sqrt{c_2 - \frac{c_1^2}{\sin^2\theta} - 2meL\cos\theta},$$

$$m\dot{r} = \frac{1}{r}\sqrt{-Wmr^2 + 2me^2r - c_2}.$$

The quanta conditions can be written down as

$$\int mr^2\sin^2\theta\dot{\phi}\,d\phi = n_1 h, \quad \cdots \quad (1)$$

$$\int mr^2\dot{\theta}\,d\theta \quad\quad = n_2 h, \quad \cdots \quad (2)$$

$$\int m\dot{r}\,dr \quad\quad\quad = n_3 h, \quad \cdots \quad (3)$$

$-W$ being twice the total energy of the system. The integrals are to be extended over the whole range within which the expression within the square root remains positive.

The integration.

From (1) we have obviously

$$c_1 = \frac{n_1 h}{2\pi} \;;$$

of the two remaining expressions, (3) can be integrated most easily : in fact,

$$n_3 h = \int \frac{1}{r} \sqrt{-\mathrm{W} m r^2 + 2me^2 r - c_2}\, dr$$

gives after integration

$$n_3 h = 2\pi \left[e^2 \left(\frac{m}{\mathrm{W}} \right)^{1/2} - c_2^{1/2} \right].$$

The second integral can be written as

$$\frac{n_2 h}{2} = \mathrm{I} = \int \sqrt{(c_2 - c_1^2) - c_2 x^2 - 2me\mathrm{L}x(1-x^2)}\, \frac{dx}{1-x^2}$$

by putting $\cos\theta = x$.

The right-hand side is to be integrated throughout the region, when the cubic remains positive. It cannot be integrated in finite terms; an approximation suitable for our purpose can, however, be made, assuming $2me\mathrm{L}$ to be small compared with $(c_2 - c_1^2) = \mathrm{A}$. To see what this means we are to remember that $c_2 - c_1^2$ is of the dimension of h^2; so that $2me\mathrm{L}$ must be small compared with h^2, or L must be small compared with $\dfrac{h^2}{me}$. Now, if α, $-\beta$, and γ are taken as the three roots of the cubic, the cubic can be written down as

$$\mathrm{D}(\gamma - x)(\alpha - x)(x + \beta),$$

where γ is the greatest of the positive roots and $\mathrm{D} = 2me\mathrm{L}$. The limits of the integral are obviously α and $-\beta$,

$$\mathrm{I} = \int_{-\beta}^{\alpha} \sqrt{\mathrm{A} - c_2 x^2 - \mathrm{D}x(1-x^2)}\, \frac{dx}{1-x^2}.$$

Hence

$$\frac{\partial \mathrm{I}}{\partial \mathrm{D}} = \frac{1}{2} \int_{-\beta}^{\alpha} \frac{-x\, dx}{\sqrt{\mathrm{D}}\left[(\gamma - x)(\alpha - x)(x + \beta) \right]^{1/2}},$$

or

$$\frac{\partial \mathrm{I}}{\partial \mathrm{D}} = \frac{1}{2\sqrt{\mathrm{D}}} \left[\int_{-\beta}^{\alpha} \frac{(\gamma - x)^{1/2}\, dx}{(\alpha - x)^{1/2}(\beta + x)^{1/2}} \right.$$
$$\left. - \gamma \int_{-\beta}^{\alpha} \frac{dx}{(\gamma - x)^{1/2}(\alpha - x)^{1/2}(x + \beta)^{1/2}} \right].$$

Supposing

$$\alpha - x = (\alpha + \beta)\cos^2\theta,$$
$$\beta + x = (\alpha + \beta)\sin^2\theta,$$

we get

$$\frac{\partial I}{\partial D} = \frac{1}{2\sqrt{D}}\left[2\int_0^{\pi/2}[\gamma + \beta - (\alpha + \beta)\sin^2\theta]^{1/2}d\theta\right.$$
$$\left. - 2\gamma\int_0^{\pi/2}\frac{d\theta}{[(\gamma + \beta) - (\alpha + \beta)\sin^2\theta]^{1/2}}\right]$$
$$= \frac{1}{2\sqrt{D}}\left[(\gamma + \beta)^{1/2}E\left(\frac{\pi}{2}, \sqrt{\frac{\alpha + \beta}{\gamma + \beta}}\right)\right.$$
$$\left. - \frac{\gamma}{(\gamma + \beta)^{1/2}}K\left(\frac{\pi}{2}, \sqrt{\frac{\alpha + \beta}{\gamma + \beta}}\right)\right],$$

where E and K are the usual elliptic integrals, defined by

$$E(\pi/2, k) = \int_0^{\pi/2}\sqrt{1 - k^2\sin^2\theta}\,d\theta,$$
$$K(\pi/2, k) = \int_0^{\pi/2}\frac{d\theta}{\sqrt{1 - k^2\sin^2\theta}}.$$

On the assumption that D is small, we have

$$\gamma = \frac{c_2}{D} + \frac{D(c_2 - A)}{c_2^2},$$
$$a = \sqrt{\frac{A}{c_2}} - \frac{D}{2c_2^2}(c_2 - A),$$
$$\beta = \sqrt{\frac{A}{c_2}} + \frac{D}{2c_2^2}(c_2 - A).$$

So that, expanding E and K and making necessary approximations, we have finally

$$\frac{\partial I}{\partial D} = \frac{\pi D}{4c_2^{5/2}}\left[c_2 - \frac{3A}{2}\right].$$

Also

$$I = \int\sqrt{(c_2 - c_1^2) - c_2 x^2}\,\frac{dx}{1 - x^2} = \pi[c_2^{1/2} - c_1].$$

So that we have

$$\frac{n_2 h}{2} = \pi(c_2^{1/2} - c_1) + \frac{\pi}{16}\frac{(2me L)^2}{c_2^{5/2}}(3c_1^2 - c_2).$$

Now, collecting all the quanta conditions, we have

$$c_1 = \frac{n_1 h}{2\pi},$$

$$c_2^{1/2} - c_1 + \frac{(meL)^2}{4c_2^{5/2}}(3c_1^2 - c_2) = \frac{n_2 h}{2\pi},$$

$$e^2\left(\frac{m}{W}\right)^{1/2} - c_2^{1/2} = \frac{n_3 h}{2\pi}.$$

So that we have

$$c_2^{1/2} + \frac{(meL)^2}{4c_2^{5/2}}\left(\frac{3n_1 h_1^2}{4\pi^2} - c_2\right) = \frac{(n_1 + n_2)h}{2\pi}$$

and

$$e^2\left(\frac{m}{W}\right)^{1/2} = \frac{n_3 h}{2\pi} + c_2^{1/2}.$$

Assuming

$$c_2^{1/2} = \frac{yh}{2\pi},$$

we have

$$\frac{yh}{2\pi} + \frac{(meL)^2(2\pi)^5}{4y^5 h^5}\left[\frac{3n_1^2 h^2}{4\pi^2} - \frac{y^2 h^2}{4\pi^2}\right] = \frac{(n_1 + n_2)h}{2\pi},$$

or

$$y + \left(\frac{2\pi^2 meL}{h^2}\right)^2 \frac{1}{y^5}(3n_1^2 - y^2) = n_1 + n_2.$$

Calling

$$\left(\frac{2\pi^2 meL}{h^2}\right)^2 = \alpha,$$

we have

$$e^2\left(\frac{m}{W}\right)^{1/2} = \frac{h}{2\pi}(n_3 + y),$$

where

$$y + \frac{\alpha}{y^5}(3n_1^2 - y^2) = n_1 + n_2 ;$$

we have approximately

$$y = (n_1 + n_2) + \frac{\alpha}{(n_1 + n_2)^3}\left[1 - \frac{3n_1^2}{(n_1 + n_2)^2}\right].$$

So that

$$W = \frac{4\pi^2 e^4 m}{h^2\left[n_1 + n_2 + n_3 + \frac{\alpha}{(n_1 + n_2)^3}\left(1 - \frac{3n_1^2}{(n_1 + n_2)^2}\right)\right]^2}.$$

So that the energy in the statical path

$$= -\frac{2\pi^2 e^4 m}{h^2\left[n_1 + n_2 + n_3 + \frac{\alpha}{(n_1 + n_2)^3}\left(1 - \frac{3n_1^2}{(n_1 + n_2)^2}\right)\right]^2}.$$

If we suppose that the spectrum is due to ionized atoms in which the field can be approximately represented as a central charge of $E = pe$ and a doublet of different strength L'.

We have, by a similar reasoning, energy in a statical path

$$= -\frac{2\pi^2}{h^2} \frac{e^2 E^2 m}{\left\{ n_1 + n_2 + n_3 + \dfrac{\alpha'}{(n_1 + n_2)^3}\left(1 - \dfrac{3n_1^2}{(n_1 + n_2)^2}\right) \right\}^2}$$

$$= \frac{-p^2 N h}{\left\{ n_1 + n_2 + n_3 + \dfrac{\alpha'}{(n_1 + n_2)^3}\left(1 - \dfrac{3n_1^2}{(n_1 + n_2)^2}\right) \right\}^2},$$

where $N = $ Rydberg number.

As a result of numerous investigations on the nature of the spectral series, it has been shown that for many elements the different series can be grouped according to the following scheme :—

P- Series :
$$\nu = (1\cdot 5, s) - (m, p_1) \atop - (m, p_2)} \quad m = 2, 3, 4 \ldots.$$

II. Subordinate Series :
$$\nu = (2, p_1) - (m + \cdot 5, s)$$
$$\nu = (2, p_2) - (m + \cdot 5, s) \quad m = 2, 3, 4 \ldots.$$

1st Subordinate Series :
$$\nu = (2, p_1) - (m, d).$$

Companion :
$$\nu = (2, p_1) - (m, d') \quad m = 3, 4, 5.$$
$$\nu = (2, p_2) - (m, d'').$$

Symbol (m, f) stands for $\dfrac{N}{(m + f)^2}$ according to Rydberg, and $\dfrac{N}{\left(m + f + \dfrac{\phi}{m^2}\right)^2}$ according to Ritz.

The frequency of the lines emitted thus appears as the difference of two terms, each of which is to be regarded as corresponding to the energy in a definite statical path, on the Quantum theory. Sommerfeld [*] has recently given reasons for assuming that in any series of statical orbits corresponding to the different kinds of s, p, and d terms the azimuthal quanta generally preserve a certain definite

[*] Sommerfeld, *Verh. d. Phys. Ges.* May 1919.

value, whereas the radial quanta can have all values from 0 to ∞; he thus shows that in s, p, and d terms the azimuthal quanta generally have values 1, 2, and 3 respectively.

Making the above assumptions in our formula, we see that the expression of the energy comes out as $-\dfrac{Nh}{(n_1 + n_2 + n_3 + A)^2}$ in the same form as required by the Rydberg formula. The constant A, however, depends only upon n_1 and n_2; it diminishes for increasing values of the azimuthal quanta; so that they decrease progressively in the s, p, and d terms. Moreover, our form shows that A depends upon n_1 and n_2 separately, so that for the same value of $n_1 + n_2$ we may have different values of the constant. Thus, if we suppose $n_1 + n_2 = 1$, we have two values corresponding to the values 1, 0 and 0, 1; for $n_1 + n_2 = 2$ we have three values; and so on. Thus we see, even on Sommerfeld's assumption, for the constancy of the azimuthal quanta we shall have two different s, three different p, four different d terms. At least two different values of p and three different values of d seem to be required by the series formula, which is essential for the explanation of doublets and triplets of constant frequency difference [*]. We thus see that our model serves at least as a qualitative explanation of the following facts :—

(1) The progressive decrease of the characteristic numbers in the s, p, and d terms.

(2) The existence of different sets of s, p, and d terms for the same element.

It is clear, however, that our simplified assumption will not fit in any actual case exactly. The complex nature of the internal field can in no case be properly represented by a simple term, $\dfrac{L \cos \theta}{r^2}$, in the Potential. Moreover, we have reason to believe that the internal arrangement of the electrons itself will be influenced, in a large measure, by the motion of the outer electron, which we have neglected in our formula. In fact, Landé [†] has tried in a recent paper to take account of this disturbance in the comparative simple case of the helium series. But at the same time, it is hoped that the calculation, in this comparatively simple

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[*] If we exclude the case $n_2 = 0$—*i. e.*, if we assume that the motion in a plane containing the axis of the doublet is excluded—we get the proper number of s, p, and d terms as observed in the case of the alkali metals and the doublet system of alkaline earths.

[†] Landé, *Phys. Zeit.* 1919.

case, will serve to illustrate at least some general principles at which we have arrived by an experimental study of the spectral series.

Summary.

In this paper an attempt has been made to deduce the laws of regularity in the spectral series of elements on the basis of Bohr's quantum theory of spectral emission. Starting from Sommerfeld's assumption that the ordinary line-spectra of elements are due to the vibration of one outer electron (the valency electron), it has been shown that the field of the nucleus and the remaining $(n-1)$ electrons may be represented by the Potential $V = -\dfrac{e^2}{r} + \dfrac{eL \cos \theta}{r^2}$: *i.e.*, the field due to a single charge plus a doublet of strength L. The axis of the doublet is variable, but the emission is supposed to take place so quickly that in that short time the axis does not appreciably change.

The quanta conditions have been applied according to Sommerfeld's rule, $nh = \int p_i dq_i$, and the energy of the system has been reduced to the quanta numbers. The energy comes out in the form

$$W = -\frac{Nh}{(n + n_3 + z)^2}, \quad n + z = y \text{ in the paper,}$$

where n_3 is the radial quantum, n is the azimuthal quantum, and z is given by an equation of the sixth degree, involving only the azimuthal quantum, and is a function of n only.

It has been next shown that if, in accordance with Sommerfeld's principle, we assume $n=1$ for the s-orbits, $n=2$ for the p-orbits, $n=3$ for the d-orbits, $n=4$ for the b-orbits, then, with a very simple assumption, we obtain a single value for the energy of the s-orbits, a double value for the energy in the p-orbit, a treble value for the d-orbit. Then, applying Bohr's law $h\nu = W_n - W_{n'}$, we arrive at Rydberg's laws of the regularity in spectral series, in the case of the alkali metals.

Exact calculations are not tried on account of the uncertainty of the value of L; but it has been pointed out that the values of s, (p_1, p_2), (d_1, d_2, d_3) progressively decrease, as is actually the case.

If the value of L be supposed to vary with n_3, the radial quantum, then probably the above calculations would lead to Ritz's law.

LXXII. *The Mass-Spectra of Chemical Elements.* (Part 2.)
By F. W. Aston, *M.A., D.Sc., Clerk Maxwell Student
of the University of Cambridge* * .

[Plate XIV.]

IN a previous paper (Phil. Mag. xxxix. May 1920, p. 611)
the apparatus for obtaining mass-spectra was fully de-
scribed and the results of analysis of eleven different elements
tabulated. The following paper deals with the analyses of
some additional elements for which the same apparatus and
method was used.

Boron (At. W. 11·90). Fluorine (At. W. 19·00). Silicon (At. W. 28·3).

It will be convenient to treat of these three elements
together. The atomic weights of boron and fluorine have
both been recently redetermined by Smith and Van Haagen
(Carnegie Inst. Washington Publ. No. 267, 1918), with the
above results. On the atomic weight of silicon there is some
divergence of opinion. The international value is quoted
above, but Baxter, Weatherell, and Holmes make it nearer 28·1
(Journ. Am. Chem. Soc. vol. xlii. p. 1194, June 1920).

After a failure to obtain the boron lines with some very
impure boron hydride, a sample of boron trifluoride was pre-
pared from boric acid and potassium borofluoride, and this
gave good results. Following the usual practice, it was
mixed with a considerable quantity of CO_2 before intro-
duction into the discharge-tube. Very complex and inter-
esting spectra were at once obtained, and it was remarked
that this gas possessed an extraordinary power of resurrecting
the spectra of gases previously used in the apparatus. Thus
the characteristic first and second order lines of krypton
were plainly visible, although the tube had been washed out
and run many times since that gas had been used. This
property of liberating gases which have been driven into the
surface of the discharge-bulb is doubtless due to the chemical
action of the fluorine, liberated during the discharge, on the
silica anticathode and the glass walls. After running some
time the corrosion of the anticathode was indeed quite visible
as a white frost over the hottest part.

After several successful series of spectra had been secured,
the percentage of boron trifluoride in the gas admitted was
increased as far as possible, until the discharge became

quite unmanageable and the tube ceased to work. Just before it did, however, it yielded two very valuable spectra which confirmed the isotopic nature of boron. These are reproduced side by side as they were taken (Spectra I. & II.). The lines at 10 and 11 are undoubtedly both first-order lines of boron. The hypothesis that these might be due to neon liberated by the action mentioned is not tenable, both on account of their relative intensities and the absence of *strong* neon first-order lines. Even if it were, it could not explain the presence of the well-defined lines at 5 and 5·5 which had never been obtained before at all, and which must be second-order lines of boron. This element therefore has at least two isotopes 10 and 11. The relative photographic intensity of the lines 5 and 5·5 does not agree well with an atomic weight as high as 10·9, and the discrepancy might be explained by the presence of a third isotope at 12 ; which would be masked by carbon, for it has not yet been found practicable to eliminate carbon from the discharge. But Spectrum IV. contradicts this suggestion for, as will be shown later, the line at 49 is mainly if not wholly due to $B^{11}F_2$, so that there should also be a line at 50 for $B^{12}F_2$. The line at 49 is very strong, but at 50 any small effect there may be can safely be ascribed to the fourth order of mercury. The evidence is clearly against the presence of a third isotope of boron.

The exceedingly accurate whole-number value for the atomic weight of fluorine suggests the probability of this element being simple. This conclusion is borne out by the strong line at 19·00 with second-order line at 9·50. The accompanying line at 20, very faint in Spectrum II., is no doubt HF, though it may be also Ne^{20} or second-order A^{40}. As there is no evidence whatever to the contrary, fluorine is taken to be a simple element with an atomic weight 19.

Having adopted these values for boron and fluorine, we may now apply them to Spectra III. and IV. taken with boron trifluoride. Consider first the group of three very strong lines 47, 48, and 49. The last two are to be expected as being due to $B^{10}F_2$ and $B^{11}F_2$ respectively, but since there is no evidence of a boron 9 or a fluorine 18, line 47 cannot be due to a compound of these elements. But line 47 only appeared when BF_3 was introduced, and so must be due to silicon fluoride formed by the action of the fluorine on the glass walls and the silica anticathode.

To test this the BF_3 was washed out and replaced by SiF_4, which has been made by the action of sulphuric acid on calcium fluoride and silica in the usual way. This greatly

reduced the lines 48 and 49, and so they must be attributed to boron compounds. At the same time line 47 remained very strong, and was evidently due to a compound $Si^{28}F$, so that silicon has a predominant constituent 28. This conclusion is further supported by the presence of very strong lines at 66, $Si^{28}F_2$, and 85, $Si^{28}F_3$.

The chemical atomic weight shows that this cannot be its only constituent. Lines at 29, 48, 67, and 86 all suggest a silicon of atomic weight 29. Practically conclusive proof of this is given in Spectrum V., which shows its second-order line unmistakably at 14·50. The only other reasonable origin of this line, namely second-order $B^{10}F$, is eliminated by the fact that there is no trace of a line at 10 in this spectrum.

The evidence of a silicon of atomic weight 30 is of a much more doubtful character. Its presence is suggested by the lines 30, 49, 68, and 87, but the possibility of hydrogen compounds makes this evidence somewhat untrustworthy, and no proof can be drawn from a second-order line 15, as this is normally present and is due to CH_3. On the other hand, if we accept a mean atomic weight as high as 28·3, the relative intensity of the lines due to compounds of Si^{28} and Si^{29} indicates the probable presence of an isotope of higher mass. These considerations taken with the complete absence of any definite evidence to the contrary make the possibility of Si^{30} worth taking into account.

Molecular lines of the Second Order.

The work of Sir J. J. Thomson on multiply-charged positive rays showed very definitely that molecules carrying more than one charge were at least exceedingly rare ('Rays of Positive Electricity,' p. 54), for not a single case was observed which could not be explained on other grounds. Up to the time of the experiments with the fluorine compounds the same could be said of the results with the mass-spectrograph. This absence of multiply-charged molecular lines, though there is no particular theoretical reason for it, has been used as confirmatory evidence on the elementary nature of doubtful lines.

The spectra obtained with BF_3 show lines for which there appears no possibility of explanation except that of doubly-charged compound molecules. The two most obvious of these may be seen on Spectrum III. and at the extreme left-hand end of Spectrum IV. They correspond to masses 23·50 and 24·50, the first being quite a strong line. Were

there no lines of lower order corresponding to these, the whole-number rule might be in question; but all doubt is removed by the fact that the lines 47 and 49 are two of the strongest on the plate. A comparison of several spectra upon which these lines occur shows a definite intensity relation which practically confirms the conclusion that the first pair of lines are true second-order lines corresponding to the first-order lines of the second pair. Now lines 47 and 49 cannot by any reasonable argument be elementary, they must in fact be due to compounds of fluorine with boron $B^{11}F_2$ or silicon $Si^{28}F$, or due to both. Further evidence of the capability of fluorine compounds to carry two charges is offered by line 33·50, which is undoubtedly the second-order line corresponding to 67, *i. e.* $B^{10}F_3$ or $Si^{29}F_2$. So far as results go, fluorine appears to be unique in its power of yielding doubly-charged molecules in sufficient number to produce second-order lines of considerable strength.

BROMINE (At. Wt. 79·92).

The results with this element were definite and easy to interpret. Its chemical combining weight is known with great certainty, and is very nearly the whole number 80. It was rather a surprise, therefore, that it should give a mass-spectrum which showed it to consist of a mixture of two isotopes in practically equal proportions. Methyl bromide was used for the experiments, and one of the results is reproduced in Spectrum VI. The characteristic group consists of four lines at 79, 80, 81, and 82. 79 and 81, apparently of equal intensity, are much the stronger pair, and are obviously due to elementary bromines. This result is practically confirmed by second-order lines at 39·5 and 40·5 too faint to reproduce, but easily seen and measured on the original negative. The fainter pair 80 and 82 are the expected lines of the two corresponding hydrobromic acids. The same difficulties as were discussed in the case of chlorine in the previous paper prevent the attainment of absolute certainty in determining the composition of bromine, or indeed that of any element capable of forming hydrogen compounds; but the conclusions stated above may be regarded as having a high degree of probability.

SULPHUR (At. Wt. 32·06).

Spectra VII. and VIII. show the effect of the addition of sulphur dioxide to the gas in the discharge-tube. Above each is a comparison spectrum taken immediately before the

gas was admitted, on the same plate with approximately the same fields. The very marked strengthening of lines 32 and 44 is no doubt due to S and CS. New lines appear at 33 SH, 34 SH_2, 60 COS, 64 SO_2 or S_2, and 76 CS_2. It may be noticed that lines 32, 60, and 76 are accompanied by a faint line one unit higher and a rather stronger line two units higher. In the first case it is certain and in the others probable that these are, at least partly, due to hydrogen addition compounds. If a higher isotope of sulphur exists, as is suggested by the chemical atomic weight, it seems unlikely that this should have mass 33, for this would have to be present to the amount of 6 per cent., and should give a line at 35 one-thirteenth the strength of 34 (normal SH_2). No such line is visible. A sulphur of atomic weight 34 present to the extent of 3 per cent. is more likely, but there is hardly enough evidence as yet to warrant its serious consideration.

Phosphorus (At. Wt. 31·04). Arsenic (At. Wt. 74·96).

The gases phosphine PH_3 and arsine AsH_3 were used in the experiments on these elements, and the results were of notable similarity. The mass-spectrum of each gas was characterized by a group of four lines. The first and strongest doubtless due to the element itself, the second rather weaker due to the monohydride, the third very faint to the dihydride, and the fourth fairly strong to the trihydride. The spectrum of AsH_3 is shown in Spectrum IX.; that of phosphorus is similar but its lines are weak, and therefore unsuited to reproduction. Both elements appear to have no isotopes, and neither give visible second-order lines.

Lines of unknown origin.

During the experiments with mass-spectra, lines have appeared from time to time to which it has been difficult to assign an origin with certainty. Three of these seem worthy of special note.

On one of the spectra taken with boron trifluoride there appeared a faint but unmistakable line at 5·33. The accuracy of its fractional value seems to insure it being triply-charged 16. If the source of the mass 16 is oxygen, it is somewhat odd that the line never appeared when oxygen was present in much greater quantity, but it may be possible that the loss of three charges only takes place when fluorine is present.

An even more baffling line is one at 6·50 which has

appeared on a chlorine plate, and also on one taken with BF_3. This is naturally put down to doubly-charged 13. If the source of the mass 13 is put down to CH, it is very surprising that the line should not appear more frequently, also that it should not be accompanied when it did appear by a line at 7·50 due to CH_3.

The third line of doubtful origin is a very faint one at 13·50 which appeared when chlorine compounds were present. The most likely explanation of this seems to be doubly-charged aluminium derived from small quantities of aluminium chloride formed by the action of the gas on the electrodes.

General Remarks.

All the seven elements whose analyses form the subject of this paper obey the " whole number " rule within the accuracy of experiment. They may be said to conclude the list of those which can be easily introduced into the apparatus in the form of gases or gaseous compounds. The following table gives a complete list of all the elements so far analysed. Some very clear results recently obtained with the mercury group of lines, *e. g.* Spectrum VIII., show that its isotopes 202 and 204 need no longer be regarded as doubtful.

Table of Elements and Isotopes.

Element.	Atomic Number.	Atomic Weight.	Minimum number of Isotopes.	Masses of Isotopes in order of intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
B	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	(2)	40, (36)
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
X	54	130·2	5	(128, 131, 130, 133, 135)
Hg	80	200·6	(6)	(197–200), 202, 204

In conclusion, the author wishes to express his indebtedness to the Government Grant Committee of the Royal Society for defraying the cost of some of the apparatus employed.

Summary.

Further experiments with the mass-spectrograph yielding provisional analyses of the elements B, F, Si, P, S, As, and Br are described.

Of these B, Si, and Br are definitely complex, the others apparently simple.

The atomic weights of all conform to the whole-number rule.

Some anomalous fractional lines are mentioned and their possible origin discussed.

Cavendish Laboratory,
    August 1920.

LXXIII. *The Ultra-Micrometer; an application of the Thermionic Valve to the measurement of very small distances. By* R. WHIDDINGTON, *M.A., D.Sc.; Cavendish Professor of Physics in the University of Leeds* [*].

[Plate XV.]

SINCE the discovery and application of the various forms of interferometer the direct and accurate measurement of small distances has been regarded, with some reason, as a problem solved.

All interferometer methods, however, are limited in accuracy of measurement by the wave-length of the light used in the production of the fringes. The present paper is an account of a new method which is not limited in this way, and which is easily capable of measuring small distances of the same order of magnitude as the atomic diameter.

The theory of the method may be put very simply.

If a capacity C be connected to an inductance L, the frequency of oscillation N natural to the circuit is given by

$$N = \frac{1}{2\pi \sqrt{LC}}.$$

If the condenser be composed of two parallel plates area A, separated by distance x,

$$C = \frac{A}{4\pi x}.$$

Whence

$$N = \left(\frac{x}{\pi LA}\right)^{\frac{1}{2}}.$$

Clearly a change in x involves a change in N, so that we may take the change in N as an indication of a change in x.

* Communicated by the Author.

For a sensitive indicator

$$\frac{d\mathrm{N}}{dx} = \frac{1}{2(\pi\mathrm{L}\mathrm{A}.r)^{\frac{1}{2}}}$$

should be as large as possible, that is, the product LA.*r* should be small.

In order to get some idea of the actual value of $\dfrac{d\mathrm{N}}{dx}$ to be expected under practical conditions we may conveniently rewrite the above in the form

$$\frac{d\mathrm{N}}{dx} = \frac{\mathrm{N}}{2x}.$$

A value of N easily obtained under conditions shortly to be described is 10^6; assuming $x = \frac{1}{1000}$ inch, say, we have

$$\frac{d\mathrm{N}}{dx} = \frac{10^9}{2}.$$

By a beat method—explained later—it is possible to observe a change in N of less than unity—assuming $\delta\mathrm{N} = 1$ we get the corresponding value of $\delta x = 2 \times 10^{-9}$ inch, $= 5 \times 10^{-9}$ cm.

With this introduction the following description of an apparatus built along such lines is put forward.

Fig. 1 shows the apparatus in diagram. A is an oscillating valve circuit involving the parallel-plate condenser (P) discussed above; T is a loud-speaking telephone shown for

Fig. 1.
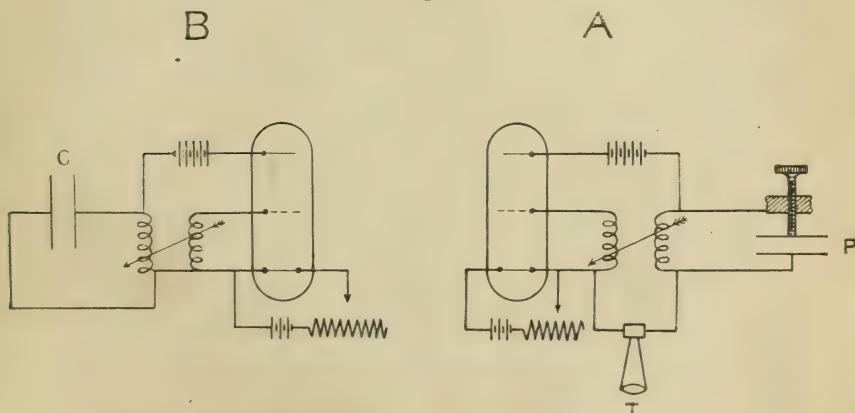
simplicity directly inserted in the valve anode circuit, although in actual practice a three-stage transformer amplifier intervened, to magnify suitably the currents passing through T.

The values of the coils in the grid and anode circuits of this part of the apparatus were so chosen as to produce oscillations of about a million frequency (N).

In order to make obvious any change in N a second valve circuit B was set up close to the one just described and shown on the left of fig. 1. The frequency of this circuit could be adjusted by means of the condenser C, so as to be nearly, but not quite, equal to N, so producing a loud audible note in T, the frequency of which could be adjusted to any desired value by a suitable choice of C.

In order to provide an unvarying standard of pitch to which the note could be adjusted, another valve circuit was set up (inducing into the amplifier), with capacities and inductances so large as to produce an audible note in T*. This note was usually kept constant, and the heterodyne note produced from the N frequency oscillation tuned to it by the condenser C.

The musical note circuit is not indicated in fig. 1, but is shown on the extreme right of the photograph of the experimental arrangement (Pl. XV.). The two large coils and standard condenser box (maximum value about 1 m.f.d.) are here clearly shown, the valve being hidden behind them. On the extreme left of the bench is shown the metal lined box containing a geometrical slide carrying two stiff vertical insulated rods and the attached condenser-plates P, one on each.

These plates were of polished steel about 5 mm. thick and about 17 sq. cm. area each.

They were set as nearly parallel as possible by an optical diffraction method, although great care in this respect is not essential to the ultimate working of the apparatus.

Just to the right of this condenser-plate box is a second box, also metal lined, containing two stiff paper bobbins (each carrying two small inductance coils) and mounted side by side, the left-hand one associated with the parallel-plate condenser P, and the right-hand one with the variable condenser C†, here shown with a pointer moving over a graduated scale. On the top of this box are seen the two thermionic valves which perform the duty of maintaining the oscillations in these high-frequency circuits.

In the left top of the photograph is the trumpet of the loud-speaking telephone, while in the centre top are shown the 100-volt lead accumulator units supplying potential to the various valve circuits.

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* The frequency of this audible note could be kept constant to about 1 part in 100,000 over a period of several hours.

† There was also another auxiliary condenser, not shown, of which C was really a fine adjustment.

It was very soon found that the apparatus just described was most extraordinarily sensitive to small changes in the value of P. Although, in anticipation, the whole arrangement was placed in a solid basement room of the University, the note emitted from T instead of being pure was rough, owing to the continuous small vibrations of the building.

It was only, in fact, in the small hours of the morning that the purity of the note could be maintained, and even then distant traffic proved troublesome at times.

Before explaining the methods used for determining the sensitiveness of the instrument, it may be mentioned in passing that the bending of the solid looking table shown in the photograph, produced by a penny placed on its edge, was clearly indicated by a change in the note from T.

A series of experiments was now carried out to find what was the smallest change in x that could be detected by this arrangement.

This involved preliminary experiments on the application of comparatively large known bending moments to the left-hand rod in the photograph*, and measuring by means of a micrometer the consequent lateral shift of the plate. A micrometer capable of measuring to 10^{-4} inch was used, contact with the plate being determined by use of a sensitive galvanometer and battery.

Two different mechanical schemes were tried shown in fig. 2 ; of these, the one marked (a) was very soon abandoned as it was found that when very small weights were used the law of proportionality between shift of plate and applied load broke down.

This was doubtless due to the frictional forces introduced at the junction J even when the finest unspun silk was used.

A method free from this defect is that of fig. 2 (b), in which the bending couple is applied by placing suitable weights on the graduated quartz rod LM.

As a result of a large number of experiments it was found that Hooke's law was obeyed to the limits of accuracy set by the micrometer.

By extrapolation it was concluded that 1·4 grams placed one inch along the rod would produce a lateral shift at the centre of the plate of exactly 10^{-6} inch.

This was a convenient number to remember from which to calculate the shift produced by any other weight at any distance.

After a long series of trials it was found that the smallest

* I am indebted to Mr. J. Gilchrist, M.Sc., for great help in this part of the work.

change that could be detected with certainty was that produced by 1 m.gm. at 5 inches—the number of beats (about 2 per sec.) changing perceptibly and by a constant amount.

Fig. 2.

(a)
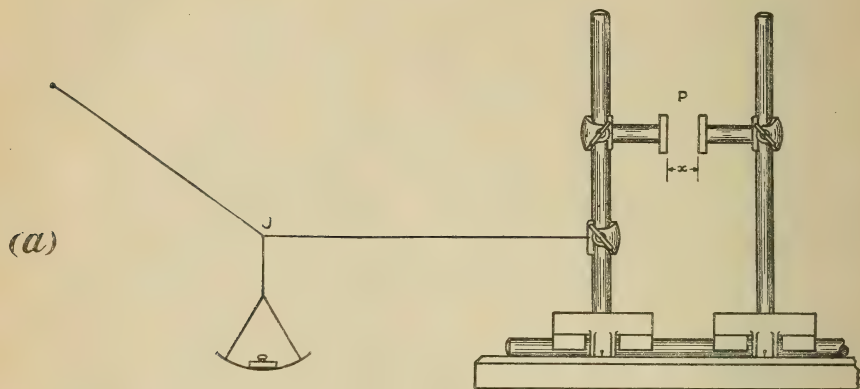
TWO METHODS USED FOR MAKING
SMALL CHANGES IN x
SCALE :- ½ FULL SIZE
(EXCEPTING x)

(b)
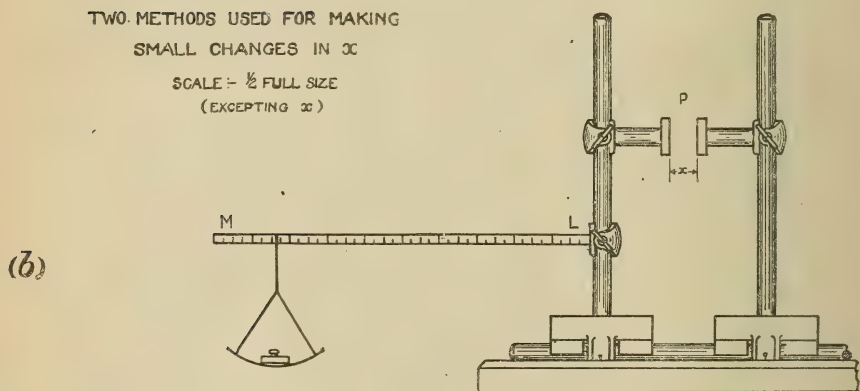
This shift is approximately

$$\tfrac{1}{1400} \times 6 \times 10^{-6} \text{ inch} = 4 \cdot 3 \times 10^{-9} \text{ inch} = 10^{-8} \text{cm. (approx.)},$$

or about $\tfrac{1}{200}$ millionth part of an inch.

It will be noticed that this figure is not so small as that estimated in the introduction (2×10^{-9})*.

* Probably due to the plates not being so close as $\tfrac{1}{1000}$ inch, the value of x assumed in the initial calculation. It is to be noted in this connexion that when oscillations occur a voltage may be set up between the plates whose mean square value can easily be of the same order as the constant voltage supplied by the anode battery—in this case 50 volts. This fact in itself sets a limit to the possible closeness of approach of the plates.

There is not the slightest doubt that an apparatus built on these lines could be made to indicate much smaller changes than that experimentally obtained here.

I have not so far attempted to push it to its practical limit, as for the purpose I have in immediate view its present sensitiveness is sufficient; there seems little doubt, however, that a sensitiveness of 100 times that just attained could be got without much difficulty.

In the previous paragraph it has been suggested how the apparatus may be used to detect extremely small distance changes, of the order of $\frac{1}{100}$ millionth of an inch. We there kept every thing constant except the variation in x and observed the consequent change in the number of beats.

When, however, we are dealing with a much larger shift in x—say $\frac{1}{100,000}$ part of an inch or so—it is possible to adopt a rather simpler scheme.

With such comparatively large changes in x a very large change in N occurs, so that a considerable change in C must be made to recover the standard note issuing from T.

With the actual apparatus shown in the photograph it was found that over quite a large range of the condenser scale —viz. from 20 deg. to 60 deg. pointer readings—a change of 1 deg. meant a change in $\frac{1}{332,800}$ inch in x. As it was possible to read $\frac{1}{10}$ degree quite easily, this scale-reading allows of a direct determination of a change in x within one three-millionth of an inch.

It is hoped to apply this extremely delicate method of observing small distance changes to various problems in the near future.

Summary.

If a circuit consisting of a parallel-plate condenser and inductance be maintained in oscillation by means of a thermionic valve, a small change in distance apart of the plates produces a change in the frequency of the oscillations which can be accurately determined by methods described. It is shown that changes so small as $\frac{1}{200}$ millionth of an inch can easily be detected. The name "ultra-micrometer" is tentatively suggested for the apparatus.

The Physics Laboratories,
     The University, Leeds.

LXXIV. *The Directional Hot-Wire Anemometer: Its Sensitivity and Range of Application.* By **J. S. G.** Thomas, *M.Sc. (Lond.), B.Sc. (Wales). A.R.C.S., A.I.C., Senior Physicist, South Metropolitan Gas Company, London*.*

Introduction.

I N a recent communication † the author described a type of hot-wire anemometer, which in addition to affording a ready indication of the direction of flow of gas in a pipe, was, on account of the almost complete elimination from the observed effect, of the influence of the free convection currents arising from the heated wires, especially applicable to the determination of the velocity of a very slowly moving current of gas.

The directional hot-wire anemometer consists of two fine platinum wires mounted parallel, and one behind the other in close juxtaposition, transversely to the direction of flow of the gas in the pipe or channel. The wires constitute two arms of a Wheatstone bridge (see fig. 7 later), the remaining arms of which are formed of a resistance of 1000 ohms and an arm capable of adjustment. A constant current is maintained in the bridge, and the battery terminals are connected through a rheostat to the appropriate ends of the platinum wires so that the maximum heat is developed in these wires. A galvanometer is inserted in the bridge in the usual manner. Further details concerning the method of mounting the wires etc. will be found in the papers referred to, wherein it is shown that as the velocity of the gas-stream to which the heated wires are exposed is gradually increased from zero, the galvanometer deflexion increases until a critical value of the velocity of the gas stream is attained. With further increase in the impressed velocity of the gas stream, the galvanometer deflexion very slowly diminishes. The direction of the galvanometer deflexion is reversed on reversing the direction of flow of the gas current, and the instrument affords an indication of the direction of flow even for extremely high values of the velocity of the gas stream. In the papers referred to, the maximum value of the galvanometer deflexion corresponded with a mean velocity of the gas stream equivalent to about 5 cm. per sec. The directional type of hot-wire anemometer possessing certain advantages in the region of low velocities—greater sensitivity, more complete elimination of the effect of the free convection current, greater

* Communicated by the Author.
† Phil. Mag. vol. xxxix. pp. 525–527 (1920). See also Proc. Phys. Soc. vol. xxxii. Part 3, pp. 196–207.

stability of zero—over those due respectively to Morris [*] and
to King [†], it appeared desirable to examine the behaviour
of the instrument further. Experiments were accordingly
made to determine (1) the relative sensitivity of the
directional hot-wire anemometer with the wires mounted
vertically compared with the sensitivity when the wires
were mounted horizontally; and (2) how the impressed
velocity of the gas stream at which the maximum galvano-
meter deflexion occurred—which may be termed the critical
velocity—was dependent upon (*a*) the heating current
employed, and (*b*) the diameter of the wires.

Experimental.

The general procedure in all the experiments was as
follows :—The two anemometer wires were cut from the
same sample of pure platinum wire supplied by Messrs.
Johnson & Matthey. In experiments connected more
particularly with the dependence of the sensitivity of the
instrument upon the inclination of the wires, it is desirable
that the resistances of the wires should be as nearly as
possible the same, in the absence of flow. This adjustment
to equality *in situ* is a matter of some difficulty and, in
general, was only achieved after a number of trials. The
following procedure was finally adopted. The sample of
wire was aged by the passage of a current sufficient to
raise it to a bright red heat for about two hours. Two
portions, as free as possible from flaws and pittings, and
of about the same length, were cut from the sample,
and attached to copper leads of diameter 0·82 mm. This
was done by filing from the end of the copper lead a
quadrantal segment about 3 mm. long. One end of the
platinum wire was inserted into the segment and joined
to the copper lead by means of the minimum amount of
silver solder affording a sound junction. The remaining
lead similarly treated was set up at a distance equal to
the diameter of the flow-tube from the end of the first
lead to which the platinum wire was soldered, and the
platinum wire affixed thereto under a tension sufficient
to maintain it quite straight. A second wire was prepared
in an exactly similar manner, and the two wires inserted
into the flow-tube as previously described. The resistances
of the wires were compared. Employing a small current
for this purpose, they were found usually to be equal to
within 0·3 per cent. When the current employed was
such that the wires were raised to a bright red heat,
their resistances were found to be, in general, within 0·5 per
cent. of one another. Occasionally agreement to within

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* Morris, Eng. Pat. 25,923/13. † King, Eng. Pat. 18,563/14.

0·1 per cent. was found. For most purposes, equality to
within 1 per cent. is amply sufficient; but when it is
desired to obtain a closer approximation in the adjustment
to equality, a current, sufficient to raise the wire of lower
resistance to a bright red heat, was passed through this
wire alone for the necessary period—extending to hours
or days—an air-stream being passed over the wires at half-
hourly intervals for about 10 minutes. In this manner the
resistances could be adjusted to equality when heated to within
0·1 per cent., and thereafter both wires were aged by the
passage for about 2 hours of a current sufficient to raise
them to a bright red heat. The ratio of the resistances
remained remarkably constant for a very considerable
period after such treatment : thus the ratio in the case
of anemometer D4 showed no greater variation than 0·1 per
cent. while the anemometer was employed in determining
about 50 calibration curves, employing various values of the
heating current. In all probability, owing to the wires
being throughout their use subjected to practically identical
conditions, no calibration would be necessary until the
instrument had been employed in the measurement of con-
siderably more than the 1000 velocities recommended by
King* in the case of the non-directional type of instrument.

The wires having been inserted in the flow-tube were
introduced into the Wheatstone bridge arrangement as
described. The wires could be placed horizontally, or at
any inclination to the horizontal transversely to the direction
of flow of the air in the flow-tube which was horizontal.
A millivoltmeter could be introduced across the ends of the
second wire of the pair so that the resistance of the second
wire could be calculated from a knowledge of the observed
drop of potential and the current in the bridge, this being
maintained constant by means of a rheostat inserted in the
battery circuit, and its value ascertained by means of a
Siemens and Halske milliammeter provided with suitable
shunts enabling current determinations to be made correct
to 0·001 amp. One of the two remaining arms of the
bridge—that connected to one end of the *second* anemo-
meter wire—was made equal to 1000 ohms and the
resistance of the first anemometer wire, when any gas-
flow was established in the pipe, was calculated from that
of the second wire of the pair, by determining the resistance
necessary in the fourth arm of the bridge to restore the
balance of the bridge. The galvanometer deflexion corre-
sponding to the flow of air was read prior to restoring the

balance of the bridge. The current of air was derived from a weighted gas-holder of 5 cubic feet capacity, provided with automatic pressure compensation, and was adjusted to any desired value by means of a micrometer cock. The air was dried by passage through a column of calcium chloride. The magnitude of the air-flow was ascertained by means of a wet gas-meter, by Sugg, of 1/12 cub. ft. capacity, this being standardized by means of the 1 12 cub. ft. bottle prescribed by the Metropolitan Gas Referees. The pressure at the meter outlet did not exceed 0·15 in. water. Further details of the experimental method may be derived from the papers already referred to.

(1) *Comparative sensitivity of the directional hot-wire anemometer when the wires are mounted* (a) *horizontally and* (b) *vertically in a horizontal flow-tube.*

The horizontal or vertical condition of the wires could, if desired, be very accurately ascertained by the electrical method devised by the author[*]. In general the horizontal position was sufficiently accurately determined by the horizontality of a generating line forming a continuation of the line joining the centres of the holes through which the wires were inserted into the flow-tube, and ruled on the tube. The vertical position was obtained therefrom by rotation of the flow-tube through 90° as indicated by an index moving over a scale engraved on the circumference of the flow-tube.

Results and Discussion.—The following particulars refer to directional anemometer D4*a* used in these experiments :—

Diameter of tube	2·0534 cm.
Diameter of wire employed (mean of 7 readings, differing by not more than 0·002 mm.)	0·101 mm.
Distance between wires	0·1 cm.
Temperature coefficient of wires .	0·003253
R_0, 1st wire (current 0·01 amp.) .	0·2556 ohm.
R_0, 2nd wire (current 0·01 amp.) .	0·2547 ohm.
Heating current in bridge . . .	1·2 amp.

The respective volumes (at 0° C. and 760 mm.) are converted to the equivalent mean velocities of the air-stream (calculated at 0° C. and 760 mm.) by multiplying the former, as given in cubic feet per hour, by 2·374. The galvanometer sensitiveness was suitably reduced by shunting with 6 ohms. The results are set out in Table I.

* Proc. Phys. Soc. 1920, vol. xxxii. Part 5, pp. 291–314.

TABLE I.—Directional Anemometer D 4*a*.

Inclination of Wires.	Temperature.		Barometer (ins.).	Vol. of Air passed (1/60 cub. ft.).	Time of Observ. (mins.)	Uncorr. volume per hour (cub. ft.).	Deflexion.		
	Air Stream. (° C.)	Meter. (° F.)					Left.	Right.	Diff.
HORIZONTAL.	24·0	75·1	29·99	1·42	3	0·47	272	227	45
	24·0	75·1	29·99	2·08	3	0·69	289	209	80
	24·0	75·1	29·99	1·84	2	0·92	310	190	120
	24·0	75·2	29·99	2·40	2	1·20	335	164	171
	24·0	75·1	29·99	3·12	2	1·56	373	128	245
	24·0	75·1	29·99	3·65	2	1·83	401	100	301
	24·0	75·2	29·99	3·98	2	1·99	423	78	345
	24·0	75·1	29·99	4·49	2	2·24	446	54	392
	24·0	75·1	29·99	6·38	2	3·19	457	44	413
	24·0	75·1	29·99	9·32	2	4·66	464	37	427
	24·0	75·2	29·99	7·74	2	3·87	462	39	423
	24·0	78·2	29·99	5·62	1	5·62	459	42	417
	24·0	75·2	29·99	18·60	2	9·30	441	62	379
	24·5	75·2	29·99	12·40	1	12·40	423	77	346
	24·5	75·2	29·99	15·0	1	15·0	410	90	320
	25·0	75·2	29·99	18·7	1	18·7	396	104	292
	25·0	75·2	29·99	20·7	1	20·7	389	110	279
	27·0	75·1	29·99	24·7	1	24·7	376	123	253
VERTICAL.	22·2	72·2	29·98	0·95	5	0·190	271	228	43
	22·2	72·2	29·98	1·73	4	0·432	302	197	105
	22·0	72·3	29·98	2·03	3	0·677	332	166	166
	22·0	72·2	29·98	2·98	3	0·993	362	138	224
	22·0	72·1	29·98	3·14	2	1·57	393	107	286
	22·0	72·1	29·98	4·54	2	2·27	422	78	344
	22·5	72·2	29·98	5·84	2	2·92	446	57	389
	22·5	72·1	29·98	3·80	1	3·80	463	41	422
	22·5	72·0	29·98	4·58	1	4·58	467	36	431
	23·0	72·0	29·98	6 30	1	6·30	463	40	423
	23·0	73·0	29·98	8·00	1	8·00	454	48	406
	23·0	73·0	29·98	12·20	1	12·20	431	72	359
	23·0	73·0	29·98	13·90	1	13·90	422	79	343
	23·5	73·0	29·98	19·7	1	19·7	400	102	278
	23·5	73·0	29·98	24·5	1	24·5	388	114	274

Heating Current 1·2 amp.

Balance Resistance (ohms).		Drop of Potential across second wire (volt).		Corr. vol. of air (dry) per hour at 0° C. and 760 mm. (cub. ft.).	Equiv. mean velocity. (cms. per sec.),	Resistance of Wires (ohm).			
						Zero flow.		With flow.	
Zero flow.	With flow.	Zero flow.	With flow.			First Wire.	Second Wire.	First Wire.	Second Wire.
1001	988	0·771	0·772	0·421	1·00	0·643	0·642	0·635	0·643
	977		0·781	0·617	1·46			0·636	0·651
	967		0·790	0·823	1·95			0·636	0·658
	952		0·796	1·07	2·54			0·631	0·663
	933		0·809	1·40	3·32			0·629	0·674
	919		0·819	1·64	3·89			0·627	0·682
	909		0·829	1·78	4·23			0·621	0·683
	896		0·825	2·00	4·75			0·616	0·687
	889		0·812	2·86	6·79			0·602	0·677
1001	880	0·771	0·770	4·17	9·90	0·643	0·642	0·565	0·642
	884		0·792	3·46	8·21			0·583	0·660
	878		0·750	5·03	11·9			0·549	0·625
	879		0·681	8·32	19·8			0·499	0·568
	885		0·647	11·09	26·3			0·477	0·539
	886		0·620	13·43	31·9			0·458	0·517
	892		0·593	16·73	39·7			0·441	0·494
	894		0·581	18·52	44·0			0·433	0·484
1001	901	0·771	0·560	22·10	52·5	0·643	0·642	0·420	0·467
1003	992	0·838	0·842	0·171	0·41	0·700	0·698	0·696	0·702
	976		0·849	0·388	0·92			0·690	0·707
	960		0·851	0·608	1·44			0·681	0·709
	945 ·		0·850	0·892	2·12			0·669	0·708
	927		0·840	1·41	3·35			0·649	0·700
	912		0·828	2·04	4·84			0·629	0·690
	897		0·810	2·62	6·22			0·605	0·675
1003	887	0·838	0·790	3·41	8·10	0·700	0·695	0·584	0·658
	881		0·770	4·12	9·78			0·566	0·642
	876		0·731	5·66	13·44			0·533	0·609
	876		0·699	7·20	17·09			0·511	0·583
	881		0·644	10·97	26·0			0·473	0·537
	884		0·629	12·50	29·7			0·463	0·524
	892		0·587	17·7	42·0			0·437	0·490
1003	896	0·838	0·567	22·0	52·2	0·700	0·698	0·423	0·472

A similar set of readings was made using platinum wires of diameter 0·202 mm. and temperature coefficient 0·003434, installed as already described in the flow-tube. In this case, owing to the smallness of the resistances of the wires, it was not so easy to adjust the separate resistances to equality when *in situ* and heated by a current, as was the case with the finer wires. The values of the resistances, the wires conveying a current equal to 0·01 amp., were 0·0753$_1$ ohm and 0·0756$_8$ ohm for the first and second wires respectively. The curves in fig. 1 show how the galvanometer deflexion depended upon the air current in the case of both thicknesses of wire. For purposes of comparison, the respective heating currents, in the cases of different thicknesses of wire, were chosen so that the wires were in the two cases, in the absence of flow, heated to approximately the same temperature. Table II. gives particulars of the heating currents employed, and the temperatures of the wires etc., in the absence of flow. Fig. 1 also gives a calibration curve for the case of the thicker wire (diameter 0·202 mm.), employed vertically and heated by a current (3·15 amp.) so that in the absence of flow, the temperatures of the vertical wires were as nearly as possible equal to their respective temperatures, with zero flow, when they were installed horizontally in the flow-tube and heated by a current equal to 3·3 amps. Fig. 1 likewise gives the form of the calibration curve obtained when the anemometer wires (diameter 0·202 mm.) were employed inclined at an angle of 45° to the vertical and heated by a current of 3·3 amps. Considering the curves obtained when using the finer wires (diameter 0·101 mm. and heating current 1·2 amp.), it will be seen from fig. 1 that the sensitivity of the arrangement is, for very small velocities of flow, considerably greater when the wires are installed vertically than is the case when the wires are employed horizontally. Corresponding to a mean impressed velocity of about 4 cm. per sec. indicated by the point P, the same deflexion is afforded by the two arrangements. Over the region of velocities embraced between values corresponding to those represented by the points P and Q, the horizontal arrangement affords the greater sensitiveness. Corresponding to values of the impressed velocity greater than that represented by Q, the sensitivities of the two arrangements are, within the limits of experimental error, equal. With regard to the greater sensitivity of the vertical arrangement for very low velocities (region embraced between the origin and P),

it may be remarked that when the wires are installed
vertically, they are each laved by their respective free

Fig. 1
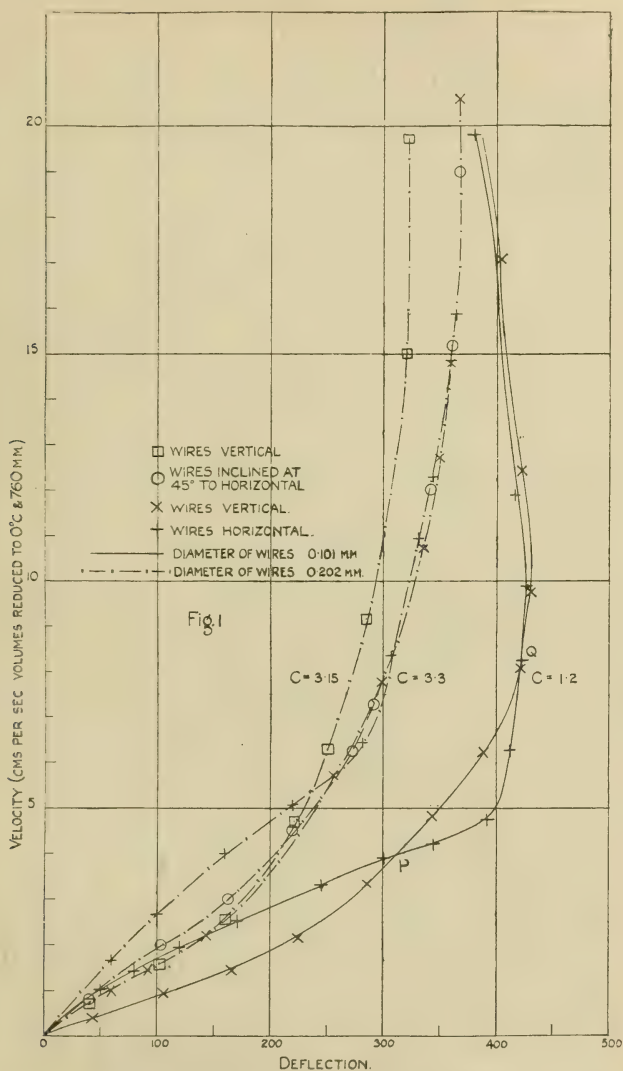
convection currents, and as shown in Table I. the wires,
in the absence of any flow, are at a considerably higher
temperature than that to which they are raised when
used horizontally and heated by the same current. The

TABLE II.

Diam. of wires (mm.).	Temperature coefficient of wires (a).	Resistance at 0°C., current = 0.01 amp. (ohm).		Heating current (amps.).	Resistance of wires when heated by bridge current with zero flow (ohm).				Excess temperature of wires above atmospheric with zero flow (°C.).			
					Wires horizontal.		Wires vertical.		Wires horizontal.		Wires vertical.	
		1st Wire.	2nd Wire.		1st Wire.	2nd Wire.	1st Wire.	2nd Wire.	1st Wire.	2nd Wire.	1st Wire.	2nd Wire.
0·101	0·003253	0·2556	0·2547	1·2	0·643	0·642	0·700	0·698	470	471	555	555
0·202	0·003434	0·0753₁	0·0756₃	3·3	0·1950	0·1976	0·2098	0·2121	469	475	535	540
0·202	0·003434	0·0753₁	0·0756₃	3·15	—	—	0·1963	0·1987	—	—	476	481

greater sensitivity of the vertical arrangement might conceivably be due to the higher initial temperature to which the wires are raised by the bridge current when installed vertically. It will, however, be clear from the sequel, and may be seen from fig. 1, that very little variation of sensitivity in the region of low velocities accompanies a change of the initial temperature to which the wires are raised. Thus in fig. 1, in the case of wires of diameter 0·202 cm., it will be seen that when the wires are vertical, the calibration curves in the region of impressed velocities between 0 and 3 cm. per sec. are practically identical when heating currents equal to 3·3 amps. and 3·15 amps. are employed, the initial temperatures of the wires in the two cases being 540° C. and 480° C. approximately. The initial greater sensitivity of the vertical arrangement, compared with the horizontal, is to be attributed to the relative disposition of the free convection currents to the wires in the two cases. With the wires vertical, the hot free convection current from each wire completely surrounds the same, whereas, with the wires horizontal, the heated free convection current rises directly away from each wire. In the case of the vertical arrangement, an impressed stream of low velocity would disturb the free convection current so that the central portion of the wire would no longer be completely protected by the hot ascending current of air. With increase of impressed velocity, the shielding effect of the free convection current would be reduced still further. The transfer of heat from the wire to the stream being in this case initially effected through the surrounding ascending free convection current, in which, moreover, the radial temperature gradient for some distance —up to something of the order of three times the radius of the wire *—is small, it is to be anticipated that any disturbance of the protecting free convection current by means of an impressed air-flow would produce a comparatively considerable reduction in the temperature of the first wire of the vertical pair. In the case of the horizontally disposed pair of wires, the heated free convection currents pass transversely over the wires, and it is evident that the first wire of the pair would experience a smaller cooling effect due to a slow air-stream than would be the case with the wires mounted vertically. The various effects can be readily discussed by the aid of fig. 2

* See Thomas, 'An Electrical Hot-Wire Inclinometer,' Proc. Phys. Soc. 1920.

and fig. 3. The former shows how the resistance of each
wire of the pair depends upon the impressed velocity of
the air-stream in the case of wires of diameter 0·101 mm.

Fig. 2.
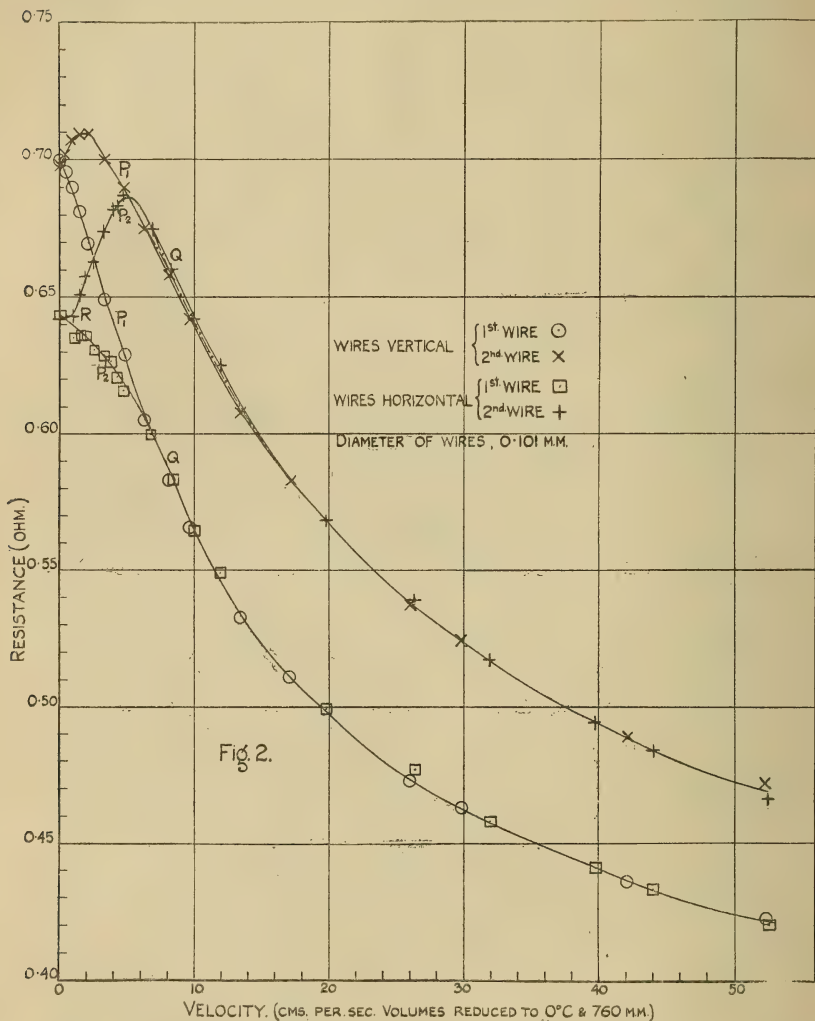
Fig. 3 shows the corresponding results for wires of dia-
meter 0·202 mm. In each case, results are given for wires
mounted both vertically or both horizontally, the experi-
mental points in each case corresponding with those given
in fig. 1. The main features of the curves shown in fig. 2

are as follows:—With the wires mounted horizontally, there is, with increasing impressed velocity of air-stream, a comparatively large *increase* in the resistance of the *second* wire. The resistance of the first wire meanwhile initially falls off comparatively slowly. On the other hand,

ANEMOMETER D 5A

1st WIRE ○

WIRES VERTICAL {
2nd WIRE X

1st WIRE □

WIRES HORIZONTAL {
2nd WIRE +

DIAMETER OF WIRE 0·202 M.M.

Fig. 3.

RESISTANCE (OHM.)

VELOCITY (CMS. PER. SEC., VOLUMES REDUCED TO 0° C & 760 M.M.)
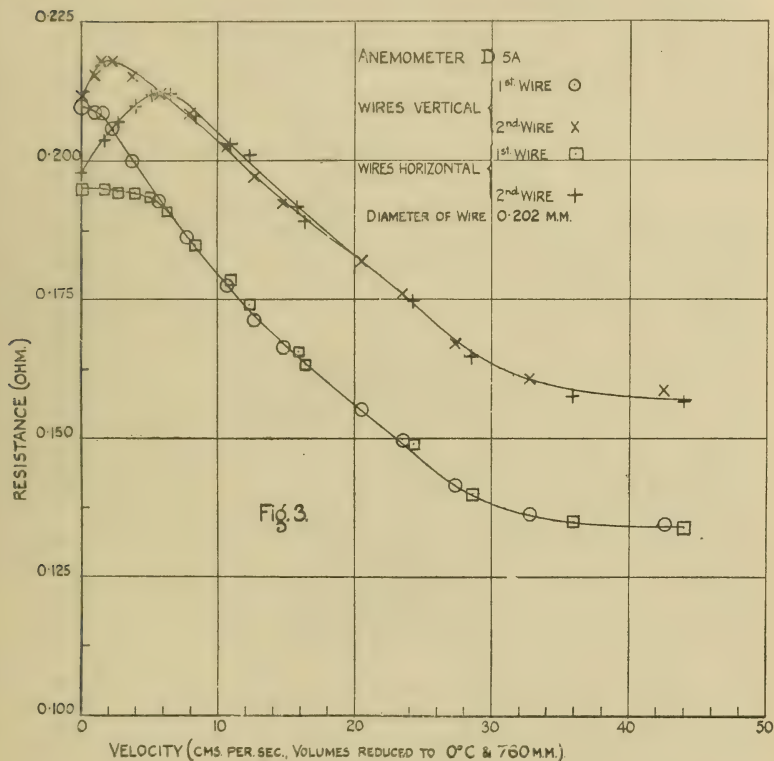
with the wires mounted vertically, with increasing velocity of the air-stream, the initial increase of the resistance of the second wire is comparatively small, while there is a very considerable decrease in the resistance of the first wire. The sensitivity of the arrangement employing horizontal wires is due, therefore, principally to the *increase* in the resistance of the *second* wire, whereas that of the arrangement employing vertical wires originates principally in the *decreased* resistance of the *first* wire. The greater initial sensitivity of the latter arrangement is now readily

2 U 2

explainable in the following manner. The passage of a
slow stream of air over the wires is accompanied, as already
explained *, by the convection of heat from the neigh-
bourhood of the first wire to that of the second, whereby
the second wire attains a higher temperature than in the
absence of the impressed flow of air. The stream of air
is, however, owing to imperfect shielding of the second
wire by the first, operative in producing some cooling
effect upon the second wire, and the resultant temperature
of the second wire is determined by the net effect of
these opposing tendencies. An impressed velocity can be
imagined of such magnitude that with suitable disposition
of the wires the temperature of the second wire remains
practically unaffected by the stream. Such a condition
of affairs is represented by the point R in fig. 1, and a
number of other illustrations are to be seen in sub-
sequent curves (see fig. 5). The initial difference in the
temperatures of the two wires when mounted horizon-
tally—an arrangement in which the sensitivity depends
mainly upon an increase of the resistance of the second
wire—is therefore small, compared with the corresponding
difference in temperature of the wires for the same impressed
velocity, when mounted vertically, as in this latter case
any reduction of temperature of the *first* wire, due to
cooling by the stream of air, is not diminished by a heating
effect operative in the counter direction. In the absence
of such considerations, considering merely heat convected
by the stream from the first wire to the second, one would
anticipate a greater difference of temperature between the
wires for a given low value of the impressed velocity of
the air-stream, when such difference of temperature is
attributable principally to cooling of the first wire, than
when it is mainly due to heating of the second wire ; for in
the latter case, owing to loss of heat by the stream of fluid
during its passage from the first wire to the second, and
owing to the fact that the whole of such residual convected
heat is not transferable, under the conditions of the expe-
riment, to the second wire, the rise of temperature of the
second wire due to this cause is necessarily less than the fall in
temperature of the first wire, the wires being assumed similar
in all respects. Now it will be remarked from fig. 2, that
when the wires are mounted horizontally, corresponding to
impressed velocities of the air-stream of from 1·6 cm. per sec.

to 6·4 cm. per sec., the resistance and consequently
the temperature of the second wire is increased by more
than that of the first wire is diminished by the same
impressed velocity of the air-stream. It is clear, therefore,
that over this region of impressed velocities, the whole
heating effect experienced by the second wire cannot
originate entirely in heat convected directly from the
first wire by the stream, but is partly due to heat derived
from the free convection current arising from the first
wire, and partly to the altered thermal conditions in the
neighbourhood of the second wire arising from the dis-
turbance of the free convection currents from the two
wires by the stream of air.

The deflexion corresponding to a velocity of about 4 cm.
per sec., indicated by P, fig. 1, in the case of a pair of wires
of diameter 0·101 mm., is seen to be the same whether the
wires are mounted vertically or horizontally. The corre-
sponding values of the respective resistances are indicated
by the points P_1, P_1, P_2, P_2, in fig. 2, the points P_1, P_1
referring to the vertical arrangement, and P_2, P_2 to the
horizontal arrangement. The equality of deflexion in this
case arises owing to the very approximate equality of the
difference between the resistances of the first and second
wires in the two arrangements (P_1, $P_2 \simeq P_2$, P_2). Equality
of deflexion corresponding to a velocity of about 8 cms.
per sec., indicated by Q in fig. 1, is seen from fig. 2 to be
due to *actual equality* of the resistances of the respective
wires in the two arrangements—*i. e.*, the resistance of the
first wire mounted either vertically or horizontally is the
same when subjected to the cooling effect of a horizontal
stream moving with a mean velocity of about 8 cms.
per sec., and similarly for the second wire. In fig. 2
the resistance of the second wire, mounted horizontally
or vertically, corresponding to an impressed velocity of
the stream of from 8 to 16 cms. per sec., is shown as
slightly different in the two cases. It is clear, however,
that the experimental results would, within the limits of
experimental error—estimated at 0·3 per cent.—be equally
well represented by equality of the resistance in the two
cases, as shown by the dotted portion of the curve in fig. 2.
It will be seen from fig. 2, that whereas when the wires
are mounted horizontally, the resistance of the second wire
increases very much more than is the case when the wires
are mounted vertically, the maximum resistance attained

by the second wire in the former case is considerably less than in the latter case, and corresponds moreover to a considerably higher value of the impressed velocity. Fig. 3 shows analogous results to those given in fig. 2, employing platinum wires of diameter 0·202 mm. The corresponding deflexion-velocity curves are given in fig. 1, together with the calibration curve for the same wires when mounted at an inclination of 45° to the horizontal. The values given in Table III. are deduced from the results represented in figs. 2 and 3.

TABLE III.

Diameter of Wires (mm.)	Plane of Wires.	Heating current (amps.).	Temperature of wires. Zero flow (° C.).	Resistance of second wire. Zero flow (ohm.).	Maximum resistance attained by second wire (ohm.).	Ratio: Max. Res. Initial Res.	Impressed velocity of stream at which maximum resistance is attained by second wire (cm. per sec.).
0·101	Horizontal.	1·2	470	0·642	0·686	1·068	5·2
	Vertical.	1·2	555	0·698	0·710	1·017	1·8
0·202	Horizontal.	3·3	472	0·1976	0·212	1·073	5·9
	Vertical.	3·3	538	0·2121	0·218	1·027	2·0

(2) *Dependence of the critical velocity—the velocity at which the maximum galvanometer deflexion occurred—upon* (a) *the heating current employed and* (b) *the diameter of the wires.*

In order to determine how the critical velocity—*i. e.*, the velocity at which the galvanometer deflexion attained its maximum velocity—depended upon the heating current employed in the bridge, a number of calibration curves of directional anemometer D4 (diameter of wires 0·101 mm.) were obtained, employing heating currents in the bridge ranging from 0·7 amp. to 1·5 amp., the temperature of the wires being thereby raised to temperatures ranging from 125° C. to 842° C. The various calibration curves obtained

employing throughout a galvanometer-shunt of 4 ohms are shown in fig. 4, and the values of the resistance of the

Fig. 4.

C = 1·5 AMP.
C = 1·4 AMP.
C = 1·3 AMP.
C = 1·2 AMP.
C = 1·1 AMP.
C = 1·0 AMP.
C = 0·9 AMP.
C = 0·8 AMP.
C = 0·7 AMP.

DIAMETER OF WIRES, 0·101 MM.

VELOCITY (CMS PER SEC, VOLUMES REDUCED TO 0°C AND 760MM)

DEFLECTION.
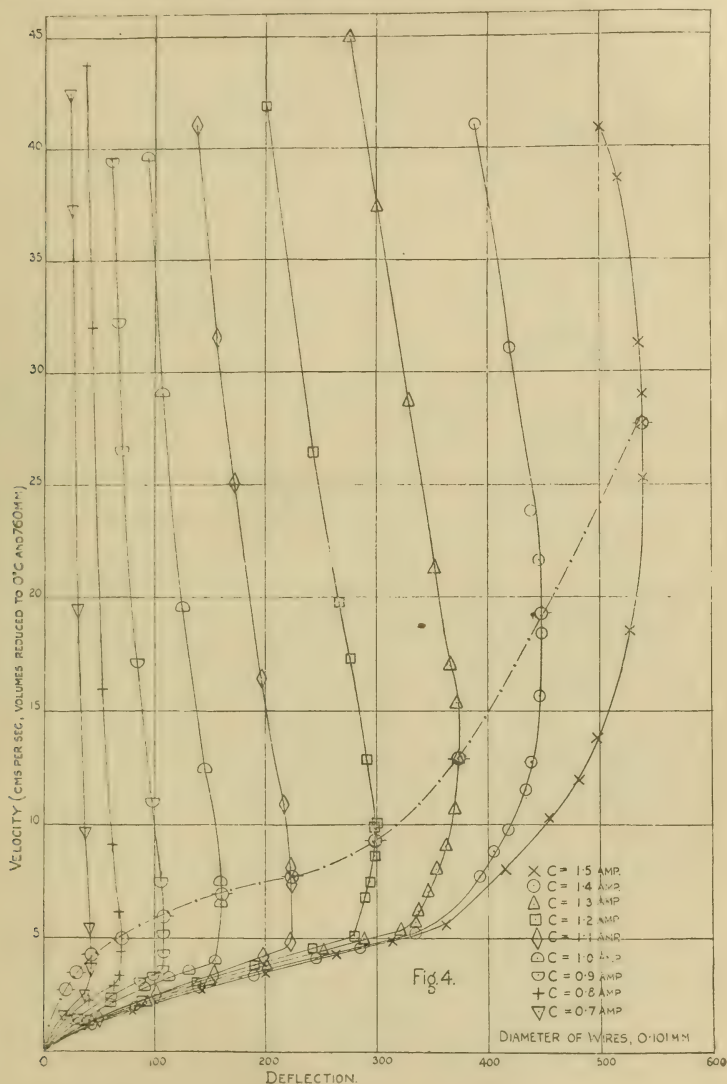
second anemometer wire, determined in the manner already described, when heated by various currents and exposed

to various rates of air-flow, are shown in fig. 5. The calibration curves shown in fig. 4, in the region of low

Fig. 5.
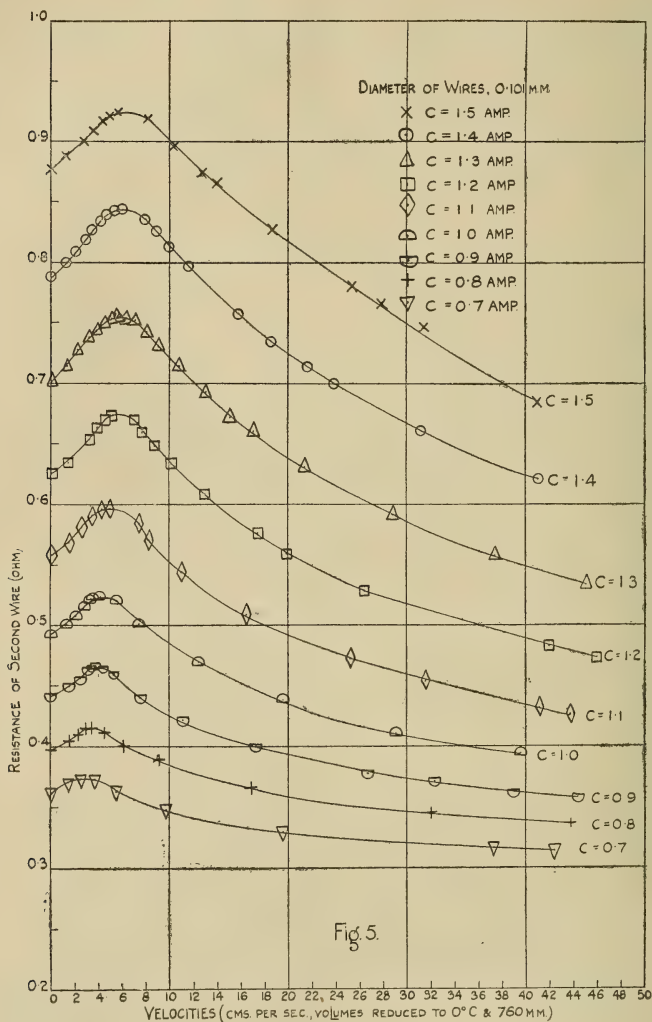
VARIATION IN RESISTANCE OF SECOND WIRE FOR VARIOUS VALUES OF HEATING CURRENT.

velocities, are markedly different from the type of calibration curve afforded by the Morris type of anemometer. Attention has been drawn to one feature of the calibration

curves in a previous paper *, indicating the more complete elimination of the effect of the free convection current in the directional type of instrument. It has likewise been shown † that in the type of hot-wire anemometer devised by Morris, the calibration curves obtained by using various heating currents in the bridge intersect in the region of velocities of the air-flow, where the velocity of the free convection current is comparable with the impressed velocity of the air-stream. The curves shown in fig. 4 are characterized by absence of such points of intersection.
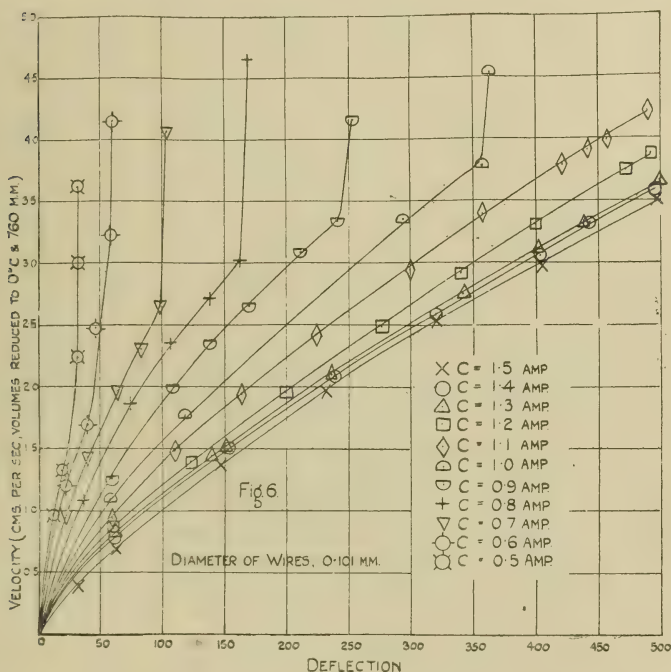
Fig. 6 shows the form of the calibration curves in the region of low impressed velocities, employing the galvanometer at its maximum sensitivity. It is clearly seen that any intersections of the respective curves, if occurring at all, must occur for values of the impressed velocity of the air-stream less than about 0·75 cm. per second.

The respective values of the impressed velocities of the

* Proc. Phys. Soc. vol. xxxii. Part 3, pp. 196–207 (1920).
† Phil. Mag. vol. xxxix. pp. 515 516, pl. x. fig. 6 (May 1920).

air-stream corresponding to the maximum galvanometer-deflexion when various heating currents were employed in the bridge could not be accurately determined from the curves shown in fig. 4, on account of the extremely small variation of such maximum deflexion accompanying alteration in the value of the impressed velocity of the air-stream in this region. The value of such impressed velocity, corresponding to the maximum deflexion, could, however, be very accurately determined by increasing the sensitivity of the galvanometer employed, whereby the rate of variation of the deflexion in the region of its maximum value could be increased as desired. For this purpose, therefore, the suspended coil galvanometer employed was substituted by a similar galvanometer of equal resistance whose sensitivity could be suitably adjusted by means of a shunt. Employing a shunt of 4 ohms, and a definite heating current in the bridge, the approximate value of the impressed flow of air corresponding to the maximum deflexion was determined in the ordinary manner. Torsion was now applied to the suspension of the galvanometer until the spot returned to the zero of the scale. (The desirability of substituting the galvanometer employed for measuring comparative deflexions by another, arises from this necessity for subjecting the galvanometer suspension to torsion.) The sensitivity of the galvanometer being now suitably increased by employing a suitable galvanometer shunt, and a constant predetermined current being maintained in the bridge, the flow corresponding to the maximum deflexion could be accurately determined. The bridge arrangement employed is such that no appreciable alteration in the heating current in the anemometer wires accompanies the alteration in the equivalent resistance of the galvanometer. This is readily seen from a general consideration of the relative magnitudes of the various resistances in the bridge. Fig. 7 shows the bridge arrangement employed, the values of the respective resistances and currents being as indicated, and the first and second anemometer wires denoted by the ordinal numbers within brackets.

It is well known that

$$y = \frac{\{G(\alpha+\beta)+\alpha(a+\beta)\}x}{G(a+b+\alpha+\beta)+(b+\alpha)(a+\beta)},$$

and as a and b are throughout, in the present experiments,

necessarily relatively small—of the order one-thousandth, at most—compared with α and β, and as moreover no

Fig. 7.
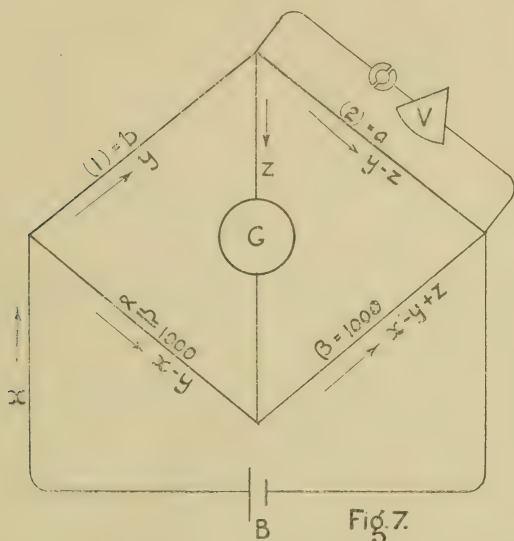
measurable alteration in their respective values accompanied an alteration of G from 0 to ∞, we have

$$\left(\frac{dy}{dG}\right)_x = \frac{\{(b\beta - a\alpha)(\alpha + \beta)\}x}{\{G(a + b + \alpha + \beta) + (b + \alpha)(\alpha + \beta)\}^2},$$

and Δy the alteration in the current through the leading anemometer wire accompanying an alteration of the galvanometer resistance from an infinite value to the value G is given by

$$(\Delta y)_x = \frac{-(b\beta - a\alpha)(\alpha + \beta)x}{(a + b + \alpha + \beta)\{G(a + b + \alpha + \beta) + (b + \alpha)(\alpha + \beta)\}}$$

and is readily seen to be very small for all values of G, under the conditions of the present experiments. It may also be readily shown that under the conditions of the present experiments, in which $\alpha \simeq 1000$, $\beta = 1000$, and $a - b$ is at the most of the order 0·1 ohm, the value of the galvanometer current alters only between the limits 0 and $10^{-4}x$ when the galvanometer resistance is altered from ∞ to zero, so that, to within 1 part in 10,000 at least, the current passing through both anemometer wires is the same. The values of the impressed velocities at which the respective maximum

deflexions occurred when various heating currents were employed are shown by the broken curves in figs. 4 and 8 in the cases of directional hot-wire anemometers D 4 and D 5 respectively, employing wires of respective diameters 0·101 mm. and 0·202 mm. In addition to determining the velocity corresponding to the maximum deflexion, it appeared desirable to ascertain the values of the velocities at which the resistance of the second wire attained its maximum value in the case of each heating current employed in the bridge. In the case of wires of diameter 0·101 mm., this was readily done from the results plotted in fig. 5. The experimental points in the neighbourhood of the respective maxima were plotted on an enlarged scale, and the maximum point accurately determined by joining the mid points of chords drawn parallel to the axis of velocities. The results obtained in the case of wires of diameter 0·101 mm. are set out in Table IV. herewith.

Referring to Table IV. and fig. 4, it will be noticed that the possible range of velocities,—determined by the impressed velocity of the stream corresponding to the maximum deflexion—within which the directional anemometer may be employed in a quantitative manner can be very considerably extended by increasing the initial temperature to which the wires are heated. Thus, while with wires of diameter 0·101 mm., employing a heating current equal to 0·4 amp., the maximum deflexion occurs at an impressed velocity of the air-stream equal to 2·57 cm. per sec., the maximum deflexion occurs at an impressed velocity equal to 27·7 cm. per sec. when the heating current is increased to 1·5 amp. The initial temperatures of the wires in these two cases were respectively 36° C. and 826° C. in excess of atmospheric. From fig. 8 it will be noted that the range of application can be still further extended by employing thicker anemometer wires. Thus in the case of wires of diameter 0·202 mm. the velocity at which the maximum deflexion occurred was increased from 4·95 cm. per sec. to 35·2 cm. per sec., when the heating current was altered from 2·0 amps. to 3·8 amps. The corresponding initial temperatures of the wires were 108° C. and 735° C. respectively above atmospheric. The sensitiveness of the anemometer employing the finer wires is somewhat greater than that of the arrangement employing the thicker wires, the wires being in each case raised to the same initial temperature above atmospheric temperature for purposes of comparison. In the case of the finer wires (diameter 0·101 mm.) the initial excess temperature is given with considerable accuracy by the relation

TABLE IV.

Directional Anemometer D4. Diameter of wires 0·101 mm. Temperature coefficient of wire 0·003253.

Galv. shunt 4 ohms. Res. β (see fig. 7) = 1000 ohms. R_0 (1st wire) = 0·2583 ohm. R_0 (second wire) = 0·2547 ohm.

Heating current (amp.)	Balance resistance (ohms). Zero flow.	At max. deflexion.	Resistance of 2nd wire. Zero flow.	At max. deflexion.	Maximum resistance of 2nd wire (ohm).	Temperature of 2nd wire (° C.). Zero flow.	At max. deflexion.	Temperature of 1st wire at max. deflexion (° C.).	Mean impressed velocity corresponding to max. res. of 2nd wire (cms./sec.).	Mean impressed velocity corresponding to max. galv. defl (cms./sec.).	Max. galvanometer deflexion (mm.).	Excess temp. of 2nd wire above atmosphere Zero flow (° C.).
1·5	1013	876	0·875	0·773	0·924	842	689	533	6·40	27·7	538	826
1·4	1014	883	0·787	0·734	0·844	708	638	495	6·10	19·2	448	692
1·3	1016	894	0·703	0·695	0·755	585	573	456	5·76	12·9	573	569
1·2	1013	903	0·633	0·642	0·675	487	499	400	5·38	9·28	299	471
1·1	1014	915	0·558	0·555	0·596	384	380	307	5·00	7·78	223	368
1·0	1016	931	0·4900	0·507	0·525	293	315	260	4·60	6·88	139	277
0·9	1017	945	0·4380	0·452	0·466	226	244	203	4·00	5·99	108	210
0·8	1016	963	0·3975	0·401	0·415	174	179	153	3·40	5·07	70	157
0·7	1016	982	0·3600	0·367	0·3738	127	137	121	2·96	4·17	46	113
0·6	1016	996	0·3333	0·340	—	95	103	95	—	3·50	30	79
0·4	1014	1008	0·2980	0·300	---	52	55	52	—	2·57	18	36

$\theta = 289 \, C^{2 \cdot 567}$, where C is the heating current measured in amperes. The corresponding relation in the case of the thicker wires (diameter 0·202 mm.) is $\theta = 12 \cdot 8 \, C^{3 \cdot 08}$.

Fig. 8.

DIAMETER OF WIRES, 0·202 M.M.

X C = 3·8 AMP
O C = 3·7 ·
△ C = 3·6 ·
□ C = 3·5 ·
◇ C = 3·4 ·
△ C = 3·3 ·
C = 3·2 ·
+ C = 3·1 ·
▽ C = 3·0 ·
C = 2·9 ·
D C = 2·8 ·
C = 2·7 ·
C = 2·6 ·
C = 2·5 ·
C = 2·4 ·
C = 2·3 ·
C = 2·2 ·

VELOCITY (CMS. PER SEC. VOLUMES REDUCED TO 0°C. AND 760 M.M.)

DEFLECTION
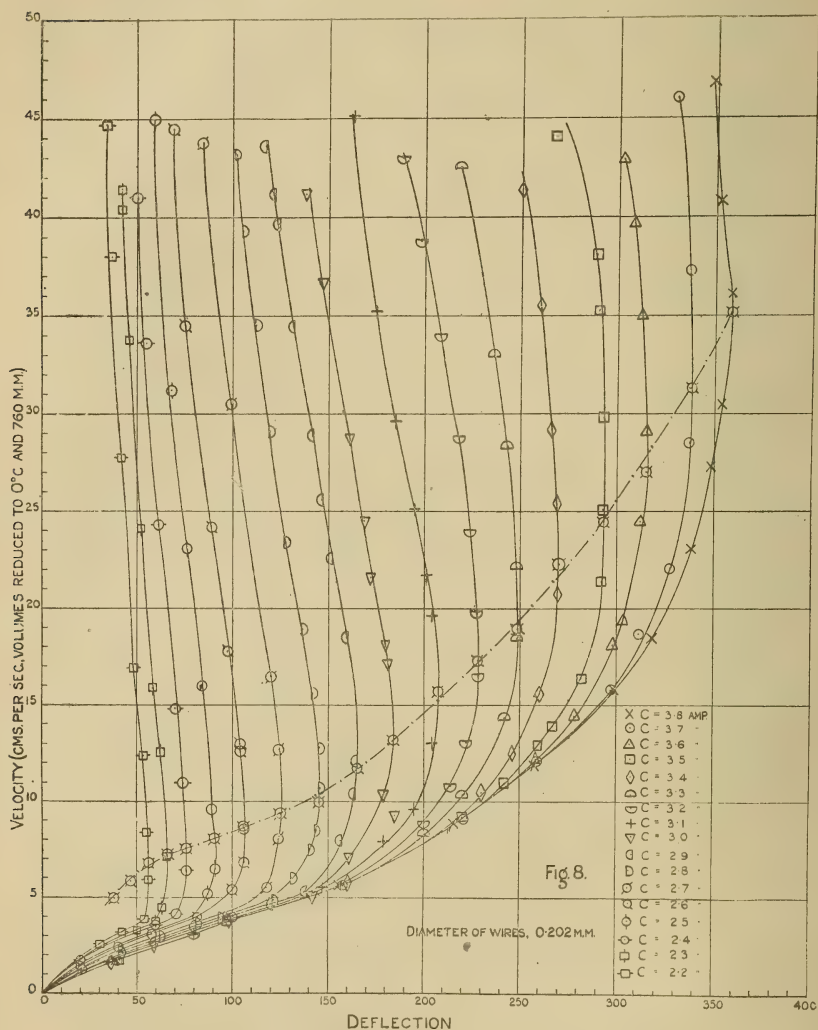
The experimental values given in the tenth column of Table IV. for the respective values of the mean impressed velocity V_m of the air-stream at which the resistance of

the second wire attains its maximum value when various heating currents are employed in the bridge, may be expressed in terms of the excess temperature θ above atmospheric, to which, in the absence of flow, the wires are raised by the respective currents by the empirical relation $V_m = 3{\cdot}95 \log \theta - 5{\cdot}14$. By virtue of the relation $\theta = 289 C^{2{\cdot}567}$ existing between the excess temperature θ and the heating current C employed, this may be alternatively expressed $V_m = 10{\cdot}14 \log C + 4{\cdot}58$.

Table V. shows the agreement between the experimental values of V_m given in column 10, Table IV., and those calculated by the above formulæ.

TABLE V.

Heating current C (amps.).	Excess temperature of wires above atmospheric. Zero flow. $(\theta.)$	Velocity of air-stream at which second wire attains its maximum resistance. (Cms. per sec.)		
		Experimental.	Calculated from $V_m = 3{\cdot}95 \log \theta - 5{\cdot}14.$	Calculated from $V_m = 10{\cdot}14 \log C + 4{\cdot}58.$
1·5	826	6·40	6·59	6·36
1·4	692	6·10	6·07	6·06
1·3	569	5·76	5·74	5·63
1·2	471	5·56	5·41	5·38
1·1	368	5·00	4·99	5·00
1·0	277	4·60	4·49	4·58
0·9	210	4·00	4·03	4·08
0·8	158	3·40	3·54	3·60
0·7	113	2·96	3·00	3·01

In the case of wires of diameter 0·202 mm. the corresponding relations were found to be

$$V_m = 3{\cdot}57 \log \theta - 4{\cdot}05 = 10{\cdot}8 \log C - 0{\cdot}10.$$

The values of the maximum deflexions given in the 12th column of Table IV. are plotted in fig. 9, as ordinates against the respective excess temperatures above atmospheric to which the wires are raised in the absence of an impressed air-stream, as abscissæ. Corresponding results for the anemometer employing wires of diameter

0·202 mm. are similarly plotted in fig. 9.   It is readily seen that in each case, excluding the range of excess temperature above atmospheric from zero to about 150° C.,

Fig. 9.

X DIAMETER OF WIRES, 0·101 M.M.
⊙ DIAMETER OF WIRES, 0·202 M.M.

MAXIMUM DEFLECTION (M.M.)

EXCESS TEMPERATURE OF WIRES ABOVE ATMOSPHERIC (°C)
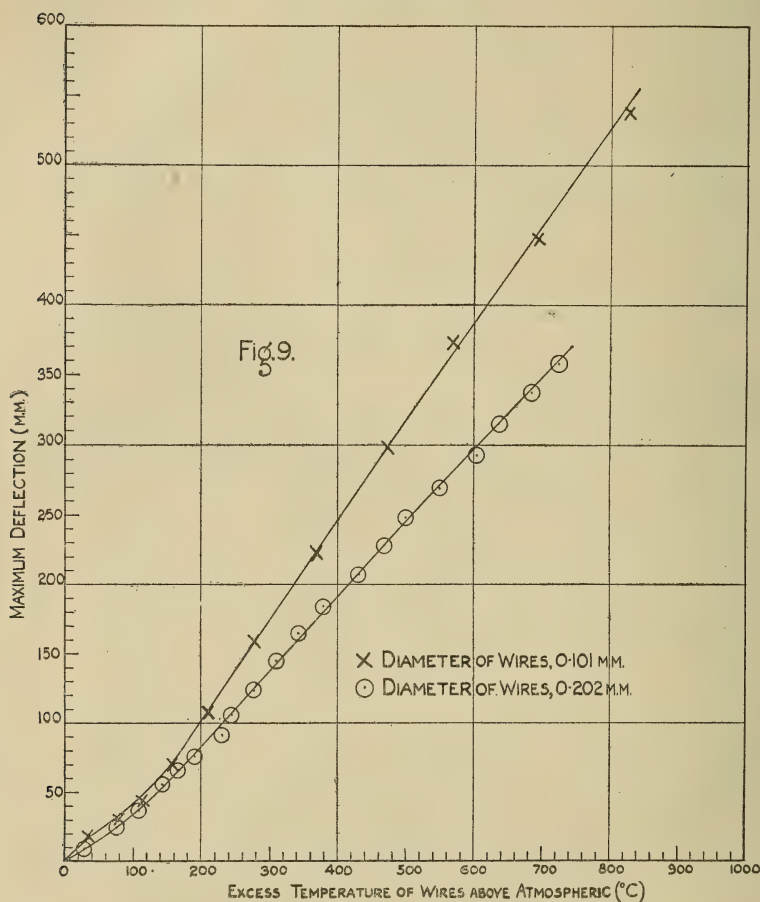
the maximum deflexion D_m is linearly related to the excess temperature θ.   Thus in the case of the wires of diameter 0·101 mm. the relation is

$$D_m = 0·708\,\theta - 42,$$

and in the case of wires of diameter 0·202 mm.

$$D_m = 0·538\,\theta - 28.$$

The departure from linearity in the relation of D_m to θ for

values of θ up to about 150° C. is probably connected with the results contained in Table IV., columns 2, 7, and 8. It will be noticed in column 2 that the ratio of the resistances of the two anemometer wires corresponding to the maximum deflexion continuously increases as the heating current is diminished, and moreover, while for large values of the heating current the temperature of the second wire, corresponding to the maximum deflexion, is considerably less than that corresponding to zero flow, for small values of the heating current, the temperature of the second wire corresponding to the maximum deflexion is greater than that corresponding to zero flow.

LXXV. *A Note on Magnetic Storms. By* S. Chapman, *M.A., D.Sc., F.R.S., Professor of Mathematics and Natural Philosophy in the University of Manchester* [*].

1. IN the Phil. Mag. for Dec. 1919, Prof. F. A. Lindemann published a paper on magnetic storms, in which certain criticisms were made of a theory of my own [†], and an alternative form of part of that theory was proposed. I have been unavoidably delayed in answering those criticisms, and the following notes will only indicate the general nature of my reply and some further conclusions, which I hope to support and extend by detailed calculations on a later occasion.

2. Prof. Lindemann criticises my theory because it postulates a stream of corpuscles "mainly or entirely of one sign of charge" [‡] projected from the sun and penetrating into the earth's atmosphere: he shows, on the basis of certain

numerical estimates of mine concerning the density &c. of the supposed stream, that if composed solely of α-particles (or *à fortiori* if composed solely of negative electrons), it would dissipate itself sideways by mutual repulsion before it could take effect on the earth : and proposes in place of the stream an ionized but electrically neutral cloud projected from the sun.

3. I concur in his conclusion that such streams as he contemplates would dissipate themselves as he describes, and though, as he recognized, I do not lay great stress on the numerical estimates referred to, I do not think they can be modified so seriously as to affect this conclusion. On the other hand, I think it is unnecessary, in order to overcome this objection, to resort to his alternative hypothesis, nor does the latter commend itself to me on its own merits. The difficulty to which Prof. Lindemann has usefully drawn attention can be met without departing from my original theory: in the latter I regarded as the essential feature of the stream the conveyance of electric current, which implies that, if charges of both sign are present, those of one kind preponderate either in density or (since both are moving in the same direction) in velocity, in order that the earth may receive charges "mainly or entirely" of the same sign. At times the qualifying words quoted may have been omitted for the sake of brevity, and the impression conveyed that I regarded the stream as consisting strictly of like charges, but if so this was unintentional : and similarly I had never definitely come to a decision (as in § 7 I now do) concerning the sign of the preponderant charge. On the other hand, it is fair to state that till the appearance of Prof. Lindemann's article I had not recognized the absolute necessity for the presence of both kinds of particles in the stream. The stream must be practically neutral electrostatically, and this condition is fulfilled if the volume density in it is the same for both kinds of charge. It is needless to require the charges also to have the same velocity, as he does, and there are definite reasons against making the assumption (§§ 5, 6).

4. On the other hand a stream such as I proposed, caused by the emission of particles mainly or entirely of one sign from some locally disturbed area of the sun, could easily adjust itself so as to become electrostatically neutral, while at the same time the neutral stream might convey a current to the earth in which the number of charges of one sign greatly preponderated. The ejection of one kind of charge from one region of the sun would leave the sun charged with the opposite sign, and this charge would presumably distribute itself uniformly over the sun with great rapidity, and then

flow outwards in all directions under its own mutual re-
pulsion : in the steady state (which is probably quickly
attained, while storm-producing streams often seem to
remain active for a month or more) the rate of escape of
the residual charge must equal the rate of emission of
the projected charge. The latter would therefore flow
through an "atmosphere" of charges of the opposite sign,
and if the velocity of escape of the latter were much less
than the velocity of projection of the locally-emitted charges
(as may well happen) the *volume-density* of charge in the
"atmosphere" might, in spite of its greater extension, equal
or exceed that in the stream. The stream would in any case
draw the slower moving charges sideways from the "atmo-
sphere," and be itself slightly expanded sideways, until within
the enlarged stream the volume-density of charge was equal
to that of the "atmosphere" outside—the stream would then
be effectively neutral and would still convey charge mainly
of one sign to the earth without having suffered any serious
lateral dissipation.

5. This establishes the *possibility* of the arrival of streams
such as I had contemplated : their origin, even their existence,
are matters concerning which little or no evidence is yet
afforded by our imperfect knowledge of solar physics. In this
respect the neutral clouds with which Prof. Lindemann deals
are on much the same footing. The real evidence for either
must at present be inferential, *e. g.* derived from the study
of terrestrial magnetism. Considered from this standpoint,
the stream hypothesis seems to possess advantages over the
cloud theory. The particles of the two signs in the neutra'
cloud are supposed to have the same velocity along the stream:
on nearing the earth they will be deflected in opposite direc-
tions in the earth's magnetic field. According to Störmer's
calculations *re* such corpuscular paths, the two sets of particles
should penetrate the earth's atmosphere (presumably to dif-
ferent levels) within two zones, one round each pole of the
magnetic axis, but so that the heavier particles fall much
nearer the poles than the lighter : also, while entering the
atmosphere all round either pole, the two sets of particles
falling near each pole will fall preferentially on opposite
sides of that pole. The phenomena of auroræ and magnetic
disturbance are not yet sufficiently well observed in polar
regions to allow any decision to be arrived at, as to whether
these two kinds of effects, corresponding to the two kinds of
particles supposed present in equal numbers, actually occur ;
but until they have been observed it seems more in accordance
with scientific procedure to adopt an hypothesis in which the
phenomena to be explained depend on one set of particles

2 X 2

only, provided the explanation afforded is equally good in respect of points which can be compared with observation.

6. On my stream hypothesis the particles entering the earth's atmosphere are mainly of one sign of charge: those of the opposite sign which also enter will be neutralized by the flow of the most mobile ions present, but this I regard as probably a secondary and unimportant part of the phenomena, and as detracting, though only slightly, from the storm-producing capacity of the preponderant charges. The latter give rise to the storm in the course of their escape from the earth : their motion would be radial, under the influence of their mutual electrostatic repulsion when brought to rest in the earth's atmosphere, did not the earth's magnetic field deflect them on their escape as at entry. But the inward and outward paths differ, because of the difference in distribution and velocity of the charge on entry and at escape. The charge spreads over the earth very rapidly and nearly uniformly, and is deflected sideways round the earth : and the magnetic storm I regard as due to this horizontal component of the outward flow of electricity. On the cloud hypothesis the two kinds of charge need not escape, but have simply to coalesce : and since both sets enter the earth near the poles, their mutual approach and neutralization would seem to be a simpler task, and one less likely (on consideration) to produce the world-wide magnetic field of a magnetic storm, than in the alternative case, where the escaping particles must redistribute themselves and also travel outwards and round the earth for great distances while making their escape.

These considerations (to be supplemented by detailed calculations later) are the chief ones which, though not urged as conclusive against the cloud hypothesis of Prof. Lindemann, yet seem to me to render that hypothesis less probable than the one I originally proposed.

7. In conclusion, though the matter has no direct relation to the foregoing, I will indicate briefly my reasons for having come to the conclusion that magnetic storms and auroræ are produced by negative charges. When writing my " Outline of a Theory of Magnetic Storms," I was of the opinion that charges of either sign would serve equally well to explain those phenomena, considering that, when they became entangled in the atmosphere, the charged layer of air rose bodily, and produced horizontal E.M.F.s and electric currents by thus cutting across the earth's horizontal magnetic field. The mean free path of an ion at auroral heights is, however, such that the ions have far less " grip " on the air molecules

in general than this view supposes : the ions have, indeed, considerable freedom to follow their own courses under the electrostatic and electromagnetic forces affecting them. Consequently, under the radial electrostatic force resulting from the mutual repulsion of the injected charges, the positive and negative ions present will at first tend to move radially in opposite directions : the vertical electric current thus produced will be unidirectional, and so also will be the horizontal electromagnetic force tending to deflect them along the circles of latitude, owing to their motion across the earth's horizontal magnetic field. This deflecting force will thus move both positive and negative ions in the same latitudinal direction, but the more mobile electrons will have much the greater velocity in this direction, both because of their smaller mass and of the greater deflecting force on them (proportional to their greater radial velocity under the electrostatic force). The horizontal current, not unidirectional for the two sets of ions as is the vertical current, will thus be directed opposite to the direction of motion of the *electrons* (opposite, because of their negative charge). Now the direction of this horizontal current is definitely known from the characteristic diminution of the earth's horizontal magnetic force during a magnetic storm : it is towards the west. Hence the motion of the electrons must be easterly, which (considering the direction of the horizontal magnetic field which deflects the electrons to the east) indicates that the radial motion of the negative electrons must be upwards.

Consequently the electrostatic field impels electrons upwards, and positive ions downwards : it must therefore be due to a negative charge on the earth.

This simple argument is supported by another which, though less weighty than the former, seems yet to have more force than most of those on which attempts to decide the sign of the injected charge have been based. The effects of magnetic storms in the middle belt of the earth are definitely greater over the afternoon than over the forenoon hemisphere of the earth, and this suggests that the injection of corpuscles is the more intense over the former hemisphere. Now the simplest paths of the particles are likely to be the more numerous, and these (as calculated by Störmer) correspond to entry of the particles on the afternoon side of the auroral zones, if the particles are negative, and on the forenoon side if positive. The circumstance mentioned is thus favourable to the view that the particles are negative.

Oct. 11, 1920.

LXXVI. *Advance of Perihelion of a Planet.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

I AM much obliged to Mr. Pearson for pointing out an error in my paper in the May number of the Philosophical Magazine.

If we take the expression

$$\gamma dt^2 - r^2 d\theta^2 - \frac{1}{\gamma} dr^2 \quad \text{for } ds^2$$

and use the transformation

$$r = r_1 \left(1 + \frac{m}{2r_1} \right).$$

we get for the new ds^2

$$\frac{\left(1 - \frac{m}{2r}\right)^2}{\left(1 + \frac{m}{2r}\right)^2} dt^2 - \left(1 + \frac{m}{2r}\right)^4 (dr^2 + r^2 d\theta^2).$$

These gravitation potentials satisfy Einstein's equations, and there is no restriction as to the magnitude of m. It is therefore quite legitimate to use this expression for ds^2, and it makes the velocity of light at any point in the sun's gravitational field independent of direction.

Using the method of the Calculus of Variations, I find that the differential equation of the path of a planet without any restriction as to the magnitude of m is

$$\frac{d^2u}{d\theta^2} + u = \frac{m}{h^2} \frac{\left(1 + \frac{mu}{2}\right)^3}{1 - \frac{mu}{2}} + m\left(u^2 + \left(\frac{du}{d\theta}\right)^2\right) \frac{2 - \frac{mu}{2}}{1 - \frac{m^2u^2}{4}} = 0,$$

where h is a constant.

If now we make m small, we have as an approximate solution

$$u = (1 + e \cos \theta)/\mathrm{L}, \quad \text{where } \mathrm{L} = h^2/m.$$

Hence the equation for a second approximation, if small terms are neglected, is

$$\frac{d^2u}{d\theta^2} + u = \frac{1}{\mathrm{L}} + \frac{2m}{\mathrm{L}^2}(1 + e^2) + \frac{6me \cos \theta}{\mathrm{L}^2}$$

which gives the correct amount for the advance of the perihelion of Mercury.

Recess,
4th Sept., 1920.

Yours faithfully,
Alex. Anderson.

LXXVII. *Note on the Theory of the Velocity of Chemical Reaction. By* F. A. Lindemann [*].

SOME years ago Professor W. C. McC. Lewis put forward an interesting theory in which he endeavoured to prove that the velocity of a chemical reaction was determined by the energy density of radiation of a certain frequency. This theory, if true, would be of such fundamental significance in all future work on the mechanism of chemical combination, that it requires most careful consideration; and it may therefore be worth while to call attention to a difficulty which appears to be fatal to the whole theory.

According to Arrhenius's well-known empirical relation, the temperature coefficient of the reaction velocity may be written A/T^2, A being a constant and T the absolute temperature. If v is the reaction velocity therefore, $1/v \dfrac{\partial v}{\partial T} = A/T^2$ or $d \log v = \dfrac{A dT}{T^2}$, whence $v = B e^{-A/T}$. It is clear, therefore, that any theory on which v is proportional to $e^{-A/T}$ will agree with the observed facts. Marcelin and Rice assume this to be the case because only molecules whose kinetic energy is greater than $\dfrac{AR}{N}$ react. The number of these is proportional to $e^{-A/T}$, so that Arrhenius's relation is satisfied. Prof. Lewis assumes that the reaction velocity is proportional to the radiation density

$$u_\nu = \frac{8\pi h \nu^3}{c^3} \; \frac{1}{e^{\frac{h\nu}{kT}} - 1},$$

which may be written

$$u_\nu = \frac{8\pi h \nu^3}{c^3} e^{-\frac{h\nu}{kT}} = B e^{-A T}$$

if $h\nu$ is large compared to kT, so that again the Arrhenius relation is bound to be found.

The only check obviously would be to establish some relation between the value of ν derived from the observed value of A by Prof. Lewis and the optical properties of the

---

reacting substances. The temperature coefficient of a reaction is usually given by chemists as the factor n by which the velocity is increased when the temperature is raised $10°$. Hence

$$1/v \frac{\partial v}{\partial T} = n^{1/10} - 1, \quad \text{so that} \quad \frac{h\nu}{kT} = T(n^{1/10} - 1)$$

and an absorption-band would be found at a wave-length

$$\lambda = \frac{ch}{kT^2(n^{1/10} - 1)} = \frac{c_2}{T^2(n^{1/10} - 1)},$$

where $c_2 = 1·46$ is the constant in Planck's radiation law written in the form

$$E_\lambda = \frac{c_1}{\lambda^5} \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}.$$

In the case of the inversion of sucrose by $0·9$ N. hydrochloric acid, Lewis finds $n = 4·13$ between $25°$ C. and $35°$ C. Therefore

$$\frac{h\nu}{kT} = 303(1·152 - 1) = 46 \quad \text{and} \quad \lambda = 1·05 \, \mu \, *.$$

The solution does absorb radiation between 1μ and 10μ, so that Lewis concludes that his theory is supported by the facts.

The fundamental difficulty to which this note refers arises from the fact that the radiation density may be profoundly modified by exposing the reaction to some external source of radiation. If Prof. Lewis's theory were true, this should completely change the velocity of reaction, but no such phenomenon has been observed. As an example, one may consider the change in radiation density produced by exposing a reaction to sunlight. If α is the apparent angular semi-diameter of the sun and T_0 its temperature, the energy density in sunlight is given by

$$u_\nu' = 2\pi\alpha^2 \frac{h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT_0}} - 1}.$$

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* Lewis finds a somewhat different wave-length, $\lambda = 1·23\mu$, presumably because he uses Perrin's value $6·85 \cdot 10^{23}$ for N; which figure one takes does not materially affect the argument.

The radiation density in the dark at temperature T is given by

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1},$$

so that the ratio of the radiation density due to sunlight to that in the dark is given by

$$\frac{u_\nu'}{u_\nu} = \frac{\alpha^2}{4} \frac{e^{\frac{h\nu}{kT}} - 1}{e^{\frac{h\nu}{kT_0}} - 1}.$$

In the above instance it has been shown that for $T = 303°$, $\frac{h\nu}{kT} = 46$, so that putting the sun's effective temperature $T_0 = 6000°$ and its apparent semi-diameter $\alpha = 16' = 4\cdot 65 \cdot 10^{-3}$, one finds

$$\frac{u_\nu'}{u_\nu} = 5\cdot 42 \cdot 10^{-6} \frac{e^{46} - 1}{e^{2\cdot 33} - 1} = 5\cdot 8 \cdot 10^{13}.$$

In other words, the energy density of the radiation which is supposed to determine the reaction velocity, namely that of wave-length $1\cdot 046\mu$, is some 10^{13} times greater in sunlight than in the dark. Yet the reaction proceeds at appreciably the same rate whether it is exposed to sunlight or not.

The obvious conclusion would appear to be that the rate of reaction is not affected by the radiation density. There are, of course, various ways in which one may attempt to escape this conclusion, but a moment's consideration shows them to be untenable, and it is therefore scarcely worth while to enumerate and disprove them here. But until and unless the above difficulty can be disposed of, it would seem to constitute a grave objection to Professor Lewis's theory.

Clarendon Laboratory, Oxford,
    Sept. 19th, 1920.

LXXVIII. *The Modification of the Parabolic Trajectory on the Theory of Relativity. By* W. B. MORTON, *M.A., Queen's University, Belfast*[*].

THE simplest case of accelerated motion, that in which a particle moves in a straight line with constant "rest-acceleration," was investigated by Born[†] who gave it the name of "hyperbolic motion" because the distance-time graph, or "world-line," has that form. The next in order of simplicity is that which corresponds to the parabolic path under gravity—*i. e.*, when the particle has rest-acceleration constant in magnitude and direction, but possesses a velocity-component perpendicular to this direction.

Let the origin be taken at the point where the velocity is perpendicular to the acceleration. It will be convenient to speak of the tangent to the path at this point as "horizontal" and the direction of the acceleration as the downwards vertical. Let the axes of x and y be taken in these directions respectively, u is the velocity at the origin, v the velocity at any point, and c the speed of light. The inclination of the tangent to the horizontal will be denoted by ϕ.

The rest-acceleration is derived from the ordinary acceleration as estimated from a "fixed" standpoint by multiplying the tangential component by γ^3 and the normal component by γ^2 where $\gamma = 1 / \left(1 - \dfrac{v^2}{c^2} \right)^{\frac{1}{2}}$.

Therefore in the present case the resultant of $\gamma^3 \dfrac{v\,dv}{ds}$ along the tangent and $\gamma^2 \dfrac{v^2}{\rho}$ along the normal is in the direction of Oy and has the constant magnitude f say. The equations of motion are

$$\gamma^3 \frac{v\,dv}{ds} \cos\phi - \gamma^2 \frac{v^2}{\rho} \sin\phi = 0 \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\gamma^2 \frac{v^2}{\rho} = f \cos\phi. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) gives $\gamma \dfrac{dv}{d\phi} = v \tan\phi$.

Put $v = c \sin\theta$ so that $\gamma = \sec\theta$, then $\operatorname{cosec}\theta\,d\theta = \tan\phi\,d\phi$, giving the relation

$$\tan\tfrac{1}{2}\theta \, . \, \cos\phi = \text{const.} = \tan\tfrac{1}{2}\theta_0, \text{ say}, \quad . \quad . \quad (3)$$

where $\sin\theta_0 = u/c$.

When θ is small this equation obviously reduces to $v \cos \phi =$ const. in accordance with the elementary theory.

The subsequent analysis is made much neater by the introduction of an angular parameter α defined by

$$\sin \alpha = \tan \tfrac{1}{2}\theta_0 = \{c - (c^2 - u^2)^{\frac{1}{2}}\}/u.$$

Using this equation (3) gives the connexion between magnitude and direction of v in the form

$$v/c = \sin \theta = 2 \sin \alpha \cos \phi/(\cos^2 \phi + \sin^2 \alpha). \quad . \quad . \quad (4)$$

From equation (2) $\rho = c^2 \tan^2 \theta \sec \phi/f$.

The linear scale of the path may be expressed in terms of the parameter of the parabola which would be described on the old theory,

$$a = u^2/2 f = 2c^2 \sin^2 \alpha/f(1 + \sin^2 \alpha)^2.$$

Using this, and the relation (3), we express the radius of curvature in terms of ϕ and the constants a, α,

$$\rho = ds/d\phi = 2a(1 + \sin^2 \alpha)^2 \cos \phi/(\cos^2\phi - \sin^2 \alpha)^2.$$

The integral of this is the intrinsic equation of the path

$$s = \frac{a(1 + \sin^2 \alpha)^2}{2 \cos^3 \alpha} \left\{ \frac{2 \cos \alpha \sin \phi}{\cos (\phi + \alpha) \cos (\phi - \alpha)} + \log \frac{\cos \alpha + \sin \phi}{\cos \alpha - \sin \phi} \right\} . \quad . \quad . \quad (5)$$

Integrating

$$dx/d\phi = \cos \phi \cdot ds/d\phi \quad \text{and} \quad dy/d\phi = \sin \phi \cdot ds/d\phi,$$

we obtain for the coordinates of a point on the path the expressions

$$x = \frac{a(1 + \sin^2 \alpha)^2}{2 \cos^2 \alpha} \left\{ \frac{\sin 2\phi}{\cos (\phi + \alpha) \cos (\phi - \alpha)} + \frac{2}{\sin 2\alpha} \log \cdot \frac{\cos (\phi - \alpha)}{\cos (\phi + \alpha)} \right\} \quad (6)$$

$$y = a(1 + \sin^2\alpha)^2 \{\sec (\phi + \alpha) \sec (\phi - \alpha) - \sec^2\alpha\}. \quad . \quad . \quad . \quad . \quad (7)$$

It only remains to find the relation between ϕ and the time. This can be obtained from (4) by writing

$$v = ds/dt = ds/d\phi \times d\phi/dt,$$

leading to

$$cdt/d\phi = a(1 + \sin^2 \alpha)^2(\cos^2 \phi + \sin^2 \alpha)/\sin \alpha(\cos^2 \phi - \sin^2 \alpha)^2,$$

the integral of which is

$$ct = \frac{a(1 + \sin^2 \alpha)^2}{2 \sin \alpha \cos^2 \alpha} \left\{ \frac{\sin 2\phi}{\cos (\phi + \alpha) \cos (\phi - \alpha)} + \tan \alpha \log \frac{\cos (\phi - \alpha)}{\cos (\phi + \alpha)} \right\}. \quad (8)$$

The following properties of the motion are seen immediately from the equations. In the first place as ϕ approaches the value $\left(\dfrac{\pi}{2} - \alpha\right)$, x, y, and t become infinite and v approaches c. That is to say, the direction of motion, instead of swerving

through a right angle and approaching coincidence with the acceleration, as in the parabolic case, is turned through $\left(\dfrac{\pi}{2} - \alpha\right)$ and the particle approaches a steady motion at the speed of light in a direction inclined at angle α to that of the constant " rest-acceleration." The following table gives the values of α for different values of u/c :—

$u/c.$	$\alpha.$
·1	2° 52′
·2	5° 48′
·3	8° 50′
·4	12° 2′
·5	15° 33′
·6	19° 28′
·7	24° 6′
·8	30° 0′
·9	38° 49′
1·0	90°

For $u/c = {\cdot}8$, $\sin \alpha = \{c - (c^2 - u^2)^{\frac{1}{2}}\}/u = \tfrac{1}{2}$.

To gain a clearer view of the terminal conditions, which have a rather paradoxical appearance at first sight, it is worth while to evaluate the components of the (ordinary) acceleration. We find, reinstating f,

$$v\,dv/ds = f \sin \phi (\cos^2 \phi - \sin^2 \alpha)^3/(\cos^2 \phi + \sin^2 \alpha)^3,$$
$$v^2/\rho = f \cos \phi (\cos^2 \phi - \sin^2 \alpha)^2/(\cos^2 \phi + \sin^2 \alpha)^2,$$
and $$\gamma = (\cos^2 \phi + \sin^2 \alpha)/(\cos^2 \phi - \sin^2 \alpha),$$

so that γ^3 times the former component and γ^2 times the latter combine to give f. This verifies the analysis.

Now put $\phi = \pi - \alpha - \chi$ where χ is small,

$$v\,dv/ds = f \cos \alpha \, . \, \cot^3 \alpha \, . \, \chi^3,$$
$$\frac{v^2}{\rho} = f \sin \alpha \, . \, \cot^2 \alpha \, . \, \chi^2,$$
$$\gamma = \tan \alpha / \chi.$$

The tangential acceleration (ordinary) is small compared with the normal, but in passing to the rest-acceleration it is multiplied by a higher power of the large quantity γ, so that the modified components are of the same order of magnitude and have the finite ratio $\tan \alpha$.

I have taken the case $u/c = {\cdot}8$, $\alpha = 30°$, and have calculated x, y for different values of ϕ and plotted the path shown on the diagram. The parabola with the same " a " is shown for comparison. The figures marked above the path give the values of v/c at the corresponding points, and those below give the time, the unit in the latter case being the time required for light to describe the parameter " a." These points were obtained by calculating the values of v/c

and ct for each ϕ and plotting against x (shown on the other curves). The points on these curves corresponding to even values of v/c and ct could then be projected on the path.

Fig. 1.
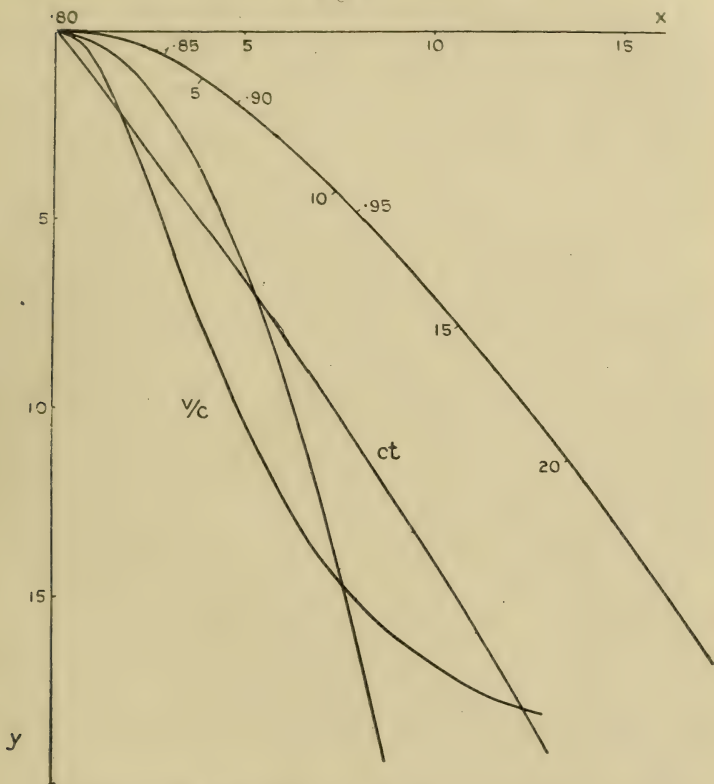
It will be noticed that the graph for ct against x is nearly straight, showing that the equable description of horizontal distance is not seriously departed from even at the high velocities taken. The analytical reason for this is seen on inspection of the formulæ (6) and (8) for x and ct. It will be seen that the expressions are built up of the same two functions of ϕ with different constant multipliers. The first term in ct is cosec α times the term in x, whereas in the second term the ratio is sin α. The two functional expressions are roughly of the same order of magnitude in x for the smaller values of ϕ, but as the limiting value is approached, the second term becomes insignificant compared with the first. Evidently the ratio of ct to x is mainly determined by the first term and approaches the constant value cosec α.

LXXIX. *Notices respecting New Books.*

Thermodynamics for Engineers. By J. A. EWING. Cambridge
University Press. Pp. xiii + 383. Price 30s. net.

THIS book is largely based upon Sir J. A. Ewing's two well-
known books on applied thermodynamics, ' The Steam Engine '
and ' The Mechanical Production of Cold.' The chapter on " First
Principles " follows closely the second chapter of " The Steam
Engine," but has gained in clarity in rewriting, and the general
treatment in the book before us of the Theory of the Steam Engine
(Chapter III.), the Theory of Refrigeration (Chapter IV.), Jets
and Turbines (Chapter V.), and Internal Combustion Engines
(Chapter VI.) does not differ essentially from the exposition given
in the books mentioned. We notice that the author restricts
the term adiabatic to reversible processes : the general practice
nowadays is rather to indicate by adiabatic a process in which no
heat is allowed to enter or leave the substance, and to specify
further whether the process in question is reversible or irreversible
in the case considered. The last two chapters, devoted to general
thermodynamic relations and their applications to particular fluids,
contain much new matter. A list of thermodynamical formulæ
is given which is very convenient for reference. The porous plug
experiment, which is often so ineffectively handled, receives
adequate treatment, and Callendar's equation, now so widely
used, is discussed in considerable detail, the author being careful
to draw attention to its limitations. The variations of the specific
heats of saturated vapours, the subject of recent papers by
Sir J. A. Ewing and Professor A. W. Porter in this magazine, are
not considered. The book is illustrated by excellent diagrams,
some of them, such as that exhibiting Witkowski's isothermals
for air, being not usually found in text-books. For the physicist
who wants to study thermodynamics from the point of view of
the engineering, rather than the physico-chemical, applications, as
for the engineer who wants to grasp the theoretical foundations
of all engine-efficiencies, the book is in every way excellent, com-
bining as it does sound theory and practical knowledge in a way
that is only too rare.

Life and Works of Sir Jagadis C. Bose. By PATRICK GEDDES.
Longmans, Green & Co. Pp. xii + 259. Price 16s. net.

EARLY in life Sir J. C. Bose set himself the task of winning a place
for the native of India in modern science, and this task he has
pursued with a steadfast and unselfish devotion in the face of
very great difficulties. The foundation of the Bose Research
Institute and the somewhat tardy award of the F.R.S. may be
said to mark the final success of his endeavours. Some twenty-five
years ago his name became known to physicists in connexion with his
work on very short electromagnetic waves, an investigation which
he carried out with the utmost experimental skill ; and although his

more recent researches have dealt almost entirely with plant-life, his methods have always been those of the physicist. Perhaps the fact that he is a physicist rather than a physiologist in training and language, may account for some of the opposition which his work and views have aroused in certain quarters. His researches on complex strain effects in metals, which he included under the title of " Response in the Non-Living," led him to extend considerably the analogy between the living and non-living which had already been expressed by the use of such terms as " fatigue " for describing non-organic phenomena. From this he passed on to the fascinating problem of plant response and irritability. Many of the astonishing results obtained with the help of his various " crescographs," or instruments for magnifying the small movements of plant-growth, were demonstrated in London early this year, and vindicated against the critics. A magnification of movement approaching one hundred million times has been obtained with the magnetic crescograph, the instrument representing the culmination of a long series of experiments. His main discoveries on plant-life have been recently discussed in the scientific press, and are still fresh in the minds of all. In the book before us Professor Patrick Geddes presents us with a very sympathetic study of the career, personality, and ideals of Sir J. C. Bose, and summarises in some detail his scientific work. He comments without bitterness on the difficulties placed in the way of a sincere and gifted student of nature, and leads us to rejoice with him in the ultimate recognition of Sir J. C. Bose's claim as a citizen and a scientist. The book is excellently produced and illustrated.

Traité de La Lumière. Par CHRISTIAN HUYGENS. Gauthier-Villars: Paris. Pp. x+155. Price 3 fr. 60.

THIS reprint of Huygens' famous treatise is one of the first volumes of a new series, appearing under the title of " Les Maitres de la Pensée Scientifique." Some sixty volumes are already announced, other classical works on light included in the list being those of Newton, Young, and Fresnel. The biological sciences are represented, but mathematics and physics claim the majority of the volumes of the series. In England we are not well provided with reprints of the classical papers. In the particular case of Huygens' " Treatise " we have, it is true, Silvanus Thompson's beautifully printed translation, which, however, is comparatively costly. The little book before us is quite well produced, and very moderately priced, and we think that the series should enjoy considerable popularity among English readers. We hope to see the list extended until there is no need to go to "*Ostwald's Klassiker*" for the original authorities. Apart from sentimental reasons French is a language more accessible to most Britons than German, and the page of the French series is more restful to the eye than the German page. We wish the new venture every success.

The Elementary Differential Geometry of Plane Curves. By R. H. Fowler, M.A. Cambridge University Press. Cambridge Tracts, No. 20. 1920. 8vo, pp. viii+105. Price 6s. net.

This tract gives a concise but clear and rigorous presentation of the differential properties of plane curves. Tangents and Normals, Curvature, Theory of Contact, Theory of Envelopes, Singular Points, and Asymptotes of plane curves are the subjects of its chapters II. to VII. The first chapter gives a good analytical Introduction to the subject. This excellent tract deserves the attention of all students of mathematics.

Lectures on the Theory of Plane Curves, delivered to post-graduate students in the University of Calcutta. By Suremdranshan Ganganli, M.Sc. Published by the University of Calcutta, 1919. 8vo. Pp. vi+350+17 (diagrams), in two Parts.

Contents: Introduction (on homogeneous coordinates, the line at infinity, line-coordinates, circular points at infinity, projection). Theory of plane curves. Singular Points. Polar Curves. Covariant Curves; the Hessian Polar Reciprocal Curves. Foci of Curves. The Analytical Triangles; Asymptotes. System of Curves (pencil of curves, envelopes, etc.). Cubic Curves (Chapters X.–XV.). Curves of the 4th order (Chapters XVI.–XX.). Appendix I, Notes on the Bicircular Quartic. Appendix II, Note on Trinodal Quartics.

This handy and easily readable work will be particularly helpful to those interested in cubics and quartics, which are treated very fully in the last eleven chapters.

Editorial Note.

In the February issue of the Philosophical Magazine we published a paper by Mr. Norman Campbell on "The Adjustment of Observations." That paper was intended to be followed by two others in which the reasons for the contentions advanced in the first would be given. We now discover that the second paper of the series, which Mr. Campbell imagined to be in our hands, has gone astray and cannot therefore be published. Mr. Campbell asks us to state that the substance of the second and third papers is to be found in his book 'Physics—The Elements' just published by the Cambridge University Press. It will be seen from that book that he does not accept the assumptions on which Dr. Meldrum Stewart, in the April issue of this Journal, based a criticism of the first paper.   W. Francis.

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[SIXTH SERIES.]

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LXXX. *On the Closure of Small Cavities in Rocks exposed to High Pressures.* By J. JOLY, *F.R.S., F.T.C.D.**

[Plate XVI.]

IT is now nearly eight years ago since I commenced experiments on the behaviour of rocks under high pressures, hydrostatic in character; the object being, more especially, to determine the stress under which cavities in these materials will close. Data bearing on this point have many applications in Geological science. These experiments extended over a period of nearly two years, from Dec. 1912 to Sept. 1914. They were all carried out at atmospheric temperature. It was intended to modify the apparatus so as to permit of the temperature being raised and maintained at moderate heights, but the outbreak of war rendered any development in this direction impossible. It appears desirable now to publish an account of what has been accomplished. The method employed seems to possess advantages on the score of directness, sensitiveness, and simplicity over any work of the kind described before or after these experiments by other observers.

The rock specimen under examination is, as truly as may be, spherical in form. But the sphere is formed of two hemispheres accurately fitted together on a plane surface. A small hemispherical cavity is ground centrally in the flat

* Communicated by the Author.

face of one of the hemispheres. The hemispheres may be cemented together by a thin varnish of Canada balsam or simply laid together. The diameter of the sphere so formed is closely 2 cm. It is highly polished on the outside as well as on the flat meeting surfaces.

The sphere of rock is enclosed in a lead cylinder having an outside diameter of 2·5 cm. This cylinder, which is about 3·4 cm. in length, is composed of two short cylinders in each of which a hemispherical cavity, having the same dimensions as the hemispheres of rock, is formed. The lead cylinder containing the sphere of rock is pushed into the crushing mortar, and exposed to pressure transmitted through a plunger. In this manner a hydrostatic pressure acts upon the sphere of rock, the lead flowing freely. The arrangements permitted of the pressure being maintained practically constant for several months at a time.

The crushing mortar is shown in section in fig. 1, to a scale of one half. It is made of vanadium steel, the outer strengthening ring being shrunk on. Messrs. Amsler of Schaffhausen were the makers, and it would be difficult to find fault with the manner in which the apparatus behaved. It will be seen that the lead cylinder is contained between a shorter plunger below and the upper plunger. The latter carries a movable cap resting on a smooth polished surface, to secure as far as possible a truly axial direction for the applied compressive force. This mortar is specified to take on the plunger one hundred tons per square inch. In order to prevent leakage of the lead past the pistons (which fit very accurately) copper washers—turned over on the edge—are provided. One of these is fitted to each end of the lead cylinder.

The shaping of the rock material to the form of two accurately fitting hemispheres was undertaken by Dr. Krantz of Bonn. This work was very beautifully and accurately carried out. The internal cavities were ground in the laboratory, using a small spherical steel ball (intended for a ball-bearing) to carry the abradent (very fine carborundum). This ball was mounted in lead, projecting just a very little more than its radial dimension, and spun in the lathe against the central point of the plane surface of the rock hemisphere. The cavity so produced had a diameter of closely 6·2 millimetres. During this operation the rock hemisphere was held in a lead cup, externally cylindrical, in which a cavity of the shape of the hemisphere had previously been formed by a special tool. Special means were employed to secure the central position of the cavity ground in the rock hemisphere.

At the pressures finally found requisite to break down the resistance of the rock, there was no reason why two spheres could not be dealt with at the one time. In this case two

Fig. 1.

spheres, as described above, were each enclosed in a separate lead container having the dimensions already given, and these containers placed in the crushing mortar. The copper flanges were applied, of course, to one end only of each cylinder.

The hydraulic press used was a Tangye Press, with Bourdon gauge attached, and capable of affording a crushing force of 400 tons; the water being pumped in by hand by two pumps, a fast low-pressure pump and a slow high-pressure pump. The crushing mortar is placed centrally on the platten of the press, and this is up-lifted by the operation of the pumps till the plunger of the mortar comes against the ceiling of the press. Further pumping now forces down the plunger.

In order to counteract the slow leakage of water around the leather collar of the press, a very simple and effective device was adopted.

In the cellar beneath the laboratory a steel gas-cylinder of the usual type, filled with compressed air, was installed. This was supported in an inverted position, *i. e.* nozzle downwards, and a high-pressure copper pipe brought up from it through the floor and tapped into the high-pressure water-chamber of the press. A screw cone-in-cone stopcock served to open connexion between the tube and the press. The action was as follows :—When the hydraulic pressure had risen above a certain point, the stopcock was opened and water from the press allowed to flow into the gas-bottle, raising the pressure in the latter. The pumping was then continued till the required pressure was attained. If, now, the whole system was left to itself, any small leakage of water was made good by water fed by air-pressure from the bottle. In short, the air acts as a spring, storing energy and replacing its loss by supplying water practically at the original pressure. This acted very successfully. For months the pressure was maintained constant with no loss detectable by the manometer. The temperature in the cellar was very uniform.

In two of the experiments the rock hemispheres were used without any cavity being formed in either of the hemispheres. A cavity common to both was provided by the device of inserting a thin steel washer between the hemispheres : this washer having a central circular opening of the same diameter as that of the cavity as formed in the hemisphere. In this case care was taken to grind the washer to a uniform thickness of about $\frac{1}{2}$ a millimetre. The washer may be cemented between the hemispheres with hard Canada balsam or used without cement.

It will be evident that by ordering the experiments as described above, directness and sensitiveness are the objects in view. The sphere is the form of highest symmetry, and the mathematical treatment of stress and strain in the determination of conditions of rupture is simpler than in any other

case. Again, the form given to the specimens under expe-
riment is such as to enable the first beginnings of yielding
to be detected. There is in every case a polished flat
surface, unsupported, in a small central area. Examination
of this by a bright reflected light affords a most sensitive
test of distortion. And, in addition to this test, examination
with the lens or microscope may readily be applied to this
polished surface and minute cracks detected in an incipient
stage. When a cavity in one hemisphere is provided rapid
yielding reveals itself in the debris which spalls off and
accumulates in this cavity.

The importance of securing the means of sensitive obser-
vation arises from the fact that in Nature time for the
accumulation and development of effects exists in a far
greater degree than can ever prevail in the laboratory. Our
only chance of detecting such effects must be such conditions
of sensitiveness as will enable their first beginnings to be
observed.

Observation soon revealed the fact that while rapid
yielding of the material to the external hydrostatic stress
was shown by the accumulation of debris in the cavity formed
in one of the hemispheres, less intense stress might show a
distinct effect in the optical distortion of the flat surface
vis-a-vis to it or by the development of cracks in the same.
It is very improbable that such signs of yielding could arise
without ultimate breakdown of all resistance and closing of
the cavity. And when we further bear in mind that the
effects of raised temperature which must prevail in Nature
are here absent, we seem justified in treating such stresses as
produce these first signs of yielding as probably exceeding
those which in Nature would result in the closing of cavities.
The use of a flat thin washer between the hemispheres was
dictated by this consideration. And although it possessed
the disadvantage of slightly disturbing the truth of the
spherical form in the specimens as prepared for these expe-
riments, it increased the number of observations possible
with the available number of specimens. War-conditions
had put an end to all possibility of obtaining others.

The rocks dealt with were of four markedly different kinds,
and all of widespread importance :—Granite, basalt, obsidian,
and Solenhofen lithographic limestone. The material has
necessarily to be fine-grained. The granite was from Selb,
Bavaria ; the basalt from Jungfernstein, Siebengebirge ; the
obsidian from Iceland ; and the lithographic limestone from
Solenhofen, Bavaria. The resistance to crushing of cubes
of the granite, basalt, and lithographic slate was made the

subject of careful experiment; and the densities of these materials were determined by accurate measurements of the dimensions and weight of the cubes. The cubes were cut by Krantz, special precautions being taken to secure the parallelism of two special faces intended to take the pressure of the hydraulic press.

The volume of the *granite* cube was $5 \cdot 07^3$ cm. $= 130 \cdot 299$, and its weight $338 \cdot 744$ gram, giving a density $= 2 \cdot 600$. A pressure of 20 tons was applied for 20 minutes with no apparent effect. The pressure was then raised to 30 tons and applied for 70 minutes without visible effect. Raised now to 35 tons one corner split off, but the cube remained otherwise sound. Next day at 36 tons it exploded violently. This is 9 tons or 20,160 lb. per square inch.

This appears to be a fairly high result. The strongest mica granite cited in Merrill's tables [*] gave 23,358 lb. per square inch, and of 59 such granites cited only 7 exceed 20,000 lb. per square inch. These tests were mostly made on 2 in. cubes as in the present case.

The volume of the *basalt* cube was $5 \cdot 05^3$ cm. $= 128,775$ c.c. Its weight was $374 \cdot 194$ grams. Hence density $= 2 \cdot 871$. 20 tons applied for 18 minutes produced no effect. At 27 tons a small crack near one side appeared, and a piece flatted out at 37 tons. Next day the pressure was applied anew and slowly increased to 59 tons, when there was a violent explosion and the cube was scattered.

This is $14 \cdot 75$ tons, or 33,000 lb. per square inch, and compares favourably with certain similar rocks, diabase, cited by Merrill, *loc. cit.*, the strength of which in no case reached 27,000 lb. per square inch.

In the case of the *lithographic limestone* the cube volume was the same as in the case of the basalt, and the weight $343 \cdot 950$ grams: giving a density of $2 \cdot 639$.

Raising the pressure at intervals approximating to 10 minutes from 20 tons, as much as 50 tons was reached by increment of 10 tons, when a small chip broke away at one corner. At 53 and 54 tons the cube began to chip rapidly— finally cracking vertically through the middle.

This is $13 \cdot 5$ tons $= 30,240$ lb. per square inch. Adams applied similar tests to this rock, his results ranging from 28,000 to 40,000 lb. per square inch [†].

The *obsidian* was not tested for crushing strength. Its specific gravity, determined by weighing one of the hemispheres in water, was found to be $2 \cdot 380$.

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[*] 'Stones for Building and Decoration,' New York, 1897.

[†] Frank D. Adams and L. V. King, The Journal of Geology, vol. **xx.** 1912.

The Experiments.

(I.) Two spheres were dealt with : one of basalt, the other granite. The hemispheres were cemented by hard Canada balsam. The pressure was raised little by little to 50 tons read on the manometer. This was maintained constant from December 26th, 1912, till March 4th, 1913, *i. e.* for 68 days. During this time the plunger sank in about $\frac{1}{2}$ mm., or possibly a little more. When pressure was relieved the lower plunger under the elastic recovery of the lead within the mortar protruded about 3 mm., lifting the heavy crushing mortar by this distance. On forcing out the lead cylinders the copper washers showed considerable flowage, where they were pressed against the plungers. The lead cylinders were easily parted, and by gentle warming the hemispheres opened.

Both basalt and granite had yielded in the same manner. The cavity held a small quantity of powdered rock—considerably more in the granite than in the basalt sphere. The debris in the basalt weighed 0·100, and in the granite 0·170 gram. Under the microscope these powders were indistinguishable from rock powdered—not very finely—in an agate mortar.

The flat polished rock surfaces covering the cavity had bulged downwards. The amount of bulge in the case of the basalt was estimated to be not more than 0·1 mm. The bulge on the granite was rather more.

It is difficult to reproduce the appearance of the specimens by photography—but the photos figs. 1 & 2 (Pl. XVI.) show that the effects are quite conspicuous. The manner in which the cavity in the basalt has been extended is remarkable. The bulge on the flat covering surface faithfully follows the outline shape of the cavity.

Examination with a strong lens of the flat, bulged, surfaces showed that the distortion was largely due to the relative displacement of the individual mineral particles. This points to the risk of error which may obtain when experiments of this nature are carried out on simple minerals only.

It may be safely inferred from this result that the pressure of 50 tons prolonged over the duration of the test is considerably in excess of what would suffice to close the cavity.

(II.) As in (I.) granite and basalt spheres were dealt with—fresh specimens being, of course, taken. The granite in this case, although from the same locality, has a felspar which is of a pale pinkish tint, and in that respect seems to differ from the granite of (I.) and as used in the crushing

test: the grain is alike. It is probable the difference is quite unimportant. In all particulars the arrangements were same as in (I.).

The test extended from March 6th, 1913, till June 24th, 1913, *i. e.* for 110 days—during which time a pressure of 30 tons on the plunger was steadily maintained. On relief of pressure it was found that there was no debris in the cavity in the basalt, but reflected light revealed a faint but unmistakable distortion of the flat covering surface. The appearance is that of a thin protuberant ring ; but close examination shows a raised circular area of the diametral size of the cavity.

The cavity in the granite sphere contains debris, but the breakdown is less than in experiment (I.). The flat surface covering the cavity shows signs of cracking

Photos of these effects are given in figs. 3 and 4 (Pl. XVI.). We must conclude from this result that 30 tons pressure, even when exerted over the brief period of 110 days, has broken down the granite and produced a distortion of the basalt which remains as a permanent set. In short, there has been something like flowage. Prolonged over years or centuries—even at these low temperatures—such distortion would very surely ultimately close the cavity.

(III.) In this experiment the arrangement was somewhat different from that of (I.) and (II.).

Two spheres were dealt with, A and B.

A consisted of a hemisphere of basalt and one of granite separated by a thin ground-steel washer, closely 0·5 mm. in thickness.

B was similarly constituted.

Canada balsam cemented the hemispheres together in both cases. It will be understood there is no cavity in any of the hemispheres. The opening in the washer is of the same diameter (6·2 mm.) as the cavity existing in (I.) and (II.), and the observation is confined to effects of distortion of the flat surfaces covering this opening at either side.

A pressure of 20 tons was applied from October 13th, 1913, till March 21st, 1914, *i. e.* for 150 days.

It was then found that both the hemispheres of A showed visible but not very definite effects. In the case of the granite there is some fine but distinct cracking around the margin of the central circular area of relief of pressure. The basalt showed one fine crack touching this central area tangentially.

In the case of sphere B there was no visible change produced in either hemisphere.

It seems as if we must conclude that at normal temperatures the pressure of 20 tons on the plunger must be near that critical pressure which will just determine the closing of small cavities. This load on the plunger, the area of which is 0·775 square inches, produces a pressure of 59,145 lb. per square inch, or 4167 kilos per square cm. The depth of the earth's surface, assuming the crust-rock to possess a density $= 2·8$, at which such a pressure might prevail, would be about 9 miles. The temperature prevailing at this depth might be about 450° C. (Adams, *loc. cit.*). It would be desirable to repeat the experiment at this temperature. It seems probable that this pressure would, under the high-temperature conditions, ultimately close every cavity.

(IV.) In this experiment the granite and basalt hemispheres used in (III.), which showed no visible injury, were re-arranged as before. No Canada balsam was used. The second sphere was composed of a hemisphere of Solenhofen limestone and one of obsidian. No balsam was used. The washers were re-ground. A pressure of 22 tons was applied from March 21st to March 23rd, 1914, *i.e.* 2 days, and then it was increased to 30 tons and left till March 27th, *i. e.* 4 days more.

The results were:—A faint raised circular area in the case of the basalt—so faint that it is not easily seen without breathing on the polished surface. The granite reveals no definite effect.

The Solenhofen limestone shows a quite distinct raised area corresponding to the opening in the washer. A straight-edge applied across the stone showed the slight central elevation. The obsidian showed a similar effect but very much fainter.

Comparing these results with (II.), we are entitled to conclude that what difference there is was due to the lesser duration of the stress in (IV.).

(V.). It was now resolved to apply the procedure of (I.) and (II.) to the limestone and obsidian, and to seek for a definite positive result at 30 tons. Two limestone hemispheres were placed vis-a-vis. One of these was that which had been used in (IV.), and which exhibited a small but distinct bulge. The other carried the cavity, and had not been previously used. The obsidian sphere was prepared in the same manner, one of the hemispheres being that which was used in (IV.). No balsam was used in either sphere.

From March 27th to March 28th, 1914, 20 tons were applied, and from March 28th to Sept. 19th, *i. e.* 175 days, 30 tons. The results were a small collection of debris manifestly spalled off the walls of the cavity, in the case of the Solenhofen rock. The covering surface was cracked and broken outwards round the edges of the circular area of no pressure. In the case of the obsidian there was a small amount of debris in the cavity, and the flat surface was very faintly bulged outwards over the central circular area.

This experiment, taken along with (II.), clearly shows that in 30 tons on the plunger, that is 38·70 tons or 88,717 lb. per square inch (=6100 kilos per sq. cm.), we have a pressure which is certainly sufficient to close cavities in granite, basalt, obsidian, or limestone.

Here the experiments had to come to an end, the prepared material being exhausted. It had been intended to apply to Dr. Krantz for additional spheres, but, of course, war conditions rendered this impossible. Modifications of the crushing apparatus permitting of prolonged application of temperatures up to about 500° C. were designed, but there was no possibility of having these carried out.

So far as they go, the experiments show that for the four different varieties of rocks tested the pressure of 88,700 lb. per square inch, *i. e.* 6100 kilos per square cm., must even in the cold close all cavities in the rock, and at the probable temperatures attending such pressures (between 800° and 900° C.) must be considerably in excess of the critical pressure. And further, that the signs of yielding in the cases of granite and basalt at the pressure of 59,100 lb. per square inch, *i. e.* 4067 kilos per sq. cm., are sufficient to justify the assumption that at the probable corresponding earth temperature (450° C.) this pressure must be near the critical pressure for these materials.

Microscopic examination of the granite and basalt shows that these rocks are quite typical varieties. The granite has two micas, a brown mica partially chloritised (and containing abundant haloes) and a limpid mica (muscovite). Most of the felspar is plagioclase; a part is orthoclase. All the felspar is fresh and limpid. There is abundant quartz showing the usual strings of fine bubbles or cavities. The structure is typically granitic. The basalt has fine olivines, augite, and basic felspar. It is very fine-grained. The phenocrysts are augite mainly. No glass was detected. The obsidian was not examined microscopically. It was obviously a very homogeneous glass. A few very minute bubbles or

cavities appear on the polished surface. The Solenhofen rock is too well known to require description.

It is hoped to continue the experiments at the earliest opportunity.

The elastic theory is readily applied to these experiments, the requisite equations having already been developed by Love and Williamson.

Taking the case of a sphere of homogeneous material with a small concentric spherical cavity, it is shown that if the sphere is externally submitted to a hydrostatic pressure p, then any diametral plane is a plane of principal stress; so that if the sphere were composed of two hemispheres merely laid together, the case is theoretically the same as that of the undivided sphere. The radial stress diminishes, of course, from p on the exterior to zero at the interior surface. The perpendicular stress (*e. g.* on the plane surface of each hemisphere) is slightly greater than p near the outer surface, and near the inner surface (*i. e.* the cavity) it increases to nearly $\frac{3}{2}p$. Rupture will tend to begin at the surface of the cavity and the planes of greatest shearing stress are at 45 to the radius.

The actual conditions of experiment differed from this ideal case in that the interior cavity was hemispherical instead of spherical. In such a case we should expect rupture to begin in the plane surface of the cavity where this first loses support from the opposed flat surface, *i. e.* at the corners where the cavity meets the overlying plane.

The elastic theory shows that for a spherical cavity, if P and Q are the stresses (measured as *pressures*) respectively radial and at right angles to the radius at a distance r from the centre, where r_1 and r_2 are the radii of cavity and sphere :

$$\mathrm{P} = \frac{r_1{}^3\, r_2{}^3}{r_2{}^3 - r_1{}^3}\left(\frac{1}{r_1{}^3} - \frac{1}{r^3}\right)p,$$

$$\mathrm{Q} = \frac{r_1{}^3\, r_2{}^3}{r_2{}^3 - r_1{}^3}\left(\frac{1}{r_1{}^3} + \frac{1}{2r^3}\right)p.$$

LXXXI. *Convection of Heat and Similitude.*
By A. H. Davis, *B.Sc.*[*]

Contents.

Introduction.

THE heat-losses from a hot body may be due to conduction, radiation, and convection. While the two former may be calculated, if the constants of the materials and surfaces be known, the loss by convection is complicated by its dependence on the geometrical form of the surface. Although for the simplest forms (spheres, cylinders, etc.) the effect may be calculable, it is obvious that in general it can only be found by experiment, using either the actual object or an object of similar form. It may be remarked here that, mathematically, convection is a combination of hydrodynamics with the Fourier equations for heat-flow, and that in the solution of the purely hydrodynamic problems presented by ships and by aircraft the value of experiments with models has been proved. One is led, therefore, to derive relations applicable to convection from the standpoint of models.

1. Natural Convection.

Formula.

Boussinesq has given a mathematical solution of the problem of heat-loss by convection, natural [†] and forced [‡]. The desirability of conducting experiments and expressing experimental results in a form applicable to models is further indicated by the fact that study of his analysis shows that he is led to consider bodies of similar form.

The equations required for this paper may be deduced from his. However, they may also be obtained from the principle of similitude. Rayleigh * has pointed this out for the case of forced convection. It is instructive to work out the case for natural convection from this alternative point of view.

Let the fundamental units be those of mass (M), length (L), time (T), and temperature (Θ). The derived units are given in brackets below. For an inviscid fluid, Boussinesq's equations show that the mean heat-loss "h" (MT^{-3}) per unit area of a body per unit time depends upon

k, ($M\Gamma^{-3}L\Theta^{-1}$)   thermal conductivity of the fluid.

c. ($MT^{-2}L^{-1}\Theta^{-1}$)   capacity for heat per unit volume of the fluid.

θ, (Θ)   temperature excess of the body.

a, (Θ^{-1})   coefficient of density reduction of the fluid per degree rise of temperature.

g, (LT^{-2})   acceleration due to gravity.

l, (L)   linear dimensions of the body.

Since we deal with the capacity for heat per unit volume of the fluid, reflection shows why the density (ρ) of the fluid does not enter. The convection currents, essentially gravity currents, depend upon the density of the heated fluid *relative* to that of the cool fluid, and not upon the absolute density.

Boussinesq regards the effect of the thermal expansion of the fluid as negligible except in so far as it alters the weight of unit volume of the fluid—that is, except in so far as "a" and "g" occur as a product. Consequently, let

$$h = k''c^v\theta^w(ag)^x l^z; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

then we readily derive :

By mass $1 = u + v,$

By length $0 = u - v + x + z,$

By time $-3 = -3u - 2v - 2x,$

By temperature $0 = -u - v + w - x ;$

whence

$$u = 1 - 2x, \quad w = 1 + x, \quad z = 3x - 1, \quad v = 2x. \quad . \quad (2)$$

* Rayleigh, ' Nature,' xcv. p. 66 (1915).

Substituting in (1) we obtain

$$h = (k\theta/l)(c^2gl^3a\theta/k^2)^x. \quad . \quad . \quad . \quad . \quad (3)$$

Since " x " is undetermined, we must write

$$h = (k\theta/l) \, \mathrm{F}(c^2gl^3a\theta/k^2). \quad . \quad . \quad . \quad . \quad (4)$$

Let us consider the assumption that expansion effects of the fluid are negligible except in so far as they alter the weight of unit volume and so set up gravity currents. With large bodies this will be fairly true. But in an extreme case of a hot thin wire, the mere volume changes of the air near the wire may be far from negligible. Indeed, observation of smoke near a hot thin wire shows that the effective diameter of the wire seems several times its true diameter. In this case we shall not expect (4) to hold. Convection data for wires, given by Langmuir [*], show on test that the relation (8) based on (4) does not hold ; and in fact Langmuir, in his theory, supposes the wire surrounded by a stationary film of fluid, of thickness several times the actual diameter of the wire. For large bodies at moderate temperatures our formula should be satisfactory.

For a viscous fluid we find, on introducing a term ν^t (ν being the kinematical viscosity coefficient with dimensions L^2T^{-1}),

$$h = (k\theta/l)(c^2gl^3a\theta/k^2)^x(c\nu/k)^t. \quad . \quad . \quad . \quad (5)$$

For gases, by the kinetic theory, $(c\nu/k) =$ const. Actually it seems constant for a given kind of gas, and varies but moderately from one kind to another. If, analogous to Rayleigh's [†] treatment of convection in a stream of fluid, $(c\nu/k)$ be supposed constant for all fluids, the result reduces to (3) as before. Viscosity, therefore, has less effect than one might expect.

On reflection this result may be made more or less clear. The kinetic theory of gases shows how increasing the viscosity (ν) of a gas is equivalent to increasing its thermal diffusivity (k/c) in the same ratio. Consequently, although increase in viscosity may decrease the speed at which cold gas sweeps over the heated body, still at the same time the thermal diffusivity is increased, and the heat escapes laterally by this means.

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[*] Langmuir, Phys. Rev. vol. xxxiv. p. 416 (1912).
[†] Rayleigh, *loc. cit.*

Examination of Formula.

$$h = (k\theta/l)\,\mathrm{F}(c^2gl^3a\theta/k^2). \quad . \quad . \quad . \quad . \quad (4)^*$$

The form of the function F may be determined experimentally by finding its variation with "θ," say, the other quantities remaining constant. Dulong & Petit[†], Péclet[‡], and Compan[§] have given formulæ in which, for the same body, $h \propto \theta^{1\cdot233}$. Hence

$$\mathrm{F}(c^2gl^3a\theta/k^2) = (c^2gl^3a\theta/k^2)^{0\cdot233},$$

whence (5) becomes

$$h \propto \theta^{1\cdot233}\,k^{\cdot534}\,c^{\cdot466}\,a^{\cdot233}\,g^{\cdot233}\,l^{-\cdot301}. \quad . \quad . \quad . \quad (6)$$

Now we may put $c = c_p\rho$, where c_p is the specific heat of unit mass of the fluid, and for air is known to be practically independent of the density "ρ." Hence, for any given body, if "k," "a," and "g" do not alter, $h \propto \rho^{\cdot466}\theta^{1\cdot233}$. In excellent agreement with this, Dulong & Petit found for air $h \propto p^{\cdot45}\theta^{1\cdot233}$, the pressure "$p$" being of course proportional to "ρ." Further, in one experiment with a very small cooling-chamber, Compan[||] found $h \propto \theta^{1\cdot154}$. Similar reasoning in this case gives $h \propto \rho^{\cdot308}\theta^{1\cdot154}$, and Compan found experimentally $h \propto p^{\cdot30}$ as his mean for this series. This is excellent agreement.

Let us return to the question of models. If, instead of attempting to determine the form of the function in (5), we so choose our models that its value is constant,

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* Equation (4) is present in Boussinesq's paper in the form

$$h \propto \theta^{4/3}(kc^2a)^{1/3} \quad \text{if} \quad l \propto (c^2a\theta/k^2)^{-1/3}, \quad . \quad . \quad . \quad (4\,a)$$

which is seen to be equivalent to (4) for

$$k\theta/l \propto \theta^{4/3}(kc^2a)^{1/3} \quad \text{when} \quad l \propto (c^2a\theta/k^2)^{-1/3}.$$

From this Boussinesq obtains an equivalent of (6), but limited to the same body so that "l" does not occur. He does not further test the equation.

† Dulong & Petit. See Preston's 'Heat.'

‡ Péclet. See Paulding's translation, 'Practical Laws and Data on the Condensation of Steam in Covered and Bare Pipes.' C. P. Paulding. Van Nostrand Co., 1904.

§ Compan, *Ann. de Chimie et de Physique*, xxvi. p. 482 (1902).

|| Compan, *loc. cit.*

we have

$$c^2 g l^3 a \theta / k^2 = \text{constant}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

and then for models so chosen in size (l)

$$h \propto k\theta/l. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

If only the temperature and size of the model are varied, c, g, a, and k, the gaseous constants, remaining the same, (7) becomes $\theta l^3 = \text{constant}.$ . . . . $(7a)$

Data are available for testing whether $h \propto k\theta/l$ when $\theta l^3 = \text{const.}$ E. Péclet has made, perhaps, the most complete experiments on heat-losses from surfaces (*Traité de Chaleur*, 3rd ed., 1860), and he measured the rate of cooling of metal cylinders and spheres filled with water. He used bodies ranging from 5 to 30 cm. in diameter and 5 to 50 cm. in length, placed in a large water-jacketed metal cylinder about 80 cm. in diameter and 100 cm. high. He worked at various values of temperature excess up to 65°.   He found for these bodies

$$h \propto A\theta^{1\cdot233},$$

where A has the value

for spheres . . . . .   A $= 1\cdot778 + 0\cdot13/r$,

for horizontal cylinders .   A $= 2\cdot058 + 0\cdot0382/r$,

" r " being radius in metres.

Also a formula is given for vertical cylinders from which the values of A can be calculated for the similar bodies we require of this shape. All spheres are similar: and in a long horizontal cylinder it is obvious that the length does not affect the heat-loss per unit area, so the formula is applicable to models, even although in the actual experiments the ratio of length to diameter may not have been constant.

From Péclet's formulæ heat-losses have, therefore, been calculated for similar bodies in the cases mentioned above. Following $(7a)$ the models have been so chosen that $\theta l^3 = \text{const.} = 6 \times 10^4$.   The result is given in Table I. This choice is such that the first seven models roughly range in temperature excess and size over the region in which Péclet's experiments were confined.   The eighth model, working at 480° C. excess, is somewhat theoretical.

TABLE I.

Heat-Loss from Models calculated from Péclet's Formulæ.

(Test of relation $h \propto \theta/l$ for a series of models in which $\theta l^3 = $ constant.)

Model.		Relative value of $h \div (\theta/l)$ *.			
Temperature, $\theta°$ C.	Linear † dimensions, l (cm.).	Sphere.	Horizontal cylinder.	Vertical cylinder ‡.	Mean.
60	10·00	1·00	1·00	1·00	1·00
50	10·62	0·99	1·01	0·99	1·00
40	11·45	0·99	1·02	0·99	1·00
30	12·60	0·98	1·04	0·98	1·00
20	14·42	0·97	1·06	0·97	1·00
10	18·17	0·97	1·11	0·96	1·01
7·5	20·00	0·97	1·13	0·96	1·02
480	5·00	1·16	0·94	1·09	1·06
0·94	40·00	—	—	0·97	0·97

* Value given, for each shape, relative to value for first model of that shape.

† For spheres and horizontal cylinders "l" is the radius, for vertical cylinders it is the height.

‡ Vertical cylinders have height $= 5 \times$ radius.

N.B.—In any test of data obtained from empirical formulæ it should be borne in mind that the formula will tend to be most reliable in the central region of the experiments on which they are based, and less reliable at the limits.

This table indicates that instead of the arbitrary form $h \propto A\theta^{1\cdot233}$, where A has complicated empirical values, Péclet's results may possibly be presented in the form suggested by (5),

$$h \propto (\theta/l) \, F(\theta l^3).$$

This could only be decided by a complete study of the whole of his *experimental* results. However, the above shows that it is fairly true for $F(x) = x^{0\cdot233}$. In any case, it would be valuable to express results in a form applicable to models, and if this were found impossible the fact is worth stating.

An alternative way of testing Péclet's data is to plot a curve with $h \div \theta/l$ as ordinate and θl^3 as abscissa. Of course, only values of l and θ are taken which fall within the range of the actual experiments.

2. Convection from a Body in a Stream of Fluid.

Formula.

Convection from a body in a stream of fluid moving with velocity v (natural convection being negligible) has been determined by Boussinesq,

$$h = (k\theta/l)\, F(lvc/k), \quad \cdot \quad . \quad . \quad . \quad . \quad (9)$$

and Rayleigh has shown the derivation from the principle of similitude.

Since from the kinetic theory of gases, as mentioned above, cv/k is constant, (9) becomes $h = (k\theta/l)\, F(lv/\nu)$, and (lv/ν) is the well-known variable in experiments on fluid resistance and flow. This raises the possibility of a useful relation between the thermal and dynamic effects of a fluid stream. It is important apart from this, however ; for if heat-loss is affected by change from stream-line motion to turbulence, it is satisfactory to find the equation for heat-loss contains the variable (lv/ν) which determines turbulence.

A formula given by Russell [*] for stream-line flow past a cylinder at right angles to the stream is readily seen to be equivalent to (9), where $F(lvc/k) \propto (lvc/k)^{1/2}$. Although such special approximate forms of the function F calculated for stream-line flow might cease to hold when turbulence set in, the formula (9) would still be satisfactory. One recalls that in dealing with purely hydrodynamic problems of the flow of viscous fluids in cylindrical pipes, Stanton & Pannell [†] investigated the resistance to flow from the standpoint of similitude. Their results show that although the relation analogous to (9) has a special form for stream-line motion, which apparently alters when turbulence sets in, the general relation holds even for turbulent motion, and is continuous through the transition region.

Examination of Formula.

Experimental work on the heat-losses from bodies in a stream of air has been carried out chiefly on thin wires, but some data are available for larger cylinders. Let us consider these two cases.

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* Russell, Phil. Mag. xx. p. 591 (1910).
† Stanton & Pannell, Phil. Trans. ccxiv. p. 199 (1914).

(1) *Thin Cylinders.*

Kennelly * and Morris † have investigated the cooling of thin wires in streams of air. King ‡ has given, perhaps, the most comprehensive investigation, working over a wide range. He used wires ranging in diameter (d) from 0·003 cm. to 0·015 cm. He worked at velocities (v) of 17 to 900 cm. per sec., and at temperature excesses (θ) (wire over air) of 200° C. to 1200° C. As a result he gives a formula, which may be written

$$H/\theta = B\sqrt{(vd)} + C. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

H is the heat-loss per cm. of wire, B and C are practically constant. B has a slight coefficient depending on the temperature excess of the wire; C has a larger coefficient, and also depends somewhat on the diameter of the wire. We may note that, in (9), "h" refers to unit *area* of the body. If the body is a long cylinder, the length obviously does not affect "h." It readily follows for long cylinders (diameter "d") that the rate of loss of heat "H" per unit *length* is given by

$$H = (k\theta)\,F(vdc/k). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

Thus King's results show that the formula (11), which for these experiments reduces to

$$H/\theta = F(vd), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

is very satisfactory, but slight corrections seem necessary. The results are in a form which readily shows this, being essentially the evaluation of the constants B and C in his theoretical formula.

(2) *Spheres and Thick Cylinders.*

Compan §, using a sphere, verified Boussinesq's approximate equation within narrow limits of temperature and air-velocity, but he did not use bodies of different size. However, Hughes ‖ has investigated the cooling of cylinders (0·5 to 15 cm. diam.) over a range of air-velocity from 2 to 15 metres per sec.

The experimental data are given in a full table in his paper, and curves are given between the heat-loss "H"

* Kennelly, Trans. A. I. E. E. xxviii. p. 363 (1909).
† Morris, 'Electrician,' Oct. 4, 1912, p. 1056.
‡ King, Phil. Trans. ccxiv. p. 373 (1914).
§ Compan, *loc. cit.*
‖ Hughes, Phil. Mag. xxxi. p. 118 (1916).

in calories per cm. of the cylinder and " v " the air-velocity :
one curve for each value of the diameter (d). They have
been re-drawn in fig. 1 in c.g.s. units. The relation between
the four curves is not obvious. However, formula (12)

Fig. 1.
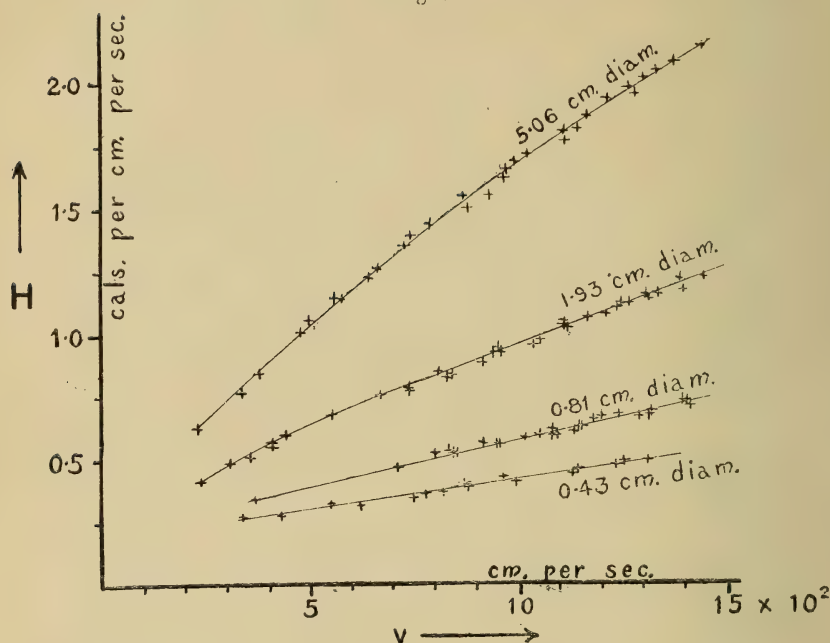
suggests that they can be replaced by one curve if " H " is
plotted against " vd ." In fig. 2 this has been attempted
from the experimental data *. It is seen that the result
is very satisfactory. It is excellent for the three smaller
cylinders (0·43–1·93 cm.) and quite good for the fourth
(5·06 cm.), although the points of the latter all seem
displaced somewhat from the line of the former.

Possible sources of this displacement may be mentioned.
In the " vd " term there is possibility of error in the
velocity " v ." Hughes's method of allowing for lack of
uniformity of distribution of the air-stream in his channel
is open to criticism from a precision point of view. A

* The points of fig. 1 are too numerous to plot individually in fig. 2,
and advantage has been taken of the natural groups (of from 2 to
6 points) which occur, and mean values have been plotted.

Pitot-tube reading is proportional to v^2, whereas the heat-loss from small and large cylinders is proportional to $v^{.55}$ and $v^{.7}$ respectively. So a value of average velocity, as deduced by Hughes, from the mean square velocity obtained

Fig. 2.

+	0·4 – 2 cm. diam.	(Hughes.)
•	5·06 " "	(")
✦	5·08 " "	(Carpenter.)
o	0·003 – 0·015 " "	(Formula. King.)
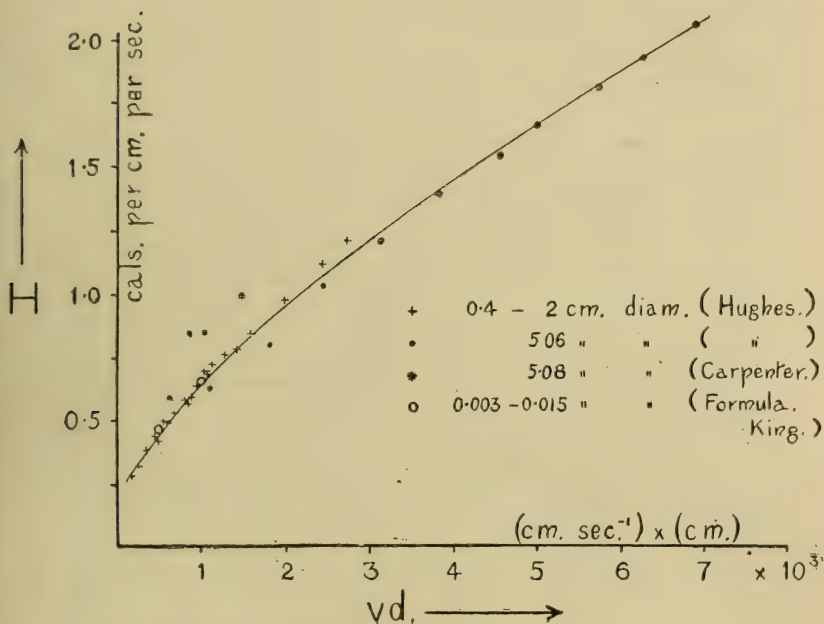
from Pitot-tube readings, is not strictly applicable. Further, the particular average required depends on which cylinder is in use. It will be noticed that the double series of points on the graph of fig. 2 come where the high-velocity values of the smaller cylinders are plotted near the low-velocity values of the 5·06 cm. cylinder. One may mention also that experience with wind channels shows that rectilinear stream-line motion is not obtained unless special precautions are taken. The entrance must be of stream-line shape, and a special metal honeycomb should be used at the beginning of the channel proper to break up vortices and ensure recti-linear delivery.

Even if there is actual discrepancy, it is obvious that the law $H \propto F(vd)$ is approximately true. Unless a better theoretical formula can be advanced, this point is worth emphasis in the form in which results are presented, even

although a slight correction factor be introduced for deviation with diameter (*d*).

Finally, Langmuir *, in his study of convection of heat, quotes from Carpenter ('Heating and Ventilation of Buildings,' Wiley & Sons, 1903) values for a 2 inch steam pipe, sensibly the same size as Hughes's largest cylinder (5·06 cm.). These convection values, calculated for a temperature excess of 85° C., are plotted as asterisks in fig. 2, and are seen to lie higher than the mean curve, although the points given by Hughes lie lower.

(3) *Long Cylinders*: *thick and thin compared.*

Hughes gave the results for his cylinders in a form $H \propto d^{\cdot 57} v^n$, where *n* varies with diameter from 0·55 to 0·7, and shows signs of depending also upon the velocity itself. Obviously, this is not a suitable formula for extrapolation. King, working over a wide range of conditions, gave the formula (10) above. It is better adapted for extrapolation. Particularly, there is no sign of variation with velocity apart from that under the root sign ; so we can work with a wire of diameter within King's range, only extrapolating the velocity.

Let us take, then, two wires approximating to the smallest and to the largest used by King, of diameter 0·003 and 0·015 cm. respectively. As with Hughes's cylinders, let them work at 100° C., in air at 15° C., this being apparently the temperature (deduced from his radiation data) at which Hughes worked. Then, if we choose velocities to give values of "*vd*" similar to those in Hughes's experiments, we may calculate from King's constants the appropriate heat-loss (H). We find for both wires

$$\text{when } vd = 500, \quad H = 0\cdot46,$$
$$\text{,, } vd = 1000, \quad H = 0\cdot66.$$

These points have been plotted on the graph of fig. 2, where remarkable agreement is seen with the curve obtained for cylinders 30 to 1600 times as thick. The extrapolation is considerable, but we recall that the most satisfactory part of the most satisfactory formula was chosen to stand the strain. It would not seem possible to conduct experiments to test this particular extrapolation, as the velocities are so great that the fine wires would oscillate or break under the mechanical strain.

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* Langmuir, Trans. Am. Electrochem. Soc. xxiii. p. 324 (1913).

SUMMARY.

1. The hydrodynamic basis of convection of heat suggests study by means of models.

2. We have the formulæ:

Natural convection . . $h = (k\theta/l) \, \mathrm{F}(c^2 g l^3 a \theta / k^2)$,

Forced convection . . $h = (k\theta/l) \, \mathrm{F}(lvc/k)$.

3. Graphs drawn with $h \div (k\theta/l)$ as ordinate and either $(c^2 g l^3 a \theta \, k^2)$ or (lvc/k) as abscissa should be independent of the size of the object; consequently, to ascertain the heat-loss for any particular body it should be necessary only to perform the appropriate experiment with a model.

4. For natural convection Péclet's data have been analysed with promising result. The formula would not be applicable to bodies where the fluid expansion caused was no longer negligible as a mere volume change.

5. For forced convection the formula, tested by data given by Hughes, is very promising. The cooling fluid is not heated so much as in natural convection, and can still be regarded as incompressible for smaller bodies at higher temperatures. The formula is good, even for thin wires, and it is satisfactory to trace in it the hydrodynamic variable determining turbulence.

6. Evidence available in published data indicates that, for heat-loss from a body, an excellent first approximation can be obtained from experiments with a model. The principle of similitude affords a convenient method of expressing experimental results.

March 1920.

LXXXII. *Space-Time Manifolds and corresponding Gravitational Fields.* By WILFRID WILSON, *B.Sc., Northampton Polytechnic Institute* *.

THE main purpose of the present paper is the investigation of the gravitational field of an infinite uniform rectilinear distribution of mass or, more precisely stated, the determination of the equations of the geodesics in a space-time manifold in which the square of the element of length has the form

$$ds^2 = -f_1 dr^2 - f_2 dz^2 - f_3 r^2 d\phi^2 + f_4 dt^2, \quad . \quad . \quad (1)$$

where the f's are functions of r only †.

† When $f_1 = f_2 = f_3 = f_4 = 1$, r z and ϕ are the ordinary cylindrical space co-ordinates.

So far as the writer is aware, the only gravitational field which has been investigated from the point of view of Einstein's theory is that of a single particle or of a number of isolated particles. On Newton's theory the intensity of the field in the neighbourhood of such an infinite rectilinear distribution of mass is equal to $\dfrac{2m}{r}$, where m is the mass per unit length, using gravitational units. The following investigation shows that the intensity as given by the general theory of relativity is, to an exceedingly close approximation, equal to the Newtonian result.

Before proceeding to the actual investigation it will be well to study the following simpler types of manifold in which the square of the line element has the forms :—

$$ds^2 = -dx^2 - dy^2 - dz^2 - 2\alpha t\,dx\,dt + (1 - \alpha^2 t^2)\,dt^2, \quad . \quad (2)$$

$$ds^2 = -dr^2 - dz^2 - r^2 d\phi^2 - 2\omega r^2 d\phi\,dt + (1 - r^2\omega^2)\,dt^2, \quad (3)$$

$$ds^2 = -\mathrm{A}\,dr^2 - dz^2 - r^2 d\phi^2 + \mathrm{B}\,dt^2, \quad . \quad . \quad . \quad . \quad (4)$$

where α, ω, A, and B are constants.

In the relativity theory of gravitation the general form of the square of the element of length is

$$ds^2 = \sum_{\kappa\tau}^{1,\,2,\,3,\,4} g_{\kappa\tau}\,dx_\kappa dx_\tau.$$

The potentials $g_{\kappa\tau}$ satisfy the equations

$$\mathrm{G}_{\mu\nu} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\mathrm{G}_{\mu\nu} \equiv \sum_{\rho\epsilon}^{1,\,2,\,3,\,4} \left(\Gamma^\epsilon_{\mu\rho}\Gamma^\rho_{\nu\epsilon} - \frac{\partial}{\partial x_\rho}\Gamma^\rho_{\mu\nu} + \frac{\partial^2}{\partial x_\mu \partial x_\nu}\log\sqrt{g} \right.$$
$$\left. - \Gamma^\epsilon_{\mu\nu}\frac{\partial}{\partial x_\epsilon}\log\sqrt{g} \right)^{*}$$

and

$$\Gamma^\alpha_{\beta\gamma} \equiv \frac{1}{2}\sum_{\delta}^{1,\,2,\,3,\,4} g^{\alpha\delta}\left(\frac{\partial g_{\beta\delta}}{\partial x_\gamma} + \frac{\partial g_{\gamma\delta}}{\partial x_\beta} - \frac{\partial g_{\beta\gamma}}{\partial x_\delta} \right).$$

In some cases the potentials $g_{\kappa\tau}$ may also satisfy the equations

$$\mathrm{B}^\rho_{\mu\nu\sigma} = 0, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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* Einstein, *Ann. d. Phys.* xlix. p. 769 (1916). Einstein only uses co-ordinates for which $g = 1$. See also Eddington, 'Report on Relative Theory of Gravitation.'

where

$$B^{\rho}_{\mu\nu\sigma} \equiv \sum_{\epsilon}^{1,\,2,\,3,\,4} \left(\Gamma^{\epsilon}_{\mu\sigma} \Gamma^{\rho}_{\epsilon\nu} - \Gamma^{\epsilon}_{\mu\nu} \Gamma^{\rho}_{\epsilon\sigma} + \frac{\partial}{\partial x_{\nu}} \Gamma^{\rho}_{\mu\sigma} - \frac{\partial}{\partial x_{\sigma}} \Gamma^{\rho}_{\mu\nu} \right).$$

The latter equation expresses the necessary and sufficient condition that, by a suitable choice of coordinates, the square of the element of length can be put in the form :—

$$ds^2 = \sum_{s}^{1,\,2,\,3,\,4} dx_s^{\,2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the gravitational field made to vanish everywhere. Such a field may conveniently be termed a non-permanent one. The manifolds (2), (3), and (4) furnish simple illustrations of such fields.

In the manifold (2) the values of the $g_{\kappa\tau}$ and $g^{\kappa\tau}$ are :—

$$\begin{cases} g_{11} = -1 \\ g_{22} = -1 \\ g_{33} = -1 \\ g_{44} = 1 - \alpha^2 t^2 \\ g_{14} = -\alpha t \end{cases} \qquad \begin{cases} g^{11} = \alpha^2 t^2 - 1 \\ g^{22} = -1 \\ g^{33} = -1 \\ g^{44} = 1 \\ g^{14} = -\alpha t, \end{cases}$$

and

$$g = -1,$$

where g is the determinant of the $g_{\kappa\tau}$.

The Christoffel expressions $\Gamma^{\alpha}_{\beta\gamma}$ all vanish with the exception of Γ'_{44}, which has the value

$$\Gamma'_{44} = \alpha.$$

The equations

$$\frac{\partial^2 x_{\sigma}}{\partial s^2} + \sum_{\alpha\beta}^{1,\,2,\,3,\,4} \Gamma^{\sigma}_{\alpha\beta} \frac{\partial x_a}{\partial s} \frac{\partial x_\beta}{\partial s} = 0, \quad \sigma = 1,\,2,\,3,\,4, \quad . \quad (8)$$

of the geodesics then give the following equations of motion :—

$$\frac{d^2 x}{ds^2} = -\alpha c^2,$$

$$\frac{d^2 y}{ds^2} = 0,$$

$$\frac{d^2 z}{ds^2} = 0,$$

$$ds^2 = 0,$$

where the constant c is given by

$$\frac{dt}{ds} = c.$$

The first of these equations may now be written

$$\frac{d^2x}{dt^2} = -\alpha,$$

showing that the manifold (2) corresponds to a uniform gravitational field in the x direction.

In the manifold (3) we have

$$\begin{cases} g_{11} = -1 \\ g_{22} = -1 \\ g_{33} = -r^2 \\ g_{44} = 1 - r^2\omega^2 \\ g_{34} = -r^2\omega \end{cases} \qquad \begin{cases} g^{11} = -1 \\ g^{22} = -1 \\ g^{33} = \omega^2 - \dfrac{1}{r^2} \\ g^{44} = 1 \\ g^{34} = -\omega, \end{cases}$$

and

$$g = -r^2.$$

The non-vanishing Christoffel expressions $\Gamma^\alpha_{\beta\gamma}$ are :

$$\Gamma'_{33} = -r, \qquad \Gamma^3_{13} = \frac{1}{r},$$

$$\Gamma'_{34} = -\omega r, \qquad \Gamma^3_{14} = \frac{\omega}{r},$$

$$\Gamma'_{41} = -\omega^2 r \ ;$$

and the equations of motion (8) are :

$$\frac{d^2r}{ds^2} - r\left\{\frac{d(\phi + \omega t)}{ds}\right\}^2 = 0,$$

$$\frac{d^2\phi}{ds^2} + \frac{2}{r}\frac{dr}{ds}\frac{d(\phi + \omega t)}{ds} = 0,$$

$$\frac{d^2z}{ds^2} = 0,$$

$$\frac{d^2t}{ds^2} = 0.$$

The last equation gives

$$\frac{dt}{ds} = c,$$

where c is a constant. Substituting this value of $\dfrac{dt}{ds}$ in the first equation, we obtain

$$\frac{d^2r}{dt^2} - r\left(\frac{d\phi}{dt} + \omega\right)^2 = 0,$$

and taking ω to be an angular velocity we have the equations of motion in a centrifugal field.

In the manifold (4) the non-vanishing Christoffel expressions are

$$\Gamma^3_{13} = \frac{1}{r} \quad \text{and} \quad \Gamma'_{33} = -\frac{r}{\mathrm{A}}.$$

The equations of motion (8) become

$$\left.\begin{array}{r}
\dfrac{d^2r}{ds^2} - \dfrac{r}{\mathrm{A}}\left(\dfrac{d\phi}{ds}\right)^2 = 0, \\[2mm]
\dfrac{d^2\phi}{ds^2} + \dfrac{2}{r}\dfrac{dr}{ds}\dfrac{d\phi}{ds} = 0, \\[2mm]
\dfrac{d^2z}{ds^2} = 0, \\[2mm]
\dfrac{d^2t}{ds^2} = 0.
\end{array}\right\} \quad \cdots \cdots \quad (9)$$

If, instead of ϕ we use ϕ', where

$$\phi = \sqrt{\mathrm{A}}\,\phi',$$

the equations (9) become

$$\frac{d^2r}{ds^2} - r\left(\frac{d\phi'}{ds}\right)^2 = 0,$$

$$\frac{d^2\phi'}{ds^2} + \frac{2}{r}\frac{dr}{ds}\frac{d\phi'}{ds} = 0,$$

$$\frac{d^2z}{ds^2} = 0,$$

$$\frac{d^2t}{ds^2} = 0.$$

We may therefore regard equations (9) as the equations of motion of a particle moving with uniform velocity in a straight line with respect to an inertia system (r, z, ϕ'),

viewed from a system (r, z, ϕ) rotating in the inertia system with angular velocity $(1 - \sqrt{A})$ times that of the particle in the inertia system.

We now proceed to the investigation of the manifold (1), where

$$ds^2 = -f_1 dr^2 - f_2 dz^2 - f_3 r^2 d\phi^2 + f_4 dt^2,$$

and the functions

$$-f_1(r), \quad -f_2(r), \quad -r^2 f_3(r), \quad f_4(r)$$

must be solutions of the equations (5).

For our purpose there is no loss in generality in using any function of r in place of r. We therefore write

$$-r^2 f_3(r) = -r'^2 \qquad \cdots \qquad (10)$$

and obtain for the square of the line element the form :

$$ds^2 = -f_1 dr^2 - f_2 dz^2 - r^2 d\phi^2 + f_4 dt^2, \quad \cdots \quad (11)^*$$

where the accent has been dropped after making the substitution (10).

It is easier to deal with the equations (5) if we write ds^2 in the form

$$ds^2 = -e^\lambda dr^2 - e^\mu dz^2 - r^2 d\phi^2 + e^\nu dt^2, \quad \cdots \quad (12)†$$

where $e^\lambda = f_1(r)$ etc., and λ, μ, and ν are functions of r which have to be determined.

The Christoffel expressions $\Gamma^\alpha_{\beta\gamma}$ are then found to be

$$
\begin{cases}
\Gamma'_{11} = \tfrac{1}{2}\lambda', \\
\Gamma'_{22} = -\tfrac{1}{2}\mu' e^{\mu-\lambda}, \\
\Gamma'_{33} = -r e^{-\lambda}, \\
\Gamma'_{44} = \tfrac{1}{2}\nu' e^{\nu-\lambda},
\end{cases}
\qquad
\begin{cases}
\Gamma^2_{12} = \tfrac{1}{2}\mu', \\
\Gamma^3_{13} = \dfrac{1}{r}, \\
\Gamma^4_{14} = \tfrac{1}{2}\nu',
\end{cases}
$$

where

$$\lambda' = \frac{\partial \lambda}{\partial r}, \quad \mu' = \frac{\partial \mu}{\partial r}, \quad \nu' = \frac{\partial \nu}{\partial r}.$$

Substituting these expressions in the equations (5) the

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* I am indebted to Dr. Wilson, of King's College, for suggesting the investigation of a line element of this type.
† Eddington, Report.

latter become :

$$\tfrac{1}{2}\mu'' - \tfrac{1}{4}\lambda'\mu' + \tfrac{1}{4}\mu'^2 = -\tfrac{1}{2}\nu'' + \tfrac{1}{2}\frac{\lambda'}{r} + \tfrac{1}{4}\lambda'\nu' - \tfrac{1}{4}\nu'^2, \quad . \quad (13)$$

$$\tfrac{1}{2}\mu'' - \tfrac{1}{4}\lambda'\mu' + \tfrac{1}{4}\mu'^2 = -\tfrac{1}{2}\frac{\mu'}{r} - \tfrac{1}{4}\mu'\nu', \quad . \quad . \quad . \quad . \quad (14)$$

$$\lambda' = \mu' + \nu', \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\tfrac{1}{2}\frac{\nu'}{r} + \tfrac{1}{4}\mu'\nu' = -\tfrac{1}{2}\nu'' + \tfrac{1}{4}\lambda'\nu' - \tfrac{1}{4}\nu'^2. \quad . \quad . \quad . \quad (16)$$

Substituting the value of λ' given by (15) in (13), (14), and (16), we obtain the equations :

$$\mu'' + \nu'' - \mu'\nu' = \frac{\mu'}{r} + \frac{\nu'}{r}, \quad . \quad . \quad . \quad (17)$$

$$\mu'' + \frac{\mu'}{r} = 0, \quad . \quad . \quad . \quad . \quad (18)$$

$$\nu'' + \frac{\nu'}{r} = 0. \quad . \quad . \quad . \quad . \quad (19)$$

From (18) and (19) we find

$$\mu' = \frac{-4m}{r},$$

$$\nu' = \frac{a}{r};$$

and therefore from (15)

$$\lambda' = \frac{-4m + a}{r},$$

where $4m$ and a are constants of integration.

Substituting these values of μ' and ν' in (17) we see that

$$a = \frac{4m}{1 - 2m};$$

whence

$$-4m + a = \frac{8m^2}{1 - 2m},$$

and therefore

$$\mu' = -\frac{4m}{r},$$

$$\nu' = \frac{4m}{1 - 2m} \cdot \frac{1}{r},$$

$$\lambda' = \frac{8m^2}{1 - 2m} \cdot \frac{1}{r}.$$

Integrating these last equations, we obtain

$$\left. \begin{aligned} \mu &= -4m \log r + A, \\ \nu &= \frac{4m}{1-2m} \log r + B, \\ \lambda &= \frac{8m^2}{1-2m} \log r + C, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (20)$$

where A, B, and C are constants of integration.

We shall see, when the equations of motion are written down, that m can be identified with the mass per unit length of the z axis. When m is zero the square of the element of length will take the form

$$ds^2 = -dr^2 - dz^2 - r^2 d\phi^2 + dt^2 ;$$

i. e., when $m = 0$,

$$\lambda = 0, \quad \mu = 0, \quad \nu = 0.$$

Therefore

$$A = 0, \quad B = 0, \quad C = 0,$$

and the values of λ, μ, and ν are

$$\mu = -4m \log r,$$
$$\nu = \frac{4m}{1-2m} \log r,$$
$$\lambda = \frac{8m^2}{1-2m} \log r.$$

The square of the element of length (1) is therefore

$$ds^2 = -r^{\left(\frac{8m^2}{1-2m}\right)} dr^2 - r^{-4m} dz^2 - r^2 d\phi^2 + r^{\left(\frac{4m}{1-2m}\right)} dt^2. \quad . \quad (1')$$

The Christoffel expressions which do not vanish are :—

$$\Gamma'_{11} = \frac{4m^2}{1-2m} \cdot \frac{1}{r}, \qquad \Gamma^2_{12} = \frac{-2m}{r},$$

$$\Gamma'_{22} = \frac{2m}{r} \cdot r^{\left(\frac{-4m}{1-2m}\right)}, \qquad \Gamma^3_{13} = \frac{1}{r},$$

$$\Gamma'_{33} = -r^{\left(1 - \frac{8m^2}{1-2m}\right)}, \qquad \Gamma^4_{14} = \frac{2m}{1-2m} \cdot \frac{1}{r}.$$

$$\Gamma'_{44} = \frac{2m}{1-2m} \cdot r^{(4m-1)},$$

Substituting these values in the equations (8), we obtain for the geodesics the equations following :—

$$\frac{d^2r}{ds^2} + \left(\frac{4m^2}{1-2m}\right)\frac{1}{r}\left(\frac{dr}{ds}\right)^2 + 2mr^{\left(-1-\frac{4m}{1-2m}\right)}\left(\frac{dz}{ds}\right)^2$$
$$- r^{\left(1-\frac{8m^2}{1-2m}\right)}\left(\frac{d\phi}{ds}\right)^2 + \frac{2m}{1-2m}r^{(4m-1)}\left(\frac{dt}{ds}\right)^2 = 0, \quad (23)$$

$$\frac{d^2\phi}{ds^2} + \frac{2}{r}\frac{dr}{ds}\frac{d\phi}{ds} = 0, \quad (24)$$

$$\frac{d^2z}{ds^2} - \frac{4m}{r}\frac{dr}{ds}\frac{dz}{ds} = 0, \quad (25)$$

$$\frac{d^2t}{ds^2} + \left(\frac{4m}{1-2m}\right)\frac{1}{r}\frac{dr}{ds}\frac{dt}{ds} = 0. \quad (26)$$

We may interpret these as the equations of motion of a particle in the gravitational field of an infinitely extended uniform rectilinear distribution of mass along the z axis. From (25) we see that if the particle is moving initially in the plane $z=$ constant, it must remain in this plane ; *i.e.*, we have always

$$\frac{dz}{ds} = 0. \quad \ldots \ldots \quad (25')$$

From (24) we have

$$r^2\frac{d\phi}{ds} = h, \quad \ldots \ldots \quad (24')$$

where h is a constant of integration. This equation simply states that a radius vector sweeps out equal areas in equal times. From (26) we get

$$\frac{dt}{ds} = cr^{\left(\frac{-4m}{1-2m}\right)}, \quad \ldots \ldots \quad (26')$$

where c is a constant of integration.

Substituting these values of $\frac{dz}{ds}$ and $\frac{dt}{ds}$ from (25') and (26') in (23), we write (23) and (24) in the form :

$$\frac{d^2r}{ds^2} - r^{\left(1-\frac{8m^2}{1-2m}\right)}\left(\frac{d\phi}{ds}\right)^2 = \left\{ \frac{-2m}{r}\frac{c^2}{1-2m}r^{\left(\frac{-8m^2-4m}{1-2m}\right)} \right.$$
$$\left. - \frac{4m^2}{r(1-2m)}\left(\frac{dr}{ds}\right)^2 \right\}, \quad (27)$$

$$r^2\frac{d\phi}{ds} = h. \quad \ldots \ldots \quad (28)$$

The Newtonian equations of motion for the type of field we are dealing with are :

$$\frac{d^2r}{dt^2} - r\left(\frac{d\phi}{dt}\right)^2 = -\frac{2m}{r}, \quad \cdots \quad (27')$$

$$r^2\frac{d\phi}{dt} = h. \quad \cdots \quad (28')$$

Comparing these with (27) and (28) we notice they are identical for a sufficiently small m. Since we are using gravitational units, m is, for any solid cylinder of laboratory dimensions, negligible compared with unity and we see that (27) takes the form

$$\frac{d^2r}{ds^2} - r\left(\frac{d\phi}{ds}\right)^2 = -\frac{2m}{r}c^2. \quad \cdots \quad (29)$$

But for small m, (26') gives

$$\frac{dt}{ds} = c,$$

and substituting $\dfrac{dt}{ds}$ for c in (29) we obtain the Newtonian equation (27'). When m, however, is very great the equations of motion are more complicated. It is instructive to put equation (27) in the approximate form obtained by neglecting small quantities of the second order. On eliminating ds by means of equation (26') we obtain

$$\frac{d^2r}{dt^2} - r\left(\frac{d\phi}{dt}\right)^2 = -\frac{2m}{r^{1-4m}},$$

neglecting quantities of the order of m^2 and assuming the radial velocity component $\dfrac{dr}{dt}$ to be small or zero. To this order of approximation therefore, and with the assumption just mentioned, we may take $-\frac{1}{2}g_{44}$ to be the gravitational potential of the field we have been investigating, since

$$\frac{\partial}{\partial r}\left(-\tfrac{1}{2}g_{44}\right) = -\tfrac{1}{2}\frac{\partial}{\partial r}\left(r^{\frac{4m}{1-2m}}\right)$$

gives for the intensity of the field the expression obtained above.

Northampton Institute, E.C. 1.
        20th July, 1920.

LXXXIII. *On some Optical Effects including Refraction and Rotation of the Plane of Polarization due to the Scattering of Light by Electrons.* By Sir J. J. THOMSON, *O.M., P.R.S.* [*]

WE begin by considering the radiation along the axis of x emitted by the electrons in a very thin slab bounded by planes at right angles to this axis; all the electrons in the slab are supposed to be moving in the same way at the same instant.

If an electron O has an acceleration f in a direction at right angles to OP the electric force at P at the time T due to this acceleration is parallel to f and equal to $-ef_1/c^2 \cdot \mathrm{OP}$, where f_1 is the acceleration at the time $\mathrm{T}-\mathrm{OP}/c$, e being the charge on the electron and c the velocity of light. Let P be a point in front of the slab on the axis of x; if the acceleration parallel to y of an electron Q in the slab is d^2y/dt^2, the electron will produce an electric force parallel to y at P at the time T equal to

$$-\frac{e}{c^2 \cdot \mathrm{PQ}}\left(\frac{d^2y}{dt^2}\right)_{\mathrm{T}-\frac{\mathrm{PQ}}{c}},$$

provided PQ is at right angles to y. Since the optical effects at P of a plane wave arise from the parts adjacent to O, where O is the foot of the perpendicular let fall from P on the plane of the wave, we may make this supposition without loss of generality.

If D is the thickness of the slab, σ the density of the electrons, Y_1 the electric force parallel to y at P at the time T is given by the equation

$$\mathrm{Y}_1 = -\frac{e \cdot \sigma \mathrm{D}}{c^2}\int \frac{1}{r}\left(\frac{d^2y}{dt^2}\right)_{\mathrm{T}-\frac{r}{c}} 2\pi \rho\, d\rho,$$

where $\rho = \mathrm{OQ}, \quad r = \mathrm{PQ}.$

Now $r^2 = \rho^2 + \mathrm{OP}^2,$

hence $r\, dr = \rho\, d\rho,$

and therefore

$$\mathrm{Y}_1 = -\frac{2\pi e\sigma \mathrm{D}}{c^2}\int \left(\frac{d^2y}{dt^2}\right)_{\mathrm{T}-\frac{r}{c}} dr.$$

Let
$$\omega = t - \frac{r}{c},$$

as throughout the integration t is constant

$$dr = -c \cdot d\omega.$$

Since at the same instant the accelerations of all the electrons in the slab are equal,

$$y = f(t),$$

$$\left(\frac{d^2 y}{dt^2}\right)_{t-\frac{r}{c}} = \frac{d^2 \cdot f(\omega)}{d\omega^2},$$

hence
$$Y_1 = \frac{2\pi}{c} \epsilon \sigma D \int \frac{d^2 f(\omega)}{d\omega^2} \, d\omega$$

$$= \frac{2\pi}{c} e\sigma D \left[\frac{df}{d\omega}\right]_{\omega_1}^{\omega_2}.$$

The limits of ω are $t - \frac{x}{c}$ where $x = OP$, and $t - \frac{R}{c}$ where R is the greatest value of PQ; when R is so large that $t - R/c$ corresponds to a time before the electrons began to be affected by the light wave,

$$\left(\frac{df}{d\omega}\right)_{\omega_2} = 0,$$

so that
$$Y_1 = -\frac{2\pi}{c} e\sigma D \left(\frac{df}{d\omega}\right)_{t-\frac{x}{c}}$$

$$= -\frac{2\pi}{c} e\sigma D \cdot v_{t-\frac{x}{c}},$$

where $v_{t-\frac{x}{c}}$ is the velocity of an electron parallel to y at the time $t - x/c$. If $k = \frac{2\pi}{c} e\sigma D$, we have

$$Y_1 = -k v_{t-\frac{x}{c}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similarly Z_1 the force parallel to z will be given by

$$Z_1 = -k w_{t-\frac{x}{c}},$$

where $w_{t-\frac{x}{c}}$ is the velocity of an electron parallel to z at the time $t - \frac{x}{c}$.

Let us now consider a plane wave travelling in the positive direction of the axis of x, let $f(x, t)$ be the value of the electric force parallel to Z at the place x and the time t. Consider now how the force at the point $x + \delta x$, at the time $t + \delta x/c$, differs from that at x_1 and t_1. The force which is at x at the time t will be found at $x + dx$, at the time $t + \delta x/c$, and in addition to this force there will be found at $x + \delta x$ the force due to the secondary waves which come from the electrons in the slab δx. This force, as we have just seen, is equal to

$$- \frac{2\pi}{c} e\sigma \left(\frac{dz}{dt} \right) \delta x.$$

Hence we have

$$f(x + \delta x, t + \delta x/c) = f(x, t) - \frac{2\pi}{c} e\sigma \left(\frac{dz}{dt} \right) \delta x.$$

This equation is equivalent to

$$\frac{df}{dx} + \frac{1}{c} \cdot \frac{df}{dt} = - \frac{2\pi}{c} e\sigma \left(\frac{dz}{dt} \right). \quad . \quad . \quad . \quad (2)$$

If the equation of motion of an electron in the slab is

$$m \left(\frac{d^2 z}{dt^2} + n^2 z \right) = ef,$$

and if f varies as $e^{\iota p t}$, then

$$z = \frac{ef}{m(n^2 - p^2)},$$

and equation (2) becomes

$$\frac{df}{dx} + \frac{1}{c} \frac{df}{dt} = - \frac{2\pi}{c} \frac{e^2 \sigma}{m(n^2 - p^2)} \frac{df}{dt}$$

or

$$\frac{df}{dx} + \frac{1}{c'} \frac{df}{dt} = 0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

if

$$\frac{1}{c'} = \frac{1}{c} + \frac{2\pi}{c} \cdot \frac{e^2}{m} \frac{\sigma}{n^2 - p^2}. \quad . \quad . \quad . \quad (4)$$

The solution of (2) is

$$f = \phi(x - c't),$$

representing a disturbance propagated with a velocity c'. If μ is the refractive index,

$$\mu = c/c',$$

hence by (4)

$$\mu = 1 + \frac{2\pi e^2}{m} \cdot \frac{\sigma}{(n^2 - p^2)}.$$

3 A 2

This is the well-known expression given by Lorentz. If the electrons have not all the same frequency, then if σ_s is the density of those with the frequency n_s, we can show without difficulty that

$$\mu = 1 + 2\pi \frac{e^2}{m} \Sigma \frac{\sigma_s}{n_s{}^2 - p^2}.$$

This expression has been used by Drude and others to determine the number of electrons in the atoms. In using it for this purpose, however, it is necessary to take account of some considerations which may be illustrated by the following example. Let us consider the case of an electron in an atom of such a character that the displacement of the electron by an electric force is not in general in the direction of the electric force. There will be three directions fixed in the atom such that a force along one of these directions produces a displacement in the same direction. If these directions are taken as the axes of ξ, η, ζ, the equations of motion of the electron may be written

$$m\left(\frac{d^2\xi}{dt^2} + n_1{}^2\xi\right) = e\mathrm{F}_\xi,$$

$$m\left(\frac{d^2\eta}{dt^2} + n_2{}^2\eta\right) = e\mathrm{F}_\eta,$$

$$m\left(\frac{d^2\zeta}{dt^2} + n_3{}^2\zeta\right) = e\mathrm{F}_\zeta,$$

where F_ξ, F_η, F_ζ are the components of the electric force in the directions ξ, η, ζ respectively. Let the axes of ξ, η, ζ cut a sphere at the points A, B, C, and the axis of z at the point Z; then, if $\angle \mathrm{ZC} = \theta$, and ϕ is the angle between ZC and CA, an electric force Z in the light wave will be equivalent to the forces

$$\mathrm{F}_\xi = \mathrm{Z}\cos\theta, \quad \mathrm{F}_\eta = \mathrm{Z}\sin\theta\sin\phi, \quad \mathrm{F}_\zeta = -\mathrm{Z}\sin\theta\cos\phi,$$

and if Z varies as $\epsilon^{\iota p t}$, we get from the equations of motion of the electron

$$\xi = -\frac{e}{m}\frac{\mathrm{Z}\sin\theta\cos\phi}{n_1{}^2 - p^2}, \qquad \eta = \frac{e}{m}\frac{\mathrm{Z}\sin\theta\sin\phi}{n_2{}^2 - p^2},$$

$$\zeta = \frac{e}{m}\frac{\mathrm{Z}\cos\theta}{n_3{}^2 - p^2}.$$

The displacement resolved along the axis of z is thus

$$\frac{e}{m}\mathrm{Z}\left(\frac{\cos^2\theta}{n_3{}^2 - p^2} + \frac{\sin^2\theta\sin^2\phi}{n_2{}^2 - p^2} + \frac{\sin^2\theta\cos^2\phi}{n_1{}^2 - p^2}\right).$$

If the atoms are orientated uniformly, the mean value of this expression is

$$\frac{Z}{3} \frac{e}{m} \left(\frac{1}{n_1^2 - p^2} + \frac{1}{n_2^2 - p^2} + \frac{1}{n_3^2 - p^2} \right).$$

So that if σ is the density of the electrons, the value of μ the refractive index will be

$$1 + \frac{2\pi}{3} \frac{e^2 \sigma}{m} \left(\frac{1}{n_1^2 - p^2} + \frac{1}{n_2^2 - p^2} + \frac{1}{n_3^2 - p^2} \right). \quad . \quad (5)$$

Thus if n_2 and n_3 were very large compared with n_1,

$$\mu = 1 + \frac{2\pi}{3} \frac{e^2 \sigma}{m} \frac{1}{n_1^2 - p^2};$$

thus the true value of σ would be **three** times that obtained by the usual formula

$$\mu = 1 + 2\pi \frac{e^2}{m} \frac{\sigma}{n^2 - p^2}.$$

The usual formula is only true when the displacement of the electron is always in the direction of the resultant force; when this is so $n_1 = n_2 = n_3$, and the expression for μ takes the usual form.

Conduction in Metals.

If we suppose that the velocity of the electrons is proportional to the electric force, then

$$\frac{dz}{dt} = \frac{Cf}{e\sigma},$$

where C is the specific conductivity of the metal; for $e\sigma \dfrac{dz}{dt}$ is the current through unit area. Using this value of dz/dt equation (2) gives

$$\frac{df}{dx} + \frac{1}{c} \frac{df}{dt} = -\frac{2\pi C}{c} f.$$

The solution of which is

$$f = \epsilon^{-\frac{2\pi C}{c} x} . \phi(x - ct).$$

Since the intensity of the radiation is proportional to f^2, the rate of decay of this intensity is

$$\epsilon^{-\frac{4\pi C}{c} . x},$$

so that the coefficient of absorption is equal to $4\pi C/c$.

Changes produced by the Electrons on the type of Polarization.

We see from equation (1) that if the electrons acquire from the primary wave a finite average velocity in any direction, secondary waves with the electric force in that direction will be emitted. Thus unless the displacement of the electrons due to the electric force in the primary wave is in the direction of that force, the electric force in the secondary waves will not be in the same direction as that in the primary, and the mixture of primary and secondary waves will differ in the state of the polarization from the primary light. The change may be one or other of two types : (1) the mixed light may differ from the primary by being elliptically polarized; or (2) it may still be plane polarized, but the plane of polarization may be rotated.

Y the force in the scattered light is by equation (1) proportional to dy/dt : hence, if y is in the same phase as Z, the force in the primary light, dy/dt and therefore Y will differ in phase from Z by a quarter of a period, so that the mixture of primary and scattered light will be elliptically polarized. If, however, dy/dt is in the same phase as Ż, Y and Z will be in the same phase and the mixture of scattered and primary light will be plane polarized, though the plane of polarization will not coincide with that of the primary light.

Unless the electrons in an atom are distributed in an exceptionally symmetrical way, a force parallel to z will produce a displacement parallel to y, but in cases similar to that discussed on page 716 the y displacement will be in the same phase as Z, and dy/dt will differ in phase from Z by a quarter of a period and the light will be elliptically polarized. The amount of ellipticity in the polarization will depend upon the orientation of the atoms or molecules, and in non-crystalline substances there may be as many molecules producing a positive effect as there are producing a negative one, so that the aggregate effect may be nil and the light will continue to be plane polarized. Thus in the case considered on page 716 the displacement parallel to y produced by the force Z is

$$\xi(\cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi)$$
$$+ \eta(-\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi) + \zeta(\sin\theta\sin\phi),$$

where θ and ϕ have the same values as before, and ψ is the angle between ZC and ZX. Substituting the values of

ξ, η, ζ given on page 716, we find that the displacement parallel to y is

$$\frac{Ze}{m} \left\{ \frac{1}{n_1^2 - p^2} \sin\theta \sin\psi (\cos\theta \sin\phi \cos\psi + \cos\phi \sin\psi) \right.$$

$$- \frac{1}{n_2^2 - p^2} \sin\theta \cos\psi (-\cos\theta \sin\phi \sin\psi + \cos\phi \cos\psi)$$

$$\left. + \frac{1}{n_3^2 - p^2} . \cos\theta \sin\theta \sin\phi \right\} .$$

If there is no order in the arrangement of the atoms or molecules, we see that the average value of each term is zero, so that the light would not be elliptically polarized.

Magnetic Rotation of the Plane of Polarization.

An important case when an electric force acting on an electron may produce motion at right angles to itself is when the electrons are exposed to a magnetic field parallel to the direction of propagation of the light. Let H be the magnitude of the magnetic force, y and z the displacements of the electron parallel to y and z respectively, Z the electric force in the light wave. The equations of motion of the electron will be of the form

$$m\left(\frac{d^2z}{dt^2} + n^2 z\right) = Ze + He\frac{dy}{dt}$$

$$m\left(\frac{d^2y}{dt^2} + n^2 y\right) = -He\frac{dz}{dt} .$$

Hence, neglecting terms in H^2, we find if Z varies as $\epsilon^{\iota p t}$,

$$\frac{dy}{dt} = \frac{ZHe^2 p^2}{m^2(n^2 - p^2)^2}.$$

We see from equation (1) that this involves the production of a wave in which the electric force is parallel to y, and that Y the magnitude of this force for a slab of thickness D is given by the equation

$$Y = -2\pi \frac{\sigma e}{c} D \frac{dy}{dt}$$

$$= -\frac{2\pi\sigma e^3}{m^2 c} . D . \frac{p^2}{(n^2 - p^2)^2} . H . Z.$$

In traversing the distance D the plane of polarization is twisted through the angle Y/Z, or

$$\frac{2\pi\sigma . e^3}{m^2 c} \frac{p^2}{(n^2 - p^2)^2} H . D.$$

If μ is the refractive index,

$$\mu = 1 + \frac{2\pi e^2 \sigma}{m(n^2 - p^2)};$$

hence the angle through which the plane of polarization is twisted is equal to

$$\frac{\mu - 1}{c} \cdot \frac{e}{m} \frac{p^2}{n^2 - p^2} \text{H} . \text{D} ; \quad . \quad . \quad . \quad . \quad (6)$$

this can be written as

$$\frac{p}{2c} \frac{e}{m} \frac{d\mu}{dp} \text{H} . \text{D}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which agrees with the expression given by Becquerel.

He/m is the angular velocity with which an electron would describe a spiral round the line of magnetic force H; let this be denoted by ω, then if τ is the time the light takes to pass across the slab D, the angle through which the plane of polarization is rotated in this time is

$$(\mu - 1) \frac{p^2}{n^2 - p^2} \omega \tau.$$

Thus when the atoms have only one intrinsic frequency the rotation is given by a very simple expression. If n is large compared with p, the rotation is proportional to $(\mu - 1)p^2/n^2$, and is thus proportional to the square of the frequency: a result which is a rough approximation to the truth in a considerable number of cases.

If, as indicated by equation (7), the rotation can be expressed as a function of the dispersion, it follows that no information as to the structure of molecules can be obtained by experiments on magnetic rotation which cannot be obtained by experiments on dispersion.

Rotation of the Plane of Polarization by substances such as quartz or sugar solution.

We cannot explain this rotation if we consider isolated electrons in an atom, but we shall see that we could account for it by a system of electrons held so firmly in position that they act somewhat as a rigid body, a force acting on one electron displacing the whole system of electrons.

We shall suppose as before that the primary beam is travelling along the axis of x, that it is plane polarized, and that the electrical force in it is parallel to z. Let the co-ordinates of an electrical charge, electron or positive particle, be x_s, y_s, z_s. If Z_s is the electrical force in the primary wave at this point, the moment about the axis of x of the forces acting on the electrical charges in the atom is $\Sigma e Z_s y_s$.

If the dimensions of the molecule are small compared with the wave-length of the light, we have, very approximately,

$$Z_s = Z_0 + \frac{dZ_0}{dx} x_s,$$

where Z_0 is the value of Z at the origin O a point inside the molecule. Thus the moment of the forces about the axis of x is

$$Z_0 \Sigma e y_s + \frac{dZ_0}{dx} \Sigma e x_s y_s.$$

Similarly there is a couple around the axis of y equal to

$$-Z_0 \Sigma e x_s - \frac{dZ_0}{dx} \Sigma e x_s^2.$$

These couples acting on the system of electrical charges considered as a rigid body will cause it to rotate, and thus move the individual charges. If the system is not symmetrical the average velocity of the charges parallel to y may be finite, and hence, by equation (1), give rise to an electric wave in which the electrical force has a component parallel to Y. The phase of this force is the same as that of $\Sigma e \frac{dy}{dt}$. The amount of rotation of the plane of rotation will depend entirely on that part of the force Y which is in the same phase as Z. There may be other parts differing in phase from Z by a quarter of a period; these will affect the ellipticity of the polarization, but not the rotation.

Though the values of dy/dt for the different electrical charges may be all in the same phase, yet, since the charges are not all in the wave-front, the secondary waves from them will not, when they arrive at a point, be all in the same phase. Thus, if x_s be the x coordinate of one of the particles, the phase of a vibration due to this particle relative to one starting from the origin will be accelerated by $x_s \frac{2\pi}{\lambda}$, so that, if the velocity of this particle were represented by

$$\cos \frac{2\pi}{\lambda} (vt - x_0),$$

the electric force due to it would have the phase corresponding to

$$\cos \frac{2\pi}{\lambda} (vt - x_0 + x_s),$$

and would be represented, since x_s/λ is small, by

$$\cos \frac{2\pi}{\lambda} (vt - x_0) - x_s \frac{2\pi}{\lambda} \sin \frac{2\pi}{\lambda} (vt - x_0).$$

Similarly, a term in $\frac{dy}{dt}$ represented by $\sin\frac{2\pi}{\lambda}(vt-x_0)$ would give rise to vibrations represented by

$$\sin\frac{2\pi}{\lambda}(vt-x_0) + x_s\frac{2\pi}{\lambda}\cos\frac{2\pi}{\lambda}(vt-x_0).$$

Treating the collection of electrical charges as a rigid body, we proceed to calculate the value of $\Sigma e\frac{dy}{dt}$ due to the rotation of the molecule produced by the couples arising from the electrical forces in the light wave.

Let the principal axes of inertia of the molecule be taken as the axes of x', y', z'; let (l_1, m_1, n_1), (l_2, m_2, n_2), (l_3, m_3, n_3) be the direction cosines of those axes with respect to the fixed axes x, y, z.

Then the moment of the forces about the axis of x' is

$$\Sigma e\left(Z_0 + \frac{dZ}{dx}.x\right)(n_3 y' - n_2 z')$$

Now $x = l_1 x' + l_2 y' + l_3 z'$,

hence the moment of the forces about x'

$$= Z_0(n_3\Sigma e y' - n_2\Sigma e z') + \frac{dZ_0}{dx}(n_3 M - n_2 N).$$
$$L = \Sigma e(l_1 x' x' + l_2 x' y' + l_3 x' z'),$$
$$M = \Sigma e(l_1 x' y' + l_2 y' y' + l_3 y' z'),$$
$$N = \Sigma e(l_1 x' z' + l_2 y' z' + l_3 z' z').$$

Similarly the moment of the forces about the axes of y' and z' are respectively

$$Z_0(n_1\Sigma e z' - n_3\Sigma e x') + \frac{dZ_0}{dx}(n_1 N - n_3 L),$$

$$Z_0(n_2\Sigma e x' - n_1\Sigma e y') + \frac{dZ_0}{dx}(n_2 L - n_1 M).$$

Let $Z_0 = \cos\frac{2\pi}{\lambda}(vt - x_0).$

If A, B, C are the moments of inertia of the molecule about the axes x', y', z', and ω_1, ω_2, ω_3 the angular velocities about these axes, we have, if we retain only the first powers of ω_1, ω_2, ω_3, and suppose that the only forces acting on the

molecule are those due to the forces in the electrical wave,

$$A \frac{d\omega_1}{dt} = \cos \frac{2\pi}{\lambda}(ct - x_0)(n_3 \Sigma ey' - n_2 \Sigma ez')$$
$$+ \frac{2\pi}{\lambda} \sin \frac{2\pi}{\lambda}(ct - x_0)(n_3 M - n_2 N),$$

so that

$$A\omega_1 = - \frac{\lambda}{2\pi c} \sin \frac{2\pi}{\lambda}(ct - x_0)(n_3 \Sigma ey' - n_2 \Sigma ez')$$
$$- \frac{1}{c}\cos \frac{2\pi}{\lambda}(ct - x_0)(n_3 M - n_2 N),$$

with symmetrical expressions for $B\omega_2$, $C\omega_3$.

The velocity of a particle due to these rotations has for components parallel to x', y', z',

$$\omega_2 z' - \omega_3 y', \quad \omega_3 x' - \omega_1 z', \quad \omega_1 y' - \omega_2 x' :$$

hence the velocity parallel to the fixed axis y is

$$m_1(\omega_2 z' - \omega_3 y') + m_2(\omega_3 x' - \omega_1 z') + m_3(\omega_1 y' - \omega_2 x').$$

Y the electric force parallel to y is, as we see by equation (1), proportional to the sum of these expressions.

Now to find the rotation we require the term in Y which is of the same phase as Z, *i. e.* we require the term in $\cos \frac{2\pi}{\lambda}(ct - x)$ and do not need that in $\sin \frac{2\pi}{\lambda}(ct - x)$.

But, as we have explained, owing to the different positions of the moving electrical charge, a term $\cos \frac{2\pi}{\lambda}(ct - x_0)$ in the expression for the velocity of a particle whose coordinate is x_r will give rise to a term

$$\cos \frac{2\pi}{\lambda}(ct - x_0) - x_r \frac{2\pi}{\lambda} \sin \frac{2\pi}{\lambda}(ct - x_0)$$

in the expression for the electric force ; while $\sin \frac{2\pi}{\lambda}(ct - x_0)$ will give rise to

$$\sin \frac{2\pi}{\lambda}(ct - x_0) + x_r \frac{2\pi}{\lambda} \cos \frac{2\pi}{\lambda}(ct - x_0).$$

Remembering this we see that the contribution of the rth

charge to the term in the expression for Y proportional to $\cos \dfrac{2\pi}{\lambda}(ct - x_0)$ is proportional to

$$- \frac{(m_3 y_r{'} - m_2 z_r{'})}{Ac} \left\{ (n_3 M - n_2 N) - x_r(n_3 \Sigma y' - n_2 \Sigma z') \right\}$$

$$- \frac{(m_1 z_r{'} - m_3 x_r{'})}{Bc} \left\{ (n_1 N - n_3 L) - x_r(n_1 \Sigma z' - n_3 \Sigma x') \right\}$$

$$- \frac{(m_2 x_r{'} - m_1 y_r{'})}{Cc} \left\{ (n_2 L - n_1 M) - x_r(n_2 \Sigma x' - n_1 \Sigma y') \right\}.$$

Thus Q the contribution of the whole molecule will be given by the equation

$$Q = - \frac{1}{Ac} \left\{ (m_3 \Sigma e y' - m_2 \Sigma e z')(n_3 M - n_2 N) \right.$$
$$\left. - (n_3 \Sigma e y' - n_2 \Sigma e z')(m_3 M - n_2 N) \right\}$$
$$- \frac{1}{Bc} \left\{ \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \right\}$$
$$- \frac{1}{Cc} \left\{ \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; , \; \right\}$$
$$= - \frac{1}{Ac} \left\{ m_2 n_3 - m_3 n_2 \right\} (N \Sigma e y' - M \Sigma e z')$$
$$- \frac{l_1}{Bc} \left\{ \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \right\} - \frac{1}{Cc} \left\{ \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \right\}$$
$$= - \frac{l_1}{Ac} (N \Sigma e y' - M \Sigma e z') - \frac{l_2}{Bc} (L \Sigma e z' - N \Sigma e x')$$
$$- \frac{l_3}{Cc} \left\{ M \Sigma e x' - L \Sigma e y' \right\}.$$

If there are σ of these molecules per unit volume, the rotation of the plane of polarization per unit path is by equation (1) equal to

$$2\pi Q \frac{\sigma}{c}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

We must distinguish between the cases (1) when the molecules are in the gaseous state or in solution, and (2) when they form parts of a crystal. In case (2) we may suppose that all the molecules are orientated in the same way so that l_1, l_2, l_3 are the same for all molecules; then equation (8) will give the rotation for light moving in the direction determined by l_1, l_2, l_3, which are the direction cosines of the path of the light relative to the axes of the

crystal. In case (1) the values of l_1, l_2, l_3 will vary from molecule to molecule. If the orientation of the molecules is quite irregular, the mean values of l_1^2, l_2^2, l_3^2 are each $1/3$, while those of l_1l_2, l_1l_3, l_2l_3 are zero: hence $\bar{Q}$ the mean value of Q is given by

$$\bar{Q} = -\frac{1}{3Ac}\{\Sigma ex'z'\Sigma ey' - \Sigma ex'y'.\Sigma ez'\}$$

$$-\frac{1}{3Bc}\{\Sigma ex'y'\Sigma ez' - \Sigma ey'z'.\Sigma ex'\}$$

$$-\frac{1}{3Cc}\{\Sigma ey'z'\Sigma ex' - \Sigma ex'z'.\Sigma ey'\},$$

and the rotation for the solution is

$$2\pi\bar{Q}\frac{\sigma}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

I obtained a similar expression, by a different method, for this rotation in a paper published in the Proceedings of the Cambridge Philosophical Society, xiv. p. 313 (1907).

We see from the expression for $\bar{Q}$ that if it is to be finite the molecule must be very unsymmetrical.

For $\bar{Q}$ vanishes

(1) if the molecule has dynamical symmetry, for then
$A = B = C$;

(2) if the centre of the electrical charges coincides with the centre of mass, for then

$$\Sigma ex' = \Sigma ey' = \Sigma ez' = 0 ;$$

(3) if the principal axes of inertia coincide with axes of symmetry of the electrical charges, for then

$$\Sigma ex'y' = \Sigma ex'z' = \Sigma ey'z' = 0 ;$$

(4) if $\quad \Sigma ey'\Sigma ex'z' = \Sigma ez'\Sigma ex'y' = \Sigma ex'\Sigma ey'z'.$

This relation would be fulfilled if the electrical charges formed a geometrically symmetrical system, even though the masses might not be symmetrical. For such a system

$$\Sigma ex'z' = \Sigma ex'y' = \Sigma ey'z' = 0$$

for all axes through the centre of figure ; hence for parallel axes through the centre of mass

$$\Sigma ex'z' = x . \Sigma e,$$

where $\bar{x}, \bar{y}$ are the coordinates of the centre of figure referred to axes through the centre of mass

$$\bar{x}\Sigma e = \Sigma ex'$$
$$\bar{y}\Sigma e = \Sigma ey' :$$

hence we see

$$\Sigma ey'\Sigma ex'z' = \bar{x}\,\bar{y}\,\bar{z}(\Sigma e)^2 = \Sigma ex'\Sigma ey'z' = \Sigma ez'\Sigma ex'y' ;$$

(5) if there is a plane of symmetry in the molecule: for if this plane be taken as the plane $z'=0$,

$$\Sigma ez' = 0, \quad \Sigma ex'z' = 0, \quad \Sigma ey'z' = 0,$$

and hence $\bar{Q} = 0$.

It follows from this that if all the atoms in a molecule are in one plane, the molecule cannot when in solution give rise to optical rotation.

It should be noticed that molecules when in a crystalline arrangement could produce optical rotation when they could not do so in solution, it being assumed that the molecules are not distorted by solution. We have seen that when in solution, *either* dynamical or electrical symmetry is fatal to rotation. Whereas in the crystalline arrangement rotation would in general exist, unless the molecule was symmetrical dynamically as well as electrically. For rotation to be absent in the crystalline arrangement the coefficients of $l_1^2, l_2^2, l_3^2, l_1l_2, l_1l_3, l_2l_3$ in the expression for Q (p. 725) must all vanish. Two important cases in which this condition is fulfilled are (1) when the centre of the electrical charges coincides with the centre of mass; (2) when the molecule is symmetrical about an axis.

For the present I shall confine myself to the case of rotation in solutions, as this is the one to which the attention of investigators has in the main been directed. As most of these have occupied themselves with substances which contained asymmetric carbon atoms, it is interesting to compare the value and sign of $\bar{Q}$ for two molecules (i.) and (ii.), where (ii.) is such that its masses and electrical charges occupy positions which are the images of their positions in (i.) in a mirror placed in one of the principal planes of (i.). Let us take this plane as the plane $z'=0$. The coordinates of the masses and charges on (ii.) will be those of the corresponding mass of (i.) with the sign of the z' coordinate reversed. Thus $\Sigma ex'$, $\Sigma ey'$ will be unaltered, while $\Sigma ez'$ will change sign. Again, $\Sigma ex'y'$ will be unaltered, while $\Sigma ex'z'$ and $\Sigma ey'z'$ will change sign: hence we see that $\bar{Q}$ will have

the same magnitude in both (i.) and (ii.), but if it is plus for one it will be minus for the other. So that if (i.) rotates the plane of polarization in one, (ii.) will rotate it in the opposite direction. Thus a molecule represented graphically by fig. 1 would rotate in the opposite direction to one represented by fig. 2, or by fig. 3.
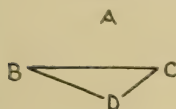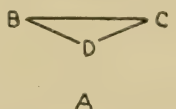
Fig. 1.   Fig. 2.   Fig. 3.
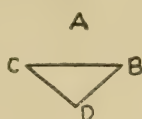
The geometrical meaning of $\overline{Q}$ is interesting. The term

$$\Sigma ey'\Sigma ex'z' - \Sigma ez'\Sigma ex'y'$$

may be written

$$\Sigma e_p e_q (x_p - x_q)(z_p y_q - z_q y_p),$$

where x_p, y_p, z_p; x_q, y_q, z_q are the coordinates of two points P, Q at which the charges are e_p, e_q; the expression may be put in the form

$$\Sigma e_p e_q PQ \cos \phi . PQ \sin \phi . p,$$

where ϕ is the angle PQ makes with the axis of x, and p the shortest distance between PQ and this axis. Since $PQ \sin \phi . p$ is the moment of PQ about the axis of x, and $PQ \cos \phi$ the component of PQ along the axis, the term is equal to the product of the charges multiplied by the product of the component of PQ along and its moment about the axis of x. Thus it vanishes if PQ is parallel to the axis, or if it is at right angles to it, or if it intersects it. The term is equal to $e_p e_q 6V$, where V is the volume of the tetrahedron whose corners are P, Q and the projections of P and Q on the axis of x. The term is to be taken as positive or negative according as the component of PQ along and its moment about the axis of x are related like translation and rotation in a right or left handed screw.

The hypothesis we have made is that the whole molecule rotates like a rigid body under the influence of the electric forces in a light wave, so that there is no displacement of the electrons relative to the atoms in a molecule. We shall now consider whether on any reasonable supposition as to the values of the quantities involved, the expressions we have found would give values for the rotation of the same order as those observed for optically active substances.

Consider first the value of Q : the terms $1/A$, $1/B$, $1/C$, will be of the order $1/Md^2$, where M will not be less than the mass of the smallest atom in the molecule, nor greater than the mass of the molecule itself, d is a length comparable with the radius of the molecule. The terms $\Sigma ex'y'$, $\Sigma ex'$, may for very unsymmetrical molecules be of the order ed^2 and ed respectively, hence Q will be of the order e^2d/M : hence we see from equation (4) that the angular rotation in circular measure per centimetre will be of the order

$$\frac{Ne^2d}{c^2M} \text{ or } NM \cdot \frac{e^2d}{c^2M^2}.$$

When there is one gramme of the substance per cubic centimetre NM will be less than unity, hence the specific rotation will be less than e^2d/c^2M^2. Now there are many active substances in which the lightest atom is heavier than OH. If we take M to be the mass of this atom, then since e is expressed in electrostatic measure, $e/cM = 10^4/17$, so that the specific rotation per cm. will be less than $d \times 10^8/289$, or taking $d = 10^{-8}$ less than $1/289$, *i. e.* less than $12'$. Many optically active substances have specific rotations greater than $10°$, so that our expression for the rotation only accounts for a small fraction of that observed. Nor is this all, the expression we have obtained does not depend upon the frequency of the light, whereas the actual rotations are approximately proportional to the square of the frequency. This discrepancy is due to the fact that we have regarded the molecule as a free system, uninfluenced by other molecules. If the influence of the other molecules is such as to make it set in a definite position and vibrate about this position with a frequency n, the displacements and velocities will be less than when the system is free in the proportion of p^2 to p^2-n^2, where p is the frequency of the light. Thus when the influence of other molecules is to be taken into account, we must multiply the expression we have obtained by p^2/p^2-n^2. If n were large compared with p, this factor would be p^2/n^2, and as this is proportional to the square of the frequency, we should get the correct variation of the rotation with the frequency of the light. There are, however, two very serious objections to the modification of the formula in this way. In the first place, it is very unlikely that the natural frequency of the motion of a heavy molecule as a whole should be large compared with the frequency of the light ; and secondly, even if it were, since the factor p^2/n^2 would then be small, the rotation, as calculated by the

modified expression, would be much smaller than that calculated by (8) which, as we have seen, is already far too small. Again, from this formula the rotation ought to tend to be smaller for heavier molecules than for light ones ; there is no indication of this in the very numerous determinations which have been made of specific rotation.

Thus we do not get sufficient movement to account for the rotation produced by optically active substances if we suppose the whole molecule to rotate as a rigid body under the electric forces in the wave of light. We may, however, regard the molecule as made up of two parts, the first part consisting of the atoms in the molecule, the second of the electrons which bind these atoms together. Thus, with a tetrahedral arrangement of the atoms round the carbon atom, the first system will consist of the carbon atom at the centre O and four other atoms or radicles, A, B, C, D at the corners of the tetrahedron (fig. 4). If we make the

Fig. 4.
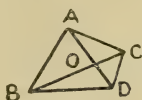
usual assumption that A, B, C, and D are bound directly to the carbon atom, then between O and each one of these atoms there must be electrons whose attractions on the positively electrified atoms will bind them together. These structural electrons will form a tetrahedral arrangement which will occupy a definite position relative to the tetrahedron A, B, C, D, and if disturbed from this position will vibrate about it with a definite frequency. When the light waves fall upon the molecule what I imagine to happen is, that in consequence of the relatively enormous mass of the atoms themselves there is but an insignificant displacement of the atomic tetrahedron, but that the much lighter tetrahedral arrangement of the electrons suffers a much greater amount of rotation, and that the motion of the electrons consequent upon this rotation gives rise to the rotation of the plane of polarization.

We have thus to regard the system of electrons as that to which we must apply the preceding analysis. It may be urged against this that since the electrons are all of the same mass, and the electrical centre of the system coincides with the mass centre, the analysis shows that the system would be far too symmetrical to give rise to optical rotation. This

would be a valid objection if all the electrons were quite
free, or even if they were all under similar conditions of
restraint. The electrons, however, are not free, they are
acted upon by forces which tend to drag them back to the
places from which they start. If these forces are different
for the different electrons, the behaviour of one electron
will be different from that of another, and this may make the
system so unsymmetrical that it may be able to produce
rotation of the plane of polarization. We may make this
clearer by considering a very simple case, that of four
electrons α, β, γ, δ at the corners of a tetrahedron, and
suppose that the restoring forces for two of the electrons,
say α and β, are very large compared with those for γ and δ.
The effect of this will be much the same as if α and β were
fixed, so that the tetrahedron would, when acted upon by
the electrical forces in a wave of light, rotate about the line
$\alpha\beta$, the two electrons γ and δ would rotate about this axis.

We see from the considerations given above that each
tetrahedron will contribute to the expression for the rotation
of the plane of polarization a term equal to

$$\frac{2\pi}{3}\frac{e^2}{c^2}\frac{[PQ]}{A},$$

where A is the moment of inertia of the two electrons γ and δ
about the axis $\alpha\beta$, and $[PQ]$ is six times the volume of the
tetrahedron whose corners are γ and δ and the feet of the
perpendiculars let fall from γ and δ on $\alpha\beta$. Let us consider
the numerical magnitude of this term. If d is a measure of
the radius of the molecule, $[PQ]$ will be of the order d^3 and
A of the order md^2, where m is the mass of an *electron*. Thus
the contribution to the rotation will be of the order

$$\frac{e^2}{c^2}\frac{d}{m},$$

and if there are N molecules per c.c., the rotation will be
of the order

$$\frac{Ne^2}{c^2m}d.$$

If M is the mass of the molecule, then when there is one
gramme of the active substance per c.c., $NM=1$, so that
the intrinsic rotation is

$$\left(\frac{e^2}{c^2m^2}\right)\frac{m}{M}d.$$

Now

$$e^2/c^2m^2 = (1\cdot8\times10^7)^2,\ d=10^{-8},\ \text{and}\ m/M = \frac{1}{1\cdot8\times10^3\cdot W},$$

where W is the molecular weight of the substance. Thus

the intrinsic rotation would be $\dfrac{1\cdot 8 \times 10^2}{W}$ radians or about $\dfrac{10^4}{W}$ degrees. This has to be multiplied by p^2/n^2, where n is the natural frequency of the vibration of the tetrahedron about the axis $\alpha\beta$. But we see that, even allowing for a small value of $p^2 n^2$, the system we have considered is able to produce rotations comparable with those excited by optically active substances. If the specific rotation is multiplied by the molecular weight of the active substance, the product is a measure of the rotation due to a single molecule, a quantity which is much more likely to throw light on the properties of the molecule than the rotation due to a gramme of the substance.

The volume of the tetrahedron which measures the contribution to the optical rotation of one molecule, when the electrons $\gamma\delta$ rotate round $\alpha\beta$, vanishes in the following cases :—

> If $\gamma\delta$ is parallel to $\alpha\beta$.
> If $\gamma\delta$ intersects $\alpha\beta$.
> If $\gamma\delta$ is at right angles to $\alpha\beta$.

From the third of these conditions it follows that no optical rotation will be produced if α, β, γ, δ are at the corners of a *regular* tetrahedron, there must therefore be some lack of symmetry in the distribution of these electrons. The rotation vanishes whenever $\gamma\delta$ is in a plane at right angles to $\alpha\beta$. Thus it would vanish if the two atoms or radicles which the electrons γ and δ bind respectively to the central carbon atom were identical ; for then by symmetry α and β would both be in the plane bisecting $\gamma\delta$ at right angles.

A shift in the position of one or both of the electrons γ, δ might change the sign of the optical rotation produced by the molecule. Thus, for example, when the electrons are
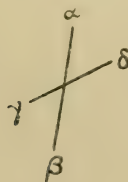
Fig. 5. Fig. 6.
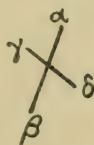
distributed as in fig. 5, the molecule would behave like a positive screw, while if they were as in fig. 6, it would behave like a negative one.

We can explain by displacements of this kind the very interesting fact that the optical rotation by a solution of an active substance may depend not merely in magnitude, but also in sign on the nature of the solvent : thus, for example, a solution of *d* acetic acid in water is dextro rotatory, while when dissolved in a mixture of acetone and ether it is lævo rotatory (Landolt). If a solvent made some progress towards ionizing the substance by weakening the attachment of one of the atoms (say D) to the carbon atom, it might make the electron δ which binds D to the carbon atom move from δ to a position more remote from the carbon atom. This change, as fig. 6 shows, might reverse the sign of the rotation.

The general conclusions to which we are led by the preceding investigation, is that the electrical system which is instrumental in producing optical rotation are the electrons which couple the atoms in the molecule to the central carbon atom, and that the most important quantities in the expression for the rotation are (1) the rigidities of those electrons, *i. e.* the intensity of the forces restoring them to their position of rest when displaced from it ; and (2) the distances of these electrons from the central carbon atom. For it is on these quantities that the dynamical and geometrical asymmetries depend respectively, and as we have seen, both these asymmetries are essential for rotation in solutions. If it were not for differences in (1) there would be no dynamic asymmetry, for the electrons have all the same mass. When, however, they are pulled back when displaced from their position of equilibrium with forces of different intensities, the effect will be much the same as if the electrons had different masses. Thus, if the frequency of the vibrations of the electron when displaced from its position of equilibrium is n_1 and p is the frequency of the light, the behaviour of the electron under the forces in the light, wave will be much the same as if the electron were free but had a mass $(p^2 - n_1^2)/p^2$ times its normal mass. When n_1^2 is large compared with p, the effective mass is approximately n_1^2/p^2 times the normal mass, and is thus much greater. Thus the dynamical asymmetry of the molecule will be measured, not as on Guye's theory [*] by differences in the atomic weights of the atoms attached to the carbon atom, for these on our view have no direct bearing on the rotation, but on the differences in the frequencies of the electrons which bind the atoms to the carbon atom.

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[*] *Ann. Chim. Phys.* (6) xxv. p. 145 (1892).

Again, the geometrical asymmetry which is necessary for rotation will depend on the distances of these electrons from the carbon atom. Thus, to predict the rotation produced by a molecule containing one unsymmetrical carbon atom and represented by $CR_1 R_2R_3R_4$, we require to know the properties of the linkages CR_1, CR_2, CR_3, CR_4; *i. e.*, we require to know the frequency of the coupling electron in the linkage CR and its distance from C.

Unfortunately our knowledge on these points is extremely meagre. We might expect to get some knowledge of the frequencies by mapping the absorption spectra of various hydrocarbons. Thus, if the coupling $C-H$ had a frequency n_1, we might expect to find in the absorption spectrum of a compound containing this coupling a band corresponding to this frequency, modified it might be by the proximity of other couplings in the molecule. A study of the spectra of compounds containing the coupling $C-OH$ might, in a similar way, lead to the knowledge of the frequency of the electrons concerned in this coupling. And in this way, by the study of the absorption spectra of a large number of organic compounds, we might hope to determine the frequency of the coupling of the carbon atom with the various atoms and radicles to which it is joined in organic compounds. Considerable progress has been made in the study of such absorption spectra. Thus Hartley (see Kayser's 'Spectroscopy,' vol. iii.), working with ultra-violet light down to the wave-length 2000, studied the absorption in the ultra-violet down to this limit, and discovered well-defined absorption bands in benzene and other aromatic compounds containing the benzene ring. Our knowledge of this subject has been greatly extended by Stark and his collaborators who, by using fluorite lenses and prisms, were able to work with ultra-violet light down to wave-length 1850, and discovered, among other things, bands which they ascribed to the linkages $C=C$ and $C\equiv C$. We are however not yet, I think, in a position to be able to say what are the fundamental frequencies of the various linkages; to do so we require observations over a wider range of frequencies extending to wave-lengths considerably smaller than those hitherto studied, for in this, the Schumann region, nearly all gases have great absorption, and some of it may well be selective. The experiments hitherto made indicate that the frequencies corresponding to the linkages $C-H$ and $C-OH$ will be very far in the ultra-violet, and consequently larger than the normal value. Now, on the view we have taken, a high frequency corresponds to a large effective mass, so that in

compounds of the type $C.H.HO$, R_1, R_2, the system of coupling electrons will tend to twist round the line joining the electrons which couple H and OH with the carbon atom.

The other condition for optical rotation is geometrical asymmetry. The electrons cannot be at the corners of a regular tetrahedron, and this arrangement, which is the one usually asssumed, is incompatible with optical rotation. The departure of the molecule from this form, in fact the shape of the molecule, is of vital importance in connexion with optical rotation, but on this subject little, if anything, seems to have been done.

If we had a theory which gave the configuration of the molecule and the periods of vibrations of the electrons, we could calculate by the expression given above the value of the molecular rotation. Inasmuch as the configuration and periods enter into these expressions in a complicated way, the effect of any one period, for example, depending on its relation to each of the other periods, the periods are not easily calculated from the rotation. Thus observations on the optical rotation are more likely to be useful as a test of any theory of the configuration and structure of the molecule than as a means of discovering this structure.

Since the above was written I have seen a paper by Stark (*Jahr. f. Radioaktivität*, xi. p. 194, 1914), in which the subject of optical rotation is also treated from the point of view of the electron theory ; the treatment is wholly qualitative, and I find it difficult to follow the reasoning ; so far as I am able to do so it seems to me to be fundamentally different from that given above.

LXXXIV. *The Charge on the Atomic Nucleus and the Law of Force. By* J. Chadwick, *M.Sc., Wollaston Student of Gonville and Caius College, Cambridge* [*].

§ 1. THE theory of the nuclear constitution of the atom, put forward by Sir Ernest Rutherford [†] in 1911, has been confirmed by evidence gathered from such various sources that it now forms the foundation on which the development of atomic physics is based. On this theory, the positive charge associated with an atom is concentrated on a massive nucleus of small dimensions, surrounded

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[†] Rutherford, Phil. Mag. xxi. p. 669 (1911).

by a distribution of electrons extending over a distance comparable with the diameter of the atom, as usually understood.

The physical and chemical properties of an element are determined by the charge on the nucleus, for this fixes the number and arrangement of the external electrons, on which these properties mainly depend. The mass of the nucleus influences the arrangement of the electrons only to a very small degree. The nuclear charge is thus the fundamental constant of the atom and the question of its actual magnitude of great importance for the development of atomic theory.

In the paper referred to above, Sir Ernest Rutherford showed—assuming that the electric forces between the nucleus and an α particle passing close to it varied according to the inverse square law—that the α particle would describe a hyperbolic path, and obtained the relations connecting the fraction of α particles scattered through any angle with the charge on the nucleus and the velocity of the α particle. From some observations of Geiger and Marsden * on the reflexion of α particles he deduced that the charge on the nucleus of an atom is roughly $\frac{1}{2}A \cdot e$, where A is the atomic weight and e the electronic charge.

In their experiments on the scattering of α particles, which proved conclusively the truth of the nuclear theory, Geiger and Marsden showed that the charge on the nucleus was equal to $\frac{1}{2}A \cdot e$ to within about 20 per cent. The large error is due to the fact that the scattered particles formed such a small fraction of the original beam that different methods of measurement had to be employed in the two cases.

Later, van den Broek † suggested that the nuclear charge might be equal to the atomic number of the element, *i. e.* the number of the element when all the elements are arranged in order of increasing atomic weight. This proved to be in good agreement with the experiments on scattering, but the importance of the atomic number was first shown by Moseley's work on the X-ray spectra of the elements. Moseley ‡ found that the X-ray spectra of the elements depended on the square of a number which increased by unity in passing from one element to the next of higher atomic weight. This number was not exactly equal to

* Geiger and Marsden, Phil. Mag. xxv. p. 604 (1913).
† Van den Broek, *Phys. Zeit.* xiv. p. 32 (1913).
‡ Moseley, Phil. Mag. xxvi. p. 1024 (1913); xxvii. p. 703 (1914).

the atomic number, but was equal to $N - a$ where N is the atomic number and a a constant for the series. For the K series $a = 1$ and for the L series $a = 7 \cdot 4$. In order to obtain perfect regularity in the X-ray spectra, it was necessary to leave three places for unknown elements corresponding to atomic numbers 43, 61, and 75, and to adjust the places of the elements A, Co, and Te, where the order of atomic weights clashed with the order of chemical properties. Then, in every case from Al, for which N was assumed to be 13, to Au, $N = 79$, the X-ray spectra of an element were defined by the number assigned to it. On the nuclear theory of atomic structure this characteristic number must be closely connected with the charge on the nucleus, and Moseley concluded that the number gave in fundamental units the actual value of this charge. He supposed that the constant a represented a disturbing effect due to the electrons in the vibrating systems, depending upon their number and position.

This is one of the most important generalizations in modern physics, and gives a starting-point for the development of the external structure of the atom. It is therefore necessary to be quite clear as to the nature of the evidence on which it rests. Moseley's discovery that the X-ray spectra of an atom are defined by a characteristic number is an empirical expression of his measurements, and is independent of any theories of atomic structure or origin of spectra. The identification of this number with the atomic number, however, is attained by an arbitrary choice of the constant a, and the statement that the atomic number gives the actual value of the nuclear charge implies a theory of the origin of X-ray spectra. The fact that the characteristic number changes by unity from element to element is, of course, very suggestive on the nuclear theory, but there is no experimental proof of Moseley's conclusion. The good agreement between the observed frequencies of the K lines and the frequencies calculated by Debye [*] and Kroo [†] on the Bohr theory afford strong presumptive evidence in favour of the correspondence between atomic number and the value of the nuclear charge, but here the assumption is made that there are no electrons between the nucleus and the K ring. (This corresponds to Moseley's choice of the constant a.) It is true that no X-ray series of higher frequency than the K series has been observed,

[*] Debye, *Phys. Zeit.* xviii. p. 276 (1917).
[†] Kroo, *Phys. Zeit.* xix. p. 307 (1918).

but this could be explained by the high voltages which would be necessary to stimulate its emission. The penetrating γ rays emitted in some radioactive transformations are known to be of far higher frequency than corresponds to the K series, and their origin is not yet clear, though it has been suggested by Rutherford that they come from the nucleus itself.

It appears, therefore, of great importance to measure the nuclear charge as accurately as possible by a direct method, and to compare the value obtained with the atomic number. Accordingly the experiments to be described in this paper were undertaken.

§ 2. *Method of Measurement of Nuclear Charge.*

The only direct method we have of measuring the charge on the nucleus of an atom is from the single scattering of α particles. Sir Ernest Rutherford has shown that, if a pencil of α particles falls on a thin sheet of matter, the number of scattered α particles which fall per second on unit area of a screen, distant r cms. from the point of incidence of the pencil in a direction making an angle ϕ with it, is given by

$$\frac{Qntb^2 \operatorname{cosec}^4 \phi/2}{16r^2},$$

where Q = number of α particles per second in the original pencil,

$\quad\quad n$ = number of atoms in unit volume of the foil,

$\quad\quad t$ = thickness of the foil,

and $\quad b = \dfrac{2E}{mu^2} . Ne,$

where Ne is the nuclear charge of the scattering atom and m, u, E are the mass, velocity, and charge of the α particle.

In this calculation it was assumed that the collision of the α particle with the nucleus does not set the atom in motion. Darwin [*] modified the calculation to include this effect, and found that if M be the mass of the nucleus and greater than m, $\operatorname{cosec}^4 \phi/2$ in the above expression must be replaced by

$$\operatorname{cosec}^4 \phi/2 - 2\left(\frac{m}{M}\right)^2 + \left(1 - \frac{3}{2}\sin^2 \phi\right)\left(\frac{m}{M}\right)^4 + \ldots.$$

* Darwin, Phil. Mag. xxvii. p. 499 (1914).

The lightest scattering atom used in the present experiments was that of copper, and the value of ϕ was about 29°. It is easily seen that the correction due to motion of the nucleus is negligible, being, in fact, only one part in 20,000.

The determination of the nuclear charge consists, therefore, in the measurement of the number of α particles in the original pencil and the number in the scattered pencil under known geometric conditions. The scattered particles, however, are an extremely small fraction of the original pencil; and, as was pointed out above, it is this which provided the chief difficulty in Geiger and Marsden's experiments, necessitating the use of different methods of measurement in the two cases.

In the experiments described in this paper both the scattered and the direct particles were counted on the same zinc-sulphide screen under the same conditions. This was made possible partly by the geometry of the arrangement adopted, but mainly by the aid of a new method of counting the direct pencil.

The fraction of scattered particles was increased by using as scattering foil an annular ring subtending a fairly wide cone at the source. There is no objection to the use of a wide angle provided that the method adopted is amenable to accurate calculation, for the law of scattering with angle has been verified to a high degree of accuracy.

In fig. 1 let R be the source of particles, AA′ the

Fig. 1.
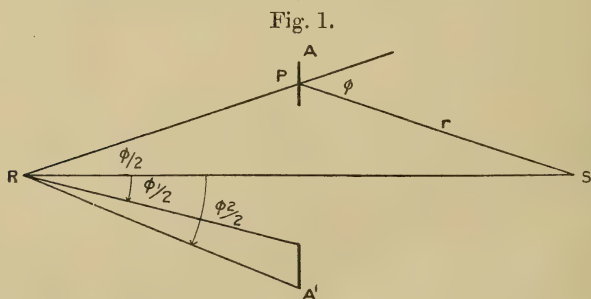
scattering foil, and let the zinc-sulphide screen be placed at a point S on the axis of the cone RAA′, such that RA = AS.

The solid angle subtended at R by an elementary annular ring at P is $2\pi \sin \phi/2 \,.\, d\phi/2$.

If Q is the number of α particles emitted per second by

the source, then the number falling per second on this elementary ring is

$$\frac{Q}{2} \sin \phi/2 \cdot d\phi/2.$$

The number scattered to unit area at S placed at right angles to RS is then

$$\frac{Q}{2} \sin \phi/2 \cdot d\phi/2 \cdot \cos \phi/2 \cdot nt \sec \phi/2 \cdot \frac{b^2 \operatorname{cosec}^4 \phi/2}{16r^2}.$$

For the whole scattering foil of angular limits $\phi_1/2$, $\phi_2/2$ the number of particles falling per second on unit area at S is

$$\frac{Qntb^2}{32r^2} \int_{\phi_1/2}^{\phi_2/2} \operatorname{cosec}^3 \phi/2 \cdot d\phi/2,$$

where $\overline{r^2}$ is a mean value.

Since
$$\int \operatorname{cosec}^3 x \, dx = -\frac{1}{2} \frac{\cos x}{\sin^2 x} + \tfrac{1}{2} \log \tan \tfrac{1}{2} x.$$

the above number is

$$\frac{Qntb^2}{64r^2} \left[\log \tan \phi_2/4 - \log \tan \phi_1/4 + \cot \phi_1/2 \operatorname{cosec} \phi_1/2 \\ - \cot \phi_2/2 \operatorname{cosec} \phi_2/2 \right].$$

The number of α particles falling per second directly on unit area at S is

$$\frac{Q}{4\pi l^2} \quad \text{where } l = \text{RS}.$$

Taking the favourable case of a heavy atom like platinum and ascribing suitable values to the dimensions involved, we find that the scattered number is still only one five-hundredth to one thousandth of the direct number. If the scattered particles were falling on the screen at the rate of 30 per minute, a convenient number for counting, the direct number would be 20,000 per minute.

The counting of this large number in the direct beam was made possible by a device suggested to me by Sir Ernest Rutherford. If a wheel containing a slit is rotated in the path of a pencil of α rays so that the particles can fall on a ZnS screen only when the slit passes it, the number of scintillations will be reduced in the ratio of the width of the slit to the circumference of the wheel at the position of the slit, and will be independent of the speed of rotation of the wheel. Thus with a slit of 2 mm. in a wheel of

10 cm. radius the reduction factor will be about 620 ; that is, if without the wheel the number of scintillations is 20,000 per minute, the number when the wheel is rotated will be 30.

This method has the further advantage that by varying the speed of the wheel the time-distribution of the scintillations can be changed. For example, suppose that, rotating the wheel, the number of scintillations is 120 per minute. If the wheel is rotated once a second, then on the average 2 scintillations will be observed every time the slit comes round. Owing to the probability fluctuations the number at each rotation will vary—sometimes 0, sometimes as many as 4 or 5 will occur,—but the observer has a second in which to collect and register his impressions. As the speed of rotation is increased, the number per rotation decreases and the interval between successive flashes gets shorter, until the ordinary time-distribution is approached. It was found that with a little practice a flash of about 6 or 7 scintillations was readily identified, provided that an interval of about half a second was allowed before the next flash. This enables counting to proceed at a far greater rate than is possible by the usual method ; in fact, with the wheel 100 scintillations per minute is quite a moderate rate, and after some practice 200 per minute can be counted with accuracy. Under the usual conditions 30 to 40 scintillations per minute is the highest rate for accurate counting.

The advantages of counting both with the direct and scattered particles on the same screen are obvious ; the chief source of error in the determination of the nuclear charge is surmounted. Provided that the scattering foil is thin and uniform, so that the correction for change of velocity of the α particle in passing through the scattering foil is small and accurately known, the accuracy of the measurement will now depend chiefly on the number of α particles counted in the experiments.

§ 3. *Apparatus.*

The experimental arrangement is clear from fig. 2. The diaphragm D defining the beam of α particles was made by suspending a circular disk 11·22 mm. in diameter in the centre of a circular opening 19·22 mm. diameter. The scattering foil was held on the support A, of similar construction to D. The circular opening had a diameter of 40 mm. and the central disk 15 mm., sufficient to prevent any particles scattered by the edges of the diaphragm from

reaching the zinc-sulphide screen. The position of A was adjusted to be equidistant from the source R and the zinc-sulphide screen S. The distance from the source to the diaphragm was 29·1 mm. and from the source to the

Fig. 2.
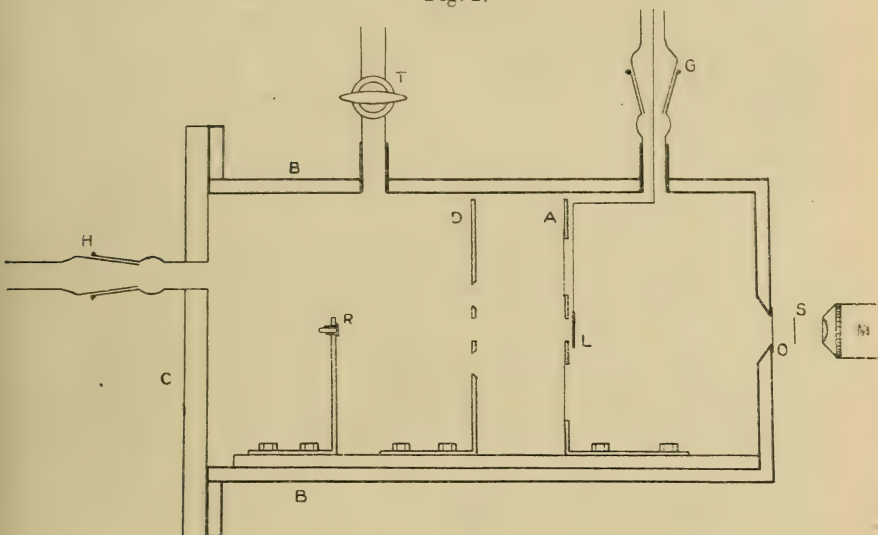
screen 99·2 mm. The source-holder, diaphragm, and foil-holder were mounted on a brass base which fitted into slides in the brass box B, 12 cm. × 6 cm. × 6 cm., and were adjusted so that their common axis was exactly central to the opening O in the end of the box. This opening, of 6 mm. diameter, was covered with a mica sheet of 2 cm. stopping power. The box was closed by the glass plate C and could be exhausted through the tap T.

The direct pencil of α rays which came through holes in the central disks of D and A could be cut off at will by the lead screen L carried by the glass joint G.

The ZnS screen was observed through the microscope M, which had a field of view of 1·5 mm. diameter.

The wheel, which was made of glass, was rotated between the end of the box and the ZnS screen, and contained besides the slit a hole 1 cm. in diameter, which was brought between the opening O and the screen when counting the scattered particles. When the wheel was rotated for the counting of the direct pencil, this hole was covered with a thick sheet of mica. The diameter of the wheel at

the effective part of the slit was 175·5 mm. Slits of width 2·80 mm., 1·24 mm., and ·622 mm. were used, giving reduction factors of 197, 445, and 886.

The source of α rays was a brass disk of 2 to 3 mm. diameter coated on the face only with Ra (B + C). The initial γ-ray activity of the source was equivalent to about 2 mgm. Ra. The preliminary manipulations of inserting the source, exhausting the box, etc., were performed in a weak light, and a further 15 minutes' wait was allowed before counting.

The scattered and the direct particles were counted alternately. The scattered number was generally about 30 to 40 per minute at the beginning, and about 300 scattered particles were counted in the course of one experiment.

In calculating the ratio of the scattered number to the direct number, the correction for decay of the source is comparatively unimportant, since each scattered number is included between two counts of the direct number. From this ratio the value of the nuclear charge of the scattering atom was deduced by substituting the known constants in the expression given in the previous section.

§4. *The Nuclear Charges of Platinum, Silver, and Copper.*

Three series of experiments were carried out, foils of platinum, silver, and copper being used as scattering materials.

Platinum.—The foil used consisted of 10 sheets of thin leaf in order to ensure a uniform thickness, and had a weight of 4·93 mgm. per sq. cm. Hence $nt = 1·520 \times 10^{19}$.

Using Geiger's relation for the decrease of velocity in passing through the foil, and Rutherford and Robinson's [*] value for the initial $\frac{mu^2}{E}$, the average value of $\frac{mu^2}{E}$ is $7·20 \times 10^{14}$.

The angles $\phi_1/2$ and $\phi_2/2$ were $10° 54'$ and $18° 16'$ respectively. We find, therefore, that the observed ratio of the number of scattered particles per minute to the number of direct particles per minute is equal to $N^2 \times 3·16 \times 10^{-7}$.

The values of N calculated from the experiments were :

80·6 (215), 79·4 (226), 79·6 (629), 76·0 (367), 77·1 (184), 78·5 (277), 77·0 (162), 76·5 (278), 75·3 (815), 76·5 (345), 76·2 (354).

[*] Rutherford and Robinson, Phil. Mag. xxviii. p. 552 (1914).

The numbers in brackets denote the number of scattered particles counted in the experiment.

The weighted mean of these results is 77·4, while the atomic number of platinum is 78. The accuracy of the determination depends chiefly on the number of particles counted, for all other quantities are given by measurements of mass and length. If a number Z of α particles is counted, the error due to probability fluctuations is $\sqrt{Z}$, *i. e.* the relative error is $1/\sqrt{Z}$. Since about 3700 scattered particles were counted and roughly 8000 direct particles, the probable error in the ratio is about $2\frac{1}{2}$ per cent. As N is proportional to the square root of the ratio, the error in the value of the nuclear charge will be a little over 1 per cent.

Silver.—The foil had a weight of 4·50 mgm. per sq. cm., giving

$$nt = 2·50 \times 10^{19}$$

and the average

$$\frac{mu^2}{E} = 7·05 \times 10^{14}.$$

The following values of N were obtained :

46·0 (453), 41·0 (156), 44·0 (190), 44·0 (307), 45·9 (529),
46·5 (411), 49·1 (224), 46·6 (416), 49·1 (297).

The weighted mean is 46·3 and the total number of scattered particles is 3000, giving a probable error in N of $1\frac{1}{2}$ per cent.

The atomic number of silver is 47.

Copper.—The foil weighed 4·78 mgm. per sq. cm. Hence

$$nt = 4·64 \times 10^{19}$$

and the average

$$\frac{mu^2}{E} = 6·85 \times 10^{14}.$$

The following values were obtained for N :

27·8 (125), 29·0 (340), 29·6 (369), 27·6 (212), 29·6 (178),
29·6 (364), 30·0 (377), 28·2 (243), 30·4 (351), 29·6 (302).

The weighted mean is 29·3 and the total number of scattered particles 2900, giving a probable error in N of about $1\frac{1}{2}$ per cent.

The atomic number of copper is 29.

§ 5. *The Law of Force.*

In his theory of the single scattering of α particles Rutherford assumed that the law of force between the α particle and the nucleus was that of the inverse square. It has been pointed out by Darwin [*] that a direct test of the law of force is given by the dependence of scattering on the velocity of the α particle. If the force around the nucleus vary with the distance as $1/r^p$, then the number of scattered α particles, other conditions remaining constant, is proportional to $\left(\dfrac{1}{u^2}\right)^{\frac{2}{p-1}}$. The experiments of Geiger and Marsden showed that the number of scattered particles depended on the fourth power of the velocity to the nearest integral power. Combined with the observed law of angular distribution of the scattered particles, this leaves no doubt as to the general validity of the inverse square law. In view, however, of the accuracy attained in the measurement of the nucleus charge, in which the inverse square law is assumed, it was considered necessary to repeat this test in a stricter manner.

The same apparatus was used, but the mica sheet at O was removed and the ZnS screen waxed on in its place. This was necessary in order that short range α particles could reach the screen. By means of a ground-glass joint H mica sheets were brought in front of the source to cut down the velocity of the α particles incident on the scattering foil. The stopping powers of the mica sheets were measured by adjusting the pressure of air in the box until the direct pencil of α rays just failed to reach the screen. The velocity was calculated from the emergent range, using Geiger's relation $u^3 = a\mathrm{R}$. A slight correction of the measured ranges was necessary, since the α particles which hit the scattering foil travel through the mica at a small angle.

The scattering foil was platinum weighing 1·58 mgm. per sq. cm. The number n of scattered particles was counted for three velocities, about 1600 particles being counted for each.

The results are given in the table :

Mica sheet.	Relative u^4.	nu^4.
0	1	100
1	·549	101
2	·232	103

[*] Darwin, *loc. cit.*

The values of nu^4 are constant within the counting error of about 4 per cent.

Taking the nuclear charge of platinum as $78e$, the distance of approach of the high-velocity α particles was about 7×10^{-12} cm. and of the low-velocity particles about 14×10^{-12} cm.

We conclude, therefore, that in the region of 10^{-11} cm. from the platinum nucleus the force varies as $1/r^p$, where p lies between 1·97 and 2·03.

§ 6. *Summary.*

1. The charges of the nuclei of three atoms, viz. platinum, silver, and copper, have been measured by a direct method depending on the scattering of α particles. The values found are 77·4, 46·3, and 29·3 respectively in fundamental units of charge. The atomic numbers of these elements are 78, 47, and 29.

2. The law of force around the platinum nucleus has been tested by the dependence of scattering on the velocity of the α particle. The results show that the inverse square law holds accurately in the region concerned, viz. around 10^{-11} cm. from the nucleus.

§ 7. *Discussion of Results.*

The good agreement between the measured values of the nuclear charges and the atomic numbers of the elements deduced from the X-ray spectra affords strong confirmation of Moseley's generalization. Owing to the probability fluctuations, it is hardly possible to attain sufficient accuracy in the measurements to prove that the charge on the nucleus is a whole number times the electronic charge. At present this is only possible in one case—that of the helium nucleus or α particle. There can, however, be little doubt that the nuclear charge does really increase by unity as we pass from one element to the next, and that its net value is given by the atomic number.

The values of the nuclear charge combined with the dependence of scattering on the velocity of the α particle indicate that the inverse square law of force holds to a high degree of accuracy in the region investigated, 10^{-11} cm. from the nucleus of a heavy atom like platinum. The experiments of Geiger and Marsden on the angular distribution of α particles scattered by gold between 5° and 150° show that the same law must hold for distances between $3 \cdot 1 \times 10^{-12}$ cm. and 36×10^{-12} cm. from the nucleus.

Further, the agreement between the experimental measurements of the K-series spectra and the theoretical values of Debye and Kroo shows that the inverse square law still holds at the K ring. In the case of platinum the radius of the K ring is about 10^{-10} cm.

Thus, measured from any point in the region between 3×10^{-12} cm. and 10^{-10} cm. from the nucleus of a heavy atom like platinum, the charge is equal to the atomic number and the law of force is the inverse square. We may therefore conclude that no electrons are present in the region between the nucleus and the K ring.

I wish to thank Sir Ernest Rutherford for suggesting this work, and for his interest and advice throughout its progress.

LXXXV. *On the Electron Theory of the Metallic State.* *By* G. Borelius, *Ph.D.*[*]

§ 1. *Introduction.*

THE well-known theory, founded by Riecke and Drude, and worked out in its further consequences by Lorentz, Bohr, and others, assumes the conducting electrons to be freely moving among the atoms of a metal, and to have the same mean kinetic energy as gas molecules at the same temperature. These assumptions gave, as a first striking result, a deduction of the laws of Wiedemann and Franz and of Lorenz. However, other consequences of the theory cannot be said to agree very well with experimental facts. There is, for example, no probable ground for the characteristic dependence upon temperature found for the electric and thermal conductivities in pure metals ; without the addition of the most improbable assumptions, it gives a wrong idea of the magnitude of the thermoelectric phenomena ; the specific heats observed require the number of free electrons to be very small compared with the number of atoms, whereas optical phenomena require these numbers to be of the same order of magnitude ; in the Hall phenomenon it gives us directly only negative signs, though both signs are actually observed, and so forth.

All these facts have caused J. J. Thomson[†], W. Wien[‡],

[†] J. J. Thomson, 'Corpuscular Theory' (1907) ; Phil. Mag. vol. xxx. p. 192 (1915).

[‡] W. Wien, *Berl. Ber.* 1913, p. 184.

Stark *, Lindemann †, and others to propose separately very radical alterations in the fundamental assumptions of the electron theory of the metallic state. The present writer, too, has made an attempt in this direction. Last year I treated in three communications ‡ the thermoelectric phenomena, the thermal and electric conduction and the magnetic and galvanomagnetic phenomena from new fundamental assumptions. I here wish to give an abstract and a revision of these papers. Especially the work published during the past year by Madelung § and Born and Landé ||, on the electrostatic forces in the atomic space-lattices in connexion with some results of X-ray analysis of metals, makes it possible for me now to treat some of the phenomena in a more concise manner.

§ 2. *Number and Arrangement of the Conducting Electrons.*

We will, as a general assumption, suppose the metallic state to be to a certain extent comparable to the state of a halogen salt according to the modern space-lattice theory, the negative ions of the salt being replaced by electrons. The great dissimilarity in the behaviour of metals and salts is then chiefly due to the greater mobility of the electrons, caused by the diminutiveness of their mass compared with that of the ions. We thus, as will be seen in § 4 for a simple case, at once get an understanding of the way in which the statical equilibrium of the metallic space-lattice is built up by electric forces in full conformity with the theory of Born and Landé.

In the simplest case the metal would be of the type NaCl, a simple cubic lattice with alternating Na and Cl atoms. The figure of symmetry for one of the components must then be a "face-centred cube"—that is, an atom at each corner of a cube and one in the centre of each of its sides. And, indeed, this symmetry is found by the X-ray analysis ¶ for a great part of the examined metals belonging to the regular crystal system, namely,

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* I. Stark, *Jahr. d. Rad.* ix. p. 188 (1912).

† F. A. Lindemann, Phil. Mag. vol. **xxix.** p. 126 (1915).

‡ G. Borelius, *Ann. d. Phys.* lvii. pp. 231 & 278 (1918), and lviii. p. 489 (1919).

§ E. Madelung, *Phys. Zeitschr.* xix. p. 524 (1918).

|| M. Born and A. Landé, *Berl. Ber.* 1918, p. 1048 ; *Verh. d. deutsch. Phys. Ges.* xx. pp. 202 & 210 (1918).

¶ W. L. Bragg, Phil. Mag. vol. xxviii. p. 355 (1914) (Cu). L. Vegard Phil. Mag. vol. xxxi. p. 83 (1916) (Ag), and vol. xxxii. p. 65 (1916) (Au, Pb). P. Scherrer, *Phys. Zeitschr.* xix. p. 23 (1918) (Al). A. W. Hull, Phys. Rev. vol. **x.** p. 661 (1917) (Pb, Fe, Ni, Na, Li, Mg, and others).

Cu, Ag, Au, Al, Pb, and perhaps one form of Ni. On the other hand, the symmetry of the " centred cube" was found to exist in the case of Na, Fe, and Ni, and probably that of the " simple cube " with two atoms connected with each corner in the case of Li. Of the non-regular metals the only one examined as yet is Mg, which shows an hexagonal symmetry.

We will in the following confine our calculations to metals of the simple type NaCl only. Some of our results will therefore be valid only for metals of the type of the face-centred cube. Many of them, however, will most probably be approximately true for any good conductor.

For a metal of this simple type the number n of free electrons in the cubic centimetre must be equal to the number n' of atoms, so that

$$n = n' = \frac{N\rho}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

($N = 6 \cdot 06 \cdot 10^{22}$, number of Avogadro, ρ density,
A atomic weight).

Though it is not *à priori* probable that this relation will hold throughout for all metals, we will adopt it for our trials, and indeed we shall find as yet no reason to alter it ; some facts rather argue in favour of its general validity.

After the present paper was nearly finished, an investigation of Haber [*] came to my notice, where he treats the compressibility and the ultraviolet characteristic frequencies of the metals making use of similar assumptions. The last problem was, moreover, treated already in 1911 [†].

§ 3. *Optical Phenomena.*

As was first shown by Drude [‡], the refraction and absorption of light in a metal enable us to calculate approximately the number of free electrons in it. Schuster [§] and later on, in another way, Drude [||] have calculated the ratio $\frac{n}{n'}$ for a number of metals from their optical properties. As a result of these investigations, it was found that this ratio is for all good conductors of the

[*] F. Haber, *Berl. Ber.* 1919, p. 506.
[†] *Verh. d. Deutsch. Phys. Ges.* xiii. p. 1128 (1911).
[‡] P. Drude, *Phys. Zeitschr.* i. p. 161 (1900).
[§] A. Schuster, Phil. Mag. vol. vii. p. 151 (1904).
[||] P. Drude, *Ann. d. Phys.* xiv. pp. 725 & 936 (1904).

order unity, or perhaps two or three times greater than unity. We can regard this fact as a further support for our theory. As is well known, it is a rather great difficulty for the classical electron theory.

§ 4. *Potential Energy of the Metallic Space-lattice.*

In full analogy with the theory of Born and Landé, the work done in bringing an electron or an atom from infinity to their place in the lattice is $-\epsilon\phi_e$ or $+\epsilon\phi_a$, where the potential functions ϕ_e and ϕ_a due to the surrounding electrons and atoms are given by

$$\phi_e = \frac{a}{R} - \frac{b}{R^\mu}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2')$$

$$\phi_a = -\frac{a}{R} + \frac{b}{R^\mu} - \frac{b'}{R^\mu}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2'')$$

where R denotes the distance between an electron and its nearest atomic neighbour, so that for a metal of the type NaCl

$$R = \sqrt[3]{\frac{A}{2N\rho}} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

The terms $\frac{a}{R}$ arise from the forces between electrons and atoms regarded as point charges. The terms $\frac{b}{R^\mu}$ arise from the repelling forces on an electron from the nearest atom-ions or on an atom from the nearest electrons, due to the arrangement of a number of electrons around and at an appreciable distance from a positive nucleus in the atom. The term $-\frac{b'}{R^\mu}$ arises from the attracting forces on the positive charge of the atom-ions caused by the mentioned arrangement of the electrons in the nearest atoms, and *vice versâ*. For ϕ_e there is, of course, no term corresponding to this. A term arising from the repelling forces between the neutral parts of the atoms is to be neglected, if the atoms' dimensions are sufficiently smaller than their distances.

The constant a may be calculated by a method of Madelung, and is for a lattice of the simple type NaCl, which we have adopted for our trial,

$$a = 1.742\,\epsilon. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The constants b and b' are deduced from the condition

for a stable state and the geometrical properties of the lattice. The condition is

$$\Sigma \epsilon (\phi_e - \phi_a) = \text{min.} \quad \text{or} \quad \frac{d}{dR}(\phi_e - \phi_a) = 0, \quad . \quad . \quad (5)$$

which gives, in combination with (2′) and (2″),

$$2b - b' = \frac{2aR^{\mu-1}}{\mu}. \quad . \quad . \quad . \quad . \quad (6)$$

The geometrical properties give approximately

$$b' : b = \frac{2 \times 12}{H(R\sqrt{2})^{\mu}} : \frac{6}{HR^{\mu}} = 2^{2-\frac{\mu}{2}}. \quad . \quad . \quad (7)$$

For different symmetries of the outer electrons in the atom, μ takes different values : 5, 9, or more. This will be discussed further in the next paragraph.

§ 5. *Compressibility.*

Born and Landé, from their space-lattice theory, found the compressibility at the absolute zero-point for salts of the type NaCl to be given by

$$\kappa = \frac{9}{8 \cdot 1 \cdot 742 \, \epsilon^2 (\mu-1)} \left(4 \frac{A_+ + A_-}{N\rho} \right)^{\frac{4}{3}},$$

where A_+ and A_- are the atomic weights of the ions. With $\mu = 9$ they find good agreement with experimental results. As the atom model of Bohr would lead to $\mu = 5$, they propose a cubic symmetry of the outer electrons in the atom that would, at least under certain conditions, give $\mu = 9$. Our fundamental equations lead, in the way shown by Born and Landé, to the same value for μ. Neglecting the weight of the electrons besides that of the atoms, we may write

$$\kappa = \frac{18}{1 \cdot 742 \, \epsilon^2} \frac{R^4}{\mu-1}. \quad . \quad . \quad . \quad . \quad (8)$$

From this equation I have calculated μ for the metals that are known from X-ray analysis to have a symmetry consistent with our premises, using values for κ and ρ [*] holding for ordinary temperatures, and have found

Cu	....	7
Ag	....	8·5
Au	....	12
Al	....	6·5
Pb	....	7·5
Ni	....	(8)

* Tables of Landolt-Börnstein-Roth.

With values for κ and ρ valid for the absolute zero-point, the values for μ would have been greater by about 1 and their mean thus equal to 9—a value that we will use in our further calculations. As the calculations of Born and Landé applied to the metallic space-lattice would give $\mu = 5$ also for a cubical symmetry, the derivation of $\mu = 9$ from the experiments seems, if our theory holds, to indicate another symmetry as more probable than that of the cube.

Haber has calculated μ in the same way also for the alkaline metals and found here much smaller values, between 2·4 and 3·5. As, however, he assumes the alkaline metals to have the same structure as their halogen salts, which is, at least for Na and Li, not consistent with the results found by Hull by the X-ray analysis, these low values are not as yet in any way definite.

§ 6. *Motions and Kinetic Energy of the Electrons at High Temperature.*

To get an understanding of the electric conduction, we must discuss the motions of the electrons in relation to the atom space-lattice—a phenomenon that has hitherto been left unconsidered. It follows from our general assumptions that this motion must be intimately connected with the motions of the atoms. To see this, we may for a moment consider what would be the case if the atoms were at rest. From the equations of § 4 it is easily seen that the energy required to overcome the hindering forces from the atoms passed by, when an electron is displaced from one point of equilibrium to another, even though all neighbouring electrons were supported in the same way, so that no forces from them were to be added, would be more than a hundred times greater than the energy of a gas molecule at ordinary temperatures. The electrons thus would not go very far away from their equilibrium positions.

In the same way, the thermal oscillations of the atoms cannot have any great amplitudes without a similar motion of the electrons. Now the atomic amplitudes are thought to be considerable, and are, in the neighbourhood of the melting-point, of the same order of magnitude as the atomic distances, so that the atoms' mean velocity is of the order $2\nu\delta$, if ν is the frequency and δ the atomic distance. The velocities of the electrons will then be of the same order. But as the electrons are much smaller and lighter than the atoms, it seems probable that there will be an irregular transport of electrons, so that the electrons' space-lattice

will be in a " fluid " state far below the melting-point of the metal.

As an electron cannot escape from between the atoms without a way being opened for it by the elastic waves of thermal agitation, and as the greatest velocities for these waves are, by the theory of Born and von Kàrmàn *, $2\nu\delta$, we may as a limit for high temperatures write the transport velocity

$$v = p \cdot 2\nu\delta, \quad \ldots \quad \ldots \quad (9)$$

where p is a constant of the order one.

The kinetic energy of the electrons must be intimately connected with the transport velocity v. It will probably not tend to a limit in the same way, but increase proportionally to the heat content of the metal, which is at high temperatures proportional to the absolute temperature. The correspondence of the kinetic energy with $\frac{mv^2}{2}$ will probably be best in the neighbourhood of the characteristic temperature θ ($=\beta\nu$, $\beta=4\cdot87\cdot10^{-11}$), where the thermal oscillations become appreciable. We are therefore led to write the two-thirds (u) of the kinetic energy corresponding to the two degrees of freedom of the motions on the (variable) equipotential surfaces as

$$u = q \cdot \frac{m}{2}(2\nu\delta)^2 \cdot \frac{T}{\theta}, \quad \ldots \quad \ldots \quad (10)$$

where the constants q have to be at least approximately of order one.

The part of the electrons' kinetic energy that exceeds $\frac{mv^2}{2}$ must, as is seen from the foregoing, give rise to oscillations with amplitudes smaller than δ. We have shown that it is probable that this surplus is at least comparable with $\frac{mv^2}{2}$, which is only about a hundredth or thousandth of the kinetic energy of a molecule at ordinary temperatures. It is perhaps worth while giving a further reason for this disproportion between the energy of oscillation of the electrons and atoms. If their kinetic energies were alike, the electron, which is many thousand times lighter than the atom, would have velocities that were a hundred times greater. Now as the amplitudes must be of the same order of magnitude, or about δ, the frequency of the electron would be about a hundred times greater than

* M. Born and v. Kàrmàn, *Phys. Zeitschr.* xiii. p. 297 (1912).

that of the atom. But according to the quantum theory such great frequencies rarely occur at ordinary temperatures, so that the supposition of equipartition of energy would lead to discrepancy with the quantum theory.

As the theory of Born and von Kàrmàn, which we have made use of, is deduced for a simple cubic space-lattice, it is not fully clear what is meant by δ. We will, however, for our approximate calculation simply put it equal to the smallest atomic distance, or $R\sqrt{2}$.

§ 7. *Electric Conduction at High Temperatures.*

The first effect of an electric field of force in the metal will be a displacement of the free electrons in a direction opposite the electric force; and this polarization in connexion with the thermal motions of the electrons will call forth the electric current. To calculate the polarization, we may in any definite way connect every electron with one of its neighbouring atoms and inversely every atom with one electron. The state of the cubic centimetre of the metal will be equivalent to n dipoles of a mean moment nearly equal to ϵR. The motions of the electrons will be equivalent to a rotation of these dipoles with an energy of rotation equal to the kinetic energy (u) of the electrons in the equipotential surfaces, corresponding to two degrees of freedom.

It is, moreover, possible that this way of description of the state of a metal will have not only a mathematical but also a physical meaning. In the statical state, dealt with in § 4, the electrons are, because of the third term in (2″), always repelled by the neighbouring atoms. But where the atoms, by their oscillations, are removed from each other, the electrons will be attracted to them; and as the electrons will seek out such places, a great number of them at least will move under the influence of a resulting attracting force from one of the neighbouring atoms.

The polarization as a function of the electric force X can be calculated in conformity with the theory of magnetism given by Langevin [*], and is found to be

$$P = P_m \frac{\epsilon R X}{3u}, \quad \cdots \quad (11)$$

where $P_m = n\epsilon R$ is the maximal moment conceivable as due to polarization, and u is given by (10). To the maximal

* P. Langevin, *Journ. de Phys.* iv. p. 678 (1905).

polarization would correspond a maximal current density,

$$i_m = n\epsilon v, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

if all the electrons travelled in a direction opposite the electric force. If now the current density i is throughout proportional to P, we must have

$$\frac{i}{i_m} = \frac{P}{P_m}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Inserting (11) and (12) in (13), and as $v = 2\nu\delta = \nu R \sqrt{8}$, we get for the specific conductivity at high temperatures,

$$\kappa = \frac{i}{X} = p \cdot \frac{\epsilon^2 \sqrt{8}}{3} \cdot \frac{n\nu R^2}{u}, \quad . \quad . \quad . \quad . \quad (14)$$

and because of (10)

$$\kappa = \frac{p}{q} \cdot \frac{\epsilon^2}{3\sqrt{2m}} \cdot \frac{n}{\nu} \cdot \frac{\theta}{T}. \quad . \quad . \quad . \quad . \quad (14')$$

We thus get the conductivity inversely proportional to the absolute temperature, in good agreement with experimental results. Further, if our premises are valid, the constants $\frac{q}{p}$, which can be calculated from (15), must be of order one. The values in the following table are simply calculated from the conductivities at $0°$ C., though that temperature cannot, for all metals, be looked upon as a rather high one. We see that the predictions of our theory are fulfilled very precisely for the best conductors in the first group of the periodic system. $\frac{q}{p}$ is here nearly equal to one. Passing to the right side of the system, this constant becomes gradually greater up to about ten for the metals in group VIII. :—

I.	II.	III.	IV.	V.	VIII.
Na 1·5	Mg 2·2	Al 1·9	Sn 3·6	(Sb 15)	Fe 7·0
K 1·1	Zn 4·5		Pb 7·8	(Bi 38)	Cu 9·7
Cu 1·6	Cd 3·8				Rh 4·8
Ag 1·1					Ir 4·2
Au 1·5					Ni 7·5
					Pd 8·2
					Pt 8·1

§ 8. *Thermal Conduction.*

Thermal conduction in non-metallic solids is generally thought to-day to be due to elastic thermal waves. The classical electron theory interprets the quantitatively superior metallic conductivity also in a qualitatively different manner, as due to an hypothetical electron gas. We are now forced to give up this standpoint, as neither the kinetic energy of the electrons nor their free paths are great enough to explain the great conductivity of the metals. We therefore are led to try if the conduction cannot in the metals as in all other solids be referred to the elastic waves ; and, indeed, we shall in this way find reasons enough for the superiority of the conductivity of the metals in their peculiar structure. In a salt of the type NaCl, for example, the lattices of positive and negative ions, as is known from the residual rays, have different characteristic frequencies and thus transport different elastic waves. Now as the two lattices have like energy, there will, at high temperatures, be a lively exchange of energy between them, so that the distance within which the intensity of the wave diminishes to an infinitely small part of its original value, will be but few atom distances, which is also in good agreement with the experimental values for the conductivity. In a metal, on the other hand, the energy of the electron space-lattice is relatively very small, so that the waves in the atom-lattice will be very little damped, and thus give a great conductivity.

For a quantitative discussion we start with a general formula * for the conductivity λ, called forth by damped elastic waves :

$$\lambda = \tfrac{1}{4}\rho cw\mathrm{L}, \quad \ldots \ldots \ldots \quad (16)$$

where ρ is the density, c the specific heat, w the velocity of the waves, and L their mean range, defined by the decrease $d\mathrm{K}$ of the intensity K over the distance $d\mathrm{S}$ by the equation

$$\frac{d\mathrm{K}}{\mathrm{K}} = \frac{d\mathrm{S}}{\mathrm{L}}. \quad \ldots \ldots \ldots \quad (16')$$

We may, for high temperatures, transform this expression for λ in the following manner. ρc is the specific heat for the unit of volume, and as a molecule in a solid has the

* P. Debye, 'Vorträge über d. kinet. Theorie,' Göttingen, 1914, p. 50.

double energy of that in a gas we can write

$$\rho c = 2\alpha n', \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$\alpha = 2 \cdot 06 \cdot 10^{-10}$ being the gas constant for a single molecule.

As is shown by Born and von Kàrmàn, most of the energy in a space-lattice is transported with velocities nearly equal to the maximal velocity $2\nu_m\delta$; so that we have approximately

$$w = 2\nu\delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

ν being as before a mean frequency nearly equal to the maximal one ν_m.

The mean range L may be calculated from (16') as follows. Every time a wave, embracing a number of atoms, advances a distance $dS = \delta$, this wave gets into an energy exchange with a like number of electrons. Now this exchange must be effected in such a way that the ratio of mean energies of the electrons ($3u$ corresponding to equipartition of energy in three kinetical and three potential degrees of freedom) and the atoms ($2\alpha T$) is kept unaltered. The mathematically simplest way in which this can be done is to assume that the mean relative loss of energy of the wave $\dfrac{dK}{K}$ is every time in this ratio. As the electrons are not able to transport the energy a long distance, the energy given off to them is lost for the regular transporting waves. We thus get

$$\frac{dK}{K} = \frac{3u}{2\alpha T} = \frac{\delta}{L},$$

and from the last equation

$$L = \frac{2\alpha T}{3u} \cdot \delta. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Inserting (17), (18), and (19) in (16), we get the heat conductivity for high temperatures,

$$\lambda = \frac{1}{p} \cdot \frac{4\alpha^2 T}{3} \cdot \frac{N\nu R^2}{u}. \quad . \quad . \quad . \quad (20)$$

As u is proportional to T, and all other quantities are constant, we find λ constant for high temperatures, in good agreement with experimental facts. The calculated value of λ is also of the right order of magnitude. We need not, however, show this separately, as the electric conduction is already discussed, and the ratio of conductivities will be the subject of the next paragraph.

§ 9. *Ratio of Conductivities.*

From equations (14) and (20) we get, as $u = N$,

$$\frac{\lambda}{\kappa} = \frac{1}{p} \cdot \frac{\sqrt{2}\alpha^2}{\epsilon^2} \cdot T. \quad . \quad . \quad . \quad . \quad (21)$$

The ratio of conductivities is thus found to be nearly constant for all pure metals (law of Wiedemann and Franz) and proportional to the absolute temperature (law of Lorenz). Also the numerical value of the constant is in good agreement with experimental facts. We find for $18°$ C.

$$\frac{\lambda}{\kappa} = \frac{1}{p} \cdot 6 \cdot 9 \cdot 10^{10} \text{ e.m.u.}$$

The measurements of Jaeger and Diesselhorst[*] gave, as a mean for eleven metals,

$$\frac{\lambda}{\kappa} = 7 \cdot 1 \cdot 10^{10} \text{ e.m.u.}$$

The agreement is good if p is, as was predicted, nearly equal to one.

§ 10. *Thermoelectric Phenomena.*

In the classical theory the thermoelectric phenomena are referred to the variations of the energy of motion of the electrons and the variations of their number with varying temperature. We have assumed this number to be constant in good conductors and thus without influence on their thermoelectric properties. But our theory gives three other origins for contributions to a specific heat of electricity or the Thomson effect σ, from which the other thermoelectric phenomena, thermoelectric power e_{ab} and Peltier coefficient Π_{ab}, of a couple of metals a and b are determined. By Thomson's thermodynamic equations,

$$e_{ab} = \frac{\Pi_{ab}}{T} = \int_0^T \frac{\sigma_a - \sigma_b}{T} dT,$$

in which, however, the lower limit of the integral is first fixed by the theorem of Nernst or the quantum theory. The three origins are :—1st, the variations with the temperature of the kinetic energy of the electrons ; 2nd, the variations of their potential energy by heating at constant volume ; 3rd, the variations of their potential energy due to

[*] W. Jaeger and H. Diesselhorst, *Abh. Phys. Techn. Reichens'alt*, iii. p. 269 (1900).

thermal dilatation. We will discuss them separately in the
three following sections.

1. The part of σ, we may call it σ_1, due to the kinetic
energy of the electrons is

$$\sigma_1 = -\frac{1}{\epsilon}\frac{d}{dt}\left(\frac{3u}{2}\right), \quad . \quad . \quad . \quad . \quad . \quad (22)$$

when u is got from (10). It is for many metals but a few
tenths of a microvolt per degree, for none of them greater
than two microvolts ; and it is but a small part of the
observed Thomson effects.

2. Of the atomic heat c_v at constant volume, one half
is thought to increase the kinetic, the other half the
potential energy. If this increase of the potential energy
were equally distributed to atoms and electrons, we should
get the corresponding part of the Thomson heat to be

$$\sigma_2 = -\frac{c}{4N\epsilon} = -43\,\frac{c_v}{c_{v\,\infty}}\,\frac{\text{microvolt}}{\text{degree}}.$$

However, such an equipartition of potential energy is not at
all probable, for the light moving electrons will be better
able than the atoms to avoid places where this potential is
increased. σ_2 is therefore probably but a little part (z) of
the value above, and we may put

$$\sigma_2 = -z\,.\,43\,\frac{c_v}{c_{v\,\infty}}\,\frac{\text{microvolt}}{\text{degree}}. \quad . \quad . \quad . \quad (23)$$

The calculation of z will not be possible without an intimate
knowledge about the external structure of the atoms.

3. From the equations of § 4 we can calculate the
variations σ_3 of the mean potential $\frac{1}{2}\phi_e$ of the electrons
due to the thermal dilatation. It is

$$\sigma_3 = -\frac{1}{2}\frac{d\phi_e}{dR}\frac{dR}{dt}. \quad . \quad . \quad . \quad . \quad (24)$$

The multipler 1/2 appears because, by summing up all
the ϕ_e, every electron is counted twice. From equations
(2) and (5) we find

$$\frac{d\phi_e}{dR} = \frac{\mu b'}{2R^{\mu+1}},$$

which for $\mu = 9$ according to (4), (6), and (7) gives

$$\frac{d\phi_c}{dR} = -\frac{0 \cdot 177 \cdot 1 \cdot 742 \, \epsilon}{2R^2}.$$

As further $\dfrac{1}{R}\dfrac{dR}{dT}$ is the linear coefficient η of dilatation, we have

$$\sigma_3 = +\frac{0 \cdot 177 \cdot 1 \cdot 742 \, \epsilon}{4} \cdot \frac{\eta}{R} = +11 \cdot 0 \frac{\eta'}{R'} \, \frac{\text{microvolt}}{\text{degree}}, \quad (24')$$

where $\eta' = \eta \cdot 10^5$ and $R' = R \cdot 10^8$ are both of order one.

We may at least for high temperatures sum up our results as to the Thomson heat in the formula

$$\sigma = A\eta - Bc_v, \quad \ldots \quad \ldots \quad (25)$$

where the second term is a sum of σ_1 and σ_2. A and B are positive constants. This formula was deduced in an earlier paper from somewhat less definite assumptions, and was also shown to be well consistent with the unfortunately rather few experimental facts that are known to-day about thermoelectric phenomena at low temperatures.

For metals with $\mu = 9$ we have

$$\sigma = 11 \frac{\eta'}{R'} - Bc_v \, \frac{\text{microvolt}}{\text{degree}}. \quad \ldots \quad (25')$$

To show the possibility of this equation, I have in fig. 1 plotted the Thomson coefficients of a number of heavy metals against the ratio $\dfrac{\eta'}{R'}$. The line in the figure corresponds to $\sigma = 11 \dfrac{\eta'}{R'}$. The experimental values are all under this line, and there also seems to be a certain orientation of them in this direction. Certainly the structure of the metals is known to be consistent with our premises only by Cu, Ag, Au, Al, Pb, and perhaps Ni; but the other metals are given because their compressibilities by means of equation (8) give values for μ of the same order as those of the named metals, so that it seems probable that our calculations are approximately valid for them. The alkaline metals, on the other hand, are excluded. The values for σ refer to temperatures greater than θ. They are taken from measurements of σ or of the thermoelectric power against Pb,

and are often very uncertain. As, however, this uncertainty is of very little importance in our figure, there is no need to give an account of authorities or way of calculation.

Fig. 1.
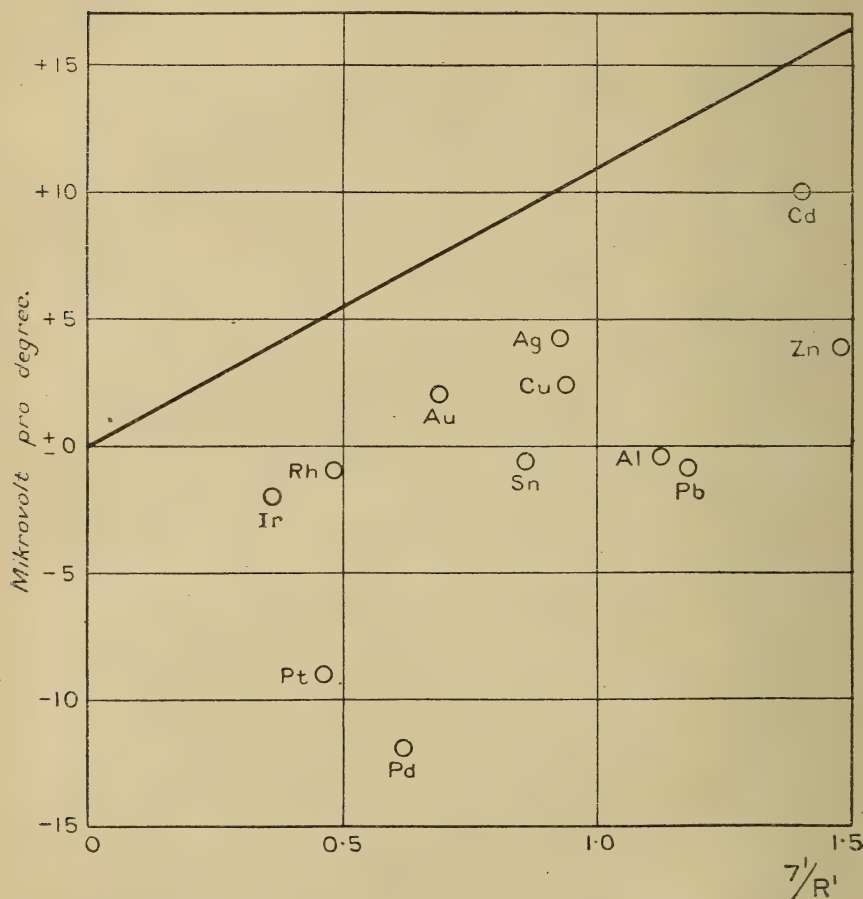
§ 11. *Specific Heat.*

From (14) we are able to calculate the mean kinetic energy $\frac{3u}{2}$ of the electrons and its contributions c' to the atom-heat. We find for high temperatures

$$c' = N\frac{d}{dt}\frac{3u}{2} = p \cdot N\epsilon^2\sqrt{2} \cdot nv R^2 \frac{dr}{dt},$$

where $r = \dfrac{1}{\kappa}$ is the specific resistance. Putting $p = 1$, and as $n = \dfrac{N\rho}{A}$ we get

$$c' = N^2 \epsilon^2 \sqrt{2} \frac{\rho\nu R^2}{A} \frac{dr}{dt} \frac{\text{erg}}{\text{degree}} \quad . \quad . \quad . \quad (26)$$

Inserting numerical values, we find in two extreme cases for Ag $c' = 0.004$, and for Bi $c' = 0.09$ calorie per degree. As the atom-heat is for high temperatures almost equal to 6 calories per degree, we see that the electrons give but an imperceptible contribution to it, which is in good agreement with the modern theory of specific heat and experimental facts.

§ 12. *Emission of Electrons from Hot Metals.*

Measurements on the density i of the electric current from the surfaces of hot metals are satisfied by

$$i = AT^\lambda e^{-\frac{b}{T}},$$

where A, λ, and b are constants. The constancy of b is well established. It is for some metals known with an uncertainty of a few tenths per cent. A has a similar uncertainty already in its logarithm. About λ we only know that it cannot be much greater than one.

On the presumption that the kinetic energy of the electrons is proportional to T, and that Maxwell's law of distribution holds, this expression is deduced theoretically, whereby λ is found to be one-half. $\dfrac{b}{T}$ is then interpreted as the ratio of the work necessary to remove an electron from the metal to two-thirds of the mean kinetic energy of the electrons. Assuming the electron energy to be equivalent to that of a gas molecule at the same temperature, and the work done when an electron is removed to be of the order of magnitude of $\dfrac{\epsilon^2}{R}$, the classical theory comes into good agreement with the experimental values for b.

We can try to calculate i in a similar way from the point of view of our theory. If the electrons are supposed to be emitted from the interior of the hot metal, we should have $\dfrac{b}{T} = \dfrac{\epsilon\phi_e}{2u}$, where ϕ_e is calculated from (2), (4), and (5) to be $1.742 \dfrac{\mu - 1}{\mu} \dfrac{\epsilon}{R}$, and u is given by (10) or (14). In this way

we should, however, since u is very small, get values for b that would be about a thousand times greater than the values known from experiment. This difficulty for our theory will, however, disappear if we assume the electrons to be emitted from the outermost layer of electrons—an assumption that is indeed well supported by the great dependance of the emission phenomenon upon small impurities of the surface. For these surface electrons, our reason from § 6 for assuming the kinetic energy of the electrons to be very little does not hold. Indeed, there will be more free impacts here with the outer atoms; so that the kinetic energy of the electrons will probably be of the same order of magnitude as for the atoms themselves.

§ 13. *Magnetic and Galvanomagnetic Phenomena.*

I shall not here treat these phenomena in detail, but will only refer to the results of my earlier investigation on this subject. The motion of the free electrons, as we have imagined it, will give rise to paramagnetic and diamagnetic phenomena with susceptibilities within the limits

$$-\frac{1}{6} \cdot \frac{\epsilon^2 N}{m} \cdot \frac{\rho R^2}{A} < k < +\frac{1}{12} \cdot \frac{\epsilon^2 N}{m} \cdot \frac{\rho R^2}{A}, \quad . \quad (27)$$

which for high temperatures must take approximately constant values. This is in good agreement with the observed magnetic properties for the metals situated in the left groups of the periodic system. The bad conductors Sb and Bi in the 5th group make an exception with great diamagnetic effects, and the ferromagnetic metals in the 8th group, at temperatures where they are not ferromagnetic, as well as their neighbours in the system have very great paramagnetic susceptibilities, which are, like the ferromagnetic phenomena, probably to be referred to the influence of the magnetic field of force on the inner electron rings in the atom.

Also the positive and negative Hall effects and their order of magnitude are, in a similar manner, deduced from our general assumptions.

§ 14. *Concluding Remarks.*

In our investigation the phenomena of thermal and electric conduction at low and very low temperatures are as yet left aside. The reason is that the treatment of these

phenomena would necessitate the theory to take into consideration the quanta conditions for the energy exchange between atoms and conducting electrons, which seems to be a rather difficult task. However, there are good possibilities for a qualitative understanding of these phenomena. Thus, for example, as we have assumed the electron lattice to be ordinarily in a "fluid" state, we have a very promising chance to interpret the transition of a metal into a supraconductor at very low temperatures as the solidifying of the electron lattice, the critical temperature being its melting-point. We thus should adopt for the supraconducting state the ideas used by Lindemann for the interpretation of conduction generally.

Lund, November 1919.

LXXXVI. *An Electrical Method for the Measurement of Recoil Radiations.* By A. L. McAulay, *B.Sc.*[*]

General.

IN the course of a research made with the object of investigating soft X radiation produced by the impact of α rays upon metal targets, it was found that there was an easily detectable increase in ionization in a chamber beyond the range of the α particles when they were fired through hydrogen instead of through air. Various tests made to determine the nature of this effect showed that it was due to a stream of hydrogen atoms set in swift motion by collisions with α particles. Sir Ernest Rutherford has investigated this radiation by the scintillation method (Phil. Mag. June 1919), but it was supposed that it would not be measurable by an electrical method, owing to its smallness, and to the large γ ray ionization necessarily present near the radioactive sources used. The above results, however, seemed to indicate that by making use of a balance method such recoil radiations might be satisfactorily investigated by the ionization they produce. An electrical method has many advantages over one based on counting scintillations. It does not involve the dark room and eye-strain inseparable from the latter, and owing to the large number of particles effective in one observation, probability variations are negligible, and a smaller number of determinations are necessary to fix a magnitude with accuracy.

[*] Communicated by Prof. Sir E. Rutherford, F.R.S.

A research was consequently undertaken with the following objects :—

(1) To develop an electrical method for the measurement of such recoil radiations produced by α rays, so far exclusively investigated by the scintillation method.

(2) To check by ionization measurements the results given by Sir Ernest Rutherford in the paper above referred to, which show that in close collisions between an α particle and a hydrogen atom, the nuclei no longer behave like point charges.

(3) To see whether any difference could be observed between the curve obtained by ionization showing the absorption of the radiation in aluminium, and that given by the scintillation method, due, for instance, to change in ionizing power with velocity of the hydrogen particle.

Description of apparatus.

Three forms of apparatus, all on the same principle, were used in succession. Only the last will be described. It consists of two main parts : the first, figure 1, is a brass

Fig. 1.
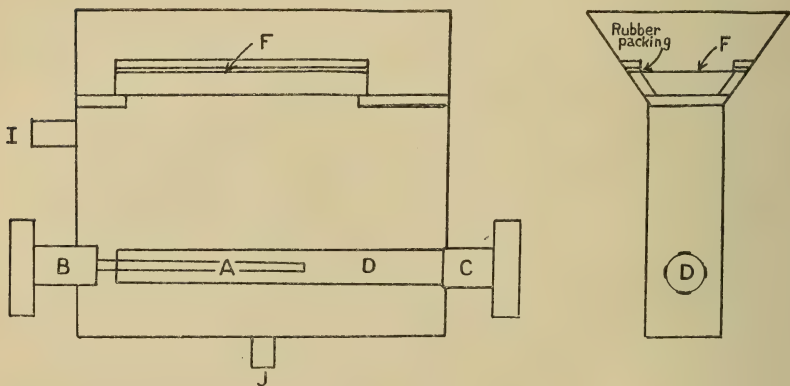
box, 8 cm. long by 2 wide by 6 deep, in which the hydrogen recoil atoms are produced. The source of rays, A generally a brass cylinder about 3 cm. long, coated with active deposit from radium, is carried on a vulcanite plug B, fitting a tube in one end of the box. In the other end, exactly opposite, fits another plug, C, carrying a hollow brass cylinder, D, in which are cut slots with aluminium screens waxed on them for intercepting the α rays. Two slots were

used, one open, and the other covered by an aluminium screen of stopping power equivalent to about 5 cm. of air. The effect is investigated by measuring the difference in ionization produced in an ionization chamber placed above the aluminium window F, when first one of these slots faces F and then the other. Hydrogen from a Kipp generator is passed through the box, by way of the side tubes I & J, throughout the experiments.

Fig. 2.
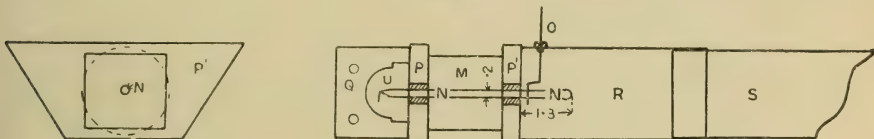
The second part of the apparatus (fig. 2), which measures the recoil radiation produced in the box, consists of electroscope, Q, ionization chamber, M, and a compensating ionization chamber, R, used to balance the current through M. P and P′ are two vulcanite slabs shaped to fit in the V of the brass box. They support the electroscope and two ionization chambers and insulate each from the others. M and part of R are over the window F. The compensating chamber, R, is merely a cylinder of thin brass (183 mgs. per sq. cm. thick) in which slides a piston, S, also of brass, so that the volume of R in which ionization is effective may be adjusted. The ionization chamber at M is a small aluminium box made of sheet aluminium soldered into a 2 cm. cube of 6·24 mgs. per square cm. thickness. The electrode N carrying the electroscope leaf passes from the electroscope through the ionization chamber into R, being supported by sulphur insulation in P and P′. The dimensions of the electrode shown in the figure were arrived at as giving a compromise between complete saturation in the ionization chamber and a low capacity. The electroscope is somewhat similar to one designed by Trepathi, working at the Cavendish Laboratory under Mr. C. T. R. Wilson. It is, however, a much rougher and less sensitive instrument. It is made of a brass plate about 2 mm. thick, in which is cut a semicircular hole, U, 1·3 cm. in diameter. The sides are of thin lead clamped by brass plates of the same shape as the main plate forming the body of the electroscope, bolts passing right through from one side to the other. The leaf is about 3 mm. long and is observed through mica windows, 3 mm. × 1 mm. by a microscope magnifying about 80 diameters.

The potentials on the various parts are as follows :—
The sides of the compensating chamber are charged to
−120 volts, the aluminium ionization chamber to +40, the
leaf through the charger, O (fig. 2), and the electrode to −40,
and the case of the electroscope is connected to earth. When
in use the whole apparatus is of course flooded with γ ray
ionization from the source, and the current which this
carries in the compensating chamber gives the leaf a higher
negative charge, while the current in the ionization chamber
tends to discharge it. The volume of the former can be
adjusted to give any strength of current, and thus any rate
of movement to the leaf.

The principal objects in view in the design were :—

(i.) To keep the capacity as low as possible while
ensuring approximate saturation.

(ii.) To use an ionization chamber as small as possible.
This is necessary to give definiteness to the absorption
curve. Dimensions at right angles to the radiation must be
small in order that hydrogens driven in the direction of the
α particles shall not enter the chamber too obliquely, and
dimensions parallel to the radiation must be small in order
that the depth of air in the chamber shall not represent more
than a small part of the absorbing material necessary to
bring the hydrogen particles to rest. A lower limit is set
to the size of the ionization chamber by the necessity of a
measurable ionization.

(iii.) To make the volume of the electroscope as small as
possible. This is important because the ionization due to
the recoil radiation must be as large as possible compared
with that due to γ rays, in order to reduce fluctuations, and
while the former is only produced in the ionization chamber,
the latter is produced in the electroscope as well.

Method.

The method employed is briefly as follows :—The brass
box is placed between the poles of a powerful electro-
magnet which prevents β rays from the source entering the
ionization chamber. The α rays are alternately cut off and
allowed to fall on the hydrogen by rotating the cylinder, D.
In the latter case, though the α particles are absorbed in the
window, F, the recoil atoms penetrate it and enter the
ionization chamber, causing a slight increase in the ionization.
The walls of the compensating chamber, being certainly
equivalent to more than 50 cm. of air absorption, are not
penetrated. With the α particles cut off, the volume of the

balancing chamber is adjusted till the leaf is almost stationary.
A reading of its rise or fall is taken, the α particles are
allowed to impinge on the hydrogen, and another reading
taken. The difference between the ionizations gives a
measure of the radiation. Readings such as these are taken
with different thicknesses of absorbing material, generally
aluminium, between the window and the bottom of the
ionization chamber.

The maximum ionization due to the recoil atoms was,
in the different arrangements used, from 2 per cent. to
10 per cent. of the total.

Tests made to establish the nature of the radiation.

Experiments were made with a gap between the box in
which the recoil particles were produced and the ionization
chamber. This gap was in an intense magnetic field,
which when varied produced no corresponding change in the
ionization. It cannot therefore be a β radiation. The form
of the absorption curves shows that it is not of γ or X ray
type.

The following experiments were made to show that it is
not a primary radiation from the source.

Source.	Screen A.	Hydrogen.	Screen B.	Ionization chamber.

Screen A is between the source and the hydrogen.
Screen B between hydrogen and ionization chamber. If
the radiation arose at the source, though a change in $A + B$
would affect the ionization in the chamber, it would be
immaterial how the total thickness of absorbers was dis-
tributed between A and B. It was found that the effect was
reduced to less than $1/5$ when A was changed from 3 cm.
air equivalent to 6 cm. air equivalent, instead of from 0 cm.
to 3 cm., although in both cases $A + B$ had changed from
6 cm. to 9 cm.

Results.

The following are the tabulated results of the absorption
experiments, plotted in curves I. and II.

Table A. This table gives the results from two typical
absorption experiments made with an a-ray tube as source.
α rays of ranges from about 5 cm. in air to zero were

incident on the hydrogen. The values are plotted as crosses on curve I.

Absorption in path of rays (between source and ionization chamber) given in equivalent cms. of air.	Ionization in arbitrary units.	Absorption in path of rays.	Ionization.
13·1	·53	9·3 cm. of air.	1
14·4	·39	10·6	·75
15·8	·23	13·1	·53
16·9	0	14·4	·41
		16·9	·11
		18·2	·08

Table B. This table gives the result of one experiment made with a later and improved form of apparatus. An *a*-ray tube was used as source, and the ranges of the

Absorption in path of rays.	Ionization.
8·7 cms. of air.	1
12·6	·48
14·4	·36
18·3	·11
20·1	·02

Curve I.
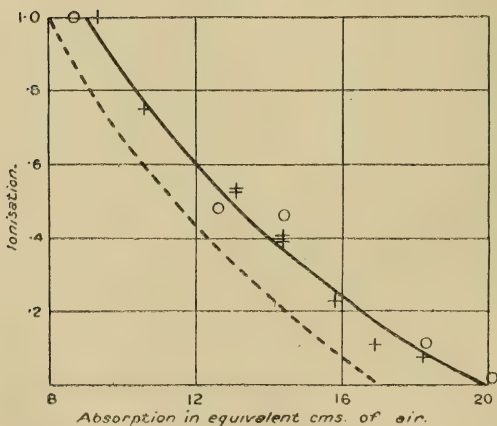
Curve I.

emerging particles were from about 5 cm. to zero as in the experiments from which table A is derived. The values are plotted as circles on curve I.

Table C. This table gives the results from four experiments made with a brass cylinder coated with the active deposit from radium as source. α rays of ranges from 7 cm. maximum to about 5·8 cm. minimum were incident on the hydrogen. The values are plotted in Curve II.

Absorption in path of rays.	Ionization.	Absorption in path of rays.	Ionization.	Absorption in path of rays.	Ionization.
11·0	·97	11·0	1·00	11·0	1·08
16·2	1·04	22·8	·75	14·9	·98
21·4	1·00	24·1	·61	16·2	1·02
25·3	·53	25·3	·51	18·9	·95
26·7	·38	28·0	·25	20·1	·91
28·0	·21	——	——	21·4	·82
29·2	·06	11·0	1·00	22·8	·81
		20·0	·95		
		29·3	·09		
		30·4	·0		

The dotted curves are replotted from figure 5, p. 550, of the paper by Professor Rutherford above referred to (Phil. Mag. June 1919). That shown with curve I. is E in fig. 5 of his paper, and that with curve II. is A.

Curve II.

Absorption in equivalent cms. of air.
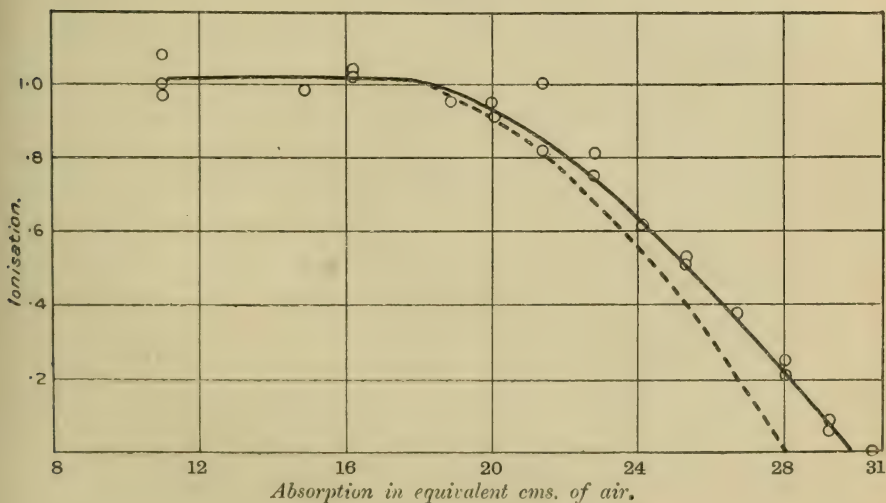
Summary of Results.

The results obtained check the main points summed up in fig. 5 of the paper above referred to (Rutherford, Phil. Mag. June 1919). Curve II. is almost directly comparable with

curve A. It will be seen that the principal difference is that the ionization curve gives a greater range for the recoil atoms than the scintillation curve. This may be because different values have been taken for the stopping powers of the absorption screens used in the two cases or to the fact that the scintillation curve was made with mixed absorptions of aluminium and mica. At the same time, in the analogous case of the absorption of a homogeneous beam of α rays, ionization is detected beyond the range of the particles as determined by scintillations, and the difference here may be due to the same causes.

Curve I. is less definite than curve II. because the glass of the α-ray tube used as the source was not of uniform thickness. Some α particles of range just over 5 cms. were present, and probably every range was represented between this and zero.

The difference between the ranges of the recoil particles given by this curve and the scintillation curve E is not accounted for by the small difference in the maximum ranges of the α particles producing them, and must be given an explanation similar to that suggested for the long range particles of curve II.

The above remarks indicate the success of the research from the point of view of two of its objects. It confirms Professor Rutherford's scintillation experiments, which show that in close collisions between α particles and hydrogen atoms, the nuclei cannot be considered as point charges, and that most of them are thrown straight forward. It does not show any essential difference between curves which plot ionization against absorption and those which plot scintillations against absorption, except the small difference in range above discussed. The effect of increase in ionizing power of a particle as its velocity decreases is probably masked by differences in the experimental arrangements used to obtain the scintillation and ionization curves.

With regard to the first object of the research, the electrical method with the apparatus as finally used is suitable for the investigation of recoil radiations, and should be capable of modification for use on an effect only about a fifth as great, with similar quantities of radioactive material. The maximum effect was about two divisions on the microscope scale per minute, for an activity corresponding to one milligram of radium.

My best thanks are due to Professor Rutherford for his continued interest and advice throughout the course of this work.

LXXXVII. *Note on Einstein's Law for Addition of Velocities.*
By W. B. MORTON, *M.A., Queen's University, Belfast* *.

THE way in which the theory of Relativity has modified
the law of combination of velocities can be shown very
clearly by an obvious graphical method, and the curves bring
out one or two points of some interest.

Take first velocities in the same line. Let u be the
velocity of the " moving platform " as seen from the
" ground " and v the velocity of a point on the platform
measured by platform standards, the velocity of light being
taken as unity. Then the velocity of the point as seen from
the ground is $(u + v)/(1 + uv)$.

Fig. 1.
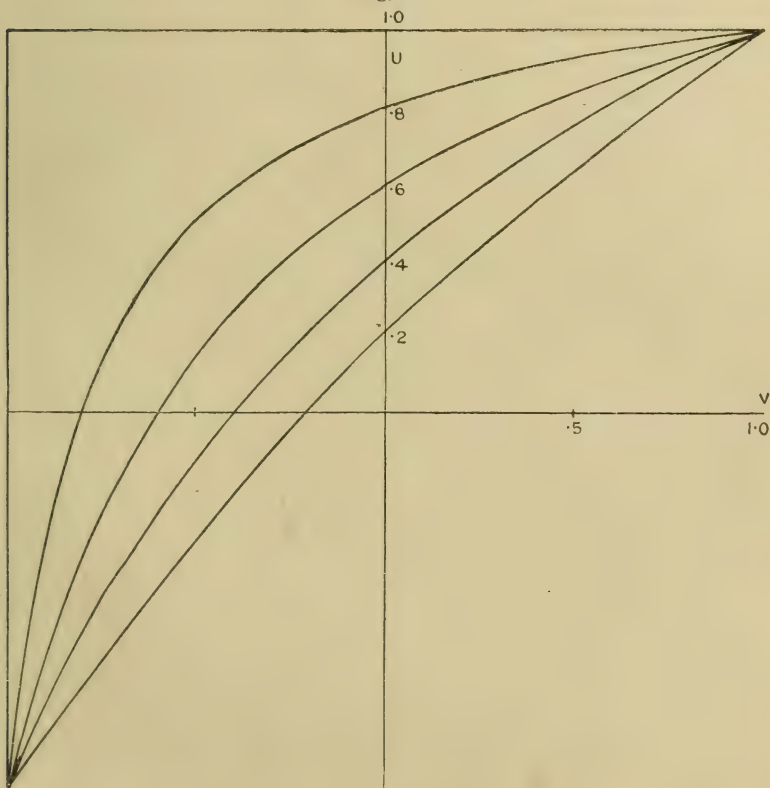
Giving u a definite value, we may plot this " resultant "
against v. This is done on fig. 1, for $u = \cdot2, \cdot4, \cdot6, \cdot8$, these

values being given by the intersections of the curves with the axis of y.

The curves are portions of rectangular hyperbolas having centres at $x = -1/u$, $y = 1/u$, and asymptotes parallel to the axes of $x\,y$. They run to the terminal points which correspond to the velocity of light in the forward and backward directions. On the old theory the graphs would, of course, be straight lines, starting from the same points on the y-axis and making 45° with the axes.

The most interesting features of the curves are in the region of negative v (backward motion along the platform). The resultant vanishes for $v = -u$, just as in the old theory, although now the "equal" speeds are measured with different standards. This is merely another way of expressing the reciprocal nature of the Lorentz transformation: the ground appears to move backward with velocity u from the platform standpoint. When $v = -1$ the resultant has the same value; a light-signal travelling backward has unit velocity to both sets of observers.

When u is large there is a very sudden increase in the resultant speed as v passes from $-u$ to -1. For example, if the platform moves at ·9 of the speed of light, a point moving backwards along it at this same speed will appear stationary from the ground. But if the speed is pushed up to the full value for a light-signal, this has its full value also as seen from the ground. On the diagram this is shown by the sudden downward plunge of the curve for ·8. As the value of u is increased towards unity the hyperbola approaches the rectangular lines along the top and down the left-hand side of the diagram.

From this consequence of Einstein's formula there follows a curious paradox which I have not seen mentioned, and which may be added to the many odd things which would happen if anything but light could be made to move as fast as light.

First let the platform have any speed, and let a point move backwards along it with the same speed as measured on the platform. Then the point is at rest as seen from the ground. Increase the common speed up to that of light and we have a light-signal moving backward along a platform which moves forward at the speed of light and appearing stationary from the ground.

But now let the backward-moving thing on the platform be a light-signal from the first. This, on the fundamental assumption of the theory, moves with the velocity of light as

seen from the ground, no matter at what rate, under light-velocity, the platform is moving. Assuming physical continuity up to light-velocity, we reach a conclusion contradictory to the last.

Mathematically the paradox has its origin in the fact that the expression $(u + v)/(1 + uv)$ is indeterminate for the values $u = -v = 1$, and approaches different limits in the two ways in which we have reached these values of the variables.

Physically it means, I suppose, that the measured speed of 300,000 kilometres per sec. cannot be attained by matter, and that, at speeds very close to this, there would be an extraordinary instability in the measured value of the resultant of opposite velocities of that order of magnitude.

Fig. 2 shows the variation of the magnitude of the resultant

Fig. 2.
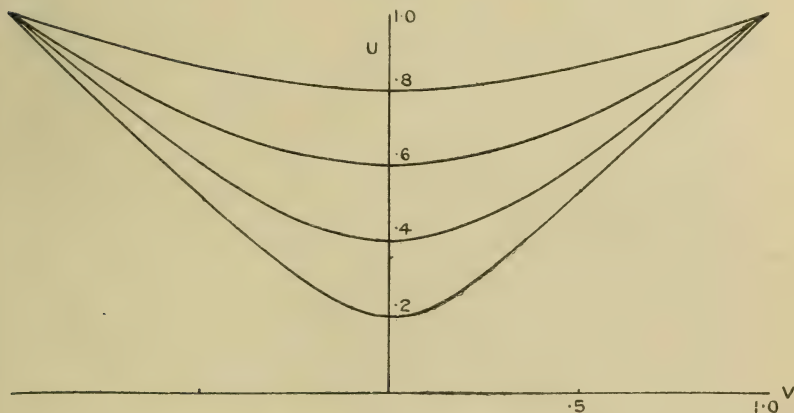
when uv are at right angles to each other, in accordance with the formula $(u^2 + v^2 - u^2 v^2)^{\frac{1}{2}}$. The curves are again hyperbolas with centres at the origin and asymptotes

$$y = \pm x (1 - u^2)^{\frac{1}{2}}.$$

On the old theory they would be hyperbolas, passing through the same points on the y-axis with asymptotes $y = \pm x$.

In the general case, when uv are inclined at an angle γ the magnitude of the resultant is

$$(u^2 + v^2 + 2uv \cos \gamma - u^2 v^2 \sin^2 \gamma)^{\frac{1}{2}}/(1 + uv \cos \gamma).$$

Two additional points may be mentioned. First:—Seeing that the curves are convex upwards in fig. 1 and downwards in fig. 2, it is evident that they may become approximately straight for an intermediate value of γ. The tangent to the curve at the axis of y is directed towards the terminal point (1 1) for $\sec \gamma = 1 + u$. In that case there cannot be much variation from the straight line—*i. e.*, the speed increases in a linear manner up to that of light as v is given larger and larger values. This is seen on the diagram (fig. 3) which is

Fig. 3.
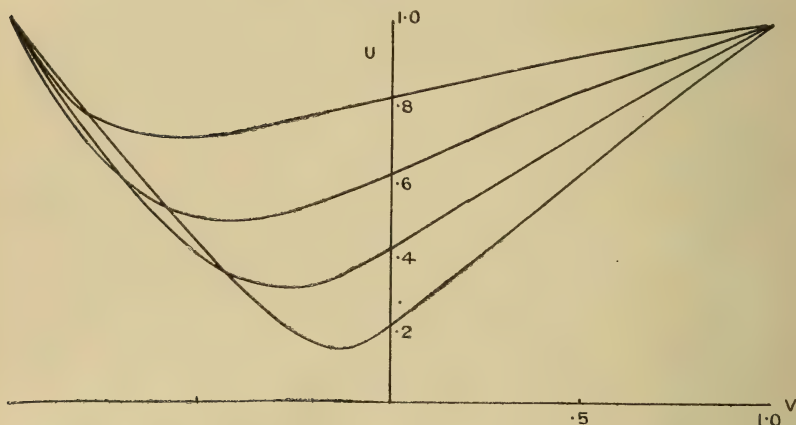
for $\gamma = 45°$; there is not much deviation from straightness in the graphs on the positive side of the origin.

Second :—It comes out that the condition for a resultant of minimum size, when $u \gamma$ are given, is identical with that found on the old theory—viz., $v = - u \cos \gamma$. The square of the resultant may be written in the form

$$1 - \frac{(1-u^2)(1-v^2)}{(1+uv \cos \gamma)^2},$$

and $(1-v^2)/(1+uv \cos \gamma)^2$ is maximum for $v = - u \cos \gamma$.

To show the continuity of passage from fig. 2, through fig. 3 to fig. 1, the parts of the curves in fig. 1 which lie below the axis must be reflected upwards so as to give the magnitude of the resultant without respect to its direction.

LXXXVIII. *The Absorption of Light by the Goldberg Wedge.*
*By F. C. Toy, M.Sc., A. Inst. P., British Photographic
Research Association, and J. C. Ghosh, D.Sc., University
College, London* * .

[Plate XVII.]

MEASUREMENTS of light absorption are now fre-
quently made by means of a thin wedge of lamp-black
in gelatine contained between inclined glass plates. This
wedge was devised by Goldberg † in 1910, and is now
available in several commercial forms. It is usually assumed
to be neutral, *i. e.*, to have a constant extinction coefficient
for all wave-lengths. As this constancy does not appear to
have been verified over any considerable range, an investi-
gation of its possible variation was made. The " gradation "
of the wedge, *i. e.* the increase of density (in the photo-
graphic sense) ‡ per unit length in a direction perpendicular
to the isopaques, is its most important characteristic, and the
variation of this gradation with wave-length was investi-
gated. For, while this variation is directly proportional
to the variation of the extinction coefficient, it cannot be
directly calculated from the latter, which is therefore of
lesser practical importance.

For the details of the method used, the reader is referred
to a previous paper §. This method is independent of the
Schwarzschild effect ‖, so that greater accuracy can be
obtained than in methods previously employed. The accuracy
of the method allows the variation of the gradation with the
wave-length to be followed very closely.

Fig. 1.
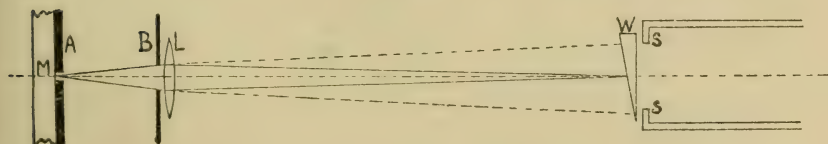
Fig. 1 shows diagrammatically the arrangement of the
apparatus. The source of light M is a quartz mercury lamp

* Communicated by Prof. A. W. Porter, F.R.S.
† B. J. P. lvii. p. 648 (1910).
‡ The density is defined as $-\log_{10} T$, where T is the photometric
transparency, *i. e.* $\dfrac{\text{Intensity of Light Transmitted}}{\text{Intensity of Light Incident}}$.
§ Proc. Roy. Soc. xcvii. p. 181 (1920).
‖ Photo. Journ. lvi. p. 11 (1916).

fitted with an iris diaphragm A, by means of which only
a small central circular portion of the lamp, about 1–2 mm.
in diameter, is used. A lens L is placed so as to project
a magnified image of this on to the slit SS of the spectro-
scope. The intensity of the image is very uniform, since it
is formed from such a small isolated patch of the source of
light. The Goldberg Wedge, W, is placed in front of the
slit and in contact with it. The length of slit used is about
1·5 cm., and a special wedge was made up between two fused
silica optical flats by Messrs. Ilford Ltd. The intensity
incident on the wedge is varied by varying the aperture of
the projecting lens L by means of the adjustable stop B.
By keeping the aperture small and the focal length large,
so that the curvature of the lens surfaces is small, the
intensity of the image is almost exactly proportional to the
square of the aperture of the lens. The current through
the lamp is of course kept constant during each experiment.
A metal filament lamp is used for experiments at the red end
of the spectrum, since there are no lines in the mercury arc
suitable for measurement in this region. The intensity is
varied in this case by changing the distance of the light
source from the wedge.

This apparatus is used by taking two spectrographs through
the wedge on the same plate with two differing intensities
in known ratio and with the same time of exposure. From
this negative the gradation at several wave-lengths can be
determined as follows. Let Δ_λ be the gradation of the
wedge for any wave-length λ, and the two incident inten-
sities be I_1 and I_2. Let the densities at the two points at
which there is the same intensity (I_t) transmitted in each
case be D_1 and D_2, and the distances of these points from
any arbitrary fixed point on the wedge be x_1 and x_2. At the
images of these points at any particular line of the spectrum
the same effect will be produced, so that on development the
densities will be equal. This equality is independent of
the exposure, the kind of plate used, or the treatment it
receives.

From the definition of density,

$$I_t = I_1 \times 10^{-D_1} = I_2 \times 10^{-D_2},$$

$$\therefore \quad \log_{10} I_1/I_2 = D_1 - D_2 = \Delta_\lambda \times (x_1 - x_2).$$

Therefore

$$(x_1 - x_2) = \frac{1}{\Delta_\lambda} \times \log_{10} I_1/I_2. \quad . \quad . \quad . \quad (1)$$

If y_1 and y_2 are the distances on the plate corresponding to x_1 and x_2 on the wedge, then

$$(y_1 - y_2)/(x_1 - x_2) = M_\lambda, \quad . \quad . \quad . \quad . \quad (2)$$

where M_λ is the magnification produced by the optical system of the spectroscope at wave-length λ.

Whence from (1) and (2)

$$\Delta_\lambda = \frac{M_\lambda}{(y_1 - y_2)} \times \log_{10} I_1/I_2. \quad . \quad . \quad . \quad (3)$$

The magnification is obtained by placing an opaque object of known length across the jaws of the spectroscope and comparing the length, at different wave-lengths, of the image obtained on the plate. If, now, y_1 and y_2 can be determined from the plate, Δ_λ can be calculated. Now, y_1 and y_2 are simply the distances from an arbitrary point, such as the image of the end of the slit, along any one line to any two points of equal density (intermediate between zero and maximum density), and can readily be measured in the following way. Fig. 2 (Pl. XVII.) is a positive printed from one of the original spectrographs. It will be noticed that the change from black to white along any one line is very gradual. The steepness of this change will, of course, depend on the gradation of the wedge and the kind of plate used. The distances y_1 and y_2 will be approximately as indicated in fig. 2. If a succession of transparencies of this spectrograph are now made, the change from black to white will be made sharper with each reproduction.

Fig. 3 (Pl. XVII.) shows the " second " positive obtained from the same original spectrograph by three reproductions. The change from black to white is now practically a sharp line, and coincides with the point of half maximum density, or any other density intermediate between the maximum and zero. The distances y_1 and y_2 can now be measured directly by means of the travelling microscope. In fig. 3 it will be noticed that towards the end of longer wave-lengths some of the lines (*e. g.* E, K, and M) are sufficiently intense to cause blackening over the whole length of the slit. These, of course, cannot be used for making measurements, but on each photograph wave-lengths can be selected at which the intensity is such that y_1 and y_2 are both of suitable length, with the ends well clear of the end of the slit. For example, lines A, B, C, D, F, G, H, and L were used in this case. The wave-lengths of the various lines can always be ascertained at once by reference to a standard spectrograph.

The value of $(y_1 - y_2)$ at any given wave-length for a given

ratio of intensities incident, is determined for several times of exposure. This variation of exposure will change the values of y_1 and y_2, but the *difference* will remain constant. The photograph shown in fig. 4 (Pl. XVII.) is taken over the same range as that shown in fig. 3 and with the same ratio of incident intensities, but with a different time of exposure. Table A is typical of the values obtained :—

TABLE A.

Ratio of Intensities 23 : 1.   Wave-length 308·8 $\mu\mu$.

Time of exposure in minutes.	$y_1 - y_2$, in cms.	Deviation of single observation from mean.
5	0·418	0·008
15	0·410	0·000
1·5	0·395	0·015
1·5	0·424	0·014
3	0·415	0·005
5	0·398	0·012
Mean	0·410	0·009

Average deviation of Mean $= \dfrac{0\cdot009}{\sqrt{6}} = 0\cdot004.$

Therefore

$$(y_1 - y_2) = 0\cdot410 \pm 0\cdot004 \text{ cm.}$$

TABLE B.

Wave-length in $\mu\mu$.	Gradation (increase of density per cm.).		
	Mercury Lamp.		M. F. Lamp.
	$I_1/I_2 = 8\cdot10$.	$I_1/I_2 = 23\cdot0$.	$I_1/I_2 = 3\cdot10$.
660	......	......	1·23
610	......	......	1·21
590	......	......	1·25
579	1·29		
570	......	......	1·28
560	......	......	1·29
546	1·42		
492	1·41		
434	1·41		
408	1·61	1·67	
398	1·61		
391	......	1·71	
379	1·75	1·78	
368	1·80	1·82	
335	2·70	2·63	
312	3·02	3·07	
303	3·22	3·29	
297	3·33	3·51	
289	4·06	3·86	

The values in Table B are plotted in fig. 5. The circles represent points determined with the metal filament lamp, the crosses and solid circles those determined with the mercury arc, but with ratios of intensities incident on the

Fig. 5.
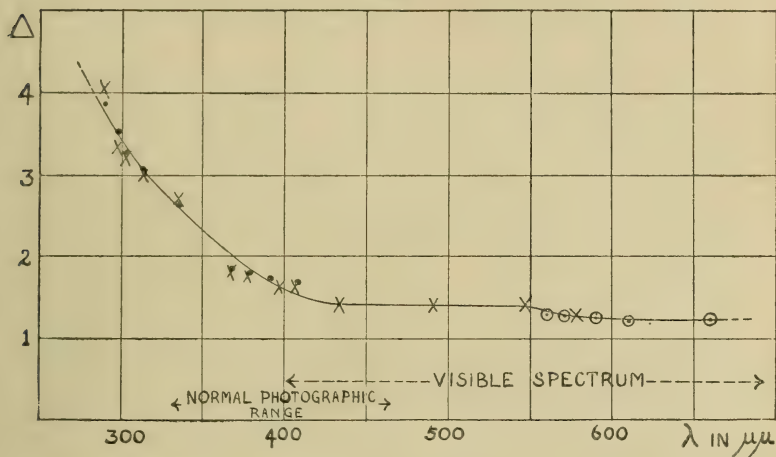
wedge of 8·1 : 1 and 23 : 1 respectively. It will be seen that the density is very nearly constant throughout the visible region of the spectrum, though there is a slight decrease from the yellow-green towards the red. In the ultra-violet, however, the density increases rapidly with decreasing wavelengths. It was thought that this might be due to the presence of gelatine in the wedge, but no absorption by the gelatine alone could be noticed above the accepted wavelength $220 \mu\mu$. The values for the gradation in the visible spectrum were verified by means of a Koenig-Martin Spectrophotometer.

It is evident from the results that while this particular type of wedge is approximately neutral throughout the visible spectrum, there is a very pronounced variation of the extinction coefficient with the wave-length in the ultra-violet part of the region which is normally used in photographic research.

LXXXIX. *On the Pressure on the Poles of an Electric Arc.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

INSERTED in your October issue is a letter from Dr. Ratner in which he objects to the argument of Prof. Duffield that any motion which ions may acquire in the field of an electric arc cannot give rise to a pressure upon its poles. It is not for me to discuss the part of his communication which deals with Prof. Duffield's work. But he goes on to make deductions from experiments upon the electric wind; and as one of the investigators of that subject to whom he refers, I think it is desirable for me to draw attention to the faulty interpretations that he places upon some of the results of their work.

In his own work which he quotes, the vane upon which he detected a pressure was placed behind a perforated electrode which received the ions. The vane therefore received some of the momentum of the wind which blew through the perforations without experiencing the compensating attraction of the ions in the discharge; this was taken entirely by the electrode. He is therefore incorrect in stating that those experiments on an electric wind give evidence of a repulsion of an electrode which has an opposite sign to the ions giving rise to the wind.

Secondly, in his remarks on the diminution of the wind with high values of current he ignores the fact that an electric current in a gas is not in general carried by one sign of ion only. In discharge at atmospheric pressure from a point or a wire with small values of current, only one sign of ion is present through the greater part of the path of the discharge. But this is not true for all values of pressure and current, and it is very improbable that it is true in arc discharge for *any* values of pressure and current.

In conjunction with Mr. H. E. G. Beer, I have been engaged for some months on an investigation of the electric wind in the arc under various conditions. We find that in general it is exceedingly minute. Its direction is from cathode to anode, a fact which under certain circumstances is in accordance with the manometric observations made by Dewar many years ago and referred to by Duffield in his paper. The results are quite consistent with the view that the effect is a residual one, being the difference between the effects which the positive and negative ionic streams would have separately

produced. Owing to the great difference between the specific
mobilities of positive and negative ions at arc temperatures, it
is only necessary to assume that through the body of the arc
a small fraction of the total current (less than $\frac{1}{2}$ per cent.) is
carried by positive ions to account for the magnitude of the
observed wind.

A full account of these experiments will be published
shortly.

<div align="center">I am, Gentlemen,</div>

Physics Laboratory,   Yours faithfully,
   University, Bristol.   A. M. TYNDALL.
   Oct. 15. 1920.

XC. *Note upon the Alternating-Current Carbon Arc.* By
Prof. W. G. DUFFIELD, *D.Sc.*, and MARY D. WALLER,
B.Sc.[*]

EXPERIMENTS carried out in the Physics Laboratory
of University College, Reading, some years ago showed[†]
that the amount of carbon lost from the cathode of a direct
current arc consisted of two parts : (1) that necessary for the
mechanism of the arc, and (2) a quantity lost by evaporation
or combustion, which, though possibly affecting the voltage,
temperature, brightness, and the current, could only be
regarded as subsidiary. Chief interest centred about the
shortest arc, less than one millimetre in length, which it was
found possible to maintain; for here the loss from the cathode
was entirely of the first category, and such that for each
carbon atom lost from that pole there was a transfer between
the electrodes of a quantity of electricity equivalent to four
electronic charges.

It was further found[‡] that, though in a normal arc the
anode loss is considerably greater than that from the cathode,
it is nevertheless possible so to cool the anode by rotating it,
that its loss of weight may be reduced, not only below that
of the cathode, but nearly to zero.

A careful examination of the contour of the poles of a
direct-current arc showed that the shape of the anode re-
mained practically unchanged, but that, even though pre-
viously burnt to shape, the contour of the cathode of a very
short arc went through a well-marked cycle of changes,
which were repeated again and again as the expenditure of
carbon proceeded.

    [*] Communicated by the Authors.
    [†] Duffield, Roy. Soc. Proc. A. xcii. p. 122 (1916).
    [‡] Duffield & Waller, Roy. Soc. Proc. A. xcii. p. 247 (1916).

The present set of experiments was undertaken for the purpose of testing the behaviour of the alternating-current arc chiefly as regards the above-mentioned features.

Since in an alternating-current arc each pole acts for half a period as anode and half a period as cathode, it seemed most likely that the loss from each pole would be intermediate between those from the anode and cathode of a direct-current arc using the same current. This we have put to the test and shown to be the case; indeed, the loss in the case of the alternating current approximates a little more closely than might be expected to the mean of the anode and cathode rates of carbon consumption.

In putting the matter briefly upon record, it is only necessary to say that the previous method of experimenting was adopted (*loc. cit.*), the special precautions being the burning to shape of the poles before the first weighing, and the prevention of absorption of moisture from the atmosphere.

The results are best shown diagrammatically. Diagram 1 shows the relationship between the loss per coulomb and the arc length for different currents. The curves possess the general shape of those obtained with the direct-current arc, rising at first rapidly, but ultimately reaching a nearly stationary value. They resemble the anode rather than the cathode curves in that they do not all diverge from a common point upon the vertical axis. Even in the case of the shortest possible arc the consumption of carbon per coulomb exceeds $3 \cdot 1 \times 10^{-5}$ gm., the theoretical limit; so it is clear that in all cases there is subsidiary as well as essential carbon loss.

Diagram 2 shows the loss from either pole of an alternating-current arc using 8 amperes, compared with the individual losses from the anode and cathode of a direct-current arc carrying the same current, and with their mean value. The latter agrees well with the alternating-current curve, but is a little higher when the arc-gap is long. For currents of 4 and 2 amperes the agreement is not so good, though of the same order of magnitude, the alternating-current consumption being definitely less than the mean value in the direct-current curves.

It thus appears that during the half-period when any given pole is acting as anode, it does not play a passive rôle like that which was, by artificial means, induced in a rotating anode, but that there is time for the pole to assume to a large extent the condition of the anode in the direct-current arc, though there is no crater; it certainly gets hotter than the cathode, and is able to lose a considerable amount of material.

Diagram 1.
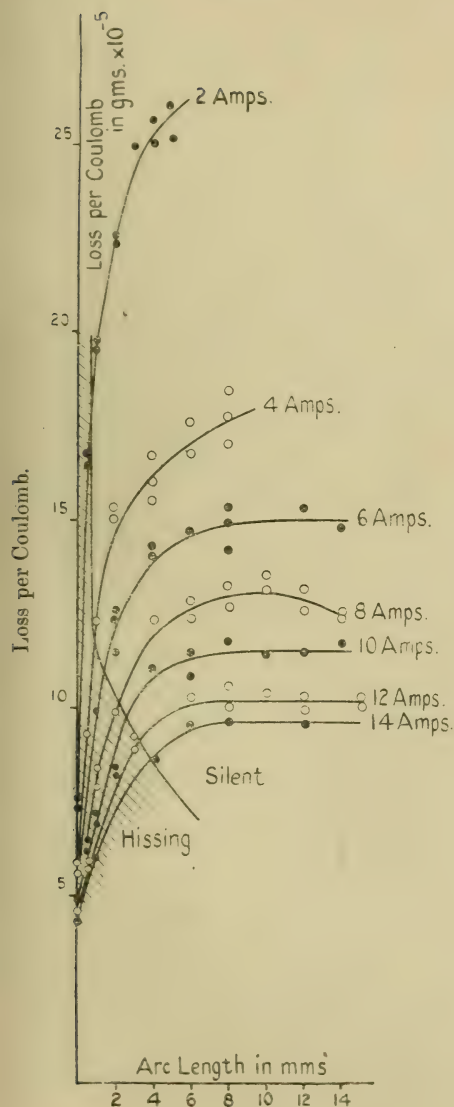
Diagram 2.
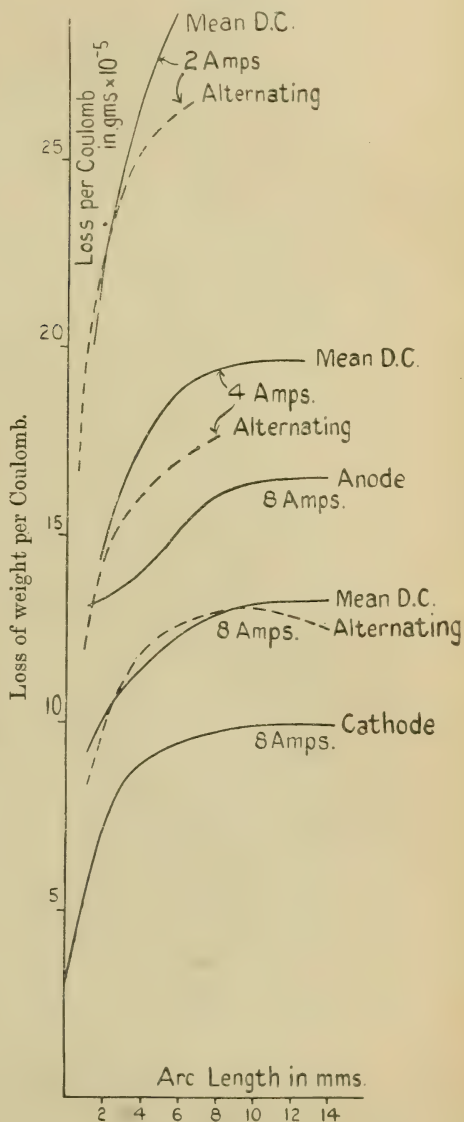
The rate of carbon consumption per coulomb plotted against arc length. The shaded area represents hissing arcs.

Comparison of Alternating- and Direct-Current consumption.

The wastage is increased by the fact that during the second half-period, when the same pole becomes the cathode, it is hotter than it would have been in a direct-current arc.

Successive contours of a very short alternating-current arc were drawn by projecting an image upon transparent paper and tracing the outlines at short intervals of time, the arc length being kept constant throughout. There is a very marked difference between the results and those obtained with the direct-current arc already referred to; here there is no cycle of changes, but a contour of practically unvarying form. No constriction develops in the rear of the pole face when the arc is short, though a tendency to form one has been observed in the case of longer alternating-current arcs. No deposition of material takes place upon either pole as it does in the direct-current arc; or, if deposition occurs in one half-period, a still larger quantity is consumed in the second half-period.

Three further points may be briefly mentioned :— We noticed that the upper and lower carbons were not equally consumed ; for short arcs the lower, and for long arcs the upper pole lost more rapidly, the value of the current not affecting the ratio seriously: the ratio of upper to lower pole loss varied in almost linear manner from 0·8 for the shortest to 1·9 for the longest arc used, 15 millimetres. This is, no doubt, due to convection currents, which have greater freedom of access to the hot under-surface of the upper carbon in a long arc.

Notes are made when the arc was hissing, and such observations have been distinguished on the first diagram, from which it appears possible to divide it into two regions, one characterized by hissing and the other by silence. Mrs. Ayrton found that hissing seemed to depend upon the access of air to the crater of the direct-current arc ; if more than a certain amount reached it, hissing ensued on account of an automatic protective mechanism which seemed designed to oppose the access of too much oxygen. Diagram 1 seemed at first sight to offer evidence in opposition to this, since silent arcs are associated with high rates of carbon consumption per coulomb; but, as we have stated elsewhere, the loss per coulomb is governed more by the time taken for the coulomb to pass between the hot poles than by the strength of the current (since it obviously takes longer with small than with large currents) ; hence the objection is not serious. If we draw out curves representing the total loss in one second against current strength for arcs of different lengths, we find that hissing arcs are, in accordance with Mrs. Ayrton's view, associated with high carbon consumption.

In conclusion, it is of interest to note the bearing of this investigation upon the pressure observed upon the poles of an alternating-current arc, which has been shown elsewhere to agree well with that for the D.C. arc. We now find the rates of carbon loss to be also approximately equal; hence the argument used in the case of the D.C. arc, that the evaporation of carbon is of the wrong order of magnitude to account for the effect, holds good in the alternating-current arc also. The reaction in the latter arc, as in the former, is believed to be occasioned by the cathodic expulsion of electrons whose momentum is propagated across the arc through the vapour to the anode, where it produces an equal pressure. In the alternating-current arc the pressure is therefore made up of a reaction consequent upon electron emission during the half-period when it is the cathode, and of the pressure consequent upon the reception of the momentum from the other pole during the second half-period when it is acting as the anode.

Physics Laboratory,
    University College,
        Reading.

XCI. *Experiments on the Nature of Discharge of Electricity through rarefied Gases. By* S. RATNER, *Research Student, University of Manchester* *.

1. IN spite of the large amount of work contributed to the study of the nature of the discharge of electricity through vacuum-tubes, the present theories fail to give a clear and adequate representation of the phenomenon. The most obscure point is the process by which, under a certain potential difference, the current begins to flow through the gas. It is usually supposed that the stray positive ions which may be present in the tube, strike against the cathode with sufficient energy to cause an electronic emission from the surface-layer of atoms of the cathode, and that these electrons, by collision with the gaseous molecules, produce sufficient ions to carry the whole current. Certain experimental facts, however, disagree with this theory. Thus, when the vacuum is sufficiently high, the potential necessary to start the discharge increases with further exhaustion of the tube, although the energy imparted to the cathode by the positive ions depends only on the potential through which

they fall. There is some evidence that α-particles from radioactive substances, by impinging upon a metal target, may set free slow electrons from the surface of the target, but the energy of α-particles is enormous compared with that of the positive ions striking the cathode in a discharge-tube. It seemed important, therefore, to investigate directly the rôle played by the positive ions in the process of the discharge, and further to carry out experiments with a view to a direct study of the conditions under which positive ions may, by impact with the surface of the cathode, give rise to an electronic emission from the latter.

2. The apparatus used in these experiments consists of a glass tube A (fig. 1) provided with two ground joints m and n, by means of which two electrodes—an aluminium plate P and a strip of thin platinum foil s—may be easily introduced into or removed from the apparatus. A third electrode r in the shape of a rod or a small plate is introduced in the bulb through the side-tube t. The platinum strip s is coated with aluminium phosphate or calcium oxide, and when electrically heated by an insulated battery of accumulators provides large supplies of positive or negative ions, according to whether it is used as an anode or a cathode. The electrodes may be raised to any desired potential by means of a battery of small cells or an induction-coil provided with a rectifying valve and a spark-gap. By means of a Gaede pump the pressure in the bulb may be reduced down to ·001 mm. of mercury in spite of some grease and sealing-wax being always present in the apparatus, and if necessary the exhaustion is carried still further by a charcoal tube immersed in liquid air. The electric current passing through the bulb, varying over a wide range between 10^{-8} amp. and several milliamperes, is measured either by one of two galvanometers of different sensitiveness or by a milliammeter.

3. In the first place experiments were made in order to ascertain whether the conditions of the discharge would be appreciably changed by a stream of positive ions produced in the vacuum-tube. It is well known that a hot cathode emitting negative carriers of electricity lowers considerably the sparking potential, and according to the theory mentioned above one could expect that the same effect would be reached by using a hot anode emitting under an intense electric force a stream of positive ions. The experiments were carried out in the following way :—The heated strip coated with aluminium phosphate is connected with the positive terminal of the induction-coil, the cathode P being earthed and the electrode r insulated, and the pressure in

the bulb reduced to a certain value. The potential of the anode is then gradually raised by means of the spark-gap, and the current carried by the positive ions from the strip

Fig. 1.
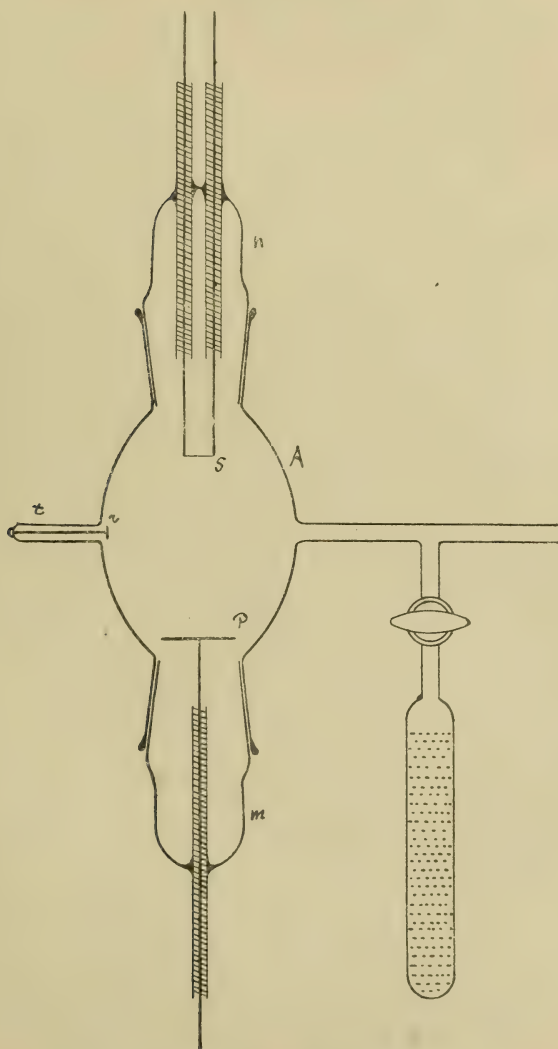
is measured. This current was usually of the order of 10^{-6} amp. When the potential of the anode becomes sufficiently high (corresponding to a spark-length of, say,

15 mm.), the discharge suddenly sets in, and the current through the tube abruptly rises to the order of a milli-ampere [*]. The external current heating the strip is then broken, and the experiments repeated with a cold anode, other conditions remaining the same. The discharge is found to take place at exactly the same potential as when the strip was heated and the cathode intensely bombarded by a stream of positive ions.

The same procedure was followed at a lower vacuum, when a potential difference of the order of 1000 v. applied to the electrodes was enough to produce the discharge. In this case the voltage was supplied by a battery of small cells, and the sparking potential could be determined with great accuracy. The results obtained were as before, and the positive emission from the strip did not lower the sparking potential by as much as one per cent.

4. These results are hardly compatible with the usual theory of discharge of electricity through vacuum-tubes, for it is equivalent to admitting that positive ions falling through a potential of more than 20,000 v. in a high vacuum do not carry with them sufficient energy to liberate electrons from the cathode on striking against its surface ; while in other cases, on the other hand, a fall through less than 1000 v. in a lower vacuum enables them to produce this effect. If we suppose that the electrons necessary to start the discharge may be bombarded not necessarily only out of the cathode, but also from the gaseous molecules by collision with the positive ions, the same difficulties will still remain in the interpretation of these experiments. One might perhaps suppose that in a high vacuum, where the number of gaseous molecules present in the tube is comparatively small, the potential necessary for the discharge is necessarily high in order to ensure ionization at every collision, but such a theory would require a *gradual* increase in the discharge current as the potential rises from about 1000 v. and goes on increasing. It is well known, however, that the discharge in a well-exhausted tube starts *abruptly* when the applied potential attains a value considerably higher than 1000 volts.

Whatever the nature of the discharge may be, the experiments described above show distinctly that it is not caused by the impact of positive ions on the surface of the cathode. It seemed important, therefore, to carry the experiments

[*] It may be mentioned here that the walls of the apparatus were previously carefully freed from occluded gases by electronic bombard-ment and heating of the strip, so that the pressure in the bulb remained sufficiently constant throughout the experiments.

further and to investigate whether positive ions by striking
against the cathode are really able to liberate electrons from
its surface, independently of the part which such electrons
may play in the process of the discharge itself.

5. In such experiments the following method of three
electrodes was adopted :—The strip *s*, coated with aluminium
phosphate and strongly heated, was connected with the
positive terminal of the battery of small cells, the cathode P
being earthed through a galvanometer, and the third elec-
trode *r* raised to a positive potential higher than that of
the heated strip. The apparatus was kept well exhausted
throughout the experiments, so that the comparatively small
potential difference applied to the electrodes (not exceeding
2000 v.) could not produce a discharge through the bulb.
The positive ions emitted by the strip move towards the
cathode P and may produce electrons either by collision with
the gaseous molecules or by impact with the surface of the
cathode. These electrons move necessarily towards the third
electrode *r* charged to a higher positive potential than the
strip, and the current carried by them is measured by a
galvanometer. The ratio of this current to that carried by
the positive ions to the cathode P, gives the rate of pro-
duction of electrons by the positive ions in the bulb.

It was evidently necessary in the first place to inquire
into the validity of the method, since it may seem doubtful
whether all the electrons produced in the bulb will actually
reach the electrode *r*. For this purpose the electrode *r* was
raised to different potentials, and curves were drawn show-
ing the current flowing through this electrode as a function
of the potential difference between it and the heated strip,
other conditions remaining the same. These curves appeared
to be similar in shape to the well-known saturation curve in
ionized gases, the current increasing at first rapidly with
the potential difference and finally remaining constant. A
potential difference of 200 v. appeared sufficient to assure
the saturation being reached, and in most of the experiments
to be described the electrode *r* was raised to a potential of
+2000 v., the strip being charged to +1800 v. Further,
it was found that the current received by the third electrode
was strictly proportional to the positive emission from the
strip, which could be varied within wide limits by changing
the temperature of the latter, so that the rate of production
of electrons by the positive ions in the bulb was constant at
a given pressure.

The experiments consisted mainly in studying the variation
in the rate of production of electrons with the pressure, in

the bulb. If the electrons present in the bulb originate solely in ionization by collision between the positive ions and gaseous molecules, then the rate of production of the electrons should be expected to vary inversely as the mean free path of the positive ions, *i. e.* it should be strictly proportional to the pressure in the bulb and should become negligibly small when the bulb is highly exhausted. If, however, electrons are also produced by impact of the positive ions against the surface of the cathode, then no such proportionality would be expected, and the current through the third electrode should remain considerable even when the highest exhaustion is reached.

In the estimation of the rate of production of electrons by positive ions an important correction must be introduced, the omission of which led to misleading results in the earlier experiments. When a molecule is ionized by collision a pair of ions is produced, so that the current through the plate P is carried not only by the positive ions from the heated strip, but also by the positive ions produced by collision. Also when an electron is set free from the surface of the cathode, a positive charge is gained by the cathode. If we denote by $C_{(-)}$ the current through the third electrode, by $C_{(+)}$ the current through the cathode P, and by R the rate of production of electrons by the positive ions from the strip, then it is easy to see that R is given not by $\dfrac{C_{(-)}}{C_{(+)}}$, as at first anticipated, but by $\dfrac{C_{(-)}}{C_{(+)} - C_{(-)}}$. This correction is small when the bulb is well exhausted and consequently $C_{(-)}$ is small compared with $C_{(+)}$.

As a result of a large number of experiments carried out in this way, it was shown distinctly that the electrons present in the bulb are produced only by collision between the positive ions and the gaseous molecules, and that there is no appreciable electronic emission from the surface of the cathode. Table I., in which the results of one set of these experiments are given, shows that the law of proportionality between R and the pressure p holds well within the limits of experimental error.

It was noticed, however, in some experiments that when the strip was raised to a very high temperature, a disproportionately large current flowed through the third electrode, even at the highest obtainable exhaustion of the bulb. This was finally found to be caused by a source of error which can, however, be easily eliminated. It was found that a strongly heated platinum strip coated with aluminium phosphate or any other salt serving as a source of positive ions,

TABLE I.

$C_{(-)}$ $\times 10^8$ amp.	$C_{(+)}$ $\times 10^8$ amp.	$R = \dfrac{C_{(-)}}{C_{(+)} - C_{(-)}}$	$\dfrac{p}{\times 1000}$ mm.
46	268	·21	28
36	280	·15	21
31	255	·14	18
24	245	·11	15
26	295	·10	14
18	235	·083	12
15	280	·056	9
13	275	·050	8
12	285	·044	6
6	260	·024	3
3	295	·010	1 (?)
1	240	·004	—

emits also a large number of negative ions when being used as a cathode. This is probably due to the fact that the salt usually does not cover the whole surface of the strip, so that the negative ions are emitted by the platinum surface itself. In the experiments described above the strip was used as an anode, but compared with the third electrode r it was always charged to a negative potential of 200 v., so that the third electrode received also the negative emission from the strip. This source of error is comparatively small and may be eliminated by insulating the cathode P and measuring the current through the third electrode, all other conditions remaining the same. When the temperature of the strip was not very high, this source of error could be neglected.

An attempt was also made to check the results by control experiments. For this purpose the heated strip was coated with calcium oxide and used as a cathode, being raised to -1800 v. The third electrode was brought to a potential of -2000 v. and the plate C earthed. The stream of electrons or negative ions emitted by the strip produced by collision with the gaseous molecules positive ions which were directed towards the third electrode charged to a higher negative potential, and the rate of production of positive ions by the electrons was measured in the same way as before. The strip was kept at a comparatively low temperature (dull red) in order to avoid the discharge setting in. Since no positive ions could be expected to be set free by the electrons from

the surface of the anode P, it was interesting to compare the results of these experiments with the results given above. The ratio R proved to be strictly proportional to the pressure in the bulb, but at a given pressure R was much smaller (about one-third) than in the case of positive ions producing electrons by collision. This is not at all surprising if we bear in mind that the free path of electrons moving with large velocities is much longer than that of the positive ions.

It may be mentioned here that the method and apparatus described in this paper proved to be useful also for the study of some questions in connexion with ionization by collision, and for the determination of the free path of electrons and positive ions in rarified gases.

6. In the experiments described in the previous chapter the energy of the positive ions was acquired by their fall through a potential difference not exceeding 2000 v. Attempts were also made, however, to carry out the same experiments by applying much greater electric forces between the heated strip and the plate P. The difficulties in such experiments mainly arise from the fact that the strip and the third electrode have to be brought to different potentials, and the potential difference between them must be kept steady and comparatively small. All attempts to use an induction-coil for this purpose were unsuccessful. The writer hopes to continue these experiments by means of a motor-generator or other source of large and sufficiently steady electromotive force.

Summary.

I. It is shown that the initial discharge of electricity through vacuum-tubes is not brought about by the impact of positive ions against the surface of the cathode.

II. A method is described by means of which the stream of ions or electrons emitted from a hot wire in a vacuum-tube may be isolated from the ions produced by collision within the tube.

III. It is shown that positive ions impinging upon the cathode with velocities corresponding to a fall through a potential difference up to 2000 volts, are unable to liberate electrons from the surface of the cathode.

XCII. *On the use of Vector Methods in the Derivation of the Formulæ used in Inductance and Capacity Measurements. By* H. H. POOLE, *Sc.D.**

THE various formulæ used in methods, such as Anderson's, for the comparison of Inductances and Capacities are usually obtained in the text-books by the use of algebraic methods. It does not seem to be generally recognized how easily these expressions can be obtained geometrically from the vector diagrams representing the currents in the various arms. This method possesses the advantage of enabling a better mental picture to be formed of the currents in the various arms and their mutual phase relationships.

A few examples are given here of the derivation of the required expressions in some important cases. We assume that an alternating current generator of frequency $\frac{\omega}{2\pi}$ is used as a source, and any form of detector, such as a telephone or vibration galvanometer. We further assume that the system is balanced, *i. e.* that the two terminals of the telephone are represented by a single point on the P.D. vector diagrams, for a pure sine wave of the given frequency. We find that in order that this may be true, certain relationships must exist between the various arms, but that these relationships are independent of ω; and hence, if the system is balanced for one frequency, it is balanced for all. Moreover, as any disturbances can be resolved into sinusoidal disturbances of suitable amplitudes and frequencies, the system will be balanced for any disturbance whatever.

This will only be the case if the inductances and capacities used are independent of the frequency. This will be very nearly true of inductances which do not contain iron, at musical or lower frequencies, but will not be true for inductances containing iron cores. The capacity of a condenser with a solid dielectric generally varies slightly with the frequency. This causes a slight variation in the balance for the various harmonics in the rather complex wave emitted by a buzzer and transformer, so that perfect silence is rarely attained, and the predominant note of the telephone changes its pitch in passing through the point of balance. A similar effect may occur with inductances owing to the capacity between different layers of windings, which may cause an appreciable change in the effective inductance for the

* Communicated by the Author.

higher harmonics. This is in some ways rather an advantage, as after a little practice one recognizes by the sound which side of the best balance has been reached.

In what follows, one point of the system O is taken as the zero of potential. Points on the circuit diagram which are at the same potential when a balance has been attained are represented by the same letter, being distinguished by suffixes. Currents are denoted by c's with suffixes. Capital R's are used for the entire resistances of arms possessing self-inductance (L). In some cases I is used for the impedance of such an arm and θ for its phase-angle, ρ being used for the total impedance of two or more arms in series or parallel. Small r's represent non-inductive resistances, M's mutual inductances, and K's capacities.

With each circuit diagram is shown the corresponding vector diagram. The vectors in every case, except fig. 8, represent falls in pressure in the corresponding arms. The diagrams are lettered to correspond, points on the vector diagrams not corresponding with any points on the circuit diagrams being distinguished by the letters P, Q, S, etc. V represents the P.D. generated by the source which is assumed to be constant in some cases. Any phase-angles employed are marked on the vector diagrams.

Comparison of Two Self-Inductances [*Maxwell's Method*].

Fig. 1.

Circuit Diagram   Vector Diagram
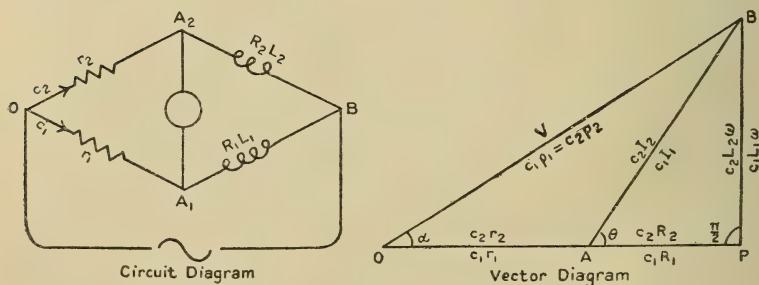
Here A_1 is at the same potential as A_2, both being represented by A on the vector diagram. The current c_1 in OA_1 also flows through A_1B, similarly the current c_2 in OA_2 flows through A_2B. It is evident that the vector diagram represents equally well the branch OA_1B or the branch OA_2B, every point on the diagram for one branch coinciding with the corresponding point for the other.

Hence

$$
\left.
\begin{array}{l}
c_1 r_1 = c_2 r_2 \\
c_1 R_1 = c_2 R_2 \\
c_1 L_1 \omega = c_2 L_2 \omega
\end{array}
\right\} \quad \therefore \quad \frac{r_1}{r_2} = \frac{R_1}{R_2} = \frac{L_1}{L_2}.
$$

Hence both these conditions must be fulfilled in order that a balance may be obtained. The method is evidently much more easily employed if one of the inductances is variable. It is further considered later.

Comparison of Two Mutual Inductances [*Maxwell's Method*].

Fig. 2.

Circuit Diagram   Vector Diagram
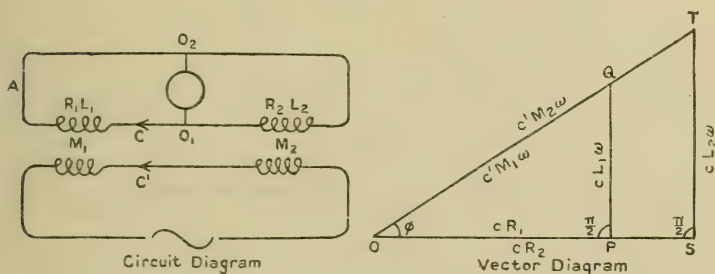
Here the points O_1 and O_2 are at the same potential, so the fall in potential due to the impedance of the arm $O_1 A O_2$ must be balanced by the E.M.F. due to the current c' in the primary of the mutual inductance M_1. The triangle OPQ represents the vector diagram of this arm. The same current c flows in the arms $O_1 A O_2$ and $O_2 B O_1$, and the current c' in the primaries of the two mutual inductances is also identical. Hence the triangle OST representing the vector diagram of the arm $O_2 B O_1$ is similar to OPQ.

Hence

$$
\frac{c R_1}{c R_2} = \frac{c L_1 \omega}{c L_2 \omega} = \frac{c' M_1 \omega}{c' M_2 \omega},
$$

so

$$
\frac{R_1}{R_2} = \frac{L_1}{L_2} = \frac{M_1}{M_2}.
$$

Hence a perfect balance can only be obtained if the self-inductances are in the same ratio as the mutual inductances. If, however, we make the non-inductive resistances in series with the coils L_1 and L_2 large, the angle ϕ will become very small and a fair balance will be attained when $\dfrac{R_1}{R_2} = \dfrac{M_1}{M_2}$.

3 F 2

In comparing two mutual inductances, there are evidently four possible arrangements, as we can interchange the primary and secondary of either coil. We see that it is generally best to use the low-inductance side of each coil as secondary except in the case where some other arrangement would make the ratio of the secondary self-inductances near the desired value.

Comparison of a Mutual with a Self-Inductance [Maxwell's Method].

Fig. 3.
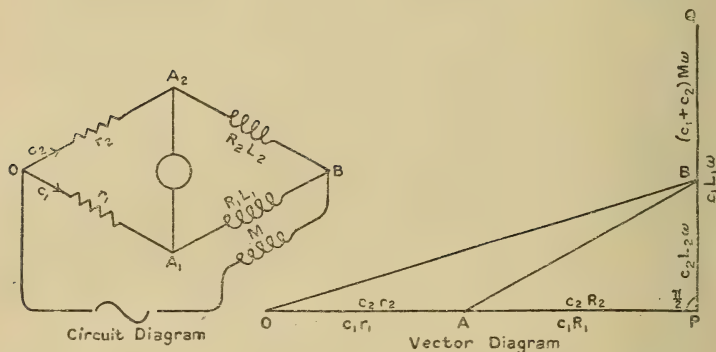
Since A_1 and A_2 are at the same potential, c_1 and c_2 are evidently in phase, so the current in the primary of M is $c_1 + c_2$. The vector diagram is obviously as shown, being identical with fig. 1 as far as the branch OA_2B is concerned. In the branch OA_1B we have a driving E.M.F., $(c_1 + c_2)M\omega$, represented by BQ. This must be subtracted from the fall of potential $c_1L_1\omega$ [PQ], with which it is in phase. The difference must be equal to $c_2L_2\omega$.

Hence

$$\left.\begin{array}{l} c_1r_1 = c_2r_2 \\ c_1R_1 = c_2R_2 \\ c_1L_1\omega = c_2L_2\omega + (c_1 + c_2)M\omega \end{array}\right\} \therefore \quad \frac{r_1}{r_2} = \frac{R_1}{R_2} = \frac{L_1 - M}{L_2 + M},$$

$$\therefore \quad L_1 = \frac{r_1}{r_2}L_2 + \left(1 + \frac{r_1}{r_2}\right)M.$$

In the Campbell Inductometer Bridge, as used with unequal arms for measuring large self-inductances, the inductance L to be measured is inserted in series with the secondary L' of the mutual coil, so that $L_1 = L + L'$.

A balancing inductance, $L_2 = \dfrac{r_2}{r_1} L'$, is inserted in the arm A_2B. This evidently cancels out with L', and we are left with $L = \left(1 + \dfrac{r_1}{r_2}\right) M$. The most convenient ratio for $\dfrac{r_1}{r_2}$ is either 9 or 99, the appropriate balancing coil being accordingly $\dfrac{L'}{9}$ or $\dfrac{L'}{99}$.

When used with equal arms for small self-inductances the secondary of M is divided, half being in each of the arms A_1B and A_2B. The vector diagram becomes slightly altered, as PB is now equal to $c_2 L_2 \omega + \dfrac{(c_1 + c_2) M\omega}{2}$ and BQ to $\dfrac{(c_1 + c_2) M\omega}{2}$, half of the mutual inductances being in each arm. [The connexions, of course, are such that when the E.M.F. induced in the lower arm is in the direction A_1B, that in the upper is in the direction BA_2.] The equations remain as before, and since the value of L' is the same in each arm this cancels, so we get $L = 2M$ where L is the self-inductance to be measured, and, as before, forms part of the arm A_1B.

Comparison of Two Capacities [*De Sauty's Method*].

Fig. 4.

Circuit Diagram
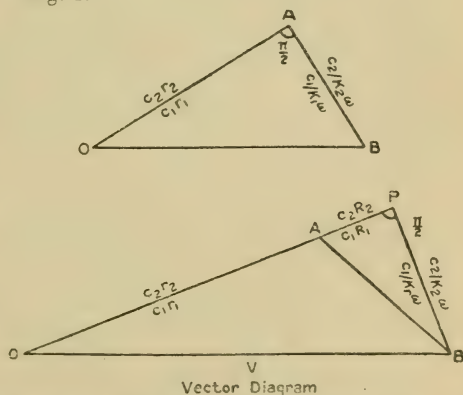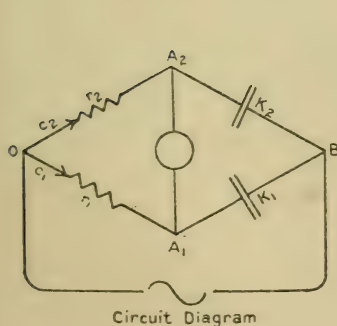
Vector Diagram

The argument is identical with that for self-inductances. The upper vector diagram refers to the case of condensers which are perfectly free from either dielectric hysteresis or leakage, so that the currents through them are in exact quadrature with the P.D.'s across their terminals.

Evidently

$$c_1 r_1 = c_2 r_2$$
$$\left. \frac{c_1}{K_1 \omega} = \frac{c_2}{K_2 \omega} \right\} \quad \therefore \quad \frac{K_1}{K_2} = \frac{r_2}{r_1}.$$

In the case of an imperfect condenser some power is absorbed and the angle OAB is obtuse. This waste of power may be due either to actual leakage or to dielectric hysteresis, or both. In any case, the current will be nearly identical with that which would pass through a perfect condenser K and a resistance R in series [or alternatively a condenser K' and a resistance R' in parallel]. K and R will probably depend somewhat on the P.D. and frequency, and the current through the actual condenser will probably not be perfectly sinusoidal, so the representation is only approximate.

If we obtain a balance with two such condensers, the conditions must be represented by the lower vector diagram. Evidently, as before,

$$\frac{r_1}{r_2} = \frac{R_1}{R_2} = \frac{K_2}{K_1}.$$

We shall almost certainly have to insert a resistance in series with one condenser in order to obtain a balance.

If we have a perfect condenser K_1 [say, an air condenser] we can use this method to measure the effective value of R_2 for another condenser K_2, and hence find its power-loss for any given frequency and voltage. We cannot hope for perfect silence, as a sinusoidal P.D. wave would probably not give rise to a sinusoidal current through an imperfect condenser.

Comparison of a Self-Inductance with a Capacity [Anderson's Method].

The branch OA_1C is similar to OA_1B in fig. 1, and is similarly represented on the vector diagram. The current c_3 through the condenser (assumed perfect) is $\frac{\pi}{2}$ in advance of the P.D. (OA); hence, as AB represents the fall in pressure due to this current passing through the resistance r_3, the angle OAB is right. The vector OB must represent the fall in pressure in the arm OB. The lengths of these vectors are

evidently as shown in the figure. The current in BC is the vector sum of c_2 and c_3, so in finding the components of BC

Fig. 5.

Circuit Diagram

Vector Diagram
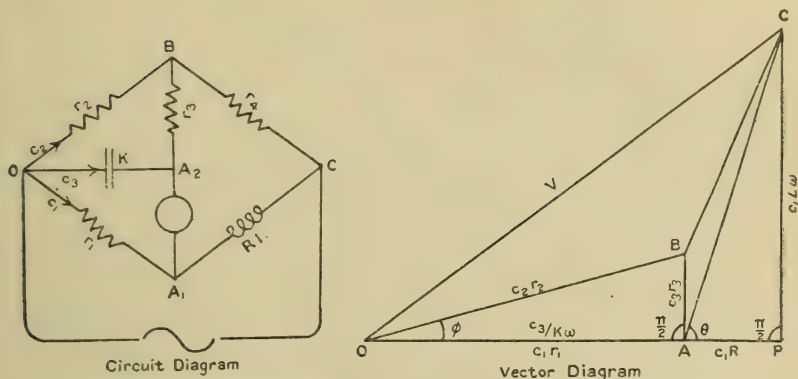
along and perpendicular to OP we may treat each current separately. Resolving along OP we have

$$c_1 r_1 = \frac{c_3}{K\omega} = c_2 r_2 \cos \phi$$

and $\qquad c_1 R_1 = c_2 r_4 \cos \phi$;

$\therefore \quad \dfrac{r_1}{R_1} = \dfrac{r_3}{r_4}$, the condition for steady current balance.

Resolving perpendicular to OP, we have

$$c_3 r_3 = c_2 r_2 \sin \phi$$

and $\qquad c_1 L\omega = c_3 r_3 + c_3 r_4 + c_2 r_4 \sin \phi,$

$$= c_3 \left[r_3 + r_4 + \frac{r_3 r_4}{r_2} \right];$$

or since $\qquad c_3 = c_1 r_1 K\omega \quad \text{and} \quad r_1 r_4 = r_2 R, \quad \text{we get}$

$$L = K \left[r_1 r_4 + r_3 (r_1 + R) \right].$$

If we can obtain a balance with $r_3 = 0$, *i.e.* the points A_2 and B coincident, we have the simpler formula $L = K r_1 r_4$. This method is, however, less convenient unless either L or K is infinitely variable.

Comparison of a Mutual Inductance with a Capacity
[*Carey Foster's Method*].

Fig. 6.

Circuit Diagram   Vector Diagram

Here, since A_1 and A_2 are at the same potential, the triangle OPA evidently represents the P.D. vectors for the arms OA_1 and OA_2. The fall in potential due to the impedance of the arm A_2BA_1, through which the current c_2 passes, must be balanced by the E.M.F. induced in it by the mutual inductance M. Now, the current in the primary of the latter is the vector sum of c_1 and c_2, therefore this E.M.F. must be the vector sum of $c_1 M\omega$ and $c_2 M\omega$, each vector being $\frac{\pi}{2}$ in advance of the corresponding current vector. [The primary of M must obviously be so connected that the E.M.F. is in the desired direction.] Hence, the figure AQST represents this part of the circuit, the lengths of the vectors being as shown. The triangles OPA and SQA are evidently similar, so

$$\sin \phi = \frac{c_2}{K\omega c_1 r_1} = \frac{c_2 R}{c_1 M\omega},$$

$$\therefore \quad M = K r_1 R :$$

and

$$\cos \phi = \frac{c_2 r_2}{c_1 r_1} = \frac{c_2(L-M)\omega}{c_1 M\omega},$$

$$\therefore \quad \frac{L}{M} = 1 + \frac{r_2}{r_1}.$$

We must remember in using this method for measuring a capacity by means of a variable mutual inductance, that if we make r_2 infinite, c_2 becomes zero, and we obtain a perfect balance with $M=0$. If we start with a very large value

of r_2, the vectors AQ, QT, and TS, which are proportional to c_2, are very small, and though a true balance is impossible, we shall obtain the least sound by making M very small. To avoid this trouble it is best to commence balancing with r_2 small or even zero.

It is fairly evident that we would not expect a very sensitive balance if the triangle SQA is very much smaller than the triangle OPA. This implies that r_1 should not be very much bigger than Mω. The latter is not likely to exceed a few ohms, even if we use the variable mutual inductance near its major limit, as is evidently the best. On the other hand, unduly reducing r_1 will considerably reduce the available P.D. OA across the condenser terminals, and may even cause the current c_1 to become so large as to cause overheating. We must remember that OA does not represent the full voltage of the generator, as the effective impedance of the mutual inductance primary must be considered.

Effect of a Small Deviation from an Exact Balance.

It is interesting to consider the application of the geometrical method to the calculation of the telephone current caused by a slight variation from exact balance. This calculation becomes somewhat cumbrous if treated exactly, all the factors being taken into consideration. If, however, we assume, as a first approximation, that the impedance of the telephone is so high that the current through it is negligible, we can, in certain cases, easily find the P.D. across its terminals. We thus arrive at certain conclusions as to the best conditions for accuracy which are probably near enough to the truth to be of use in practice, at least in cases where a high-resistance telephone is used. We can then consider the effect of the current passing through the telephone, and also the loss of voltage due to the impedance of the generator. These impose further conditions which must be approximately satisfied if the most sensitive arrangement is required.

The method is best suited to measurements not involving mutual inductance. Two such cases are considered below.

Comparison of Self-Inductances.

Suppose we are measuring a self-inductance L_1 by comparison with a standard L_2. We want to arrange that a given error in L_1 should produce the maximum effect on

the telephone.   We must also consider the effect of a small change in one resistance, say R_1.

(1) Let L_1 become $L_1 + \delta L_1$, all the other quantities remaining as before.   Neglecting the telephone current, the vector diagram of fig. 1 now becomes as shown in fig. 7. The points O, A_2, P_2, and B are unchanged from their original positions, but A_1 and P_1 have separated as shown from A_2 and P_2.

Fig. 7.
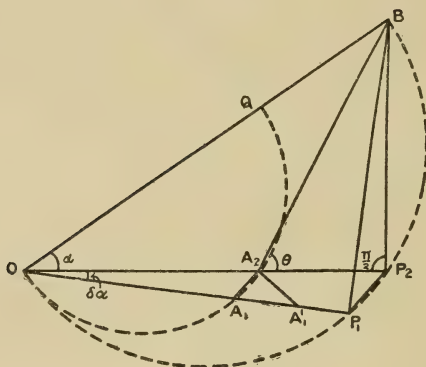
It is evident that as the angle OPB is always right, P moves on a semicircle on OB as diameter.   Also, since the resistances are unchanged, the triangle OA_1A_2 is clearly similar to OP_1P_2, so that A_1 lies on the semicircle OA_2Q on OQ as diameter, where

$$\frac{OQ}{OB} = \frac{r_1}{r_1 + R_1} = \frac{r_2}{r_2 + R_2}.$$

For a very small motion A_1A_2 is a tangent to this circle, so that it is evident that the angle OA_2A_1 is equal to $\frac{\pi}{2} - \alpha$.

Let δE be the P.D. (A_1A_2 on the figure) across the telephone terminals due to the increment δL.

Then

$$\delta E = \frac{c_1 r_1 \delta \alpha}{\cos \alpha} = c_1 r_1 \cos \alpha \, \delta (\tan \alpha).$$

Now $\cos \alpha = \dfrac{r_1 + R_1}{\rho_1}$, where ρ_1 is the total impedance of branch $\hat{O}A_1B$,

and $\tan \alpha = \dfrac{L_1 \omega}{r_1 + R_1}$, so $\delta(\tan \alpha) = \dfrac{\omega \delta L}{r_1 + R_1}$.

Hence $\delta E = \dfrac{c_1 r_1 \omega \delta L}{\rho_1} = \dfrac{V r_1 \omega \delta L}{\rho_1{}^2}$.

(2) Let R_1 become $R_1 - \delta R_1$, the inductances and all the other resistances remaining at the balancing values. P again moves in the same direction along the semicircle OP_2B to some point P_1 (fig. 7). Let A_1' be the corresponding position of A so that $A_1'A_2$ represents the P.D. $\delta E'$ across the telephone. Since r_1 and L_1 are unchanged,

$$\frac{OA_1'}{OA_2} = \frac{BP_1}{BP_2} = \frac{c_1 + \delta c_1}{c_1}.$$

Also angle $P_1OP_2 =$ angle P_1BP_2, so the triangles $OA_2A'_1$ and BP_2P_1 are evidently similar, so that when $\delta \alpha$ is small the angle $OA_2A_1' = \pi - \alpha$.

Hence we see that A_2A_1 is perpendicular to A_2A_1', *i.e.* the P.D. across the telephone due to a small difference between $\dfrac{L_1}{L_2}$ and $\dfrac{r_1}{r_2}$ is in quadrature with that caused by a small difference between $\dfrac{R_1}{R_2}$ and $\dfrac{r_1}{r_2}$. This fact greatly helps the operation of balancing, especially if our standard inductance is variable, as, even if $\dfrac{R_1}{R_2}$ has not exactly the right value, the inductance ratio which gives the least sound is very nearly $\dfrac{r_1}{r_2}$. Similarly, if this adjustment is imperfect, the value of $\dfrac{R_1}{R_2}$ which gives the least sound is $\dfrac{r_1}{r_2}$. Hence we can make the final adjustments independently and successively, repeating the steps until the best balance is reached.

We have

$$\delta E' = \frac{c_1 r_1 \delta \alpha}{\sin \alpha} = \frac{c_1 r_1 \cos \alpha \cdot \delta(\tan \alpha)}{\tan \alpha}.$$

Hence, as $\delta(\tan\alpha) = \dfrac{L\omega\delta R_1}{(r_1+R_1)^2}$, δR_1 being a decrement in R,

$$\delta E' = \frac{c_1 r_1 \delta R}{\rho_1} = \frac{V r_1 \delta R}{\rho_1{}^2}.$$

If there are errors δL_1 and δR_1 in L_1 and R_1 respectively, the resultant P.D. across the terminals of the telephone is evidently

$$\frac{V r_1}{\rho_1{}^2}\sqrt{\omega^2\delta L_1{}^2 + \delta R_1{}^2}.$$

In order to measure a given inductance as accurately as possible, we must arrange that a given error δL_1 in it shall produce the maximum value of δE_1.

R_1 should evidently be as small as possible since $(r_1+R_1)^2 + L_1{}^2\omega^2$ occurs in the denominator. Unless our standard inductance L_2 is variable, it will probably be necessary to introduce a non-inductive resistance in series with the coil L_1 in order to effect a balance, but this should be as small as possible.

It is obvious that $\dfrac{\delta E_1}{\delta L_1}$ vanishes if r_1 is either zero or infinity, so there must be some value of it for which this quantity is a maximum.

Since

$$\frac{\delta E_1}{\delta L_1} = \frac{V\omega r_1}{\rho_1{}^2} = \frac{V\omega r_1}{(r_1+R_1)^2 + L_1{}^2\omega^2},$$

$$\frac{\partial}{\partial r_1}\left(\frac{\delta E_1}{\delta L_1}\right) = \frac{V\omega}{\rho_1{}^4}\left[(r_1+R_1)^2 + L_1{}^2\omega^2 - 2r_1(r_1+R_1)\right];$$

so for a maximum value of $\dfrac{\delta E_1}{\delta L_1}$ we must make

$$r_1{}^2 = R_1{}^2 + L_1{}^2\omega^2 = I_1{}^2,$$

where I_1 is the impedance of the arm A_1B. This implies that on the vector diagram (fig. 1) $OA = AB$. The same condition evidently ensures a maximum value of $\dfrac{\delta E'}{\delta R_1}$.

We see that for a given value of ω it is best to make $r_1 = I_1$, so that

$$\frac{\delta E}{\delta L_1} = \frac{V \omega I_1}{\rho_1^2},$$

but $\qquad \rho_1^2 = r_1^2 + I_1^2 + 2 r_1 I_1 \cos \theta \quad \text{(see fig. 1),}$

$$= 2 I_1^2 (1 + \cos \theta) \quad \text{when} \quad r_1 = I_1,$$

and $\quad I_1 \sin \theta = L_1 \omega$;

$$\therefore \quad \frac{\delta E}{\delta L_1} = \frac{V \sin \theta}{2 L (1 + \cos \theta)} = \frac{V}{2 L} \tan \frac{\theta}{2}.$$

Hence we should use the highest available frequency in order to make θ as large as possible.

In the case considered above the available voltage V is assumed to be fixed and the telephone impedance infinitely high. In this case it is evident that the points O, A_2, and B on the vector diagram being fixed independent of L_1, the sensitivity is independent of the magnitudes of r_2, R_2, and L_2, and all we need do is to make the ratios of these quantities correct.

In practice, a current flows through the telephone and reduces the P.D. δE, the amount of this reduction depending on the resistances and reactances of the bridge-arms as compared with the telephone. It is not necessary to consider the question very exactly, as it is obvious that the smaller r_2, R_2, and L_2 are, the lower will be the impedance to this transverse current and the smaller the reduction in δE. We do not, however, gain much by making r_2, R_2, and L_2 much smaller than r_1, R_1, and L_1 respectively. The latter quantities may be regarded as already fixed, since it has been shown above that r_1 should be approximately equal to I_1.

On the other hand, it is evident that the smaller r_2, R_2, and L_2 are, the larger will be the current c_2, and, if the generator resistance is appreciable, the smaller the available voltage V. There is not much use, however, in attempting to reduce the total generator current by making the impedance ρ_2 very much greater than the parallel impedance ρ_1.

Hence we see, in a general way, that it is best to have r_2, R_2, and L_2 of about the same size as r_1, R_1, and L_1 respectively.

Summarizing these points, we see that in measuring a given inductance L_1 by comparison with a standard L_2 we should endeavour to satisfy the following conditions :—

(1) The frequency used should be as high as possible.
(2) The resistances R_1 and R_2 should be as small as possible compared with the reactances $L_1\omega$ and $L_2\omega$.
(3) The resistances r_1 and r_2 should be about equal to the impedances of the corresponding inductive arms.
(4) The inductances L_1 and L_2 (and hence the corresponding resistances) should not differ greatly in magnitude.

The first three conditions may be further summarized by the statement that the triangle OAB should be approximately isosceles and as nearly as possible right angled.

Comparison of a Self-Inductance with a Capacity.

Suppose we are measuring a given self-inductance by comparison with a standard condenser, it is evident that if we neglect the current through the telephone and assume V constant, the points O, A_2, B, and C (fig. 5) are unaffected by the changes of L and R, while A_1 moves exactly as in the last case, and we arrive at the same conclusions.

As before, the current that actually flows through the telephone renders it expedient to make the transverse impedance as low as possible. In this case it is perhaps worth while considering the magnitude of this impedance more fully. Strictly speaking, we should also consider the angle between this impedance vector and that for the telephone, but this would involve a knowledge of the angle of lag of the telephone. As, however, this angle of lag seems unlikely to be very large, and hence the angle between the two impedance vectors will probably be small compared with a right angle, it will suffice to make the network impedance as low as possible and disregard its phase-angle.

Let us neglect the generator impedance, so that as far as the small transverse current, which may be regarded as superimposed on the main currents, is concerned, we may treat the network as two impedances ρ' and ρ'' in series, ρ' being the impedance of the branches A_2BO and A_2BC and the arm A_2O in parallel, and ρ'' that of OA_1 and CA_1 in parallel.

The resistance of A_2BO and A_2BC is $r_3 + \dfrac{r_2 r_4}{r_2 + r_4}$, but since

$$r_3 = \frac{\dfrac{L}{K} - r_1 r_4}{r_1 + R} \quad \text{and} \quad \frac{r_2 r_4}{r_2 + r_4} = \frac{r_1 r_4}{r_1 + R},$$

this reduces to $\dfrac{L}{K(r_1 + R)}$.

The reactance of A_2O is $\dfrac{1}{K\omega}$;

$$\therefore \quad \frac{1}{\rho'^2} = \frac{K^2(r_1 + R)^2}{L^2} + K^2\omega^2 = \frac{K^2\rho^2}{L^2},$$

where ρ is the impedance of the branch OA_1C.

So $\rho' = \dfrac{L}{K\rho}$, and if α is the angle of lead of the joint current $\tan\alpha = \dfrac{L\omega}{r_1 + R}$, so α is equal to the angle POC (fig. 5).

ρ'' is most easily obtained from the admittance vector diagram for the arms OA_1 and CA_1 in parallel.

Fig. 8.
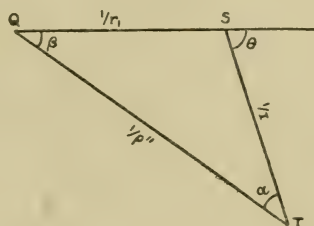
Here I is the impedance of A_1C and θ its angle of lag. We have

$$\frac{1}{\rho''^2} = \frac{1}{r_1^2} + \frac{1}{I^2} + \frac{2\cos\theta}{r_1 I} = \frac{\rho^2}{r_1^2 I^2}; \qquad \therefore \quad \rho'' = \frac{r_1 I}{\rho},$$

also $$\sin\beta = \frac{\rho''}{I}\sin\theta = \frac{r_1}{\rho}\sin\theta\,;$$

so β, the angle of lag of the total current in these arms, is

evidently equal to the angle OCA in fig. 5. The triangles QST (fig. 8) and CAO (fig. 5) are clearly similar, so angle QTS (fig. 8) is equal to angle α above, and $\alpha + \beta = \theta$.

Hence, to find the total impedance to the transverse current we must compound the two vectors ρ' and ρ'', the angle between them being θ. Now, this angle is always acute, and the vector ρ'' may be regarded as fixed by the condition that r_1 should be equal to I, so to obtain a minimum transverse impedance we should make ρ' as small as possible, *i.e.* K should be large.

Two rather interesting conclusions have here been reached.

> (1) Given r_1, R, and L, the transverse impedance depends solely on the value of K, and not on the distribution of the resistance necessary for balancing between the arms r_2, r_3, and r_4.
>
> (2) Owing to the angle θ being acute, no reduction in the transverse impedance by " tuning " is possible, *i.e.* there is no value of K giving a minimum impedance for a given frequency.

Under the best conditions of working, $r_1 = I = L\omega$ nearly and $\cos\theta$ is small, so

$$\rho = L\omega\sqrt{2}, \quad \rho' = \frac{1}{K\omega\sqrt{2}}, \quad \text{and} \quad \rho'' = \frac{L\omega}{\sqrt{2}};$$

so the total transverse impedance is not much greater than

$$\sqrt{\frac{1}{2}\left(\frac{1}{K^2\omega^2} + L^2\omega^2\right)}.$$

In most cases $\dfrac{1}{K\omega}$ will be greater than $L\omega$. For example, if $\omega = 3300$, corresponding to the Note C in the treble clef, and our largest available condenser is 1 microfarad, $\dfrac{1}{K\omega} = 300$ ohms. If $L = 0{\cdot}05$ henry [which is a comparatively large value for a coil without an iron core], $L\omega = 165$ ohms. Hence in most cases we should use the largest available condenser, though little would be gained by the use of one whose capacity greatly exceeded $\dfrac{1}{L\omega^2}$, even if it were available.

It must be remembered that a large value for K entails a small value for $r_1 r_4 + r_3(r_1 + R)$. As before, it is a disadvantage to have r_2 and r_4 small, as this causes excessive

current and reduces the available voltage ; hence r_3 should be as small as possible, in order that for a given condenser r_2 and r_4 may be as large as possible.

If we have to measure a condenser, it is easily seen, as before, that we should choose a self-inductance coil with a large value of $\dfrac{L}{R}$; so if we employ a variable self-inductance, it should be used near its upper limit. The larger the value of L the higher will be the transverse impedance, but the less the "lost volts" due to generator impedance. It is probable that the largest available self-inductance will be considerably smaller than $\dfrac{1}{K\omega^2}$; so the transverse impedance due to it will not be very important, and its use will be advantageous.

We may conclude by summarizing these points as follows :—

(1) The frequency should be as high as possible.

(2) R should be as small as possible.

(3) r_1 should be about equal to I, the impedance of the inductive arm.

(4) r_3 should be small.

(5) Since K is in most cases considerably smaller than $\dfrac{1}{L\omega^2}$, it is best to use the largest available condenser for measuring a given self-inductance and *vice versâ*.

Physical Laboratory,
　Trinity College, Dublin.
　　September 8, 1920.

XCIII. *Elements in the Sun**. (Paper B.)　*By* Megh Nad Saha, *D.Sc., Lecturer on Physics and Applied Mathematics, University College of Science, Calcutta* †.

IT is a matter of common knowledge that the continuous spectrum from the photosphere of the sun is crossed by a number of dark lines, which are called Fraunhofer lines in honour of their eminent discoverer. The correct inter-

* Much of the introduction is taken, *mutatis mutandis,* from Fowler's Report on the subject; *vide* 'Journal of the British Astronomical Society,' May 1918.

† Communicated by the Author.

pretation of these lines was given by Kirchhoff in 1859, who showed that most of the principal lines can be attributed to the absorption of light of proper frequency by the cooler layers of the vapour lying above the photosphere. Since this epoch-making discovery, it has become a part of the routine work of astrophysicists to catalogue and properly measure the wave-length of these lines, and identify them with the emission lines of elements obtained in the laboratory.

The most extensive mapping of the Fraunhofer spectrum is due to Rowland, who counted and catalogued about 20,000 lines, but of these only 6000 have been identified with the lines of known elements. By this means, the presence of thirty-six elements has been definitely established in the sun, with doubtful indications of eight or more. The following are the elements of the existence of which in the sun no evidence has yet been obtained * :—

(A). Rubidium, Cæsium; Nitrogen, Phosphorus, Boron, Antimony, Bismuth, Arsenic; Sulphur, Selenium; Thallium, Praseodymium.

Doubtful indications have been obtained of the existence of the following elements :—

(B). Radium † ; elements of the inert group with the exception of Helium, which is obtained in the flash spectrum, Osmium, Iridium, Platinum, Ruthenium, Tantalum, Thorium, Tungsten, Uranium.

The following elements are represented by very faint lines in the Fraunhofer spectrum :—

(C). Potassium, Copper and Silver; Cadmium and Zinc; Tin and Lead; and Germanium.

(D). Chlorine, Bromine, Iodine, Fluorine, Tellurium, and many other elements have not been investigated at all.

No satisfactory explanation has yet been offered of the complete non-existence of the lines of elements mentioned in group (A) or (B), or of the faint occurrence of the lines of elements mentioned in group (C). Similarly, it has not yet been made clear why certain elements like Ca, Fe, V, Ti are so unusually prominent in the solar spectrum. They are represented not only by the absorption lines of the neutral atom, but also by the absorption lines of the ionized atom (enhanced lines).

It is sometimes assumed that these phenomena are due to the chemical composition of the sun—in other words, the

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* Pringsheim, *Physik der Sonne,* p. 116.

† For the controversy regarding the existence of Radium, and the members of the inert group in the flash-spectrum, see 'Observatory,' vol. xxxv. pp. 297, 357, and 402.

elements of which no lines are found either in the Fraunhofer or the flash spectrum are totally absent from the sun. But this view is most unsatisfactory, and can only be regarded as a stop-gap. There is, *à priori*, no reason why, in the sun, certain elements should be preferred to the exclusion of others. On the contrary, it seems natural to infer that the sun is composed of the same elements as the earth, and contains all the 92 elements known to the chemists on the earth.

It therefore becomes increasingly necessary to investigate why certain elements should entirely fail to be recorded on the Fraunhofer or the flash spectrum. It may be supposed that certain elements fail to be recorded because, on account of their heavy atomic weight, they are practically confined to the photosphere. But it is not merely a question of atomic weight, for in the list of missing elements we find light elements like boron and nitrogen side by side with a heavy element like thallium.

The view which is urged in the present paper is *that the varying records of different elements in the Fraunhofer spectrum may be regarded as arising from the varying response of these elements with regard to the stimulus existing in the sun. The stimulus existing in the sun is the same for all elements, viz., that arising from a temperature of about* $7500°$ K., *but owing to different internal structure, elements will respond in a varying degree to this stimulus.* The manner in which we can quantitatively estimate the effect of the stimulus has been sketched in papers A and C*. In paper A, the effect of the stimulus on the alkaline earths Ca, Sr, and Ba was estimated. It was shown that while on the photosphere 30, 40, and 57 per cent. of the atoms are respectively ionized, the percentage of ionization increases with height and becomes practically complete for Ca at a pressure of 10^{-6} atm., for Sr at a pressure of 10^{-3}, and for Ba at a pressure of 10^{-2} atm. In this connexion it may prove interesting to compare the results with the following remarks of Fowler :—

" We find further, that while many of the metals are represented by both arc and enhanced lines, there are some which are identified only, or mainly, by their enhanced lines alone. Thus, although Ca shows both classes of lines strongly, Sr and Ba practically show enhanced lines alone."

Fowler ascribes the different behaviour of Ca on the one

* Paper A—" Ionization in the Solar Chromosphere," Phil. Mag. Oct. 1920 ; Paper C—" On the Temperature Radiation of Gases " (to appear shortly).

hand, and Sr and Ba on the other hand, to their differences in atomic weight, but according to the view presented in paper A, this is mainly due to the varying values of the *ionization potential*. The author's belief is that in the sun and the stars, the attraction due to gravity is largely compensated by selective radiation pressure, and atomic weight is of much less consequence than can be supposed.

The method sketched in paper A has been extended to the alkali metals, and a few other elements. It will be seen that the theory accounts in a most gratifying manner for the varying behaviour of sodium lines in the Fraunhofer spectrum, and its intensification in the sun-spot spectrum, for the faint occurrence of the potassium lines, and for the complete absence of the lines of Cs and Rb, and for the varying behaviour of the lines of Mg and Mg^+, though, on this last point, the results are not so satisfactory. There is very little doubt that if proper data be available, the method can be extended to the explanation of all the details of the Fraunhofer spectrum.

For the explanation of the method, the reader is referred to Sections 2 and 3 of paper A. The temperature of the photosphere has been taken to be $7500°$ K., the pressure 1 to 10^{-1} atm., while for the high-level chromosphere a temperature of $6000°$ K. has been used.

1. The Alkali Elements in the Sun.

(a) *Sodium.*

The following table shows the ionization of sodium in per cents. under varying conditions of temperature and pressure :—

Ionization Potential $= 5\cdot12$ volts $= 1\cdot17 \times 10^5$ calories.

Pressure	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
Temp.						
5000	6	19	53	89	98·5	
6000	21	56	90	98·5		
7000	46	85	98			
7500	60	72	99		Complete	
8000	72	96			Ionization.	
9000	87	98·5				
10000	97					

The table shows that under the solar conditions, 60 per cent. of sodium atoms are ionized in the photosphere, and ionization is practically complete at a level where the pressure falls to 10^{-3} atm. The result is in very good agreement with observational facts, for according to Mitchell the D_1 and D_2 lines reach a level of only 1200 kms. Over this height, only ionized Na atoms are present, the chief emission lines of which lie, according to Goldstein *, in the remote ultra-violet, and so escape detection.

Taking the temperature of the spot $=5000°$ K.†, we see from the tables that only 6 to 19 per cent. of the atoms are ionized. So over the spot, there is a great increase in the proportion of unionized Na-atoms, and we should expect a much stronger absorption of the D_1 and D_2 lines. The following table (taken from Kayser's *Handbuch der Spektroskopie*, vol. vi. p. 114) shows that this is actually the case :—

Line.	Series-Description.	Intensity in the Sun.	Intensity in Sun-spot Spectrum.
$D_1 - 5896 \cdot 15$	$(1, s) - (2, p_2)$	20	60
$D_2 - 5890 \cdot 19$	$(1, s) - (2, p_1)$	30	90
$5682 \cdot 90$	$(2, p_2) - (3, d)$	5	12
$5688 \cdot 26$	$(2, p_1) - (3, d)$	6	12
$6154 \cdot 44$	$(2, p_2) - (3, s)$	2	8
$6161 \cdot 95$	$(2, p_1) - (3, s)$	3	9

(b) *Potassium.*

The identification of Potassium is rather doubtful. Rowland has identified only two faint Fraunhofer lines $\lambda = 4047 \cdot 36$, $4044 \cdot 29$, with the emission lines $(1, s) - (3, p_1)$, $(1, s) - (3, p_2)$ of potassium. The following table shows that owing to the low value of the ionization potential, potassium is highly ionized throughout the whole of the solar atmosphere.

* Goldstein, *Ann. d. Physik*, vol. xxvii. pp. 773–796; Schillinger, *Wien. Ber.* p. 608 (1919); Nelthorpe, Astrophysical Journal, Jan. 1915.

† Emden, *Gas-kugeln*, p. 443. See also numerous papers on the spectra of sun-spots by Fowler, Hale, and others.

Ionization of Potassium.

Ionization Potential $= 4\cdot318$ volts $= 1\cdot00 \times 10^5$ calories.

Pressure	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
Temp.						
3000			2·5	9	28	66
4000	3	11	32	72	97	
5000	15	44	83	98		
6000	41	81	97·5			
7000	70	95				
7500	81	98		Complete		
8000	87	99		Ionization.		
9000	94					
10000	98					

The identification of potassium is to be carried by the lines $(1, s) - (3, p_1)$, $(1, s) -- (3, p_2)$ which under all circumstances are likely to be much less intense than the leading pair $(1, s) - (2, p_1)$, $(1, s) - (2, p_2)$ which lie in the infra red, $\lambda = 7665\cdot3$, $7699\cdot3$. This fact, combined with the high proportion of ionization, tends to make the identification rather difficult. The lines of the ionized atom lie in the ultra-violet, and so escape detection (Goldstein, Astro. Journal, xxvii. pp. 25–34 (1908) and *Ann. d. Phys.* loc. cit.).

Over the spots, the potassium lines ought to be strengthened, but no observation seems to have been made on this point.

(c) *Rubidium.*

As has been mentioned in the introduction, no lines of Rubidium have been identified in the Fraunhofer spectrum of the sun, though in the usual flame and arc spectrum there are many strong lines within the available range.

The following table shows the ionization of rubidium. It will be apparent from the tables that in the sun rubidium is completely ionized. Consequently, even if it be present, we shall get the lines due to the ionized atoms only, which, according to Goldstein [*], lie in the ultra-violet. The spot spectrum should show some faint rubidium lines. But no observation seems to have been made on this point.

* Goldstein, *loc. cit.*

Ionization Potential U = ·96 × 10⁵ calories = 4·16 volts.

Pressure	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
Temp.						
2000						1
2500				2	6	20
3000		1	4	13	37	78
4000	4	17	39	80	98	
5000	19	51	87			
6000	46	85	98			
7000	75	97			Complete	
7500	84	98			Ionization.	
8000	90					
9000	96					
10000	99					

(d) *Cæsium.*

No Cæsium lines have been identified in the Fraunhofer spectrum. The case is identical with that of rubidium, only in a more marked degree. A table of the ionization of cæsium is appended below:—

U = 3·88 volts = ·90 × 10⁵ calories.

Pressure	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
Temp.						
2000					3	8
2500			1	4	11	34
3000		1	4	12	35	75
4000	7	20	53	89	98·5	
5000	25	62	92			
6000	56	90				
7000	81	97·5			Complete	
7500	88	99			Ionization.	
8000	92					
9000	98					

Oxygen.

The presence of oxygen in the sun was a matter of great controversy until a few years ago. The well-known bands A, B, α were shown by Jansen [*] to be of telluric origin— *i. e.*, caused by the absorption of the solar light by the molecular oxygen of our own atmosphere. But Runge and Paschen identified the weak Fraunhofer triplet, λ = 7772·20,

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[*] Pringsheim, *Physik der Sonne*, p. 119 *et seq.*

7774·43, and 7775·62, lying in the extreme red, with the three emission lines of oxygen, having the series formula

$$(2, s) - (m, p_1), \quad (2, s) - (m, p_2), \quad (2, s) - (m, p_3).$$

In the sun, therefore, oxygen exists in the atomic state.

The heat of decomposition of the oxygen molecule is not yet known with certainty. From Langmuir's [*] observation that at 2400° K. and 10^{-1} atmospheric pressure oxygen is completely dissociated, I have calculated provisionally the heat of decomposition to be less than 50,000 calories, which is less than the corresponding value for hydrogen (84,000 cal.). Since the equation of chemical equilibrium is almost the same in both cases [†], it follows without any calculation that oxygen should be completely decomposed into atoms in the sun. The ionization potential of oxygen is probably large, and no lines due to ionized oxygen seem to occur in the sun.

The lines of O^+ and O^{++} have been qualitatively studied by Lunt, Fowler [‡], and Brooksbank, but no series-formulæ have yet been obtained for these lines. But Fowler's identification of certain of these lines in the Bo-class of stars and in Wolf-Rayet stars respectively seem to indicate that the first step ionization of oxygen is reached at an approximate temperature of 20,000° K. and second step ionization at probably not less than 30,000° K.

Magnesium.

The wave-lengths of the strongest lines of the emission-spectrum of Mg, viz. lines $(1, S) - (2, P)$, $(1, S) - (2, p_2)$, lie beyond the range of atmospheric absorption, so that we have to fall upon the next strongest lines, the triplet

$$(2, p) - (3, d_i), \quad i = 1, 2, 3, \quad \lambda = 3838·34, \ 3832·46, \ 3825·51,$$

which are very prominent in the flash spectrum, and reach, according to Mitchell, a level of about 7000° km. The height reached by the line $(1, S) - (2, P)$, $\lambda = 2852$, if it were available for observation, would probably be somewhat higher, say about 9000° km. The brief is strengthened from an examination of the table of ionization given below.

[*] Langmuir, Journ. Chem. Soc. vol. xxxiv. pp. 864, 1030 (1912).
[†] *Vide* Hydrogen in the Sun, paper A, p. 483.
[‡] Fowler and Brooksbank, Month. Not. Roy. Astr. Soc. April 1917.

Ionization of Magnesium.

Ionization Potential $= 7\cdot65$ Volts $= 1\cdot76 \times 10^5$ calories.

Pressure	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.
Temp.					
4000		2.10^{-3}	1	2	9
5000	5.10^{-2}	1	4	11	32
6000	2	6	18	50	87
7000	6	20	54	89	98
7500	11	32	73	96	——
8000	17	47	85	98	
9000	34	75	96	———	
10000	56	90	98		
11000	75	96	———		
12000	86	98			
13000	93	99		Complete	
14000	96	——		Ionization.	
15000	98				
16000	99				

As the ionization potential of magnesium is rather high, it is ionized to a lesser extent than the other alkaline earths. Total ionization is reached at a pressure of about 10^{-6} to 10^{-7} atm. in the chromosphere. This is in excellent accord with observational results.

The lines of ionized magnesium have been studied by Fowler. The lines which should theoretically * turn out to be the strongest, all lie in the ultra-violet, as the following table shows :—

$$(1, s) - (2, p_1)\ldots\ldots 2795\cdot5 \text{ Å.U.}$$
$$- (2, p_2)\ldots\ldots 2802\cdot7$$
$$(2, p_1) - (3, d_1)\ldots\ldots 2798\cdot1$$
$$(2, p_2) - (3, d_2)\ldots\ldots 2790$$
$$(3, d_1) - (4, f)\ldots\ldots 4481,$$

so that the only line available for observation is the leading member of the Bergmann series $\lambda - 4481$ Å.U. According to observation, this reaches a level of 450 km. only.

According to the considerations presented in paper C, lines of this description under all circumstances require not only a higher stimulus, but also a high density of the

* Fowler, Phil. Trans. vol. ccxiv. The intensity given for 4481 is relatively much greater than the intensity of the $(1, s) - (2, p)$ lines.

radiant particles. Though the upper layers of the chromosphere favour relatively stronger ionization, yet the density is so small that such lines fail to be recorded. They are recorded only from the lower regions where the density is sufficiently great, and the stimulus is not much weakened.

Nitrogen in the Sun.

The emission spectrum of Nitrogen is a rather difficult matter to deal with. Under the stimulus in which most of the other elements can be made to emit their characteristic line spectrum or even their enhanced lines, nitrogen gives only several classes of band or molecular spectra. The line spectra seem to require a very great stimulus for their production. But the existing knowledge on the subject is too meagre to allow the discussion of the line emission of atomic nitrogen from the present standpoint According to a recent paper, the ionization potential of N is 17–18 volts, but this must be made up of the energy of dissociation of the molecule plus the energy of ionization of the atom.

If the so-called cyanogen band having its head at $\lambda = 3883$ * be really due to molecular nitrogen, the conclusion follows that in the sun nitrogen occurs in the molecular state. There may be a fair proportion of atomic nitrogen, but the stimulus is not sufficiently strong to make it emit the lines we are familiar with. All these characteristics are in very good accord with the chemical inertness of nitrogen, which is again due to the high value of the heat of dissociation of the N_2 molecule. The fact is only qualitatively known. According to Langmuir †, less than 5 per cent. of nitrogen is dissociated at $3500°$ K. and at atmospheric pressure. From this we may calculate the heat of dissociation in the following manner. The reaction takes place according to the scheme

$$N_2 \rightleftharpoons N + N - U,$$

and if x be the fraction dissociated, P the partical pressure, we have

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2\cdot3RT} + \frac{3}{2} \log T + \Sigma C.$$

Now $$\Sigma C = 2C_N - C_{N_2}.$$

---

* This is the opinion of Runge and Grotian (*Phys. Zeits.* vol. xv. 1914). Fowler, on the contrary, believes that the band is due to CN (cyanogen). See also Barratt, Proc. Roy. Soc. Lond. vol. xcvii.

† Langmuir, Journal of the American Chem. Soc. vol. xxxiv. p. 860 (1919).

According to the Tetrode-Sackur formula,

$$C_N = -1{\cdot}6 + \frac{3}{2} \log M = {\cdot}119,$$

and $C_{N_2} = -{\cdot}05$ *.

Taking $x = {\cdot}03$ in Langmuir's experiment, we can calculate U from the above formula ; we obtain

$$U = 1{\cdot}50 \times 10^5 \text{ calories, in round numbers.}$$

Taking $T = 7000°$ C., we can now calculate the value of $\log \frac{x^2}{1-x^2} P$. This becomes $1{\cdot}390$. If $P = 1$ atm., almost 98 per cent. of the nitrogen ought to be completely broken up into atoms. For $P = 10$ atms., the proportion is 83 per cent.

Thus the calculation does not seem to favour the suggestion that a certain percentage of nitrogen occurs in the sun in the molecular state. But the data used for calculation are of the roughest nature, and nothing definitely can be said until better data are available.

Helium.

It is well known that none of the Helium lines occur in the Fraunhofer spectrum, though occasional reversals of the D_3 have been observed in the spectra of the penumbra of sunspots †. But in the flash spectrum, helium lines are very prominent, the D_3 reaching a height of 7500 km. in the chromosphere. These facts may be explained in the following manner :—

The lines by means of which helium is detected belong to the series-combination $(2, p) - (m, d)$, or $(2, s) - (m, p)$. These lines cannot be absorbed by the ordinary He-atoms, which possess $(1, s)$ orbits, but by such atoms as possess the $(2, p)$ or $(2, s)$ orbits. These orbits can only be produced under very great stimulus. It is known from the 'Harvard Annals' (vol. xxviii. 91) that the absorption lines of helium disappear below stars of the Ao class. Hence a temperature of about $11,000°$ K. (temperature of the Ao class) is required for producing a sufficient number of He-atoms with $(2, p)$ orbits, when the pressure is one atmosphere. These conditions are not attained on the photospheric level ; but at great heights, owing to

* Laski, *Phys. Zeits.* xx. p. 269 (1919).
† Pringsheim, *Physik der Sonne*, p. 123.

diminished concentration, not only (m, p), but also (m, d) orbits are produced. As these absorbing atoms occur only at large heights in regions of low concentration, they are not in sufficient number to produce a weakening of the corresponding regions of the continuous spectrum by absorption.

The occasional reversals of He-lines in the penumbra of sun-spots seem to be an effect of diminished concentration without a corresponding loss in temperature. The temperature of the penumbra is intermediate between those of the spot and the undisturbed photosphere, and may be supposed to lie between 6500° K. and 7000° K. We have no direct observational result which can give us some idea of the pressure, but Evershed * has found that gases are flowing through the penumbra radially outwards, parallel to the surface of the sun, with velocities ranging from rather small values to about three or four kilometres per second. As the mass-motion of a quantity of gas is always attended with a fall in pressure, the penumbral regions certainly possess lower pressure than the undisturbed photosphere. The physical conditions in the penumbra are therefore favourable to the production of a larger percentage of He-atoms with the $(2, p)$ orbits. Probably this accounts for the occasional weak reversal of He-lines over the penumbra.

The Flash Spectrum.

From paper A and the foregoing part of the present paper, it will be seen that the Fraunhofer spectrum can mainly be regarded as function of a single physical condition, viz., the temperature. The flash spectrum is, on the other hand, a function of temperature and concentration, a low concentration favouring a greater percentage of ionization, and consequently a *relative* intensification of the enhanced lines. Special attention is called to the word "relative" when terrestrial sources of limited extent are considered, for though the percentage of ionized atoms becomes greater, the absolute number of particles becomes less, and hence all lines, as a rule, become fainter. But the lines of neutral atoms would become much fainter than the enhanced lines.

All this was substantially stated in paper A, but at the time of writing this paper I was acquainted with no experimental work which could be cited in support of the view. I have since come across some works which support my case.

* Evershed, Astrophysical Journal, vol. xxv. (1909).   Hale, *loc. cit.* vol. xxviii. (1910).

The following is an experimental work by Loving on the comparative intensities of Ca and Mg lines in ordinary arc and vacuum arc. (Astrophysical Journal, vol. xxii. p. 300, 1905.) Fowler also noted that the enhanced lines of Mg, Zn, and Cd are greatly intensified in a vacuum arc (Fowler and Payn, Proc. Roy. Soc. lxxii. 1903).

Element.	Open arc.	Vacuum arc.	Relative weakening.	Spark.	Chromo-sphere.
K − 3934	500	25	$\frac{1}{20}$	1000	75
H − 3968	300	20	$\frac{1}{15}$	500	60
g − 4227	1000	8	$\frac{1}{125}$	100	8
Magnesium. 2852	500	8	$\frac{1}{60}$	100	—
4481 (+ Mg)	0	20	—	50	1

Thus the tables show that in the vacuum arc the ratio Ca$^+$/Ca is 6–8 times its value in the ordinary arc. Unfortunately the pressure, which is a vital point, is not stated. In the case of Mg, the stimulus at the open arc is not even sufficient to excite the ionized line 4481. But a diminution in concentration brings about ionization. This case is rather remarkable because it affords an experimental basis for the view that temperature remaining the same, a diminished concentration can bring about a higher stimulus.

Conclusion.

The foregoing work will probably make it clear that the theory of temperature ionization developed by the author in paper A, and more fully applied in the present paper, is capable of throwing much light on many obscure and puzzling questions of solar physics. We are precluded from making further applications owing to lack of necessary data, viz., the value of the ionization potential of elements or the value of the term or terms $(1, s)$. If this and the spectral properties of all elements were known with as much certainty and exactness as in the case of the alkaline earths, details of the Fraunhofer spectrum could be very satisfactorily explained.

We can, however, make the following suggestions with

regard to future work on the subject :—Elements like Fe,
Ti, V, Ni have probably ionization potentials varying from
6 to 9 volts, so that their behaviour is almost parallel to that
of calcium and magnesium.   Elements which are missing
from the sun can be broadly subdivided into two groups : 1st,
those which are completely ionized, *e. g.* Rb, Cs, and pro-
bably thallium ; 2nd, elements of which the ionization and
radiation potentials are so high that they are not in a state
capable of absorbing those of their characteristic lines which
occur in the continuous photospheric spectrum (*vide* paper
C). Helium and most of the inert gases fall within this
group. The case of helium has already been considered.

Neon, Argon*, and other inert gases have very high ioni-
zation potentials, the value being 16 volts for argon.   Their
principal emission lines $(1, s)-(2, p)$ lie in the ultra-violet,
and identification is to be carried on by lines $(2, s)-(m, p)$,
or $(2, p)-(m, d)$ or $(2, p)-(m, s)$. As the intensity of the
photospheric radiation in the region $(1, s)-(2, p)$ is very
small, the compensating value of the radiation-pressure is
also small, and the elements fail to reach great heights.   In
the lower regions, the stimulus is not sufficient enough to
convert the atoms to the states $(2, s)$ or $(2, p)$ and hence
these lines do not occur in the Fraunhofer spectrum †.

The case of the unidentified Fraunhofer Lines.

As has been mentioned in the introduction, about 60 per
cent. of the Fraunhofer lines catalogued by Rowland still
remain to be identified.   According to Fowler, a large
proportion of these are due to molecules and molecular com-
pounds.

The best known example is the so-called cyanogen band
with its head at $\lambda=3883$, now attributed by Grotian and
Runge to molecular nitrogen.   Other examples are Newall's
identification of the G-group of the Fraunhofer spectrum with
the band-lines of hydrocarbons, and Fowler's detection of
ammonia and water-vapour bands in the ultra-violet part
of the solar spectrum.

These identifications raise a very important point, viz., Is
it possible, under the conditions prevailing in the sun, for

---

* For the spectral grouping of the lines Ne and A, see Paschen, *Ann.
d. Physik*, vol. lx.

† Probably the metalloids As, Sb, Bi, etc., fall in this category, for
it is well known that they can be made to emit their line spectrum at a
comparatively low temperature, *vide* paper C, Introduction.

any molecule or molecular compound to exist in the undissociated state? The problems are essentially of the same nature as those which are treated by the physical chemist in the laboratory, only repeated on a scale which is not available on the earth. But thanks to the recent developments in thermodynamics by Nernst, Planck, Sackur, and others, we can now handle these problems from the theoretical side in a very satisfactory manner, if only proper data are available. Examples have already been given; it has been shown that in the sun, hydrogen and oxygen are in wholly dissociated conditions, while some proportion of nitrogen may remain in the molecular state.

The chief data which are required are heats of dissociation, the specific heat of the components, and the value of the chemical constant of the components. Thus to take a concrete case, let us consider the chemical equilibrium of NH_3. The reaction is of the type

$$NH_3 \xrightleftharpoons{} N + 3H - U_1,$$
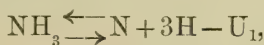
and the chemical equilibrium is given by the law

$$\log \frac{P^3 x^4}{(1+3x)^3 (1-x)} = -\frac{U_1}{2 \cdot 3RT} + \frac{\Sigma \nu C_p}{R} \log T + \Sigma C,$$

where x is the fraction dissociated.

Now $\qquad \Sigma \nu C_p = (C_p)_N + 3(C_p)_M - (C_p)_{NH_3}$

and $\qquad \Sigma \nu C = C_N + 3C_H - C_{NH_3}.$

All of these quantities can be calculated theoretically excepting C_{NH_3}. (The theory of the chemical constant for polyatomic gases is yet to be developed—see paper mentioned below *.)

It should be remembered that U_1 is different from the energy evolved in the reaction,

$$2NH_3 = N_2 + 3H_2 - U_2,$$
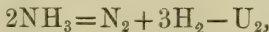
if $\qquad N_2 = N + N - U_N,$

and $\qquad H_2 = H + H - U_H,$

it is easy to see from the energy principle that

$$U_1 = \frac{U_N + 3U_H + U_2}{2}$$

and cannot be estimated before all these quantities are known.

---

* "On the Chemical Constant of Diatomic Gases." Leon Schames, *Phys. Zeits.* vol. xxi. p. 41 (1920).

For a chemical reaction of the type

$$Ti + O_2 = TiO_2 + U,$$
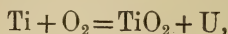
the equation of chemical equilibrium is given by the formula

$$\log \frac{P^2 x^3}{(1+2x)^2(1-x)} = -\frac{U}{2\cdot30RT} + \frac{\Sigma\nu C_p}{R}\log T + \Sigma\nu C,$$

which reduces to

$$\log \frac{P^2 x^3}{(1+2x)^2(1-x)} = -\frac{U}{2\cdot30RT} + 3\log T + C_{Ti} + 2C_O - C_{TiO_2},$$

if, in accordance with the kinetic theory of specific heat, we put $(C_p)_{TiO_2} = \frac{9R}{2}$.

This class of chemical reaction is likely to have wide application in the treatment of the spectra of sun-spots, for a large number of spot-lines were identified by Fowler, Hale, and Olmsted with the band-lines of MgH_2, TiO_2, and CaH_2 (Tri-atomic compounds) [*].

It appears that no attention has yet been paid to the study of the spectra of the faculæ, which are believed, on the basis of very sound physical arguments, to be regions of higher temperature than the photosphere. Supposing the temperature of the faculæ to range between 8000° K. and 9000° K., their spectra are likely to show very important differences from the spectra of the ordinary photosphere, and to be similar to the spectra of the Fo to F_5G classes of stars, just as the spectra of sun-spots are similar to those of the Antarian stars (K-class). At any rate, the subject seems to offer a very rich field for investigation.

If the necessary data be available, these questions will be taken up in a future communication.

I have much pleasure in recording my best thanks to my students of the Post-graduate classes in Physics for much useful help in the preparation of this paper.

University College of Science,
Calcutta.
May 22, 1920.

* Pringsheim, *Physik der Sonne*, pp. 211 to 217.

XCIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 284.]

January 21st, 1920.—Mr. G. W. Lamplugh, F.R.S., President,
in the Chair.

Mr. RICHARD DIXON OLDHAM, F.R.S., V.P.G.S., gave a de-
monstration on a Model to Illustrate the Hypothesis of a
somewhat Rigid Crust resting on a somewhat Yielding
Substratum, as applied to the Problem of the Origin
of Mountain-Ranges.

He remarked that geodetic measurements in the Himalayas, the
Pamirs, and the Andes show that in each case there are systematic
departures from equilibrium, in the form of parallel zones in which
the surface-level stands alternately above and below the level of
equilibrium, the differences being very considerable, and amounting
to the equivalent of somewhat over 2000 feet thickness of rock of
average density. These zones run parallel to the direction of the
axis of greatest elevation of the range, and are explicable by an
hypothesis that the elevation of the ranges was due to direct uplift
produced by changes in volume of the material underlying the
crust, if this material be supposed to possess a certain limited
amount of compressibility or plasticity and the crust to have a
certain amount of rigidity, which would offer resistance to an
exact adjustment of the uplift of the surface to the varying amount
of uplifting force developed in the material below the crust.

The model is designed to visualize the consequences of such an
hypothesis. It consists of two strips of spring steel, supported at
regular intervals by connecting links to a series of blocks capable
of vertical movement. For one strip these links are of fixed
length, representing a condition in which surface-elevation will be
exactly equivalent to the magnitude of the uplifting force. For
the other the links have a limited possibility of variation in length,
representing a condition where the rigidity of the crust is given a
certain possibility of influence on the resulting elevation of the
surface. On giving differences in height to the elevating blocks,
to represent the varying amount of uplifting force supposed to
exist under the mountain-range, it is found that the two strips do
not run at the same level, but the second runs alternately higher
and lower than the first, just as geodetic measurements have shown
is the case in the great ranges of mountains. The model is of no
value as evidence in favour of the hypothesis which it was designed
to illustrate, but is regarded as of some interest in visualizing the
consequences of an hypothesis which seems worthy of closer in-
vestigation than it has yet received.

February 4th.—Mr. G. W. Lamplugh, F.R.S., President,
in the Chair.

The following communication was read:—

'Geological Sections through the Andes of Peru and Bolivia:
II—From the Port of Mollendo to the Inambari River.' By
James Archibald Douglas, M.A., B.Sc., F.G.S.

The paper gives a description of a geological section across the
Andes of Southern Peru, from the port of Mollendo to the Inam-
bari River, a tributary of the Madre de Dios.

The deflection of the Pacific coast-line of South America north
of Arica towards the north-west brings to light a zone of ancient
granite and gneiss comparable with the rocks of the coastal
Cordillera of Chile. These rocks are shown to be of 'alkaline'
type, and are contrasted with the 'calcic' granodiorites forming
the batholitic core of the Western Cordillera. It is suggested that
their formation preceded the uplift of the folded chains.

The Jurassic zone of Northern Chile has been almost entirely
stripped from the underlying plutonic core, but its continuation
has been proved at more than one locality, and in the inter-Andean
region strongly-folded fossiliferous beds of Bajocian age are found
beneath an unconformable Cretaceous series. The batholitic core
is shown to comprise at least three distinct phases of plutonic
intrusion, represented by granodiorites, diorites, and adamellites.

The volcanic cones of the Western Cordillera have given rise to
an extensive series of lavas and tuffs comparable with the Mauri-
River Series of Bolivia.

Cretaceous limestones here take the place of the red gypsiferous
sandstones farther south, and are transgressive on to Devonian
rocks. The latter contain abundant fossils of Lower Hamilton
age.

The post-Cretaceous line of dioritic intrusion, formerly described
as running through Coro Coro and Comanche, once more appears
on the line of section.

The Permo-Carboniferous fauna of Bolivia has not been dis-
covered in the district here described, but beds of similar lithological
character are found overlying fossiliferous limestones assigned to
the highest part of the Avonian sequence. The eastern flanks of
the Cordillera are composed of a great thickness of barren shales,
slates, phyllites, and mica-schists, the only fossils discovered being
graptolites of Llanvirn age.

This area is further characterized by a well-marked 'alkaline'
province of igneous rocks, comprising elæolite-syenite-porphyry
and rocks closely related to laurvikite, ditroite, and durbachite. A
comparison is made with a section drawn through Northern Chile
and Bolivia (from Arica to the Bolivian Yungas), and an attempt
is made to reconstruct the history of the Cordillera.

JOLY.

Phil. Mag. Ser. 6, Vol. 40, Pl. XVI.

Fig. 1.
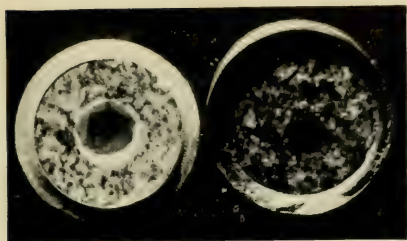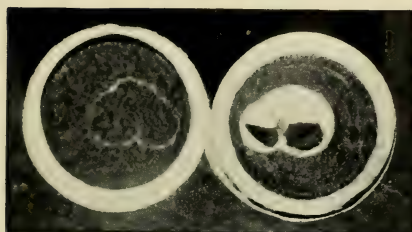
Granite. (I.)

Fig. 2.

Basalt. (I.)

Fig. 3.

Granite. (II.)

Fig. 4.

Basalt. (II.)

Fig. 2.

Fig. 3.

Ratio of Intensities=23 : 1.

Fig. 4.

INDEX to VOL. XL.

END OF THE FORTIETH VOLUME.

FOOTE & MEGGERS.

Phil. Mag. Ser. 6, Vol. 40, Pl. I.

Applied accelerating potential in volts

Low voltage arc spectra of caesium vapor

True accelerating potential in volts

ELECTRO

g .TICAL BASE LINE 50 FT. LONG.

m ce. Resistance of Circuit 50 ohms.

SEA SLIGHT

G H.

12   3   6   9   12

NOON
5 -9 -18

9

SEA SLIGHT.

OBSERVED TIDE (1'2 KNOT)
ESTIMATED DIRECTION OF TIDE.

N W

-0 8 m υ   WATER.

12   3   7.

it 235 ohms

TOV

B

Start Bay, ECTRODES.

Observ 00 Yards.

BY E →   rance, 29th July, 1918

nst Tide)   knot W. by S.

g W. BY S →   Turning N. BY W. →
to
starboard

20   25

TACTICALLY N

8.

Fig. 1.

Fig. 2.

ENTRANCE TO DARTMOUTH HARBOUR.
SHOWING POSITION OF MOORED ELECTRODES.
Depths shown in Feet.

Fig. 3.

MOORED ELECTRODES M₁ AND C₁ 2000 YARDS APART.

Resistance of Circuit 530 ohms. Deflexions ↓ indicate M₁+ve with respect to C₁.

Fig. 4.

MOORED ELECTRODES M₁ AND M₂ 200 YARDS APART.

Resistance of Circuit 235 ohms. Deflexions ↑ indicate M₂+ve with respect to M₁.

Fig. 5.

MOORED ELECTRODES ON VERTICAL BASE LINE 50 FT. LONG.
Upper Electrode 4 feet below Surface. Resistance of Circuit 50 ohms.

Fig. 6.

TOWED ELECTRODES.
Base Line 100 Yards,
East of Portland, 10th Oct. 1918.

Fig. 7.

TOWED ELECTRODES.
Base Line 100 Yards.
Start Bay, Bell Buoy, 25th July, 1918.
Observed Tide 1 knot S.W. by W.

Fig. 9.

TOWED ELECTRODES.
Base Line 100 Yards.
Dartmouth Harbour Entrance, 29th July, 1918
Observed Tide ½ knot W. by S.

Fig. 8.

BRAGG.

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Sodium chloride.   Calcium carbonate (Calcite).
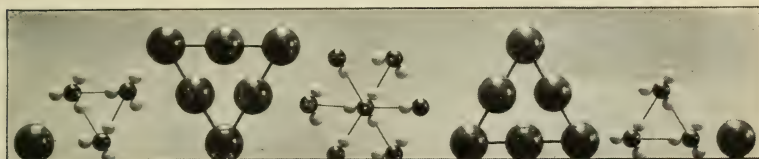
Planes (III) of Calcite.

Zinc sulphide (Zinc-blende).
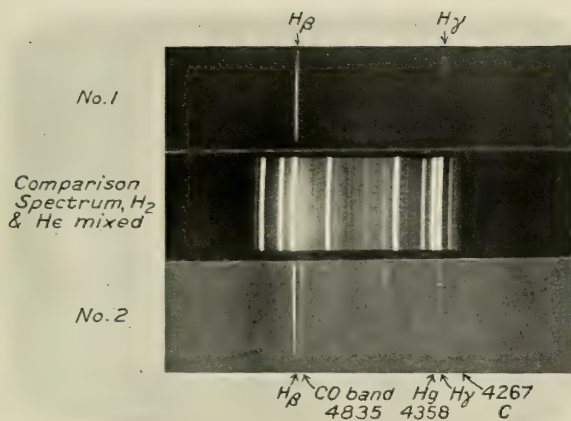
All lines in No. 2 not otherwise marked belong to the
second spectrum of hydrogen.

° 4
CND MICA
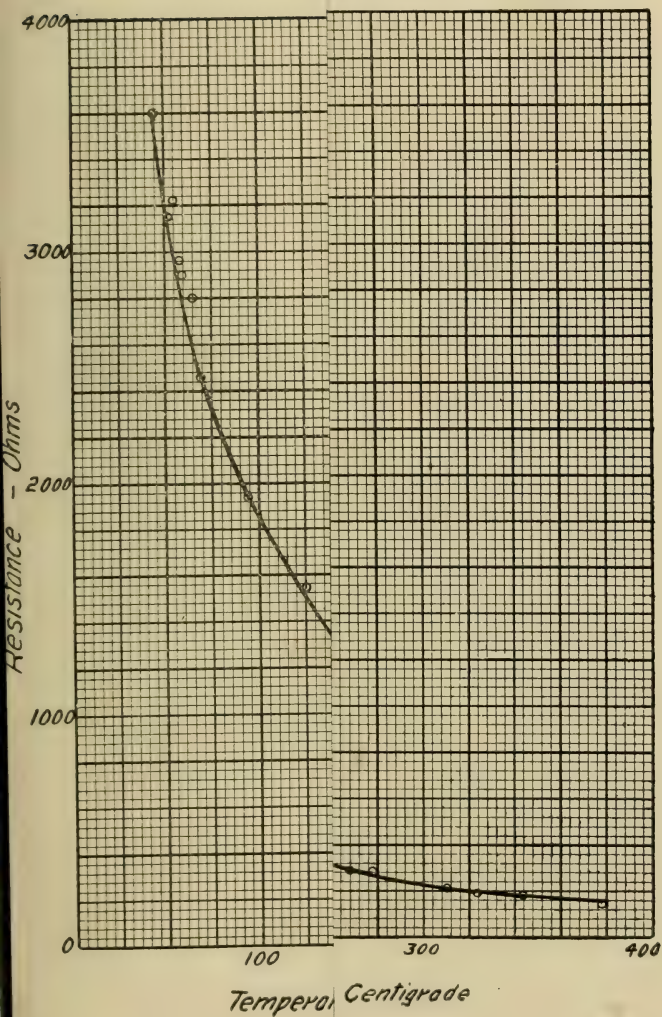
Graph Nº 1.
COPPER – MICA
RESISTANCE-TEMPERATURE CURVE
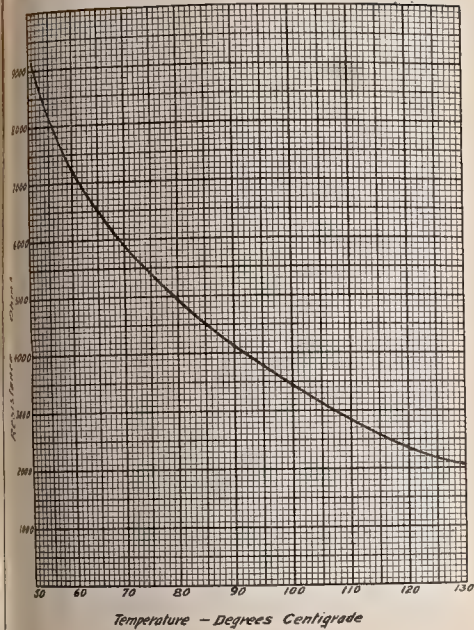
Graph Nº 2
COPPER – MICA
RESISTANCE-TEMPERATURE CURVE
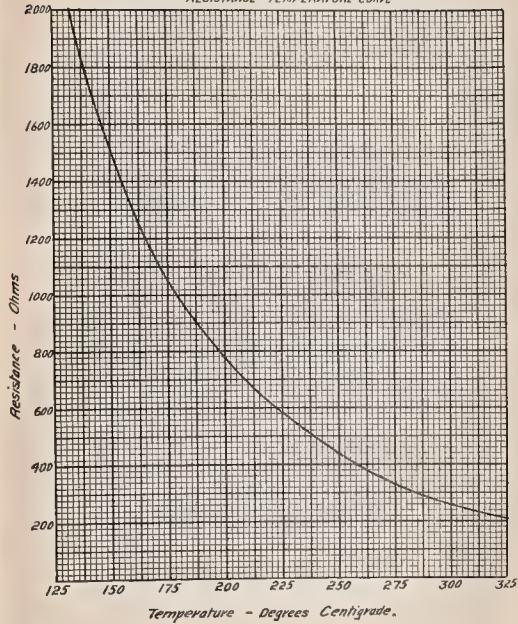
Graph Nº 3
COPPER AND MICA
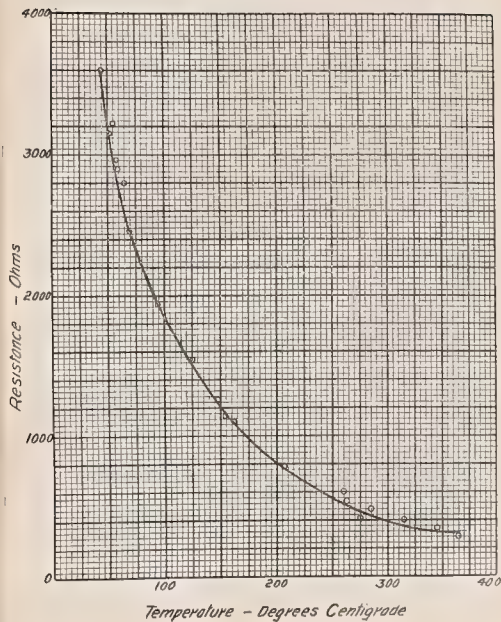
Graph Nº 4
COPPER AND MICA

Temperature – Degrees Centigrade

Temperature – Degrees Centigrade.

Temperature – Degrees Centigrade

Temperature – Degrees Centigrade

b Nº 8

AND SELENIUM

·09

·08

·07

Resistance - Ohms

0   100 200   300

Temperat grees Centigrade
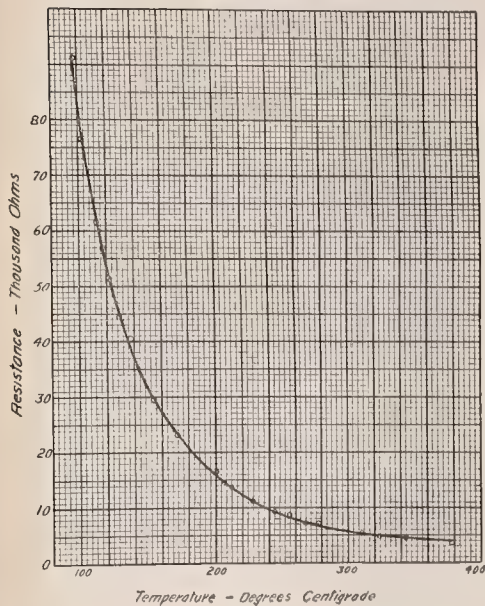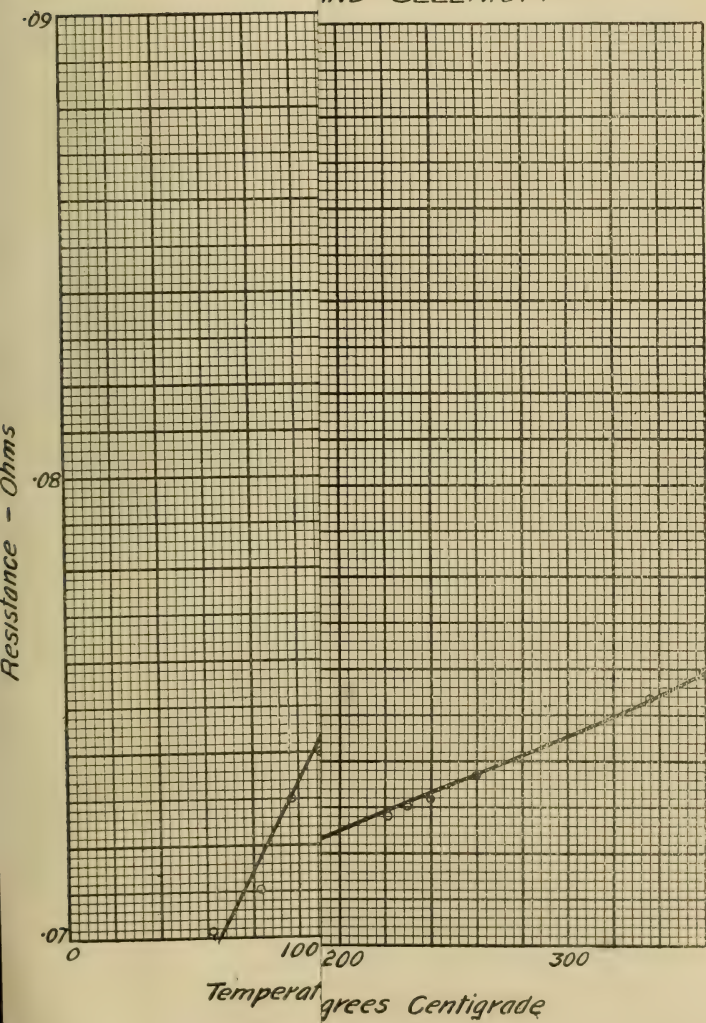
Graph N° 5
IRON AND MICA
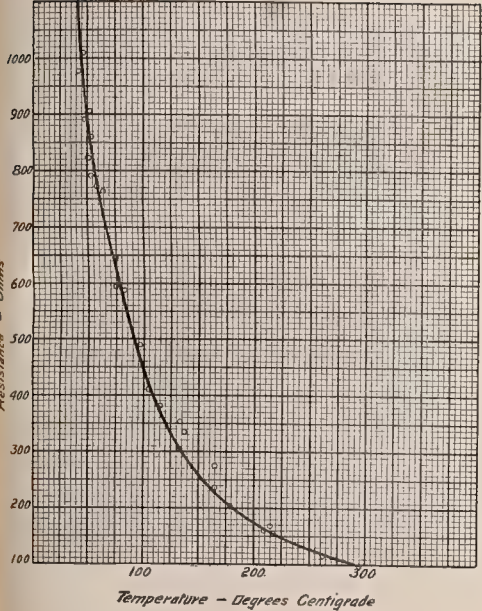
Graph N° 6
IRON AND MICA
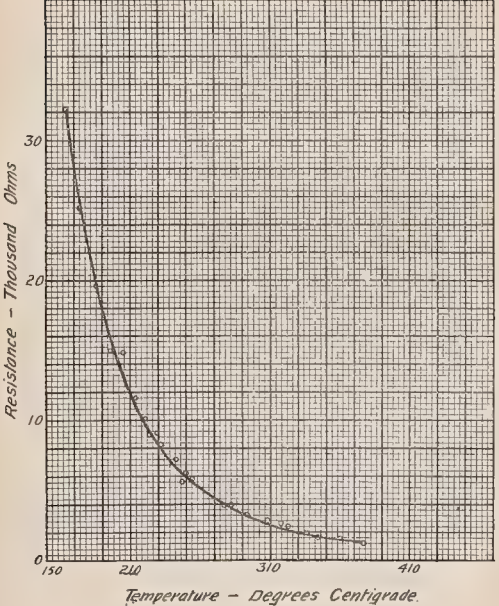
Graph N° 7
FERRO-SILICON
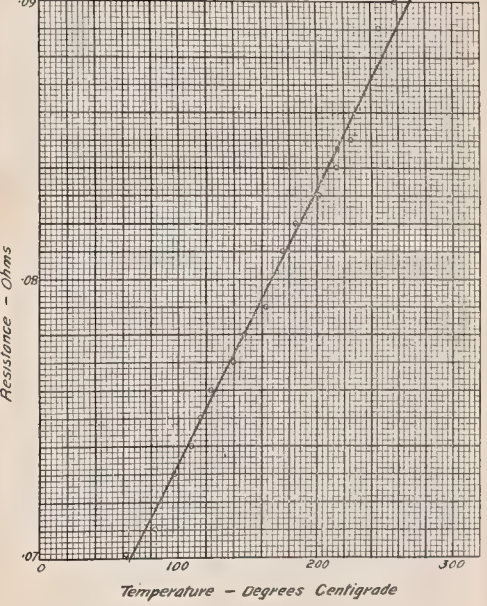
Graph N° 8
COPPER AND SELENIUM
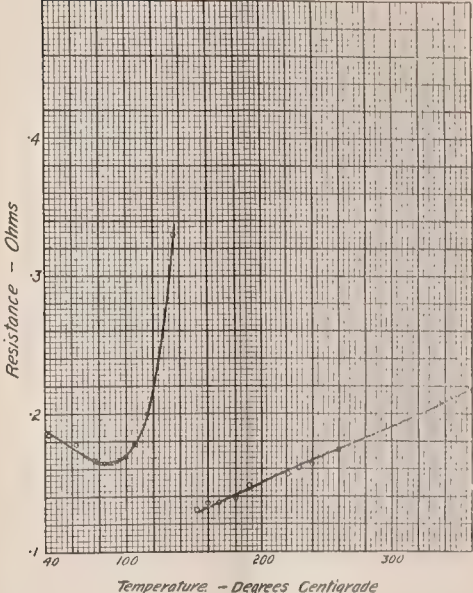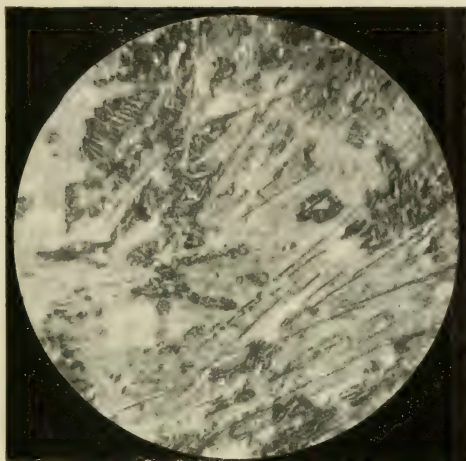
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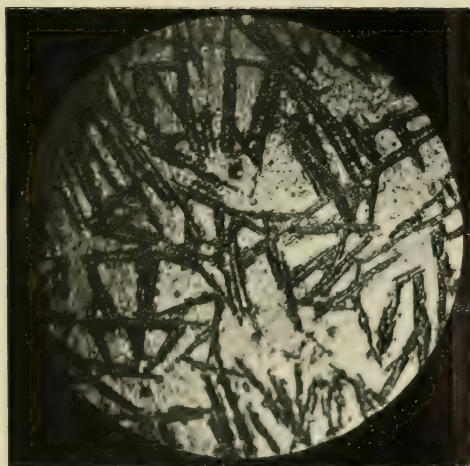
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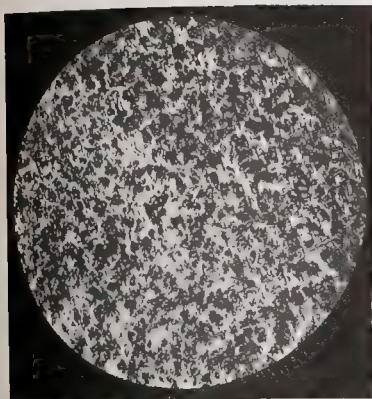
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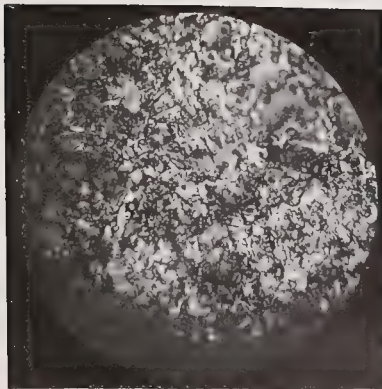
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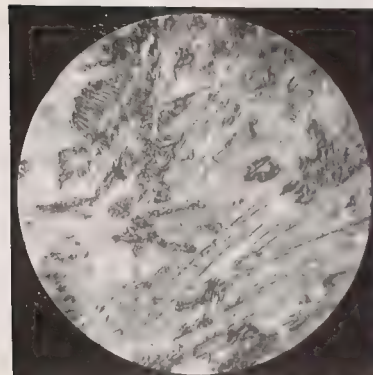
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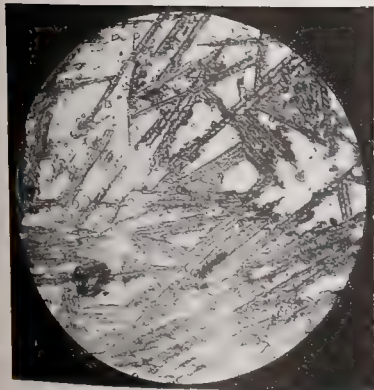
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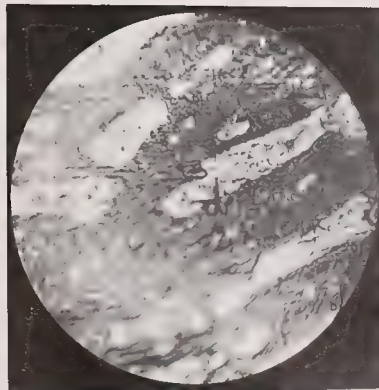
5
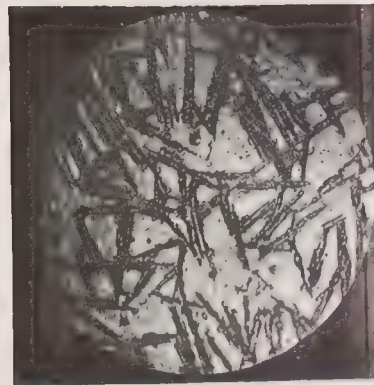
6

Red Bands of Calcium in Fringe and Luminous Vapour.
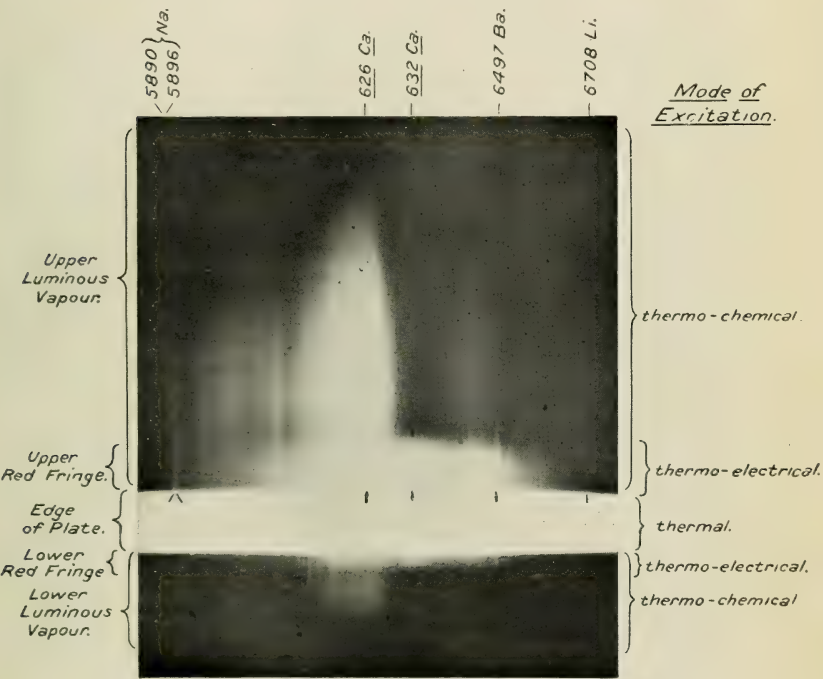
Plate temperature : about **3000°** C.   Drop of Potential along plate : about **8** $\frac{\text{volts}}{\text{cm.}}$

Hemsalech.

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Thermo-chemical and Thermo-electrical Excitation of Light Radiations in Metal Vapours.
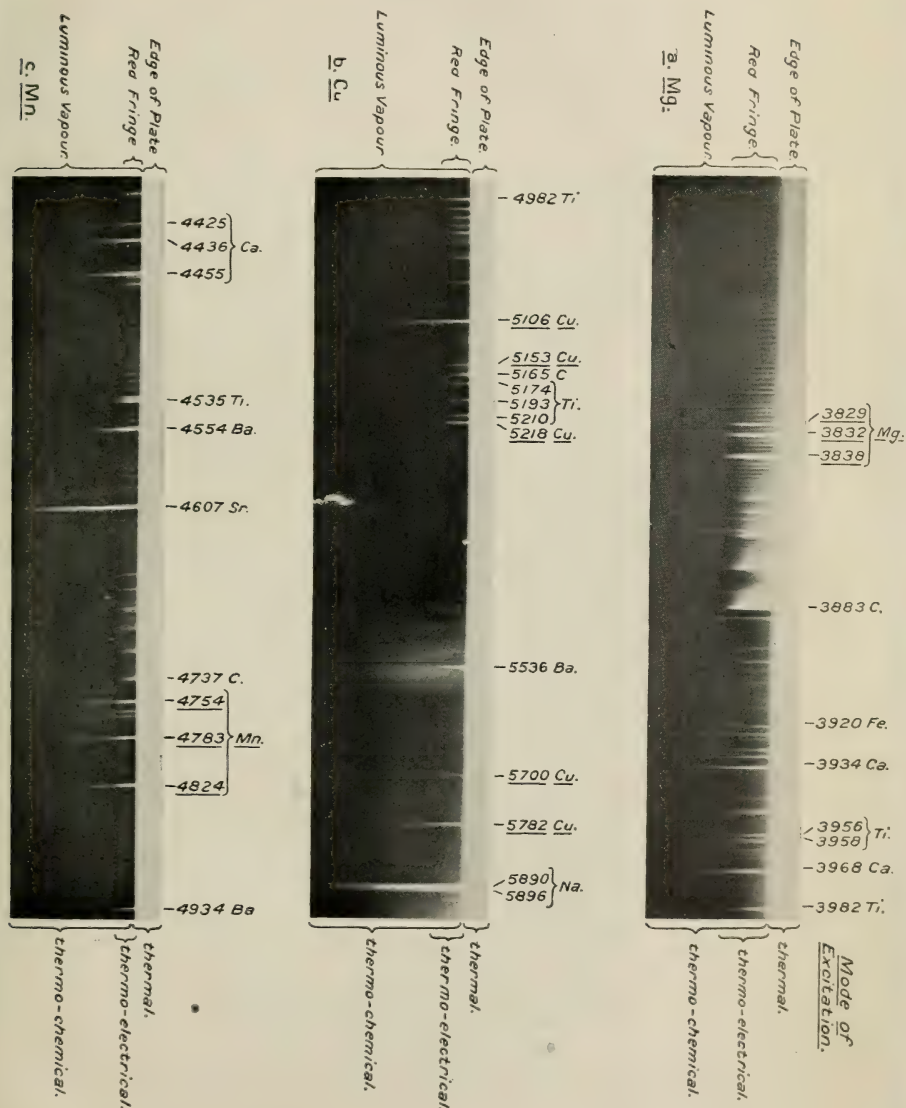
Plate temperature : about **3000°** C.　　Drop of Potential along plate : about **8** $\frac{\text{volts}}{\text{cm}}$.

Traces of Vibrations for $\rho = 1\cdot 5$ and $\eta = 0\cdot 571$.
Traces of Vibrations for $\rho = 0\cdot 67$ and $\eta = 1\cdot 45$.
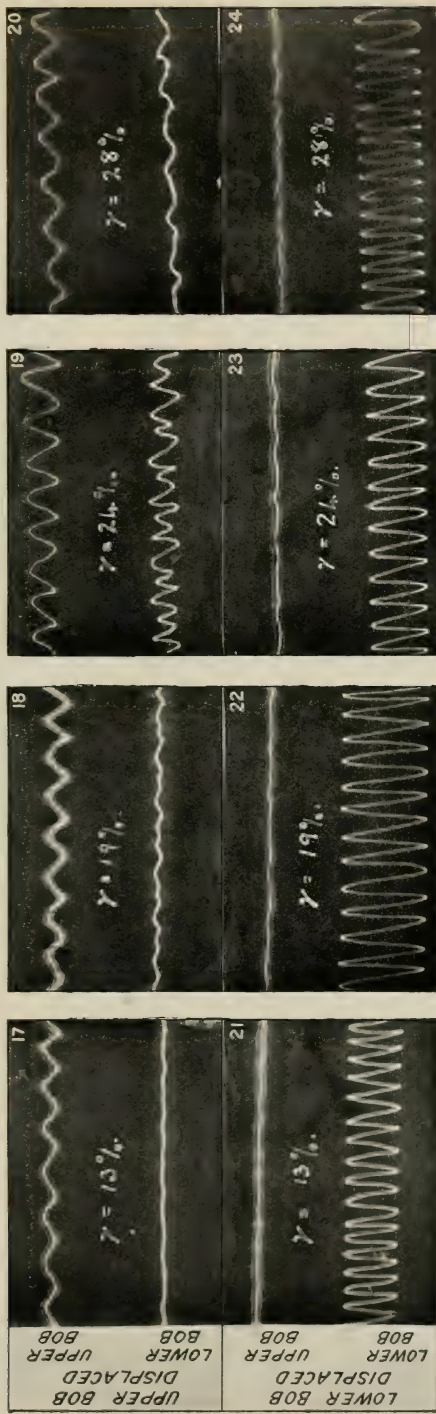
Traces of Vibrations for $\rho=1\cdot5$ and $\eta=0\cdot571$.
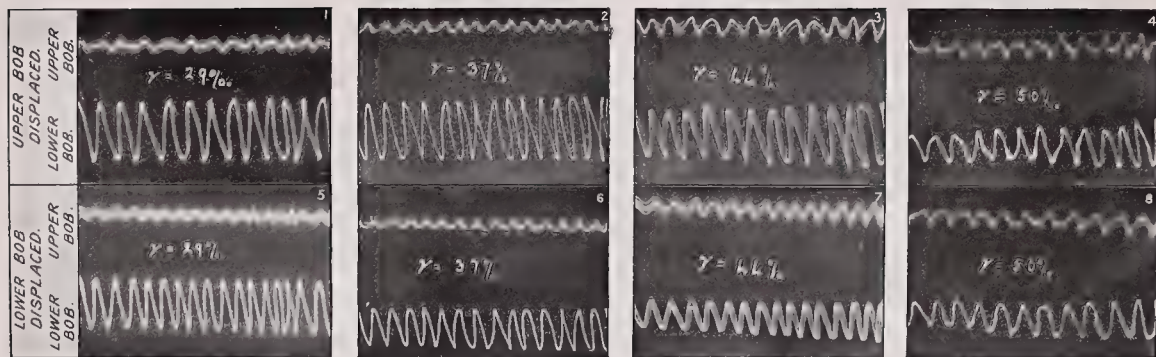
Traces of Vibrations for $\rho=1$ and $\eta=1\cdot083$.
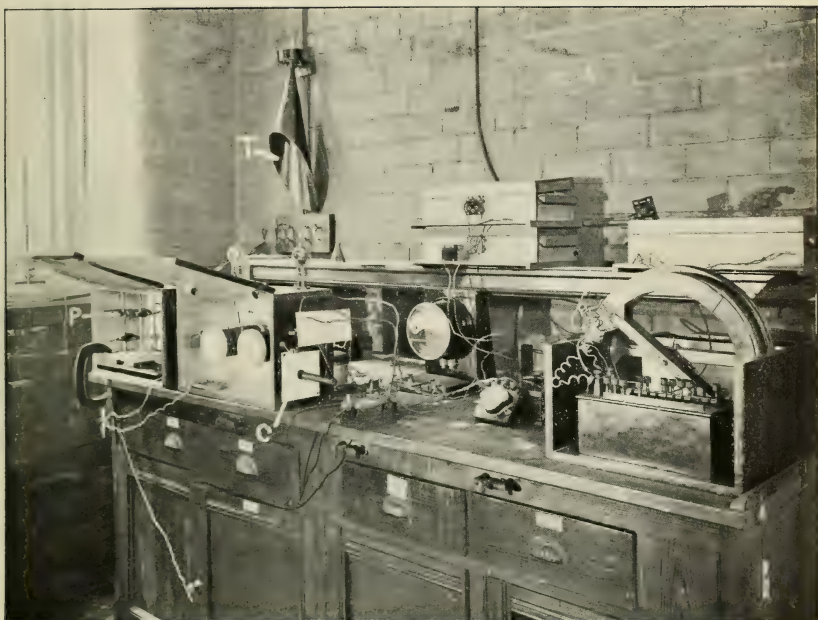

Traces of Vibrations for $\rho=0\cdot67$ and $\eta=1\cdot45$.

Aston.

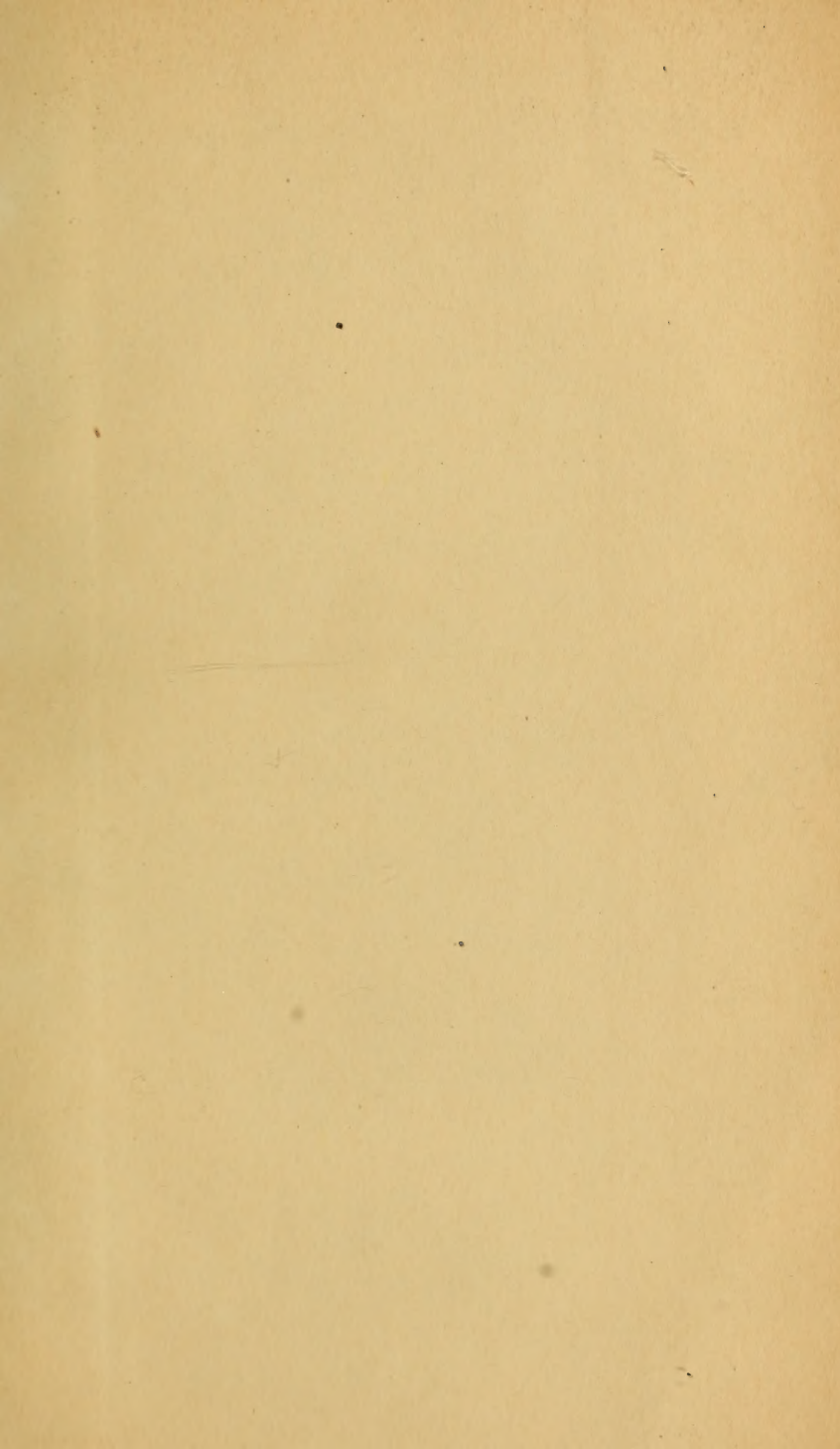Phil. Mag, Ser. 6, Vol. 40. Pl. XIV.
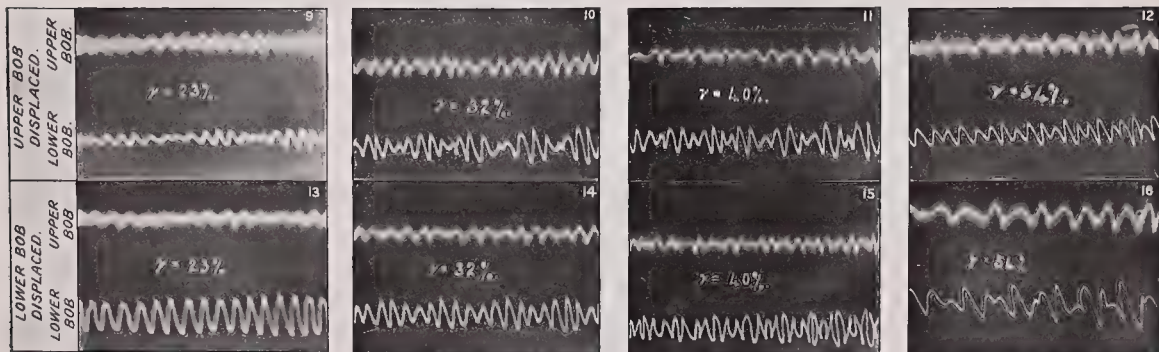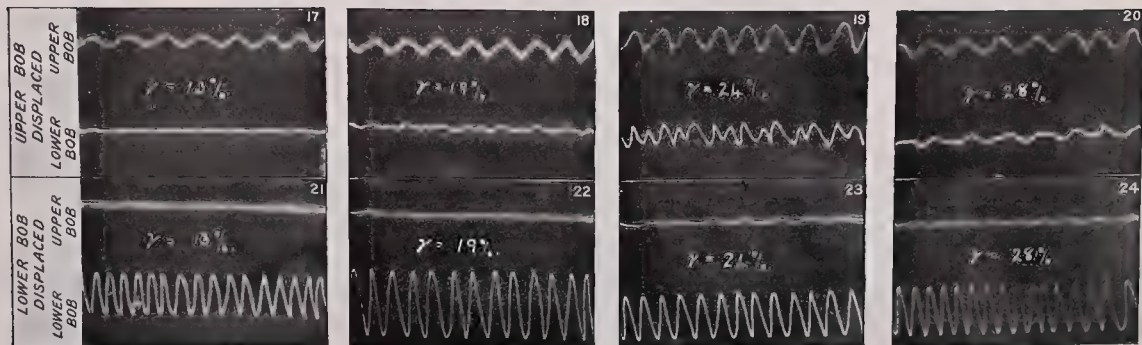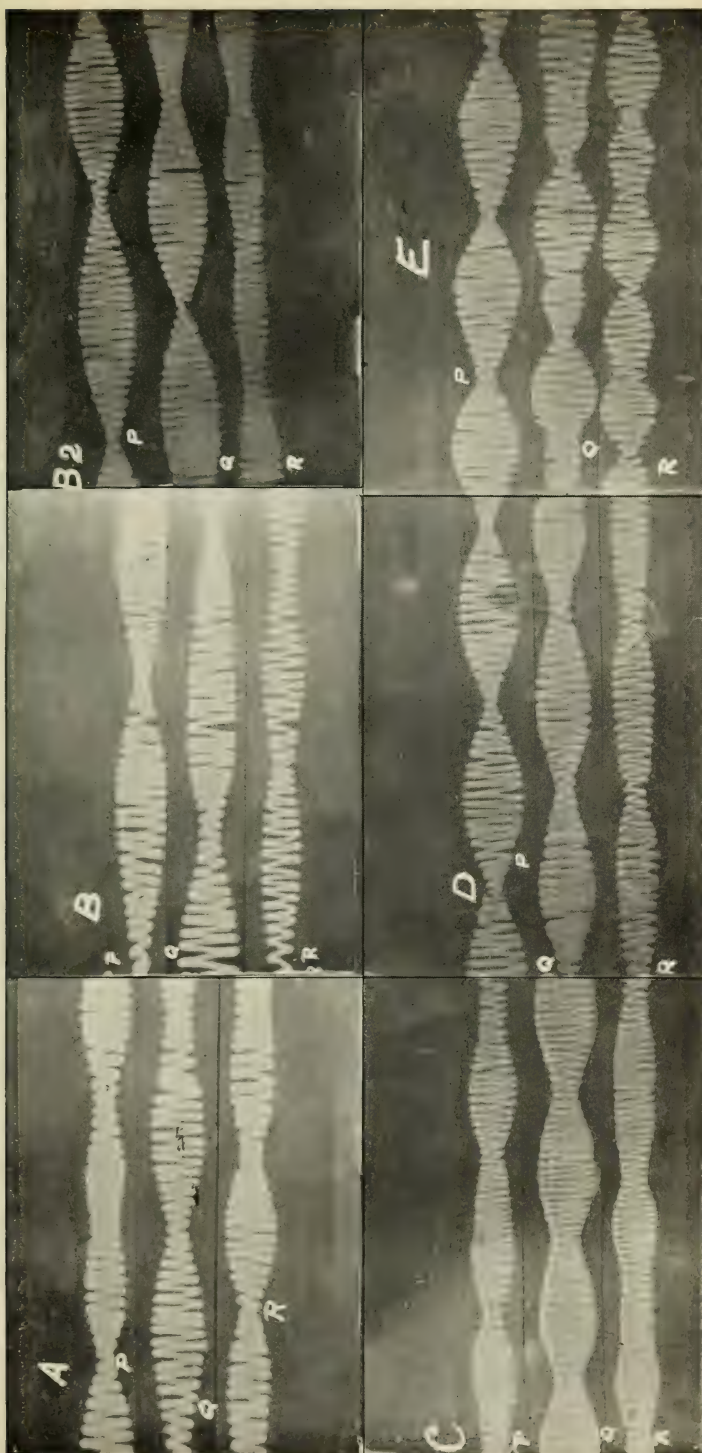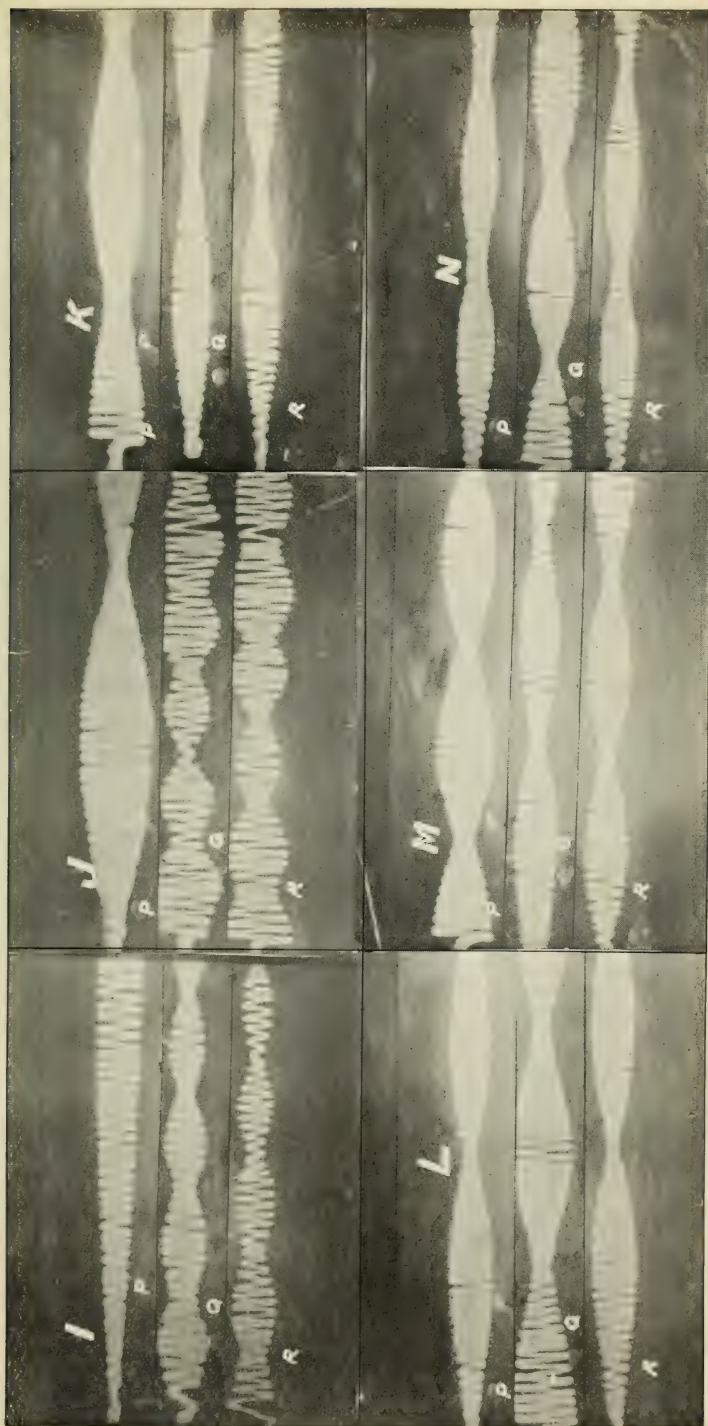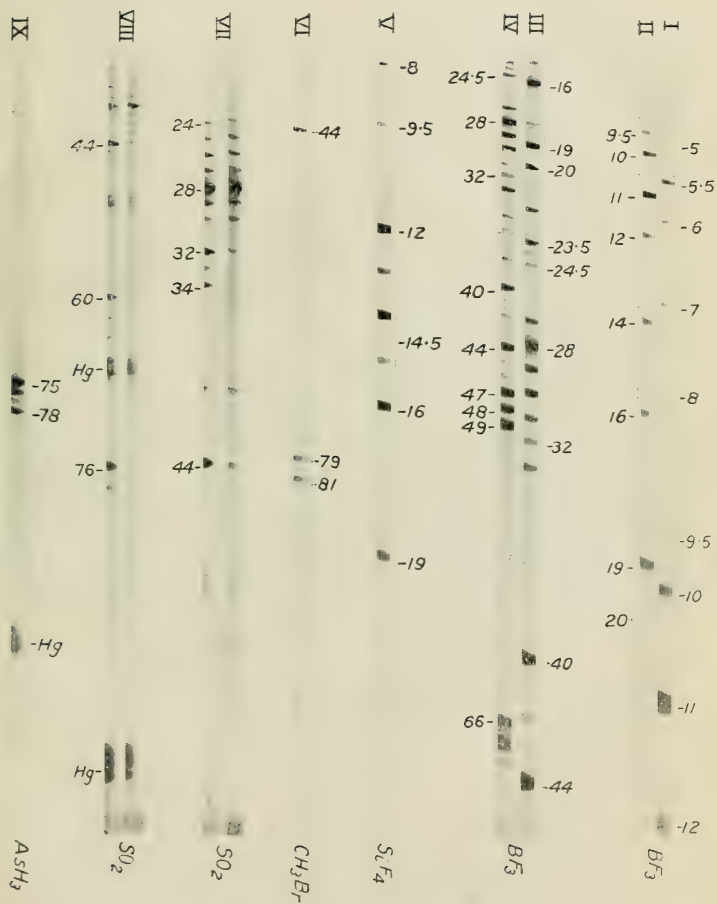
General view of apparatus shown diagrammatically in Figure 1. Metal boxes
containing circuits A and B shown open. The letters correspond to those
used in Figure 1.