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AND

WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

"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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"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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[SIXTH SERIES.]

JULY 1902.

I. *Comparison of the Radiations from Radioactive Substances.*

By E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, and* Miss H. T. Brooks, *M.A., McGill University, Montreal* *.

ALL the radioactive substances possess in common the power of acting on a photographic plate and of ionizing the gas in their immediate neighbourhood. The intensity of the radiations may be compared by means of the photographic or electrical action; and in the case of the strongly radioactive substances by the power of lighting up a fluorescent screen. Such comparisons, however, do not throw any light on the question whether the radiations are of the same or of different kinds. It is well known that such different types of radiation as the short waves of ultra-violet light, Röntgen and cathode rays all possess the property of producing ions throughout the volume of the gas, lighting up a fluorescent screen and acting on a photographic plate. None of the radiations from the various radioactive substances show any trace of regular reflexion, refraction, or polarization †.

There are two general methods of differentiating to some extent between the various types of radiations.

(1) By observing whether the rays are appreciably deviated by a magnetic field.

(2) By comparing the relative absorption of the rays by solids and gases.

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* Communicated by the Authors.

† A very complete and admirable account of radioactive substances by Henri Becquerel and P. & Mme Curie is given in vol. iii. of the Reports of the Congrès International de Physique held at Paris, 1900.

The first method has been utilized by Giesel, Becquerel[*], Curie, and others. Of the radioactive substances which have been most closely examined, viz. uranium, thorium, polonium, and radium, the latter has been shown by many observers to give out rays deflectable by a magnet. Debierne[†] states that the radioactive substance which he has termed actinium also gives out some rays deflectable by a magnet. In all cases these deflectable rays are similar in every respect to cathode-rays, and are thus probably streams of negatively charged particles moving with very great velocities. Becquerel[‡] has shown that the ratio $\frac{e}{m}$ of the charge to the mass of these negatively charged carriers is about 10^4, which is about the same value observed for the cathode-rays produced in a vacuum-tube.

Radium, in addition to the deflectable rays, also emits non-deviable rays. The ionizing and fluorescent action of radium rays in air at atmospheric pressure, at a distance of from 5 or 6 cms. from the surface of the radium, is very largely due to the rays deflected by a magnetic field. For distances less than this, the ionization is partly due to the deflectable rays and partly to rays which are not acted on by a magnet. Close to the surface of the radium the ionization due to the non-deviable rays greatly preponderates over that due to the deviable rays. This is due to the fact that the non-deflectable rays are very largely absorbed in passing through a few centimetres of air at ordinary pressure.

Action of a Magnetic Field on Uranium Rays.

Becquerel has examined the rays of uranium in a magnetic field by the photographic method, and found that some of them are deflectable. We have confirmed these observations by the electrical method, and found that only the penetrating rays of uranium are deviable.

One of us[§] has shown several years ago that the radiation from uranium was complex, and could be divided into two types of radiation, which were called for convenience the α and β radiations. The β radiation is far more penetrating in character than the α radiation, but is difficult to examine accurately on account of the small conductivity produced by it in the gas, compared with that due to the α radiation. In

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[*] Paris Report, 1900.

[†] *Comptes Rendus*, cxxix. (1899), & cxxx. (1900).

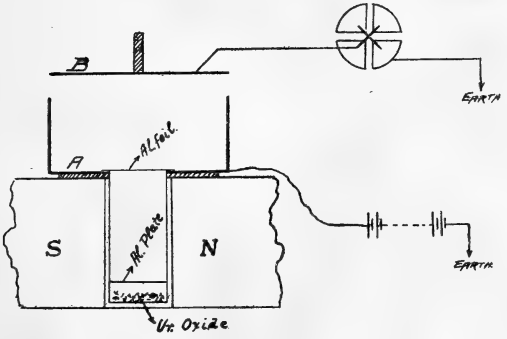
[‡] *Loc. cit.*

[§] E. Rutherford, Phil. Mag. Jan. 1899.

order to measure with certainty the very small rate of leak involved, a very sensitive electrometer was employed. The instrument is described by Dolezalek* in a recent paper, and was constructed by Herr Bartels of Göttingen. It was of the usual quadrant type, but was provided with a very light needle suspended by a fine quartz fibre. When the needle was charged to 200 volts it gave a deflexion corresponding to 1500 mms., with the telescope and scale at a distance of about 150 cms, for 1 volt between the quadrants. For the special purpose for which it was employed, it was found necessary to improve the insulation of the quadrants and to alter the quadrant connexions. The instrument was easy to work and gave accurate results. It has been employed recently by one of us† to measure the small spontaneous ionization produced in the air, which has been shown by the experiments of Elster and Geitel‡ and C. T. R. Wilson§ who used specially designed electroscopes for that purpose.

In the experiments on the action of a magnetic field on uranium radiation (fig. 1) a thick layer of uranium oxide was

Fig. 1.



placed on the bottom of a rectangular lead box 5·7 cms. long, 1·8 cm. wide, and 4·0 cms. deep, which was placed between the flat pole-pieces of a large electromagnet. The rays, after passing out of the lead box, passed between two parallel insulated plates A and B. One of these plates A was charged to a P.D. of 50 volts above the earth by means of a battery. The other plate B was connected to one pair of quadrants of an electrometer in the usual manner.

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* *Verh. d. D. Physik. Ges.* iii. (1901).

† Rutherford and Allen, *Phys. Zeit.* No. 11, 1902.

‡ *Phys. Zeit.* Nov. 24, 1900.

§ Proc. Roy. Soc. March, 1901.

Electrostatic disturbances were completely eliminated by covering the electromagnet and wires leading to it with tinfoil connected to earth.

There was always a small current observed between the plates on account of the spontaneous ionization of the air in the testing vessel when the uranium oxide was removed to a distance.

The layer of uranium oxide was covered with several thin layers of aluminium of sufficient thickness to completely absorb all the α radiation. The open end of the lead vessel was covered with thin aluminium-foil. In that case the rate of leak of the electrometer was due to ionization produced between the plates by the β radiation together with the ions spontaneously produced by the air itself. The latter was accurately determined before the lead vessel containing the oxide was placed between the poles of the electromagnet.

As the magnetic field was increased, the rate of leak observed by the electrometer steadily diminished, until with a strong field the rate of leak was reduced almost to that due to the spontaneous ionization of air. This diminution of the rate of leak between A and B is due to the curvature of the path of the rays by the magnetic field before they reach the testing vessel. Since the rate of leak, due to the action of the β radiation, with a strong magnetic field is reduced to a small fraction of its value when no magnetic field is acting, we may conclude that the β radiation is composed almost entirely of rays deviable by a magnetic field.

A comparison experiment with radium showed that the β rays of uranium were deflected to about the same extent as the radium rays for the same strength of field.

No action of a magnetic field on the α radiation of uranium was observed. Both radium and uranium resemble one another in emitting two types of radiation, one of which is deviated in a magnetic field, and the other not.

Absorption of the β Radiation by Substances.

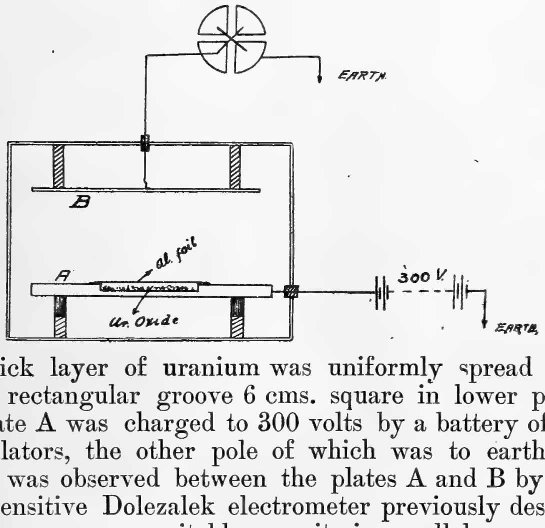
Since the β radiation of uranium is acted on by a magnetic field to almost the same extent as radium rays, we may conclude that the deviable rays are due to negatively charged particles emitted with high velocities; for Becquerel has shown that some of the radium rays move with a velocity of at least $1{\cdot}6 \times 10^{10}$ cms. per second. The penetrating power of the β rays is greater than that of the similar radiation for radium in our possession. It readily passes through 2 mms. of glass before complete absorption.

Lenard, in his well-known experiments on cathode-rays, has shown that the absorption of cathode-rays in substances depends only on the density of the material through which they pass, and is approximately independent of its chemical constitution. On account of the constancy of the uranium rays, it is possible to determine their absorption in different media with accuracy.

A few experiments were consequently made to see how closely the absorption varied with the density for the high-velocity particles emitted by uranium.

The experimental arrangement is shown in fig. 2, where the dotted lines represent insulators.

Fig. 2.



A thick layer of uranium was uniformly spread over a shallow rectangular groove 6 cms. square in lower plate A. The plate A was charged to 300 volts by a battery of small accumulators, the other pole of which was to earth. The current was observed between the plates A and B by means of the sensitive Dolezalek electrometer previously described, with, if necessary, a suitable capacity in parallel.

In order to completely absorb the α radiation an aluminium plate ·003 cm. in thickness was fastened tightly over the layer of uranium. The P.D. of 300 volts between A and B (6 cms. apart) was sufficient to carry over all the ions to the electrodes before appreciable recombination occurred.

The rate of movement of the electrometer-needle was observed, for different layers of material of uniform thickness successively placed over the uranium.

If λ is the coefficient of absorption of the radiation in a material, the intensity I of the radiation after passing through a thickness d is given by

$$I = I_0 e^{-\lambda d},$$

where I_0 is the intensity of the radiation at the surface before the plate was applied. The absorption of the radiation in a layer of air is negligible compared with that of an equal thickness of solid matter. The maximum current* between the plates is proportional to the intensity of the radiation.

Preliminary experiments showed that the current diminished very approximately in G.P. with the distance of material traversed, so that the value of λ determined was independent of the thickness of the plate.

This shows that most of the rays emitted have approximately the same penetrating power. The rays of radium, examined in a similar manner, did not fall off regularly, showing that the rays emitted consist of particles having a wide range of velocities, and consequently a wide range of penetrating power. This is clearly shown by Becquerel, who examined (by the photographic method) the amount of deflexion of the rays in a magnetic field after passing through different thicknesses of various metals.

The following table represents the results obtained.

Substance.	λ.	Density.	$\frac{\lambda}{\text{Density}}$
Glass	14·0	2·45	5·7
Mica	14·2	2·78	5·1
Ebonite	6·5	1·14	5·7
Wood	2·16	·40	5·4
Cardboard	3·7	·70	5·3
Iron	44	7·8	5·6
Aluminium	14·0	2·60	5·4
Copper	60	8·6	7·0
Silver	75	10·5	7·1
Lead	122	11·5	10·8
Tin	96	7·3	13·2

It will be observed that the value of the coefficient of absorption divided by the density is very approximately the same for such different substances as glass, mica, ebonite, wood, iron, and aluminium. The divergences from the law are, however, great for the other metals examined, viz. copper, silver, lead, and tin. In tin the value of λ divided by the density is 2·5 times its value for iron and aluminium. These differences show that the law of the absorption of cathode-rays depending only on the density, is not true for all substances.

Experiments are at present in progress to see whether there is any simple numerical connexion between the values of λ divided by density for different metals, and to extend the

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* Rutherford, Phil. Mag. Jan. 1899.

results so as to include a variety of substances in the solid and liquid state.

Absorption of the Rays by Solids and Gases.

The rays not acted on by a magnetic field can be distinguished from each other by their power of penetrating through thin layers of metal, and their absorption in gases. If, on examination, the penetrating power of two types of radiation proves to be the same in each case for all substances, it is extremely probable that the two radiations are identical. By examining the diminution of intensity of the radiation when sheets of metal of the same thickness are placed over the radioactive substance, the homogeneity or complexity of the radiations can be tested. If the intensity I of the radiation after passing through a distance of metal is given by $I_0e^{-\lambda d}$, where I_0 is the original intensity and λ the coefficient of absorption, we can conclude that the radiation is homogeneous in character. If this condition is not fulfilled the radiation is complex.

One of us* has at different times given results for the absorption of some of the different radiations in solids and gases. In this paper we have extended the results and compared the different types of radiation under, as far as possible, the same conditions.

In the case of both uranium* and thorium† it has been shown that the absorption of the radiation is the same for all the different compounds of each element examined. When the types of radiation are complex, the relative amount of rays of different types may vary for different compounds, but so far there is no evidence that the actual radiations themselves are altered. It is only necessary therefore to examine one compound of each element for the purpose of comparison of the types of rays emitted.

The following substances have been employed in the experiments :—

Uranium Oxide & Thorium Oxide.—Two different samples of each obtained from Schuchart of Germany and Eimer and Amend of New York gave similar results.

Polonium.—This substance was kindly prepared for me by Dr. Walker of McGill University from pitchblende, after the method described in Curie's first paper. Since that time the intensity of the radiation given off has steadily diminished; but the type of radiation has been unaltered.

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* E. Rutherford, Phil. Mag. Jan. 1899, Feb. and March 1900.

† Owens, Phil. Mag. Oct. 1900.

Radium.—Two different specimens were employed. One was of impure radium chloride kindly presented to me by Elster and Geitel two years ago ; this did not give off any emanation and only a small proportion of deflectable rays. The other, from P. de Haen, Hannover, was not very strong in deflectable rays, but gave out a large amount of emanation when slightly heated.

In the course of the paper we shall examine the following types of radiation.

A. Uranium.
 (1) The α or early absorbed radiation.
 (2) The β or deflectable rays.

B. Thorium radiations.
 (3) The simple radiation given out by a thin layer.
 (4) The radiation from the "emanation."
 (5) The excited radiation.

C. Polonium.
 (6) Simple radiation.

D. Radium.
 (7) Radiation not affected by a magnetic field.
 (8) Radiation from the emanation.
 (9) Excited radiation.
 (10) Magnetically deflected rays.

Absorption of Radiation by Metals.

In examining the absorption of the radiation by metal-foil and other substances, the apparatus shown in fig. 2 was employed. The active compound in the form of fine powder was uniformly spread over a shallow depression 6·5 cm. square in a large lead plate. This corresponds to plate A in fig. 2. The rate of leak was observed by means of an electrometer between plates A and B with, if necessary, a suitable capacity in parallel. The plate A was connected to one pole of a battery of 300 volts, the other pole of which was earthed. Preliminary experiments showed that with this voltage the maximum or saturation current between the plates was obtained for all the radioactive substances examined.

In most of the experiments described in this paper an Ayrton electrometer was used. In some of the later experiments, however, the White pattern of Kelvin electrometer was used. The former electrometer could be readily arranged to give 200 mm. divisions for 1 volt P.D. between the quadrants. As most of the experiments were carried out during the very dry Canadian winter, it was very essential to screen the electrometer and connexions with testing apparatus by wire gauze. Unless precautions of this kind were taken, every movement of the observer produced sufficient frictional electrification to disturb the electrometer. For the same reason and also for convenience the quadrants were separated by a cord connected to a suitable key and operated at a distance.

The method of observing the rate of leak was as follows:—A seconds-pendulum was placed before the observer. At the instant of passing the middle point of its swing the quadrants were separated by a sudden pull of the cord. After ten or more swings the connexion between testing-apparatus and the electrometer was broken by means of an insulated key, operated by a second cord. The deflexion of the electrometer-needle when it came to rest was then observed.

The number of scale-divisions passed over, divided by the time between the separation of the two keys, was taken as a measure of the rate of leak. This method is more accurate than the usual one of observing the time the electrometer-needle takes to pass over say 100 divisions of the scale. The final deflexion is independent of the amount of damping and of any oscillation or irregularity in the movement of the electrometer-needle.

In experiments with uranium, thorium, and polonium a very thin layer of the material was employed. This is essential in the case of thorium oxide, in order that the rate of leak *due to the emanation* from it may be negligible compared with the rate of leak produced by the ordinary radiation. In dealing with radium a very small amount of material was dusted by means of a gauze as uniformly as possible over a platinum plate. For the specimen of radium employed the rate of leak due to the emanation and rays deviable by a magnet was in this way rendered negligible compared with the rate of leak due to nondeviable radiation. Suitable capacity was, if necessary, placed in parallel with the electrometer to reduce the rate of leak.

In figs. 3 and 4 (p. 10) curves are given for the absorption of the different radiations by thin aluminium foil and Dutch-metal respectively. In order to plot the curves on the same scale the rate of leak for the bare radioactive plate is in each case taken as 100. The average thickness of aluminium-foil was ·00036 cm., and of Dutch-metal ·00012 cm. The curves are given for two specimens of radium, marked C and E, which corresponded to two specimens of radium from P. de Haen, marked "concentrated" and "einfach" respectively. The curve for the specimen sent by Herrn Elster and Geitel was not very different from the two shown. Curves obtained from specimens of the minerals "thorite" and "orangite" gave practically the same curves as for thoria.

Fig. 3.

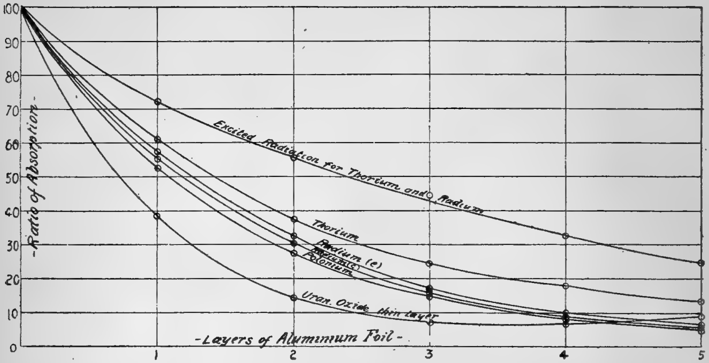
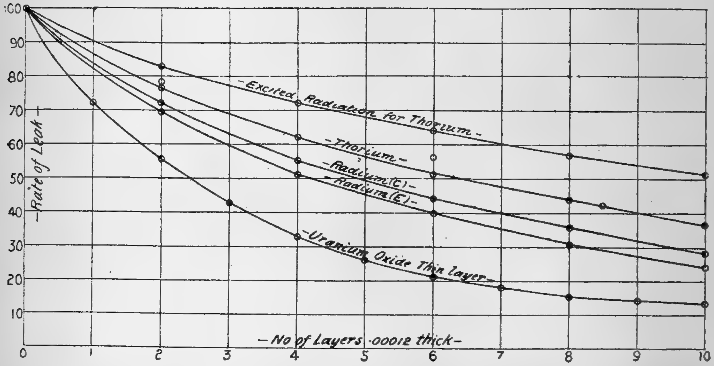


Fig. 4.



The radiations may be arranged in the following order as regards the power of penetration, beginning with the most penetrating.

Excited radiations due to Thorium and Radium:

Thorium
Radium
Polonium
Uranium.

The same order of penetration is observed for all the substances examined, viz. aluminium and Dutch-metal, tin-foil, and paper.

The same order, as will be shown later, holds also for the penetrating power of radiations in air.

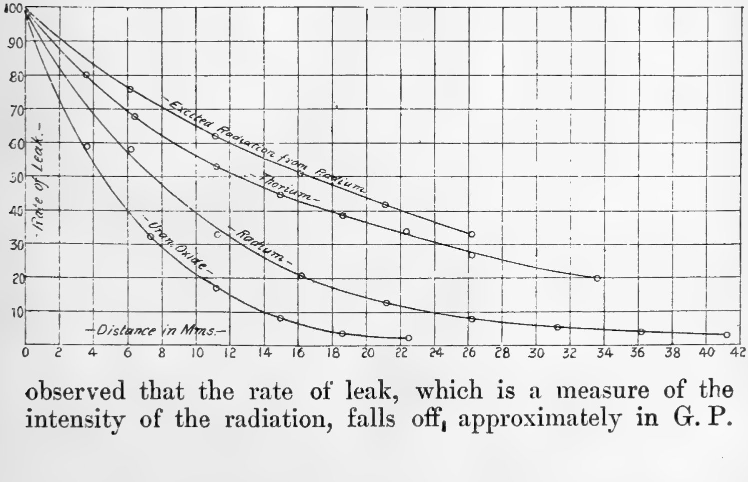
Absorption of the Radiation in Air.

The method employed of determining the absorption of the radiation in air was similar to that explained in a previous paper (Phil. Mag. Jan. 1899, p. 124).

Two insulated parallel plates kept a fixed distance of 2 cm. apart, could be moved by means of a screw to different distances from the parallel radioactive surface. The radiation from the active surface passed through a circular opening in the lower plate, covered with thin aluminium-foil, and was stopped by the upper plate. The current between the two fixed plates for a voltage sufficient in all cases to give the maximum or saturation current, was determined for different distances from the radioactive plate. If the radius of the active surface is large compared with the distance of the lower of the pair of plates from it, the current between two fixed plates for a distance x of the lower plate from the radioactive surface, can be readily shown from the theory of ionization (loc. cit.) to vary as $e^{-\lambda x}$, where λ is the coefficient of absorption of the radiation in the gas.

The results of the experiments are given in curves fig. 5. For each radiation the maximum rate of leak between the plates at a distance of about 2 mm. from the active surface is taken as 100, for the purpose of comparison. It will be observed that the rate of leak, which is a measure of the intensity of the radiation, falls off, approximately in G. P.

Fig. 5.



with the distance. The thickness of air through which each radiation passes before the intensity of the radiation falls to half its original value, is given in the following table.

Radiations.	Distance in cms.
Excited radiation from radium and thorium.	1·65
Thorium	1·0
Radium	·75
Uranium	·45

The penetrating power of the different radiations in air thus follows the same order as metals and solid substances.

Connexion between Absorption and Density.

From the curves of absorption of the radiations in metals and air, the coefficient of absorption λ can be readily determined. The following table gives the value of λ for aluminium and air for the different radiations.

Radiation.	λ for aluminium.	λ for air.
Excited radiation.........	830	·42
Thorium	1250	·69
Radium	1600	·90
Uranium	2750	1·6

Taking the density of air at 20° C. and 760 mm. as ·00120 compared with water, the following table shows the value of λ divided by density for the different radiations.

Radiation.	Aluminium.	Air.
Excited	320	350
Thorium	480	550
Radium	620	740
Uranium	1060	1300

Comparing aluminium and air the absorption is thus roughly proportional to the density of all the radiations. The divergence, however, between the absorption-density numbers is large when we compare two metals like tin and aluminium.

The coefficient of absorption for tin is not much greater than for aluminium, although the density is nearly three times as great.

The result for the nondeviable radiations is in this respect exactly opposite to that for the deviable uranium rays, for in that case we have shown that the absorption is more than twice as great as would be expected on the absorption-density law.

Results of this kind point to the conclusion that the mechanism that causes absorption is different for the deviable and nondeviable rays.

The result of Strutt*, that the relative ionization of hydrogen compared with that of air and other gases is quite different for the deviable and nondeviable rays of radioactive substance, also supports such a view.

Emanating Power of Thorium and Radium.

In a previous paper by one of us it has been shown that thoria gives off a radioactive emanation which behaves in all respects like a radioactive gas. It can be carried along with a current of air, passes readily through tightly packed cotton-wool, and is not appreciably absorbed by bubbling through solutions. The radiating power of the emanation rapidly diminishes, falling to half its value in about one minute.

Dorn † later found that a preparation of radium from P. de Haen also gave out an emanation which decayed far more slowly than the thoria emanation.

The specimens of radium used by us gave out very little emanation at atmospheric temperature.

On heating radium, however, the amount of emanation increased very rapidly. In *Physikalische Zeitschrift*, April 20, 1901, one of us has given an account of the effect of temperature on the emanating power of both thorium and radium. The radioactive substance to be tested was placed in a platinum tube (see fig. 6) through which a slow current of air was passed. The emanation was carried with the air into a metal cylinder, where the rate of leak produced by the emanation was tested by an electrometer in the usual way.

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* Phil. Trans. 1900.

† *Abh. der Nat. Ges. zu Halle,* 1900.

It was found that in the case of thorium compounds the emanating power increased to three or four times before a dull red heat of the platinum tube was reached, and remained constant if the temperature was unchanged. On heating to a white heat the emanating power was to a large extent destroyed.

The amount of emanation from radium increased over 10,000 times by heating below a red heat. Like thoria, if the temperature was raised to a white heat, the emanating power could not be recovered on cooling.

Unlike the thoria emanation, the radium emanation loses its radioactive power very slowly, with time.

The emanation kept in a closed metal vessel still preserved appreciable radioactivity after an interval of 14 days. The rate of decay of the emanation from radium does not appear to be the same under all conditions. The emanations from the two different radium compounds showed appreciable differences in this respect. The rate of decay also seems to depend on the temperature at which the emanations are produced.

Further experiments on this subject are delayed until preparations of radium of more definite composition are obtained.

Connexion between Emanation and Excited Radioactivity.

There is a very close connexion between the emanation from radium and thorium and their property of causing excited radioactivity. The presence of the emanation is necessary to produce excited radioactivity, and the amount of the latter depends upon the amount of emanation present.

Thoria, for example, which has been ignited to a white heat loses its power, to a large extent, of giving off an emantion, and its power of producing activity is diminished in a like ratio.

Excited radioactivity can be produced at long distances from the radioactive material provided the emanation is carried to that point. Intense excited radioactivity can be obtained from a radium emanation which has been left standing in a closed vessel for over a week, far removed from the radium compound from which the emanation was originally obtained.

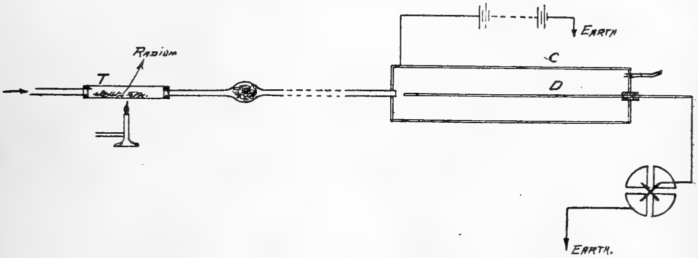
Excited radioactivity is due to the conveyance of some kind of radioactive matter to surrounding bodies. This radioactive material is either derived from the radioactive emanation itself, or in some way produced by it out of the surrounding gas.

This radioactive material is always associated with a positive charge and so can be concentrated on the cathode in a strong electric field.

A fuller discussion of the connexion between emanations and excited radioactivity, and the method of transmission of the latter, is reserved for a later communication.

Some experiments were made which illustrate the quantitative connexion between the rate of production of ions on the excited body, and the rate of production of ions by the emanation itself. Fig. 6 shows the general arrangement of the experiment. The radium was placed inside a platinum tube T through which a slow current of air was passed into the testing cylinder C. The platinum tube T was heated by a gas-burner until a large supply of emanation was carried into the testing cylinder with the current of air. The openings of the cylinder were then closed, and by means of the electrometer, the ionization current was observed between the outer cylinder and the brass rod D fixed centrally along the axis of the cylinder. A strong electric field (P.D. 300 volts) was applied and the excited radioactivity concentrated on the central rod. After several hours' exposure the amount of excited radioactivity on the rod reaches an approximate maximum. The rod was then removed and placed in a testing cylinder of the same dimensions, with the same P.D. between electrodes. The rate of leak was observed with the electrometer. A fresh rod was immediately placed within the emanating cylinder, and the rate of leak observed as soon as possible. This rate of leak is a measure of the number of ions produced by the emanation in the surrounding gas.

Fig. 6.



For radium (*e*) the rate of leak due to the excited radiation was about $\frac{1}{5}$ of that due to the emanation. For radium (*c*) the ratio was as high as $\frac{4}{5}$ after a long exposure. Since half the energy of the excited radiation in the rod is absorbed in the rod itself, the rate of production of ions due to the excited radiation is thus greater than that due to the emanation which causes it.

An experiment was tried to see whether the application of an electric field had any effect on the rate of production of excited radioactivity. The emanation was introduced into a long closed cylinder with an insulated central electrode and allowed to stand undisturbed for several hours with no electric field acting. The excited radioactivity in such a case was distributed by the processes of diffusion to all parts of the interior surface of the cylinder. On account of the small area of the central rod very little excited radiation was produced on it. After several hours a steady state is reached, such that the rate of conveyance of fresh radioactive material to the surface is balanced by the decay of radiating power of the matter already deposited. A P.D. of 300 volts was then applied so as to make the central rod the cathode, and the ionization current, observed with the electrometer, was immediately determined.

The excited radioactivity now decays on the inside of the cylinder and is concentrated on the brass rod. No appreciable change of the current was observed with time, although the rate of leak due to the excited radioactivity was quite comparable with that due to the emanation. This experiment shows that the rate of production of the excited radiation for a fixed quantity of emanation is the same whether an electric field is acting or not.

Excited Radioactivity due to Radium and Thorium Compounds.

The excited radiation from thorium compounds was obtained by placing a platinum plate, charged negatively, in a closed vessel containing thoria in the manner explained in a previous paper (*loc. cit.*). After about a day's exposure, the platinum plate was removed and placed inside the testing vessel in place of the radioactive material, and the diminution of the rate of leak observed for successive layers of thin metal foil. The same amount of absorption of the radiation was observed, if the platinum plate was made radioactive by being placed near some thoria in a closed vessel with no electric field acting. In such a case the excited radiation is not confined to the platinum plate, but is spread over the whole interior of the vessel in which the thoria is confined.

Two methods were adopted to obtain excited radiation due to radium. In one case, as with thorium, the platinum plate was made the cathode in a closed vessel containing radium.

With the sample of radium obtained from P. de Haen, Hannover, the amount of excited radiation obtained in this way was small. In order to obtain intense excited radiation the following course was adopted.

A small amount of the radium compound was placed on a small platinum plate which rested on a larger iron plate. A sheet of asbestos with a rectangular hole in the centre, smaller in area than the platinum plate, was placed over it. The platinum plate to be radioactive was placed over the hole in the asbestos and an iron plate placed on top of it. The top platinum plate was connected to the negative pole of a battery of 300 volts and the lower platinum plate to the positive pole. The iron plate was then slowly heated with a bunsen. After a short interval the top platinum plate was removed and found strongly radioactive.

Effects not much differing in intensity were obtained if the plates were uncharged. The only advantage in charging the top plate negatively is to concentrate to some extent the radioactivity on its surface. If the radium was not heated too strongly, the same specimen could be used several times before its power of exciting radioactivity was much diminished. If, however, the radium was heated to a red heat, its power of exciting radioactivity afterwards was to a large extent destroyed.

Some difficulty was experienced in determining the absorption of the excited radiation due to radium, on account of the rapid diminution of the intensity with time.

In order to correct for the loss of intensity with time, the rate of leak due to the bare excited plate was taken before and after the substance whose absorption was being examined was placed over it. The observations were taken at regular intervals as rapidly as possible. The mean of the two rates of leak due to the bare plate was taken as a measure of the intensity of the radiation for the intermediate time when the rate of leak due to the excited plate, covered with the absorbing substance, was being examined.

The absorption of the excited radiation due to both thorium and radium is shown in fig. 3 for aluminium foil, in fig. 4 for Dutch-metal, in fig. 5 for air at atmospheric pressure and temperature.

It was found that, for all the substances examined, the absorption of the excited radiation due to thorium compounds was the same as for the excited radiation due to radium, at any rate within the limits of experimental error. This points to the conclusion that these two radiations are the same.

It is of interest to observe that the power of penetration of the excited radiations is much greater than that of the ordinary nondeviable rays of thorium and radium, which give rise to the emanations. The radiations are apparently fairly homogeneous in character.

The penetrating power of the radium-excited radiation is independent of the substance in which it is produced.

Decay of Excited Radioactivity.

In a previous paper it has been shown that the excited radiation due to thorium compounds decays regularly with the time, falling to half its value in about eleven hours. The decay of excited radioactivity due to radium is irregular and depends upon the sample of radium employed.

Fig. 7.

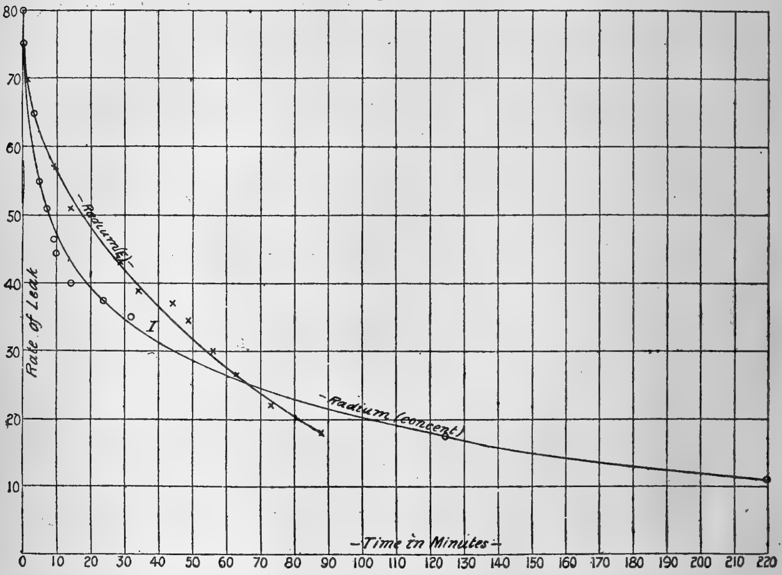


Fig. 7 shows the decay curves for the two samples of radium labelled "einfach" and "concentrated" respectively. The decay curve for the former is more regular than that for the latter. Fig. 8 is for radium (*c*) when the plate had been excited by exposure for a short interval to its emanation. In obtaining the curve of fig. 7 the plates were exposed for several hours in the presence of the emanations.

Curie* has given a curve of decay for excited radioactivity

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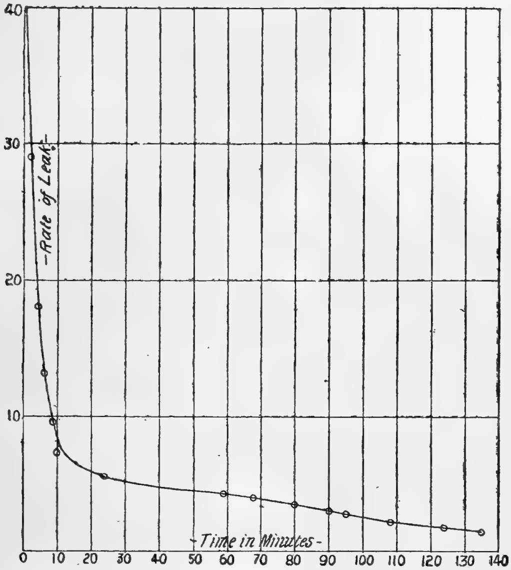
* Paris Report, 1900.

due to radium which is very similar to the curve for radium (*e*) fig. 7.

Fig. 8.



The decay-curves shown all exhibit to a greater or less degree the following peculiarities :—

(1) An initial rapid rate of decay for about 10 minutes after removal.

(2) A very slow decrease for the next 20 minutes. Then follows

(3) A more rapid decrease till radioactivity disappears.

The rate of diminution of intensity thus passes through a minimum about 20 to 25 minutes after removal of the excited plate from the presence of the emanation.

An explanation of these changes can be given in the light of some recent experiments by one of us on thorium-excited radioactivity.

It has been found that the excited radiation from a plate exposed for a short interval in the presence of thorium emanation increases to three or four times its initial value in the course of a few hours after removal. A preliminary account of these experiments is given in *Physikalische Zeitschrift*, No. 11, 1902.

No increase is observed when a plate has been exposed for many hours in the presence of thoria. This is to be expected, since the rate of decay of the excited radiation as a whole more than compensates for the increase of radiation due to radioactive particles deposited in the last few hours of exposure.

The general shape of the decay-curves for the two specimens of radium points to the conclusion that two kinds of radiation are emitted by the excited body which decay at different rates. The relative amount of excited radiation due to the two kinds is different for the two samples of radium. The amount of that radiation which decays more rapidly is greater for specimen (*c*) than for specimen (*e*).

If, in addition, we suppose, as in the case of thoria, that the excited radiation which has the slower normal rate of decay does not reach its maximum for some time after deposit of the radioactive matter, the general shape of the decay-curves can be satisfactorily explained.

The observed curve of decay is in that case due to the addition of the effect of two types of radiations, one of which decays regularly with the time, while the other increases at first, passes through a maximum, and then decays. Such a combination would completely explain the peculiarities exhibited by the experimental curves of the excited activity from radium (*c*) and (*e*).

It will be observed that the shape of the decay-curves for radium depends upon the time of exposure to the emanation. The initial decrease of excited activity with time is greater for a body exposed a short interval (see fig. 8) than for a body exposed several hours (see fig. 7, curve I.).

From general theoretical considerations the rate of rise of excited activity with time of exposure can be deduced from the rate of decay and *vice versa*. In a recent paper * it has been shown that excited radioactivity is due to the conveyance of radioactive matter of some kind on positively-charged carriers, which travel through air in an electric field with about the same velocity as the positive ions produced in air by Röntgen and Becquerel rays.

Suppose n_0 is the average number of ions produced per second by a single radioactive carrier at the instant of deposit. Let n = number after a lapse of time t.

Suppose $n = n_0 f(t)$ where $f(t)$ is a function of t,

such that $$f(t)=1 \text{ when } t=0,$$ $$f(t)=0 \text{ when } t=\infty;$$

$f(t)$ may in some cases pass through a maximum value greater than unity.

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* *Phys. Zeit.* No. 10, 1902.

The variation of the rate of production of ions from a particle with the time of deposit, is supposed to include the effect of different kinds of radiations emitted, which may also have different rates of decay, and any effects of excited radioactivity on the body on which it is deposited.

For simplicity, suppose that the radioactive carriers are deposited at a uniform rate of q per second. (This is the case in practice where the amount of emanation present does not vary with the time)

The number of ions produced per second after a time t by the radioactive particles deposited for the first short interval of exposure dt is given by

$$qn_0 f(t)\, dt.$$

The number of ions N produced per second by the radioactive matter deposited during the time t is given by

$$N = qn_0 \int_0^t f(t)\, dt.$$

A steady state is reached when the rate of supply of fresh ions per second, by the addition of radioactive material, is equal to the rate of diminution due to decay of excited radiation as a whole.

This steady state is reached after a long interval of exposure, and the maximum rate of production of ions N_0 is given by

$$N_0 = qn_0 \int_0^\infty f(t)\, dt.$$

If the curve of decay of excited radiation due to a single particle is plotted with the ratio $\frac{N}{N_0}$ as ordinate and t as abscissa, the value of these integrals can at once be obtained.

The rise of excited radioactivity with time can thus be at once deduced from the decay-curve of a single particle, and *vice versa.*

The rate of production of ions N_1 due to the excited radiation, after removal for a time t_1 from the emanation, is given by

$$N_1 = qn_0 \int_t^{t+t_1} f(t)\, dt,$$

where t is the time of exposure.

If N is the rate of production of ions immediately after removal, it follows that

$$\frac{N_1}{N} = \frac{\int_t^{t+t_1} f(t)\,dt}{\int_0^t f(t)\,dt}.$$

The decay of excited radioactivity is thus a function of the time of exposure, and in some cases may vary very greatly for different values of t.

The decay-curve for a long time of exposure may be quite different in general shape from that of the individual particle which gives rise to excited radioactivity.

This is seen to be the case for radium (*c*) (compare figs. 7 and 8). It is, however, much more marked in the case of excited activity from thoria, where the radioactivity for a few minutes' exposure increases after removal to three or four times its value in the course of a few hours, and then decays at the normal rate. For a long exposure the radioactivity on removal at once begins to decay.

The decay-curve of the individual particle on which we have based the predetermination of the curves of decay and rise of excited radioactivity, is obviously very nearly the same as the decay-curve for a body which has been exposed for a short interval in the presence of an emanation. The only condition to be fulfilled is that the time of exposure is to be so short that the radiation from the individual particle does not appreciably vary.

This condition can readily be fulfilled in the case of thorium-excited radiation; but in the case of radium the initial rapid rate of decay introduces experimental difficulties.

As a rule it takes a minute or two to remove the excited conductor from the vessel containing the emanation, and to place it in position in the testing apparatus. During this time the radioactivity has appreciably diminished.

Fig. 8 shows approximately the decay-curve of a radioactive particle for radium (*c*). The plate was only exposed a short time and then immediately tested.

Some experiments have been made on the *rise* of excited radioactivity with time in the case of radium (*c*). A curve for thoria is given in a previous paper. From the general shape of the decay-curve we should expect the radioactivity to increase rapidly for about the first ten minutes and then more slowly afterwards. This was experimentally found to be the case. The results obtained were only approximate on account of the initial rapid decay after removal.

Summary of Results.

From the differences observed in the behaviour of the radioactive substances most closely studied, viz. uranium, thorium, and radium, it will be seen that radioactivity is a very complicated phenomenon. Both uranium and radium * emit negatively charged particles with high velocities, similar in all respects to cathode-rays. In addition, uranium, radium, and thorium emit rays non-deviable by a magnetic field, which are readily absorbed by gases and thin layers of metal. These non-deflectable rays differ from one another in penetrating power and cannot consequently be ascribed to any radioactive impurity common to all these substances. In addition, thorium and radium possess the remarkable property of continuously emitting radioactive emanations which behave in all respects like radioactive gases. The emanations from thorium and radium differ greatly in their rates of decay of radiating power. The presence of an emanation gives rise to the complicated phenomenon of "excited" radioactivity. The nondeviable "excited" radiations due to thorium and radium, although apparently of the same penetrating power, decay at very different rates.

"Excited" radioactivity is not confined to radium and thorium, for Elster and Geitel † have recently shown that a negatively-charged wire, exposed in the open air, free from all possible contamination by radioactive substances in the laboratory, becomes strongly radioactive. This excited radioactivity ‡ decays at a different rate from that due to the emanations of thorium and radium, and also is of greater penetrating power.

Macdonald Physics Building,
McGill University, March 6, 1902.

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* It has recently been found that thorium also emits some rays deviable by a magnetic field. The excited radiations produced by thorium and radium also possess the same property. (Rutherford and Grier, Amer. Phys. Soc. April 21, 1902.)

† *Phys. Zeit.* 1901.

‡ Rutherford & Allen, *Phys. Zeit.* 10, 1902.

II. *The Sizes of the Water Particles producing the Coronal and the Axial Colours of Cloudy Condensation.* By C. Barus [*].

THE following table contains a summary of my data for the sizes of water globules producing coloured cloudy condensation either by the diffraction of diverging rays, or by absorption of the strictly axial pencil. A brief account of the general method of work will be found elsewhere [†]. The nuclei used came from glowing charcoal, though the corresponding result for sulphur nuclei will also be instanced. In the table N' denotes the relative number of particles per cub. centim., N the absolute number, $1/N^{1/3}$ the edge of a cube containing one particle, d the diameter of the particle, all referred to centimetres. Experiment showed that in successive adiabatic exhaustions between fixed pressures, $N'=N_0'10^{n(1+bt)\log y}$, where n denotes the serial number of the exhaustion, b is the coefficient of the time losses alone, y is the ratio of the density of distribution of nuclei before and after each exhaustion regarded as an adiabatic process, but corrected for the heat evolved by the precipitation.

In measuring the diameter, d, of the particles, the normal (white-centred) coronas succeeding the 20th exhaustion were used directly, by comparing their angular apertures, s, with the coronas due to lycopodium particles under like conditions. I assumed for the latter $d_0=\cdot0032$ centim., while by trial $s_0=\cdot45$ centim., seeing that the radius of the goniometer falls out. Hence numerically $d=\cdot00144/s$. In these experiments the source of light and the special goniometer were each 250 centim. from the receiver of water globules.

The diameters of the earlier coronal particles, *i. e.*, those corresponding to smaller values of n, were computed from N', as this was the immediate result of the experiments. If when $n=0$, $d=D$, then $d=DN'^{-1/3}$ and $D=\cdot00144\,N'^{1/3}/s$. In this way I found in case of the globe :—

$D=\cdot000263$ centim. for punk nuclei, $D=\cdot00035$ centim. for sulphur nuclei, and in the drum, $D=\cdot00036$ centim. for punk nuclei.

These data give the number of nuclei arbitrarily put in at the outset, but they seem to have an upper limit. The datum for the drum was reduced from those of the globe by the aid of the accompanying coronas.

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[*] Communicated by the Author.

[†] American Journ. of Science, [4] xiii. pp. 81–94 (1902); Science, xv. pp. 175–178 (1902). For allied experiments *cf.* American Journ. of Science, [4] xii. 1901; "Experiments with Ionized Air," Smithsonian Contributions, pp. 1–95 (1901).

The precipitation for adiabatic expansion was computed from $rx = s\theta - C\theta \ln \theta$, where θ is the absolute temperature, r the latent heat of evaporation, C the specific heat of the liquid, S the constant entropy, and $x/(1-x)$ the ratio of vapour and of liquid in the chilled mixture. In each exhaustion in the globe $m = 79/10^8$ gram was precipitated per cub. centim. of air, and for the drum similarly $m = 36/10^8$ grams of water per cub. centim. of air.

Finally the size of the water globules was found from $m = N\pi d^3/6 = N\pi D^3/6N'$, where N is the absolute and N′ the relative number of particles per cubic centim. In this way for coronas in the globe,

$$N = 8{\cdot}3 \times 10^4 \times N' \quad \ldots\ldots \quad \text{(punk nuclei)},$$
$$N = 3{\cdot}6 \times 10^4 \times N' \quad \ldots\ldots \quad \text{(sulphur nuclei)};$$

and for axial colours in the drum and weaker nucleation,

$$N = 1{\cdot}5 \times 10^4 \times N' \quad \ldots\ldots \quad \text{(punk nuclei)}.$$

If $N' = N_0' = 1$, or initially ($n = 0$), $N_0 = 83000$ and 36000, for punk and for sulphur nuclei, respectively, found in the globe. This nucleation was made as dense as I conveniently could. It is interesting to note, therefore, that these data lie between 10^4 and 10^5, the limits found for phosphorus nuclei in my earlier papers under very different conditions * The table has been constructed for punk (glowing charcoal) nuclei only, as these seem to be more uniform and give rise to a greater wealth of coronal display.

General Remarks and Deductions.

With regard to the two sets of colours, it appears that the coronas must in large measure be diffraction phenomena; the axial colours (which are rigorously axial) cannot be so explained, but seem to be evoked by some unknown kind of absorption. The contrast is sharply brought out by the experiments. Only after about 20 partial exhaustions (76–58 centim.) are the ordinary white-centred coronas encountered. After n exhaustions all the preceding coronas and axial colours from 0 to n are flashed through, and after hovering over the limit for a brief time show a tendency to a retrograde movement (n to 0), though this soon vanishes beyond recognition. The coronal centre (uniformly coloured patch or disk, in which lies the coloured point-source of light) surrounding the first axial blues and greens is not determinable as to colour, in the

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* Phil. Mag. [6] vol. iii. p. 91 (1902).

Diameters and Numbers of Water Particles,

$N'=N_0'10^{n(1+bt)\cdot\log y}$; $b=\cdot1$;

For coronas (globe, 30 cm. in diam.),

For axial colours (doubly conical drum, 187 cm. long,

Exh. No. *n*.	Corona.	$N'\times10^3$.	$d\times10^6$. cm.	$N\times10^2$. $1/\text{cm.}^3$	$\sqrt[3]{1/N}\times10^3$. cm.
0.	Nucleation.	1000	260	830	23
1.	Fog.	791	280	660	25
2.	Fog.	626	310	520	
3.	Fog.	495	330	410	
4.	Yellowish, Reddish.	392	360	320	
5.	Do., smaller.	310	390	260	34
6.	Wh-yl, prp, gr-yl.	245	420	200	
7.	Bluish, gr-bl, or, rd.	194	450	160	
8.	Greenish, gr, prp, gr.	154	490	130	
9.	Gr-yl, prp, gr, rd.	122	530	100	
10.	Yl, or-rd, gr, prp.	96	570	80	50
11.	Yl, or, rd, gr, viol, gr.	76	620	63	
12.	Wh-viol, prp, bl, gr, rd.	60	670	50	
13.	Wh, prp, gr, rd, gr.	48	730	39	
14.	Gr, bl-gr, rd, gr.	38	780	31	
15.	Gr-yl, br, gr, rd.	30	850	25	74
16.	Yl-wh, or-rd, gr, viol.	24	920	20	
17.	Wh, prp, gr.	19	990	15	
18.	Wh, gr-yl, bl-gr, rd, gr.	15	1070	12	
19.	Wh, rd-br, gr, bl, rd.	12	1160	10	
20.	Wh, rd, gr.	9·2	1250	7·7	111
21.	Wh, br, bl, gr, rd, gr.	7·3	1350	6·0	
22.	Do.	5·8	1460	4·8	
23.	Do.	4·6	1580	3·8	
24.	Do.	3·6	1710	3·0	
25.	Do.	2·9	1850	2·4	161
26.	Do. (faint).	2·3	2000	1·9	
27.	Do.	1·8	2160	1·5	
28.	Do. (very faint).	1·4	2340	1·2	
29.	Vanishing.	1·1	2530	·9	
30.	Do.	·9	—	—	—

Note:—Wh, white; yl, yellow; or, orange; rd, red; gr, green; bl, blue;

drum. In the globe it appears as a diffuse, tawny, red-rimmed fog. The first pronounced contrast appears in the orange-red axial colour and the blue-green or green-blue field. This is usually definite and complimentary in character. The axial colours then move toward the violet and *producing Coronal and Axial Colours.*

nuclei from glowing charcoal.
corrected $y=\cdot 819$; $t=1\frac{3}{4}$ min.
37 cm. in equatorial diam.), corrected $y=\cdot 916$; $t=3\frac{1}{2}$ min.

Exh. No. *n*.	Axial Colour.	Corresponding Corona.	$N'\times 10^3$.	$d\times 10^6$.	$N\times 10^2$.	$\sqrt[3]{1/N}$ $\times 10^3$.
				cm.	$1/\text{cm.}^3$	cm.
0.	Nucleation.		1000	360	150	40
1.	Viol-bl.	Fog.	889	370	130	42
2.	Bl.	Fog.	790	390	120	
3.	Bl.	Fog.	702	410	105	
4.	Bl-gray.	Fog.	624	420	94	
5.	Yl-gr.	Fog.	555	440	83	49
6.	Gr-yl.	Fog.	493	460	74	
7.	Yl.	Bl-gr.	438	470	66	
8.	Or.	Do.	389	490	58	
9.	Or.	Do.	346	510	52	
10.	Or-rd.	Do.	308	530	46	60
11.	Prp.	Gr-yl.	273	550	41	
12.	Prp.	Gr-yl.	243	580	36	
13.	Viol.	Yl.	216	600	32	
14.	Viol-bl.	Or-rd.	192	620	29	
15.	Do. *	Rd.	171	650	26	73
16.	Gr.	Prp.	152	670	23	
17.	Yl.	Do.	135	700	20	
18.	Yl.	Viol.	120	730	18	
19.	Viol?	Gr.	106	760	16	
20.	Viol.	Yl-gr.	95	790	14	89
21.	...	Or-rd.	84	820	13	93
22.	...	Viol-prp.	75	850	11	96

* Succceeding axial colours extremely faint, almost white; surrounding coronas strong.

prp, purple; br, brown; annuli read off from within, outward.

the field colours toward the yellow. After this the axial colours are already nearly white; the tinge of colour is so faint that it would be hard to recognize it if the sequence of colour were not known from the steam-jet. Nevertheless the march of colour into bluish, greenish, and yellowish tints, corresponds to a march of the field from yellows to reds and purples. The colours thus follow each other around the circle, apparently diametrically opposed in position. The axial yellows, oranges, etc., of the first order, seen so splendidly in the steam-jet, were not obtained with the drum in any case.

The data found may be sustained by independent estimates. It may be noted that the order of size of particle is about ten times larger than would follow if the same (axial) colour were produced by interference in thin plates.

When the coronas begin to vanish, the increased rapidity of removal of particles from gravitational subsidence is noticeable. In case of sulphur nuclei there were about 33 particles per linear centim. initially, and 5 particles per centim. finally; in case of punk nuclei, 44 per centim. initially and 4 per centim. finally. The attempt to use subsidence methods was abandoned. Such data are seriously complicated by the evaporation at the surface of the fog and by the fact that the air cleared by the warmer sides of the vessel rises convectively to the top. Both causes produce apparent but false subsidence. Again, the use of Kelvin's vapour-tension equation breaks down quantitatively for the present purposes, in practice.

With particles as near together as they are intially (say ·02 to ·03 centim.) one might anticipate some optical effect due to their mutual action. The normal or white-centred coronas do not appear until the particles are somewhat less than one millimetre apart. The edge of the cube containing one particle and the diameter of the particle are proportional quantities, the ratio being $N^{-1/3}d^{-1}$, or about 87 for the globe. The density of suspended water is thus about $\cdot 8 \times 10^{-6}$.

For the drum the uniform successive exhaustions were smaller and the ratio of diameter of particle to the edge of the cube was about 113; but the length of the column (now 187 centim. as compared with 30 centim. for the globe) more than makes up for the difference. Therefore a cube whose edges are ·04 centim., at the outset contains one particle ·00036 centim. in diameter; and $(113)^2$ cubes of this kind *on end* would, virtually, fill up the square content normal to the line of vision to the first order of small quantities. In other words, about 5 metres of column would be needed to effectively blot out the white light. At the end of the experiment, a column $\cdot 096(113)^2 = 1280$ centim. in length would be needed. In the above experiments with axial colours, the column was nearly 2 metres long, and this proved to be quite insufficient. The axial colours completely vanish (become white) before even one half of the coronas have been passed. Experiment shows, therefore, conformably with the given interpretation, that the condition of optical saturation (removal of the original white light) is a line of vision quite blocked by water particles all of rigorously the same size. Thus it would seem as if each single water particle colours the area of its projection.

Now what kind of absorption is this which occurs for particles of such surprisingly large dimensions relatively to the wave-length of light, which occurs moreover in just as marked a degree if the particles are electrical insulators like the precipitates from benzine and petroleum vapours? For though one cannot regard a water particle captured by a saline nucleus as quite an insulator, there seems to be no electrical conduction possible for the case where a sulphur nucleus condenses benzine vapour. But the discussion of this question is beyond the present purposes.

Brown University, Providence, U.S.A.

III. *Lenard Rays.* *By* J. J. E. Durack, *B.A.* (*Syd.*), 1851 *Exhibition Scholar, Trinity College, Cambridge* [*].

THE first experiments here described were undertaken with the object of measuring the velocity of the Lenard Rays as the pressure of air in the discharge-tube is altered. The variation of the energy of the rays, as shown by the intensity of the photographs taken for this purpose, led to an investigation of :—

(1) The variation of the ionization produced by the rays with the pressure in the discharge-tube;

(2) The change in the Lenard-ray current in the same circumstances; and

(3) The ionizing power of the Lenard rays, *i. e.* the number of ions one Lenard-ray ion produces in travelling unit distance through a gas at some standard pressure.

These experiments will be described in the above order.

§ 1. The discharge-tube, together with the apparatus used for determining the velocity, is shown diagrammatically in fig. 1 (p. 30).

The cathode rays were produced in a discharge-tube similar to that originally used by Lenard. A plane aluminium disk *c* served as cathode; the rod of aluminium connected with *c* was inclosed in a thick-walled glass tube

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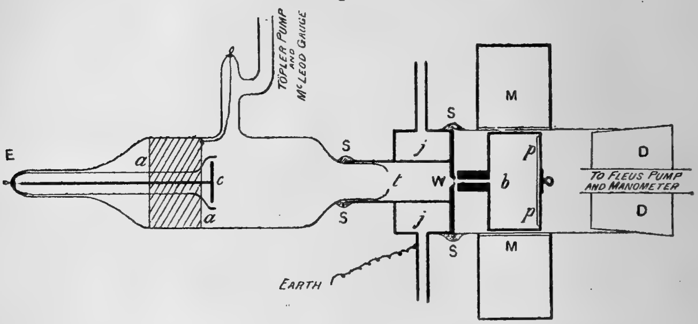
[*] Communicated by Prof. J. J. Thomson.

to prevent the discharge taking place from the rod, and it was also found necessary to cover the back of the disk with glass (as shown in the diagram) when intense Lenard rays were required. An aluminium cylinder *a a* was used as anode.

Fig. 1.



The end of the discharge-tube facing the cathode was drawn down and a brass tube *t* cemented on with sealing-wax coated on the outside with a layer of (Munich) soft wax*. An aperture about 1·5 mm. in diameter was bored in the end of the brass tube, the brass being rather thick to prevent heating, and the hole bevelled on the inside; on the outside a piece of aluminium-leaf, ·0043 mm. thick, was fastened with soft wax. This constituted the window W.

A water-jacket *j j* surrounded the tube *t* to keep the window cool and so prevent melting of the soft wax. The discharge-tube was kept connected to a Töpler pump and McLeod gauge.

An outside tube, which, following Lenard, I shall call the observation-tube, was cemented on to the tube *t* with sealing-wax; this tube contained the camera *b*, was closed at the end with a rubber stopper D, and connected to a Fleuss pump and manometer.

The velocities were found by measuring the magnetic

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* Sealing-wax joints, if properly made, are absolutely air-tight, that is to say I was unable to detect any leak in a discharge-tube with such joints when the tube was left unused for three weeks, the pressure of air in the tube during that time being less than ·01 mm. To make these joints, the parts to be joined should first be heated sufficiently to melt the sealing-wax (as has been before pointed out by several experimenters), the parts can then be pressed together while the wax is soft, and a uniform joint made by heating the wax till it flows smoothly, *care being taken not to burn the sealing-wax*: if the sealing-wax is burnt little bubbles break on the surface and probably allow the air to leak in; the soft wax serves to cover up these holes if any are formed.

deflexion of the rays, the electromagnet M M being used for that purpose.

The camera consisted of two brass cylinders about 1 cm. long and 3 cm. diameter, and fitted nicely in the observation-tube. One of the two brass cylinders fitted tightly into the other so as to shut out all stray light; the photographic plate *p p* was stuck on to the flat end of one of these tubes, while the other had a hole 2·2 mm. bored in the centre of the end and had a neck 1·5 cm. long attached, the end of the neck being pushed right up to the window.

An induction-coil with an Apps interrupter was used to work the discharge-tube, the tube and coil being inclosed in a metal box; the anode, water-jacket, and box were connected to earth. The observation-tube projected through a hole in the side of the box, so that the camera could be easily placed in position for taking photographs; sheets of lead screened off stray light and Röntgen rays coming from the discharge-tube directly.

The terminals of the secondary coil were provided with spheres of 1 cm. diameter, so that a rough measurement of the potential-difference required to send the discharge could be made, the distance between the spheres being adjusted till the coil seemed to spark at the terminals and discharge through the tube about equally.

In making the observations, the discharge-tube was pumped down to a pressure of about 60 × ·0002 mm., the furthest limit at which the Lenard rays produced an image on the plate *. The equivalent spark-length (measured between the terminals of the coil) was about 4·5 cm. for this pressure.

The camera was placed in position, and the observation-tube exhausted to a pressure of about 5 mm. of mercury; the coil was then turned on, and an exposure varying from 5 to 15 seconds given to the plate with the magnet M M "on"; the camera was then removed and the centre marked to obtain the position of an undeflected spot. After developing, the deflexion of the ions could be measured.

The discharge always increased the pressure in the discharge-tube, gas being given off probably by the brass struck by the cathode-rays, the potential required to produce the discharge was then less, and the Lenard rays "softer," than before.

The camera was then replaced and another photograph taken. In this way a series was obtained throughout the range at which Lenard rays were produced, this range being from spark-lengths of about 4·5 cm. to 3 cm.

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* This limit depends on the form of discharge-tube and the working of the coil.

To obtain the velocity from these measurements we have the formula given by J. J. Thomson*,

$$v = \mathrm{H} \cdot \frac{e}{m} \cdot \frac{d^2+\delta}{2\delta},$$

where

v is the velocity of the ions;
H is the magnetic field producing the deflexion δ;
d is the distance travelled from the neck of the camera to the plate;
e/m is the ratio of the charge on an ion to its mass, which has been measured by several experimenters and found to be approximately 10^7 in electromagnetic units.

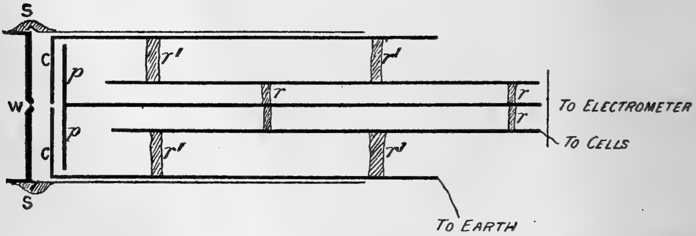
The magnetic field was varied so that the deflexion was nearly the same in all cases, it was measured with a small coil of known dimensions and a ballistic galvanometer.

The velocities as determined in this way varied from 5.10^9 cm. per second for the high discharge potentials to $3{\cdot}2\ 10^9$ for the lower; none of the velocities measured were smaller than this, but probably higher velocities could be obtained with good discharge-tube insulation.

The photographs varied very much in character, being very faint for the higher velocities and most intense just before the Lenard rays disappeared altogether. At this point double images were obtained, the one deflected, due to the Lenard rays, the other undeflected, due to Röntgen rays or to the lighting up of the aluminium window.

§ 2. To test further the variation of the energy with discharge-tube pressure, the apparatus shown in fig. 2 was used to measure the ionization produced by the rays.

Fig. 2.



An aluminium cylinder with a flat end CC, also of aluminium, fitted into the observation-tube and could be moved along it; the end was 1 mm. thick and had a hole 1 mm. in

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* J. J. Thomson, Phil. Mag. Oct. 1897.

diameter bored in its centre to face the window W. A plate of aluminium, *p p*, was placed inside parallel to the end and 4 mm. from it; this plate was connected to an electrometer and the connecting-wire screened from electrostatic effects with a metal tube: this tube was kept at a constant potential equal to the initial potential of the plate from which the leak was measured. The leaking system was supported by this tube with rods of sealing-wax, *r r*, and the outer earthed cylinder supported the shield also with sealing-wax rods $r' r'$, so that the insulation of the leaking plate was good. An initial potential-difference of 440 volts was put on between the plate and the cylinder so that a field of 1100 volts per cm. was applied to the gas; this was considered sufficient to saturate it*.

When necessary an auxiliary capacity was placed in parallel with the quadrants of the electrometer, to decrease the fall of potential while the rays were on.

Some difficulty was experienced in getting constant readings, even when the pressure of the discharge-tube was kept the same: this was thought to be due to the interrupter, but different forms of mercury-break made practically no difference. Finally, consistent readings were obtained by cutting down the current in the primary circuit and allowing the interrupter to work easily. The E.M.F. of the primary circuit was 8 volts; an additional ohm resistance was added to the ½ ohm of the primary, making the total resistance of the circuit 1·5 ohms.

Some of the Lenard rays proceeding from the window enter the aperture in the end of the cylinder, and make the gas a conductor. By this means only the ions produced between the plate and the end of the cylinder are collected, and we are able to find the ionization at different distances from the window.

With this apparatus it was found that the conductivity increased greatly with decreasing discharge-tube pressure, being a minimum for the low pressures (corresponding to high Lenard-ray velocities), and increasing steadily to a maximum at the point where the Lenard rays begin to disappear: here the conductivity began to decrease and quickly fell to zero.

This shows that the increasing energy, as shown by the photographs, was due to increasing Lenard-ray current, or, perhaps, to increasing ionizing power. More experiments will be described to settle this point later.

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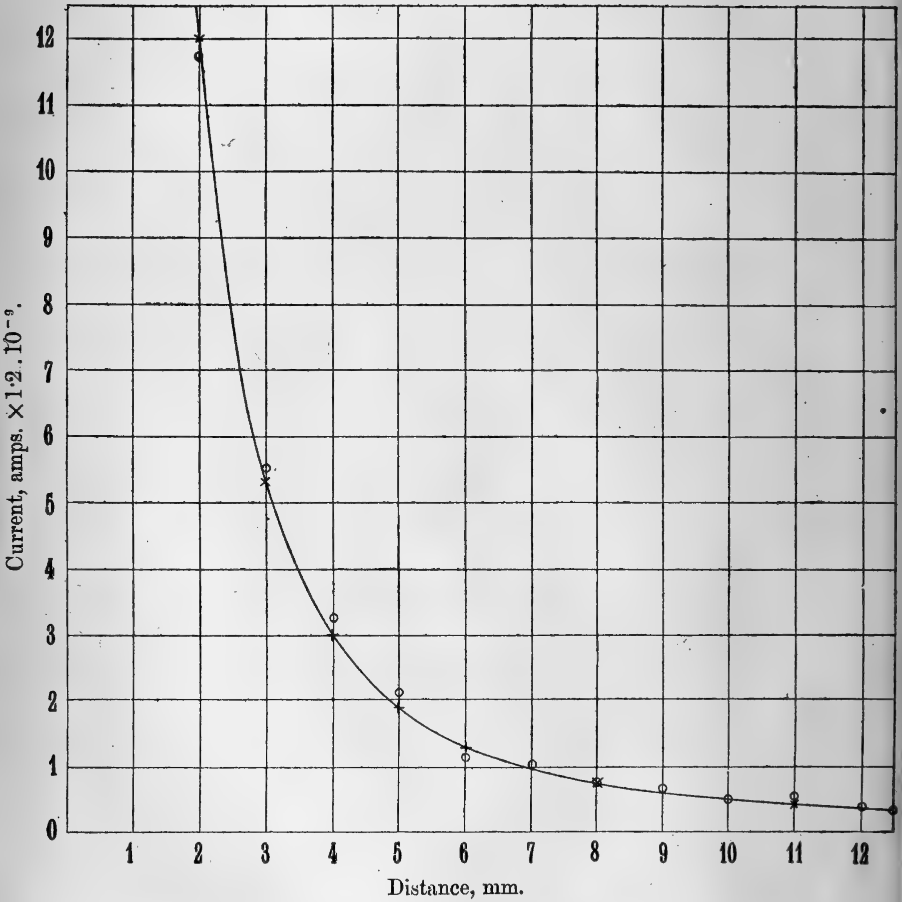
* The E.M.F. required to saturate the gas of course depends on the number of ions formed in 1 c.c. of the gas, *i.e.* on the intensity of the Lenard rays.

As the apparatus here employed was very convenient for measuring the conductivity at different distances from the window, observations were made to find the rate of decrease in the ionization with increasing distance.

Readings of the leak produced in 10 seconds were taken at different distances, the discharge-tube pressure being kept constant and such as to produce the maximum leak.

Curve I.



The following table gives the results of these readings. Distances are measured from the window to the inside edge of the end of the cylinder.

Current, amps. 1·2 . 10^{-9}.	Distance, mm.	Current.	Distance.
11·75	2	0·75	8
5·50	3	0·63	9
3·50	4	0·50	10
2·10	5	0·50	11
1·15	6	0·35	12
1·00	7	0·30	12·5

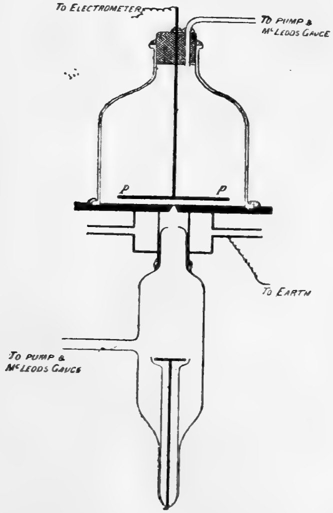
These numbers are shown by the circles ○ in curve I.; the curve is drawn from the formula

$$(\text{Current})\,(\text{Distance})^2 = \text{const.},$$

the constant being found by assuming the point distant 8 mm. from the window to lie on the curve; it will be seen that the circles lie nearly on the calculated curve: the crosses × give the calculated values.

§ 3. Experiments were next undertaken to find the current carried by the Lenard rays themselves, and at the same time the ionizing power of the rays.

Fig. 3.



The apparatus is shown in fig. 3; the old discharge-tube having been pierced by the discharge, a new one was made and the cylindrical anode omitted, the window serving as anode. With the new tube the intensity of the Lenard rays was increased and also the amount of gas given off by the tube during a given time of discharge. The amount of gas given off was found to increase with the intensity of the rays. Hence when it is desirable to keep the pressure pretty constant and very intense Lenard rays are not required, the cylindrical anode will be found useful.

The brass tube and water-jacket were soldered to a zinc plate about 9 cm. square and 5 mm. thick, a bevelled hole was bored in the zinc plate opposite the cathode, and the aluminium window stuck on with soft wax as before.

A bell-jar was fastened to the zinc plate and supported an aluminium plate *p p* which was parallel to the zinc plate and 2 mm. from it; aluminium was used for this plate to make the secondary ionization, if any exists, as small as possible. The plate, 7 cm. in diameter and 2 mm. thick, was supported by a rod passing through the ebonite stopper (shown by the shading in fig. 3) in the mouth of the jar; the rod was then connected to an electrometer and screened from electrostatic effects, as in former experiments. The jar was connected to a second pump and McLeod gauge *.

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* The McLeod gauge used has worked so satisfactorily that it is perhaps worth while describing it.

In order to measure small pressures with the McLeod gauge it is necessary to have

(i.) a large ratio of volumes.

To avoid capillary errors one must have

(ii.) tubing of the same bore inside at the zero and outside where differences in level are measured.

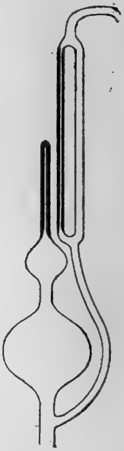
To avoid having to wait a long time for the pressure to equalize in the gauge and apparatus one must have

(iii.) a tube of large bore connecting the bulb of the gauge with the rest of the apparatus.

These three conditions can be realized by having the bulb of the gauge and the connecting tubes large, but this is objectionable, since it adds so much capacity to the apparatus and consequently requires so much more work in pumping.

By using capillary tubes inside the gauge and outside, we can keep the bulb small and at the same time have conditions (i.) and (ii.) fulfilled; condition (iii.) is then very easily fulfilled by having a wide tube for the air to pass through in parallel with the capillary as shown in fig. 4; by blowing a second small bulb above the first the range of pressures that can be measured by the gauge is greatly increased. With the gauge used in these experiments, pressures from 30 mm. to ·001 mm. can be easily measured, assuming, of course, Boyle's Law to be true throughout this range.

Fig. 4.



When the Lenard rays leave the window they strike the plate and give it a negative charge; on the way, however, they ionize the gas between the plates. By putting on a saturating E.M.F. we may collect all the ions formed.

Let p be the pressure of the gas in the bell-jar; d the distance from the plate to the window; α_p the number of pairs of ions produced by one Lenard-ray ion in travelling 1 cm. at the pressure p; N_0 the number of ions leaving the window per second; e the charge on an ion.

The current due to the Lenard rays is

$$-N_0e$$

(calling a motion of positive ions from the window to the plate the positive direction of current).

If a saturating E.M.F. is applied, the plate being charged positively, then all the negative ions formed move to the plate so that the current is

$$\begin{aligned}\gamma_1 &= -N_0e - N_0\alpha_p de \\ &= -N_0e\,(1+\alpha_p d),\end{aligned}$$

assuming that the Lenard rays travel straight across from the window to the plate.

Now if the plate be charged negatively we have, since we now collect the positive ions,

$$\gamma_2 = -N_0e\,(1-\alpha_p d);$$

hence

$$\gamma_1+\gamma_2 = -2\,N_0e,$$

which gives the Lenard-ray current.

Also

$$\gamma_1-\gamma_2 = -2\,\alpha_p d N_0 e,$$

hence

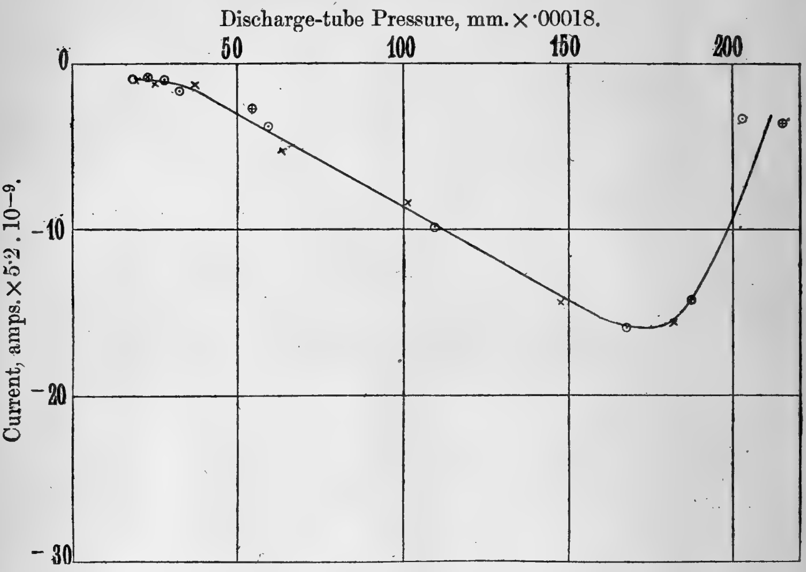
$$\frac{\gamma_1-\gamma_2}{\gamma_1+\gamma_2} = \alpha_p d;$$

which gives α_p.

We may, if we choose, pump the air in the bell-jar down to a very low pressure, so that α_p is small compared with 1, and then we should obtain the current carried by the Lenard rays no matter what is the direction of the field or its value.

Curve II. (p. 38) has been drawn in this way: the abscissæ represent the pressure in the discharge-tube, and the ordinates the Lenard-ray current. The points shown by the circles ⊙ and ⊕ have been plotted from readings taken with no E.M.F. applied to the gas, so that the plate pp was originally at the same potential as the zinc plate, and gradually charged up negatively as the Lenard rays fell on it. If the air is appreciably ionized between the plates the charging plate will collect positive ions from the gas; also if negative ions are given off by the plate, as when ultra-violet light falls on a zinc plate, these negative ions will leave the charging plate with a positive charge.

CURVE II.



Both these possible causes of error will make the Lenard-ray current too small.

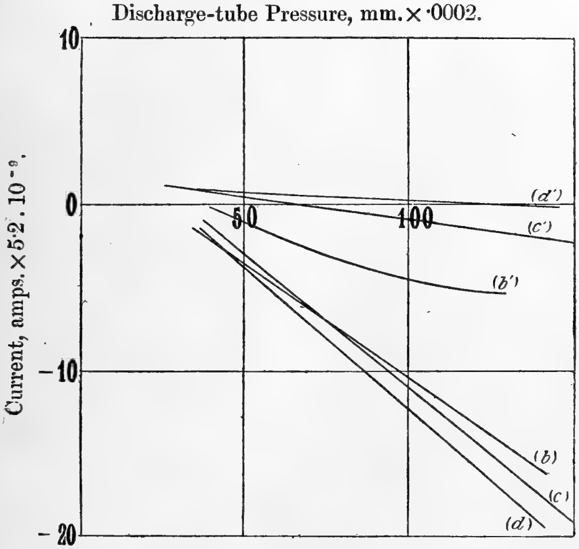
Now let the leaking plate be charged positively: the negative ions are now collected from the gas, and this will make the Lenard-ray current too large; but the negative ions which leave the plate, as in the case of ultra-violet light, will be attracted back to it if the electric intensity is sufficiently great, so that they will be without effect in this case. The curve II. proves that neither of these possible sources of error exists to any appreciable extent; for, as has been said, the two circles show the current as measured when the plate is charging up negatively, the crosses × the current when the plate was charged positively, a field of 630 volts per cm. being applied to the gas, and all three series fit the curve about equally well. The pressure in the bell-jar was always less than ·06 mm.

We can, then, state that the current carried by the Lenard rays at first increases as the pressure in the discharge-tube decreases, and that then there is a sudden falling off in the current, as we were led to suspect from the photographs.

Having measured the current carried by the Lenard rays and found that it kept fairly constant, it is only necessary to take readings of the total current with the field in one direction in order to find α_p for any pressure in the bell-jar. However, as it was thought that the pressure of gas in the jar might alter the Lenard-ray current, α_p was found by reversing the field between the plates. We then have α_p from the formula

$$\alpha_p = \frac{1}{d}\left[\frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2}\right].$$

CURVES III.



The curves III. have been drawn to show the saturation-currents for different discharge-tube and bell-jar pressures, as indicated in the following table:—

Curve.	Field. Volts per cm.	Bell-jar pressures, mm.
b	+64*	5·2
b′	−64	,,
c	+110	9·5
c′	−110	,,
d	+110	10·7
d′	−110	,,

* A + field indicates that the plate was charged positively.

The curves have only been carried up to the point where the Lenard rays reach a maximum, past this the presence of Röntgen rays prevents one from giving a proper interpretation to the values of the saturation-currents.

We can now find a_p for any type of radiation (indicated by the pressure in the discharge-tube). I have selected the type given out when the pressure was 105 × ·0002 mm., as this is well removed from the point where Röntgen rays are given off, and is considered likely to be most accurate.

Calculating α_p in this way we get the following numbers:—

Pressure mm.	α_p.	α_p/p.
10·7	5·1	·48
9·4	4·0	·43
5·2	2·0	·39

The mean of these three values of α_p/p is ·43, that is the number of pairs of ions one Lenard-ray ion makes in travelling 1 cm. of air at a pressure of 1 mm. of mercury is ·43.

Professor Townsend[*] in his experiments found 21 for the number of ionizing collisions one ion (produced in air by Röntgen rays) makes under the same conditions, or about 50 times the number obtained here.

This difference I was unable to account for by any experimental errors, but before seeking an explanation it was thought desirable to confirm the result. I therefore carried out further experiments, using a D'Arsonval galvanometer instead of an electrometer to measure the currents.

The arrangement was very simple; the cells, plates, and galvanometer were connected in series and the window always to earth.

Measurements of the Lenard-ray current were first made by pumping the bell-jar down to a pressure of about ·01 mm. It was found to make no difference whether a field + 10·5, − 10·5, or 0 volts per cm. was applied to the gas; the variation of the current was also in agreement with the electrometer observations.

α_p was next determined from the same formula as before for two pressures, as shown in the table :—

Bell-jar pressure, mm.	Field. Volts per cm.	α_p.	α_p/p.
10·1	500	7·5	·74
27·6	625	15·5	·56

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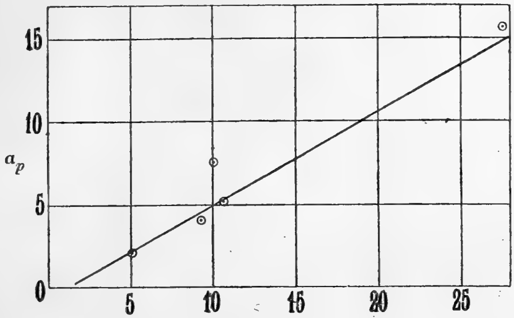
[*] Townsend, Phil. Mag. Feb. 1901.

The five values of a_p taken from these two series have been plotted in curve IV. It will be seen that four of them lie

Curve IV.



Pressure, mm.

on a straight line; this line does not pass through the origin. This may be due to an error in setting the zero of the McLeod gauge or in measuring the ratio of volumes.

These figures justified one in believing the correctness of former results obtained for a_p/p; they are larger than those obtained in the former series, probably because larger E.M.F.'s were applied to the gas.

To avoid the trouble of taking current-E.M.F. curves in all cases and yet be sure the gas was saturated, an E.M.F. was applied to the gas which was a little less than sufficient to give a free fall of 1 volt between collisions of the ions with molecules of air as these ions move towards the plate. This 1 volt free fall has been shown by Prof. Townsend [*] to give the ions just sufficient velocity to produce others by collisions. This was the plan adopted in working with the galvanometer, and I think it is probable some additional ionization due to the Townsend effect has come in to make a_p too large.

This conclusion that we have come to, viz., that very fast moving ions are less efficient ionizers than slower ones, is in agreement with the discovery of Becquerel, viz., that of all the deflectable Becquerel rays the slower ones are most easily absorbed. But it has been shown by several observers that ionization is proportional to absorption: hence we would expect the slow Becquerel rays to be more efficient ionizers than the fast ones.

As an explanation of this the following theory was proposed

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[*] Townsend, *loc. cit.*

by Prof. J. J. Thomson some time ago at a meeting of the Cavendish Physical Society.

Suppose a force to act between an ion and a molecule when the former approaches the latter, the force varying inversely as the square of the distance.

Let r be the radius of the sphere of action of a molecule, that is, an ionizing collision will just occur when an ion comes within this distance from its centre.

Let an ion carrying a charge e and of mass m be projected from an infinite distance with velocity v in the direction of the molecule.

The initial kinetic energy of the ion is

$$\tfrac{1}{2}mv^2.$$

The work done by the forces when the ion is distant r from the centre of the molecule is $\dfrac{e^2}{r}$.

Now the projected ion will just have sufficient energy to produce a pair of ions when

$$\tfrac{1}{2}mv^2 = \frac{e^2}{r}.$$

Hence collisions just occur when

$$r = \frac{2e^2}{mv^2}.$$

But the number of collisions in unit distance is proportional to r^2.

Hence $$\alpha_p = cr^2 = \frac{4ce^4}{m^2v^4},$$

or α_p varies inversely as the fourth power of the velocity.

On comparison of my experiments with those of Prof. Townsend, α_p does not appear to decrease so fast as is given by the inverse fourth power of velocity. However, this depends on the law of force assumed to act between an ion and a molecule; the argument is the same if we assume (as Maxwell did for the law of force between molecules) the inverse fifth power, in which case α_p varies inversely as the velocity. As far as one can estimate from Townsend's results and my own, this seems not improbable.

I have tried to give an explanation of the variation of α_p with velocity based on the consideration of the induced charge on a molecule when an ion passes close to it.

Let us assume that a molecule is a sphere, capable of having a charge induced on it.

When an ion approaches the molecule there will be an attraction between them owing to the induced charge on the molecule. If the mass of the ion is small compared with that of the molecule the force will be directed to the centre of the molecule, and at a distance r is equal to

$$F=\frac{e^2a^3}{r^3}\,\frac{2r^2-a^2}{(r^2-a^2)^2},$$

where a is the radius of the molecule, and e is the charge on the ion. The potential at the point r is therefore

$$V=e^2a^3\int_\infty^r\frac{2r^2-a^2}{r^3(r^2-a^2)^2}=-\frac{e^2a^3}{2r^2(r^2-a^2)}.$$

Let an ion be projected from an infinite distance with a velocity which is large in comparison with the velocity of translation of the molecules; let p be the perpendicular from the centre of the molecule to the direction of the initial velocity.

Let $r=$ the length of the apse,
$v'=$ the velocity at the apse.

Then
$$\tfrac{1}{2}mv^2=\tfrac{1}{2}mv'^2-\frac{e^2a^3}{2r^2(r^2-a^2)},$$

where m is the mass of the ion.

Also $vp=v'r$;

hence
$$\tfrac{1}{2}mv^2=\tfrac{1}{2}m\frac{v^2p^2}{r^2}-\frac{e^2a^3}{2r^2(r^2-a^2)}$$

or
$$p^2=r^2+\frac{e^2a^3}{mv^2}\cdot\frac{1}{r^2-a^2}.$$

Let p_1 be the value of p for which a collision just occurs, *i. e.* when $p=p_1$ the ion is drawn inside the sphere of action by the attracting forces. Also let r_1 be the radius of the sphere of action, N the number of molecules in 1 c.c. of the gas.

We have the mean free path of the ion

$$=\frac{1}{\alpha}=\frac{1}{\pi p_1{}^2N},\quad\text{or }\alpha=\pi Np_1{}^2,$$

but
$$p_1{}^2=r_1{}^2+\frac{e^2a^3}{mv^2}\cdot\frac{1}{r_1{}^2-a^2}$$

Hence

$$\alpha_p=\pi N\left[r_1^2+\frac{e^2a^3}{mv^2}\,\frac{1}{r_1^2-a^2}\right]^*.$$

If we suppose, as is very frequently done, that the radius of the molecule and of the sphere of action are identical, *i. e.* that actual contact takes place at a collision, the formula for α_p becomes

$$\alpha_p=\pi N\left[1+\frac{e^2}{mv^2}\,\frac{1}{2\rho}\right]a^2,$$

where ρ is the radius of an ion.

The experimental evidence available is not sufficient to test the truth of this formula, but we can make a rough estimate of ρ from the values of α_p obtained by Professor Townsend and myself.

$$\frac{21}{\cdot 4}=\left(1+\frac{e^2}{2m10^{17}}\,\frac{1}{\rho}\right)\Bigg/\left(1+\frac{e^2}{32m10^{18}}\,\frac{1}{\rho}\right).$$

Taking the velocity giving Townsend $\alpha=21$ as $3\,.\,10^8$ cm. per sec., and the velocity in the case of the Lenard rays as $4\,.\,10^9$.

From this we get $\rho=10^{-11}$ cm.

From the values of e/m for cathode rays and for hydrogen in electrolysis we know that m the mass of an ion is approx. 10^{-3} times the mass of an atom of hydrogen, and so if the densities are equal the radius of an ion would be of the order 10^{-9} cm.; but on Prof. Thomson's view of an atom, viz. that it is made up of ions, the density of an atom would be much less than the density of an ion; hence 10^{-9} is too large for the radius of the ion.

Also we know that the radius of the ion must be greater than 10^{-13}, for it has been shown by J. J. Thomson †, and also by Searle ‡, that the inertia due to a moving charge e on a sphere of radius ρ is

$$m_2=\frac{2}{3}\,\frac{e^2}{\rho},$$

when the velocity is small compared with that of light,

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* It was pointed out to me that this form $A+\frac{B}{v^2}$ is the same as that deduced by Sutherland in calculating the influence of cohesion on the free path (v. Meyer, Kinetic Theory of Gases, p. 425), and hence it is not necessary to assume any more than that the force is central.

However, I have assumed *less* than this, having merely supposed a charge could be induced on the molecule, that the force is central, and the actual law of force follows from electrostatics; moreover, we deduce a definite form for a in terms of quantities which may be experimentally determined, and thus we can test the theory.

† J. J. Thomson, Rec. Researches, p. 21.

‡ Searle, Phil. Mag. xliv. 1897.

e being expressed in electromagnetic units. As the velocity increases m_2 increases; hence m, what is usually taken to be the mass of an ion consisting of the ordinary mechanical mass together with the apparent mass due to the moving charge, is greater than m_2.

Hence
$$m > \frac{2}{3}\frac{e^2}{\rho},$$

i. e.
$$\rho > \frac{2}{3}\frac{e^2}{m},$$
$$> \frac{4}{3}10^{-13}.$$

The value therefore that we have calculated for ρ lies between the limits that can be assigned to it in other ways.

The experiments described in this paper were carried out in the Cavendish Laboratory, and I have much pleasure in expressing my gratitude and best thanks to Professor Thomson for many suggestions and kindly advice given during the progress of the work.

IV. *On the Magnetostriction of Steel, Nickel, Cobalt, and Nickel-Steels.*

By H. Nagaoka, *Professor of Physics, and* K. Honda, *Lecturer in Physics, Imperial University, Tōkyō* *.

§ 1. Introduction.
§ 2. Magnetization of Steel, Nickel, Cobalt, and Nickel-Steels.
§ 3. Change of Length by Magnetization in (*a*) Steel ovoid, (*b*) Nickel ovoid, (*c*) Cobalt (cast and annealed) ovoids, (*d*) Reversible Nickel ovoids containing 46, 36, 29, 25 per cent. of Nickel, (*e*) Reversible Nickel-Steel wires containing 46, 35 per cent. of Nickel in low fields.
§ 4. Effect of Mechanically Elongating Cobalt and Nickel-Steels on Magnetization, and the reciprocal relations with the change of length.
§ 5. Change of Volume by Magnetization in Steel, Nickel, Cobalt, and Nickel-Steel ovoids.
§ 6. Wiedemann Effect in Iron, Nickel, and Nickel-Steel wires.
    (*a*) Twist produced by the interaction of circular and longitudinal magnetizations, (*b*) circular magnetization produced by twisting a longitudinally magnetized wire, (*c*) longitudinal magnetization produced by twisting a circularly magnetized wire, (*d*) application of Kirchhoff's theory to Wiedemann effect and reciprocal relations.
§ 7. Summary of the Results.

§ 1. INTRODUCTION.

IN the course of our researches on the magnetostriction of different ferromagnetic bodies, questions of various character presented themselves, both with regard to the method

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* Communicated by the Authors.

of measurement and the nature of the sample. The minuteness of the effect necessitated precautions against diverse sources of error, such as the non-homogeneity of the magnetizing field, and the non-uniformity of temperature. All these different sources of error, however intricate they may at first sight appear, can, by properly arranging the measuring apparatus, be eliminated. In the present investigation we have used the method of observing the change of length and of volume already described in our former papers*, with slight modifications.

Apart from these instrumentalities, the diversity in the character of magnetostriction with different samples is hardly to be avoided. Experiments by Rhoads† with rolled and stretched sheets of iron sufficiently prove that the treatment of ferromagnetic bodies has great influence on the change of length accompanying the magnetization. In our former experiments on the magnetostriction of iron, steel, and nickel, the soft iron was what may be practically considered homogeneous, but the nickel ovoid was turned into shape from a thick plate. It thus seemed advisable to repeat the experiments with more homogeneous metals. In addition to this, our investigation did not include the magnetostriction in cobalt, the only specimen hitherto examined being an ovoid, which was broken in two pieces, and firmly fixed together by wrapping thick paper over the broken edge‡. Unlike other experimenters, we tested cobalt in the present investigation in the cast and annealed states, and found an extraordinary difference in the change of length.

The curious property of irreversible nickel-steel as regards magnetization has been known for a long time by the experiment of Hopkinson. The question of magnetostriction in reversible nickel-steel was a tempting subject of investigation, especially in connexion with the remarkable small thermal expansion possessed by the metal, and its practical utility in the construction of scales and other instruments, which will not be affected by the variation of temperature. Moreover it was very interesting to examine the nature of the magnetostriction in nickel-steel, as it is composed of two substances, whose length-change by magnetization is of opposite character in weak fields, but similar in strong. A simple conjecture may suggest that the changes produced by magnetization are according

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* Nagaoka, Phil. Mag. Jan. 1894; Wied. *Ann.* liii. p. 487 (1894); Nagaoka & Honda, Phil. Mag. Sept. 1898, April 1900; Nagaoka, *Rapports presentés au Congrès International de Physique,* Paris, ii. p. 536 (1900). For literature on magnetostriction see *Rapports.*

† Rhoads, Phys. Rev. vii. p. 65 (1898); Phil. Mag. Nov. 1901.

‡ Nagaoka, Wied. *Ann.* liii. p. 487 (1894).

to the relative proportion of the magnetostriction of the constituents, but the phenomena are of a very complex nature.

Associated with the change of length and of volume comes the Wiedemann effect, which is measured by the amount of torsion caused by the interaction of circular and longitudinal magnetizations. The measurement in cobalt must at present be postponed, as the metal cannot be brought to a geometrical shape suitable for experiment on account of its brittleness. Investigation of the effect in nickel-steel of different percentages presents the phenomenon in the same aspect as for the length-change, and the sense of twist is determined by that of iron in weak fields.

A singular characteristic of magnetostriction is its reciprocity with the effect of stress on the magnetization of different ferromagnetic substances. In the present instance, we have specially turned our attention to cobalt and nickel-steels. As will be expected from the nature of the length-change, the former metal is characterized by the existence of a minimum point closely analogous to that bearing the name of Villari for iron, while with the latter the effect of the longitudinal pull always results in the diminution of magnetization. The parallel statements giving the correlation between the magnetization and the effect of torsion, first noticed by G. Wiedemann, can thus be extended to other effects of stress and the strain resulting from the magnetization.

§ 2. INTENSITY OF MAGNETIZATION IN STEEL, NICKEL, COBALT, AND NICKEL-STEEL OVOIDS.

In all of our experiments we noticed the change of dimensions by magnetization and the strength of the field $\mathfrak{H}$ ($\mathfrak{H}=\mathfrak{H}'-N\mathfrak{I}$, where $\mathfrak{H}'$ is the external field, N the demagnetizing factor, and $\mathfrak{I}$ the intensity of magnetization). It will therefore be not out of place to make a digression on the magnetization of the ferromagnetic substances here examined, in order to enable us to examine the various changes, considered as functions of the intensity of magnetization.

The following table gives the dimensions as well as the

Metal.	a (cm.).	c (cm.).	v (c.cm.).	ρ.	N.
Steel	0·493	10·00	10·40	7·85	0·0836
Nickel	0·493	10·00	10·40	8·87	0·0836
Cast Cobalt	0·493	10·00	10·38	8·26	0·0836
Annealed Cobalt	0·495	10·02	10·52	8·20	0·0836
Nickel-Steel (46 p. cent. Ni)	0·494	10·01	10·45	8·15	0·0836
„ „ (36 p. cent. Ni)	0·496	10·01	10·48	8·11	0·0836
„ „ (29 p. cent. Ni)	0·492	10·01	10·43	8·12	0·0835
„ „ (25 p. cent. Ni)	0·494	10·02	10·40	8·05	0·0836

demagnetizing factor N of the ovoids examined in the present experiments. *a*, semi-minor axis of ovoid; *c*, semi-axis of rotation of ovoid; *v*, volume; *ρ*, density, determined by hydrostatic balance.

The difference in the volume of ovoids is to be attributed to the slight deviation from exact geometrical shape. As most specimens of cobalt contain more or less quantities of nickel, the cast and annealed samples were chemically analysed by Mr. Y. Suzuki, student in chemistry, with the following result:—Cast cobalt, Co 93·36, Ni 5·05, Fe 1·20, C 1·38, Si 0·39, Cu 0·17, Mn 0·12; Annealed cobalt, Co 92·74, Ni 4·07, Fe 1·07, C 1·64, Si 0·28, Cu 0·15, Mn 0·04.

The magnetization was determined magnetometrically[*] as given in the following table:—

Cast Steel.		Nickel.		Cobalt (cast).	
$\mathfrak{H}$.	$\mathfrak{J}$.	$\mathfrak{H}$.	$\mathfrak{J}$.	$\mathfrak{H}$.	$\mathfrak{J}$.
0·8	44	1·0	14	2·7	30
1·3	135	2·7	76	5·6	83
1·6	319	5·5	139	14·7	274
3·1	633	7·8	198	19·4	340
7·4	878	11·7	252	30·0	467
23·0	1122	18·2	314	44·7	572
140	1433	33·3	377	89·8	778
302	1555	59·9	426	256	984
511	1627	116	459	474	1080
597	1644	482	484	643	1119
672	1648	796	486	720	1136

Cobalt (annealed).		Nickel-Steel (46 p. cent. Ni).		Nickel-Steel (36 p. cent.).		Nickel-Steel (29 p. cent.).	
$\mathfrak{H}$.	$\mathfrak{J}$.	$\mathfrak{H}$.	$\mathfrak{J}$.	$\mathfrak{H}$.	$\mathfrak{J}$.	$\mathfrak{H}$.	$\mathfrak{J}$.
3·6	4	0·9	36	1·7	38	1·2	24
13·4	22	2·7	102	4·8	134	2·6	81
22·4	38	4·2	241	9·4	352	6·4	139
42·6	90	6·2	465	14·6	524	13·3	188
77·5	188	16·9	926	30·4	720	24·7	224
195	367	35·5	1108	85·5	900	46·2	243
281	439	120	1274	150	934	68·8	249
364	527	231	1308	262	953	140	256
461	568	380	1323	367	962	325	264
617	633	557	1333	510	971	575	273
788	699	778	1345	818	992	893	280

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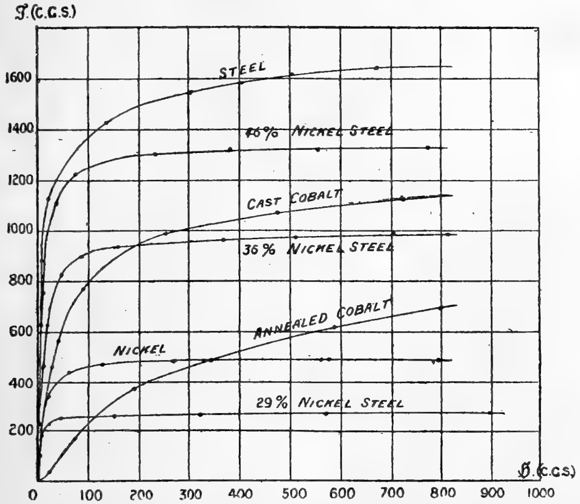
[*] The magnetizing coil had the following constants;—Length = 30 cm. diam. of the core = 3·2 cm., $4\pi n = 379·7$, resistance = 0·63 ohm. The ovoid was placed axially, so that the extremities of the axis were at 5 cms. distance from the ends of the coil, thus insuring the uniformity of the field.

The curves of magnetization are represented in fig. 1. The most magnetic of the metals here examined is cast steel, whose magnetization comes very near to that of soft iron. Of the two kinds of cobalt the cast specimen lies between steel and nickel; but with the annealed specimen the susceptibility is small in weak fields, and less than in nickel, and the differential susceptibility $\left(\frac{d\mathfrak{J}}{d\mathfrak{H}}\right)$ is greater in the strong, so that the intensity of magnetization becomes greater than in nickel.

Fig. 1.



Of the three kinds of reversible nickel-steels the 46 per cent. Ni specimen approaches steel, the 36 per cent. Ni lies near cast cobalt, and the 29 per cent. Ni is less magnetic than pure nickel. The magnetization reaches asymptotic value in fields less than those for steel or cobalt. The 25 per cent. Ni specimen is only feebly magnetic, so that its magnetization is scarcely to be detected by the magnetometer. Here we notice a singular fact, that the intensity of magnetization in nickel-steel is not proportional to that of the constituent metals.

§ 3. CHANGE OF LENGTH BY MAGNETIZATION.

(a) *Cast Steel* (fig. 2).

Dr. H. du Bois was kind enough to give us a piece of cast steel which was regarded as the most homogeneous specimen at present obtainable. The rod was turned into an ovoid, and its change of length measured in the manner already described in our former paper.

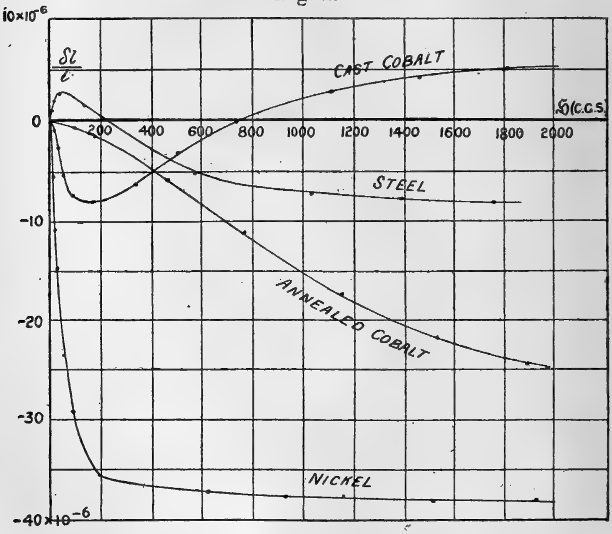
In low fields the ovoid elongates and reaches a maximum, whence it gradually diminishes, till it indicates no elongation. The decrease goes on steadily, but the rate of change becomes gradually less, and ultimately assumes an asymptotic value. As will be seen from the curve of the length-change (see fig. 2), the general feature resembles that of iron, with slight difference in quantitative details.

(b) *Nickel* (fig. 2).

The nickel ovoid which we formerly used for the measurement of length and volume changes was prepared from a thick plate of the same metal. Although the ovoid was heated in a charcoal fire for several days lack of homogeneity was undeniable. To guard against such mischances we have tested a new specimen supplied by Johnson and Matthey, shaped into an ovoid from a cylindrical rod.

The nature of the change does not materially vary from the former specimen. In weak fields the contraction takes place at first slowly, but gradually at an increased rate. Between fields 5 and 100 the rate of diminution is very rapid, but the change becomes at last asymptotic, when it amounts to about 38×10^{-6}. It appears from the curve (see fig. 2)

Fig. 2.



that the further diminution of length will be but slight, even if the field be increased to several thousand units.

(c) *Cobalt* (fig. 2).

One of us has already examined the change of length in a cobalt ovoid, which unfortunately was broken in two pieces. The result was notwithstanding in close conformity with that already discovered by Bidwell.

Rods of cobalt, obtained from Johnson and Matthey, were turned into ovoids of the same dimensions as for the two former metals. One of the ovoids was examined in the state just as it issued from the lathe, while the other was annealed in a charcoal fire for about four hours, after carefully wrapping it with asbestos paper. As the change of length by magnetization and the intensity of magnetization were characterized by a remarkable difference in character, it would be well to describe the phenomena separately for cobalt ovoids which underwent different treatments.

Cast Cobalt.—The behaviour of cast cobalt, as regards the length-change, is similar to that of nickel in weak fields. Instead of reaching an asymptotic value, as in nickel, the contraction of cobalt reaches a maximum at about $\mathfrak{H}=160$, from which the metal gradually recovers with increase of field-strength, till it attains its initial length in $\mathfrak{H}=740$. The metal, however, goes on elongating but at a less rapid rate up to $\mathfrak{H}=2000$, which is the strongest field employed in the present experiment. Representing the change of length by means of a curve (see fig. 2) we notice a singular trend, somewhat resembling the inverted form of the curve showing the same change for iron and steel. If the existence of the maximum elongation in iron warrants the existence of the Villari point, a point of opposite character will exist in cobalt if the metal be subjected to loading.

Annealed Cobalt.—The cast cobalt has a silvery hue, similar to nickel only lacking the yellowish lustre of the latter. By annealing cobalt the surface-colour turns ashy grey, and the permeability of the metal diminishes (see § 1) in a remarkable degree, as will be seen from the curves of magnetization (fig. 1). The change of length by magnetization takes place at first slowly, but goes on steadily increasing till it amounts to nearly 25×10^{-6} for $\mathfrak{H}=2000$. The curve (see fig. 2) representing the change is therefore very simple, approximating to a straight line. As will be found later on, we found the reciprocity between the strain caused by magnetization and the effect of stress on the magnetization again established, since the longitudinal pull only produces diminution of magnetization.

(d) Reversible *Nickel-Steels.*

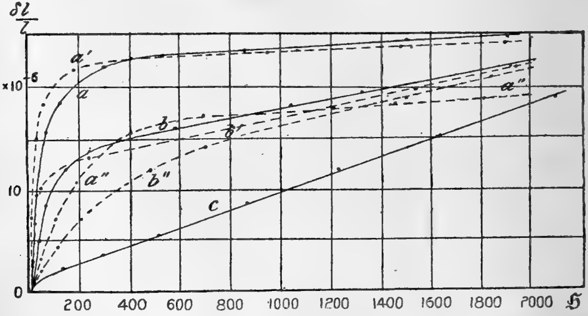
Through the kindness of Messrs. Ch. Ed. Guillaume and Dumas, who supplied us with the different samples of reversible nickel-steels, manufactured by Commentry-Fourchambault at Decazeville, we were enabled to examine the magnetostriction of reversible nickel-steels in its various aspects.

The samples to be tested were either turned into ovoids of the same dimensions as for the other metals, or used in the form of wires. These two sets of metal of different shape do not show serious discrepancies in the observed results, which are given below for specimens containing different percentages of nickel, either in the form of ovoids or wires. It is to be remarked that the annealing of nickel-steel was conducted in a glass tube, through which hydrogen was kept in constant circulation, and heated to 500° C. upwards for more than three hours.

The curves of the length-change are plotted in fig. 3.

All the nickel-steels indicate increase of length in fields up to about $\mathfrak{H}=2000$. The character of the change for 46 per cent. Ni resembles that for nickel with opposite sign, inasmuch as the curve of elongation in the former has great resemblance to that of contraction in the latter, and is similar to that for the intensity of magnetization. The elongation in very weak fields takes place slowly, but in fields of about 30 units the rate of change is most rapid, and soon reaches an inflexion-point, whence to increase in length very slowly and finally in an asymptotic manner.

Fig. 3.



a=nickel-steel ovoid (46 p. c. Ni).
b= ,, ,, ,, (36 p. c. Ni).
c= ,, ,, ,, (29 p. c. Ni).
a'=nickel-steel wire (46 p. c. Ni) annealed.
a''= ,, ,, ,, ,, unannealed.
b'= ,, ,, ,, (35 p. c. Ni) annealed.
b''= ,, ,, ,, ,, unannealed.

With the 36 per cent. Ni we observe similar features in the curve of elongation. The inflexion-point lies in higher fields, but the elongation is less than in 46 per cent. Ni. After this stage is over the ovoid goes on elongating at an almost constant rate, which is greater than for the 46 per cent. Ni. Although the field at which the curves for 46 per cent. and 36 per cent. Ni intersect has not yet been reached, we can easily infer that if the field be sufficiently increased, the elongation in 36 per cent. Ni *, which is the least expansible by rise of temperature, will exceed that for 46 per cent. Ni. The contrast between 46 per cent. and 36 per cent. Ni is similar to that between 36 per cent. and 29 per cent., so that what has just been remarked with respect to the two former alloys equally applies to the relation between the two latter. It is also remarkable to observe that the 29 per cent. Ni, which will apparently indicate the largest increase of length if the field be made sufficiently strong, is the least susceptible of the three nickel-steels. With the 25 per cent. Ni we could not detect any change which is within the scope of measurement now attainable with the present arrangement.

The nickel-steel wires in the annealed state present similar changes of length to the ovoids. In the hard drawn state the change is decidedly less than for the annealed.

The curves of the length-change in iron or nickel, placed side by side with those in nickel-steel, present a singular contrast. As is well known, nickel contracts instead of elongating like iron, the amount of contraction being several times that of iron. The feature here presented by nickel-steel is similar to nickel as regards the amount and the character of the change, but as to the sense of elongation it is similar to iron in weak fields, increasing instead of diminishing as in nickel. It thus appears that the length-change by magnetization is not of a simple nature, and not to be easily determined from the percentages of the constituent metals.

(e) *Nickel-Steel wires in low fields.*

Urged by the question of the practical utility of the metal we made special investigation into the change of length in low fields, such as may habitually occur in the neighbourhood of electric installations or in the terrestrial magnetic field. The question will be of great importance in deciding the effect of the terrestrial field; as one instance, we may mention that in using Jäderin's wire of nickel-steel in geodetic measurements. One may suspect, from what has already been described, that the effect of the magnetic field will not be

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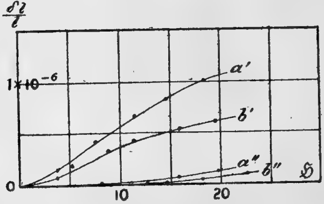
* The expansion-coefficients a for nickel-steel are as follows :—

For 29 per cent. Ni : $a=0\cdot000010$.
„ 36 per cent. Ni : $a=0\cdot000001$.
„ 46 per cent. Ni : $a=0\cdot000009$.

of the same magnitude as that of thermal expansion, which, as is well known, is of very minute amount. Experiments in low fields show that the magnetostriction plays no important part in the use of nickel-steel scales; only in measurements of extreme accuracy it will be necessary to add a very small correction to the measured values, according as the scale is placed in the magnetic meridian or perpendicular to it. As will be seen from the curves of elongation (fig. 4) the difference in a metre will generally be less than $\frac{1}{10}\,\mu$ for measurements made in the said directions.

Fig. 4.



a' = nickel-steel wire (45 p. cent. Ni) annealed.
a'' = Ditto, unannealed.
b' = nickel-steel wire (35 p. cent. Ni) annealed.
b'' = Ditto, unannealed.

One distinct feature in the curves of elongation is the effect of annealing. In both 45 and 35 per cent. Ni the wire elongates much more in the annealed than in the hard drawn state, so that in cases where the change caused by magnetization is to be feared we shall be able to eliminate the errors due to magnetostriction in a considerable degree by using the unannealed metal.

§ 4. EFFECT OF MECHANICALLY ELONGATING COBALT AND NICKEL-STEELS.

A remarkable feature in the magnetostriction is the reciprocal relation between the strain caused by magnetization and the effect of stress on magnetization. We have already examined the different changes from this standpoint for iron and nickel. In the present experiment we made special examination into the effect of longitudinal pull on the magnetization of cobalt and nickel-steels in the same light.

Magnetometric measurement of the change of magnetization of a cast cobalt cylinder by loading shows decrease in low fields (see fig. 5). As the field strength is increased the amount of the decrease reaches a maximum and then gradually lessens. Ultimately the field at which the longitudinal pull does not affect the magnetization is reached. When this stage is over the magnetization increases by loading, so that the effect is reversed. The existence of a critical point in cobalt, analogous to that of Villari in iron, is thus established (see fig. 5). With annealed cobalt the effect is simpler. As will be seen from the curves in fig. 6 the longitudinal pull always causes diminution of magnetization which increases with the field. Thus the behaviour of cast and annealed cobalt stands in correlation with the change of length caused by magnetization.

Fig. 5.

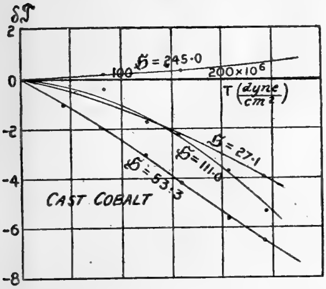
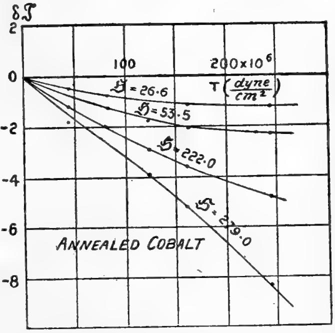
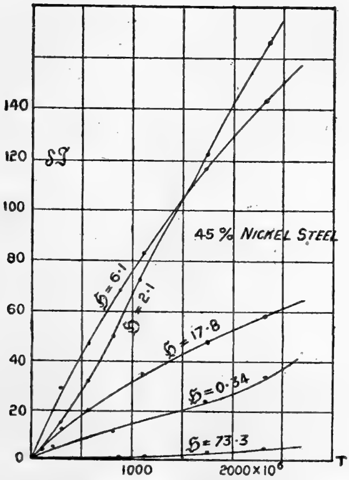


Fig. 6.



Loading nickel-steel wires always results in the increase of magnetization, as will be seen from fig. 7. The following parallel statements will clearly show the reciprocity between the change of length due to magnetization and that of magnetization wrought by the mechanical stretching.

Fig. 7.



Cast Cobalt.

Magnetization produces diminution of length in low fields, which, after reaching a maximum, gradually decreases, and finally increase of length is produced in strong fields.	Mechanical elongation produces diminution of magnetization in low fields, which, after reaching a maximum, gradually decreases, and finally becomes an increase in strong fields.

Annealed Cobalt.

Magnetization produces diminution of length, which gradually increases with the strength of the field.	Mechanical elongation produces diminution of magnetization, which gradually increases with the strength of the field.

Nickel-Steel.

Magnetization produces increase of length.	Mechanical elongation produces increase of magnetization.

§ 5. CHANGE OF VOLUME BY MAGNETIZATION.

It was suggested by Rhoads that the change of volume by magnetization may, in a great measure, be due to the heterogeneity in the material under examination, while in some experiments the arrangement was not free from errors, which, though very small, are sufficient to disguise the minute effect. One serious drawback in these experiments was the use of a disproportionately large mass of iron, which, had the ratio of dimensions been sufficiently great, would not have been altogether objectionable, but as it mostly happened to be, did not give the expected result. Non-uniformity of the field is another source of error, which unfortunately has too often been neglected; the result obtained in fields which are not uniform will indeed be difficult of interpretation. If the material under test be not placed axially in the direction of magnetization and the mechanical force urging the magnetic substance in one or other direction comes into existence, the change of shape of the volumenometer will in some cases be of such amount that it not only deteriorates the measured change, but screens the desired effect. These various sources of error may, by proper construction of the volumenometer, be easily eliminated.

The arrangement of the volumenometer has already been described in our former researches, so that it would be superfluous to enter anew into the details of the apparatus; suffice it to say that the axis of the ovoid coincided with that of the magnetizing coil, which was all the while waterjacketed.

As announced by Quincke [*], change of volume in the liquid

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[*] Quincke, *Sitzb. d. Berliner Akad. d. Wiss.* xx. p. 391 (1900).

filling the volumenometer may be caused by the pressure in the magnetic field. To guard against this source of error we have specially examined the volumenometer readings by simply filling it with water or ferric chloride. The result was in the negative within the range of field used in the present experiment, as will be easily expected, since the pressure is proportional to the square of the field strength.

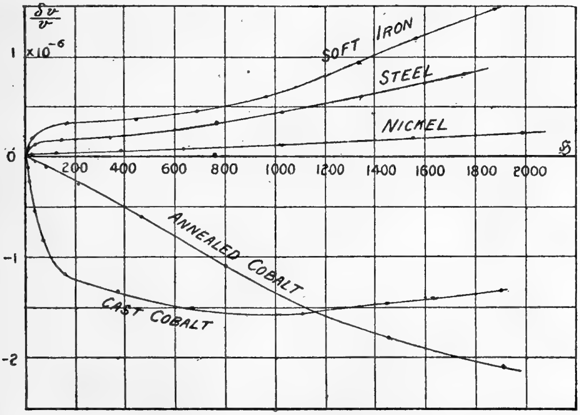
(a) *Cast Steel* (fig. 8).

The metal shows increase of volume in fields up to $\mathfrak{H}=2000$. In weak fields the change is very small, but the rate is tolerably large; as the field increases the curve reaches an inflexion-point. The change goes on somewhat slowly for fields amounting to a few hundred units; it again reaches an inflexion-point, whence to increase steadily and almost at a constant rate as the field is farther increased.

(b) *Nickel* (fig. 8).

In our two former experiments we noticed a discrepancy in the nature of the volume-change in this metal. With a bar of square section we noticed a diminution, while an ovoid showed an increase. That this may be easily accounted for we have already discussed in our former paper, so that it would be unnecessary to enter into the subject anew.

Fig. 8.



With the present specimen, which may be considered as more homogeneous, we noticed a slight increase of volume, which is about the same in amount as that observed in the former experiment. The character of the change is similar to that in steel, the curve of the change presenting two inflexional points. These points do not appear in such a remarkable degree as in steel, but their whereabouts can be ascertained at a glance.

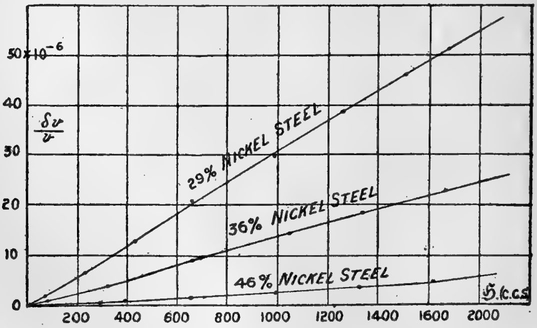
(c) *Cobalt* (fig. 8).

Just as we have noticed a difference in the length-change and the intensity of magnetization in the cast and annealed metals, we notice a difference in the volume-change for these two bodies. The results of observation are plotted in curves (fig. 8). The behaviour of cobalt is unlike other ferromagnetic substances—instead of showing increase the magnetization causes diminution of volume, which in the annealed state bears close resemblance to the character possessed by nickel, indicating glimpses of two inflexion-points in the curve of volume-change. With the cast specimen the feature is still more different from the other ferromagnetic substances. The diminution of volume takes place quite rapidly in weak fields, so that the curve soon reaches an inflexion-point. The rate of diminution after passing this point is very small, the curve passing on almost parallel to the axis of the field. This state continues for a large range of fields, but the curve, instead of showing another inflexion-point, reaches a point of maximum diminution of volume. The course of the curve turns and proceeds in the same direction so far as the present experiment goes. This character is possessed by cast cobalt only among the numerous specimens of ferromagnetic substances hitherto experimented upon. Further, we may notice that the amount of the change is, to a certain extent, greater in cobalt than in iron, steel, or nickel.

(d) *Nickel-Steel* (fig. 9).

The volume-change in nickel-steel is simple but extremely large compared to other ferromagnetic substances. The common feature of the change, as will be seen from the

Fig. 9.



graphical representation, is the approximate proportionality of the effect to the magnetizing force.

The magnitude of the change is, however, not directly proportional to the intensity of magnetization, as the 46 per cent. Ni shows a smaller effect than the 29 per cent. Ni, which is the least magnetizable among the specimens with the exception of 25 per cent. Ni, whose magnetization is scarcely to be detected by ordinary means. In fields of 1600 C.G.S. units the change amounts to

$\frac{\delta v}{v} = 3{\cdot}8 \times 10^{-6}$ for 46 per cent. Ni.
$= 22{\cdot}0 \times 10^{-6}$,, 36 ,, ,,
$= 48{\cdot}9 \times 10^{-6}$,, 29 ,, ,,
$= 0{\cdot}2 \times 10^{-6}$,, 25 ,, ,,
$= 1{\cdot}2 \times 10^{-6}$,, soft iron.

The difference between steels containing different percentages of nickel is indeed remarkable, as the changes here noted far exceed that hitherto observed in simple ferromagnetic substances. The change in 29 per cent. Ni is nearly 40 times greater than in soft iron; in fact, the motion of the capillary meniscus can be easily followed by the naked eye, as the displacement, which takes place almost instantaneously with the making of the current, is nearly 5 mm. in the capillary tube of 0·4 mm. diameter in the strongest field at our disposal. Even the 25 per cent. Ni shows a volume-change which, in spite of the minute magnetizability, is distinctly visible with a microscope.

From the above result, it follows that there is a certain alloy, whose percentage content will lie somewhere between 25 per cent. and 36 per cent., that will indicate greatest change of volume; the change will indeed be the greatest that we can observe in the ferromagnetic substances of common occurrence.

When we consider that the alloys of nickel and iron show increase of volume, we at once perceive that the sense of the change is not common to both the constituent metals. When we further consider the magnitude of the change and compare it with that observed in iron or nickel, we are struck with the immensity of the effect, which is not shared in such an extraordinary degree by either of the constituents of the alloy. A similar remark applies to the magnetizability of the different specimens; that the alloy of two strongly magnetic substances should give rise to an almost neutral body is in no way a matter for surprise, when considered in the same light as the enormous effect of magnetization on the bulk of the alloy. In the present instance, we are at a loss to find which of the two metals plays a predominating part in the magnetostriction of nickel-steel; perhaps a complete study of the subject from the lowest percentage to the pure nickel, and the comparative investigation of the phenomena in the succeeding stages, will reveal to us the groupings of the constituent metals while entering into an alloy, and the part played by them in the magnetization and the various phenomena attending it.

It may at first sight appear that the smallness of thermal expansion in nickel-steel necessarily entails the minuteness of the change of length and of volume by magnetization, but no connexion seems to exist between the magnetostriction and the deformation due to temperature variation, as illustrated in the preceding experiments.

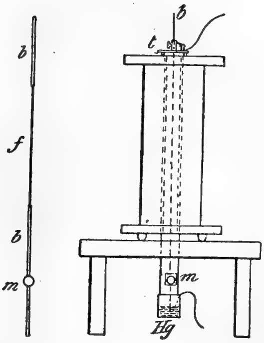
§ 6. WIEDEMANN EFFECT IN IRON, NICKEL, AND NICKEL-STEEL WIRES.

(a) *Twist produced by the interaction of circular and longitudinal magnetizations.*

The subject was first studied by G. Wiedemann, who established remarkable reciprocal relations with the longitudinal magnetization produced by twisting a circularly magnetized wire. Dr. Knott found that the direction of twist in iron is opposite to that in nickel; Bidwell afterwards discovered that the twist in iron is reversed in high fields. Unfortunately some of these experiments were undertaken with wires which were longer than that of the coil, so that the magnetization was far from being uniform.

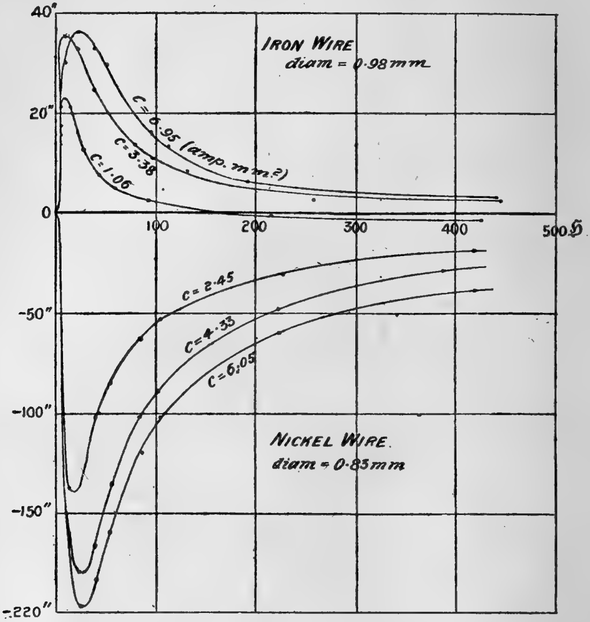
The twist produced by longitudinal magnetization of a circularly magnetized wire was measured in the following way (fig. 10). To the extremities of a ferromagnetic wire (f) 21 cm. long were brazed stout brass wires (b, b), and a light plane mirror (m) was attached to the lower one. The end of the lower brass wire dipped in a mercury pool, while the upper brass wire was clamped to a small tripod (t), which rested on the top of a magnetizing coil, provided with hole-, slot-, and plane-arrangement. One end of the accumulator was connected with the tripod, while the other was led to a mercury pool. The wire hung vertically in the axial line of the coil, which was used for all the preceding experiments. The vertical component of the terrestrial magnetic field was compensated by placing another coil in the interior of the magnetizing coil. The lower part of the wire to be tested was protected against air-currents by inclosing it in a wide brass tube with a small window, just where the reflecting mirror was attached. The twist was measured by scale and telescope method, by which the deflexion of $0''\cdot3$ per cm. was easily read. The current was measured by Kelvin graded amperemeters, whose constants were from time to time checked by means of an ampere balance. Before each experiment, care was taken to demagnetize the wire completely, either longitudinally or circularly, by passing an alternate current of gradually diminishing intensity.

Fig. 10.



Twist by varying the longitudinal field.—The direction of twist in iron, so long as the longitudinal magnetizing field is not strong, is such that if the current is passed down the wire from the fixed to the free end and the wire is magnetized with north pole downwards, the free end, as seen from above, twists in the direction of the hands of a watch. By keeping the circular field constant, the amount of twist increases at first, till it reaches a maximum in a field of about 20 units (fig. 11); it then goes on diminishing till it ultimately changes direction and continues to twist in the opposite direction with increasing fields. The field at which the twist is reversed increases with the circularly magnetizing field. In nickel, the direction of twist is opposite to that in iron, but the general feature is similar to iron, the only difference being that even in strong longitudinal fields the twist is not reversed. For wires of equal thickness, the amount of twist in nickel is greater than in iron—the maximum twist in iron wire of 1 mm. diam. by passing 6 amperes through it amounts to about 28″ per cm., while with nickel wire of 0·83 mm. diam. under similar conditions, the maximum twist amounts to about 200″.

Fig. 11.



Three different kinds of nickel-steel wires, for which our thanks are due to Dr. Ch. Ed. Guillaume, were tested. The results of the measurements are shown in fig. 12.

The sense in which a nickel-steel wire twists is the same as for iron. The amount of twist increases with the magnetic field, but it soon reaches a maximum, to decrease afterwards quite slowly as the field becomes stronger; and the twist is generally reversed in high fields. With the specimens tested, the twist increases with the percentage of nickel. The 23·6 per cent. Ni and 39·2 per cent. Ni were examined in a hard drawn state; but the 45·2 per cent. Ni wire was examined after annealing it in hydrogen, as already described.

Twist by varying the circular field.—In iron the twist increases with the strength of the circular field if the longitudinal field remains constant. Such is also the case with nickel in moderate and strong fields. In low longitudinal fields, however, the twist does not continue to increase with the circular, but we notice a maximum as will be clear in the

Fig. 12.

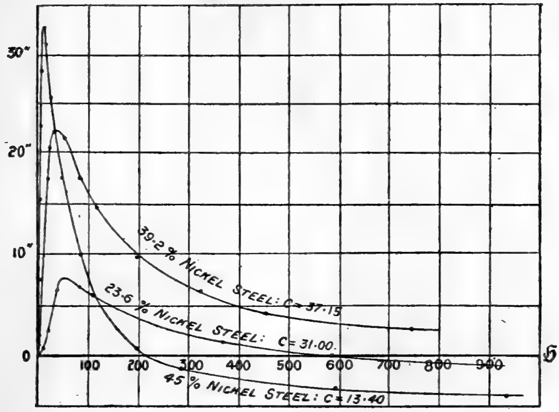


Fig. 13.

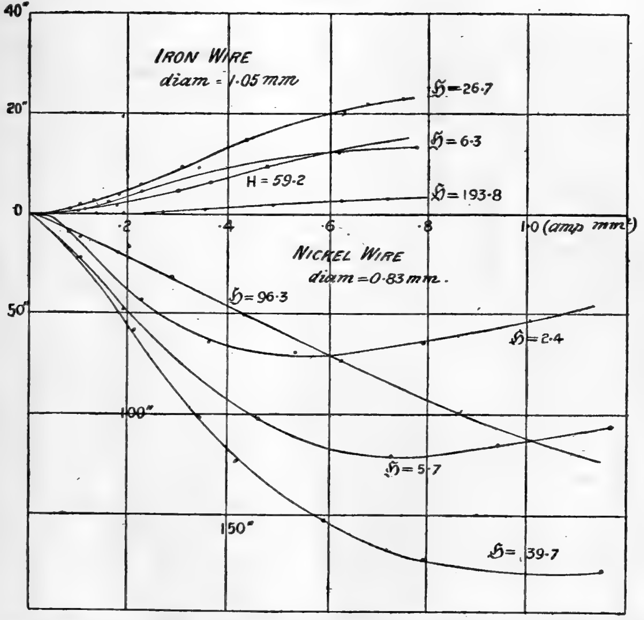


figure (see fig. 13). There is great experimental difficulty in increasing the circular field, inasmuch as the wire becomes heated and the result is materially affected.

The hysteresis accompanying the cyclical change of the circular magnetization deserves special notice. If the longitudinal field be such that with the increase of the circularly magnetizing force, the twist reaches a maximum, the curve of twist goes below its former course on weakening the circular magnetization. The twist, however, goes on slowly increasing, till it crosses the *on*-curve and then reaches a maximum, whence it gradually diminishes and ultimately vanishes in a negative field. The course after passing this point is exactly the reverse of that already described. The character of twist is exactly the same for iron as for nickel, when we take the opposite character of twist into account. The nature of the hysteresis is nearly the same when the longitudinal magnetizing field is made to vary while the circular field remains constant.

The results are in accordance with the experiments of Wiedemann and Dr. Knott, with the discrepancy in the position of maximum twist in nickel, which occurs in a tolerably strong field according to Dr. Knott.

(b) *Circular magnetization produced by twisting a longitudinally magnetized wire.*

By twisting a longitudinally magnetized wire, circular magnetization is developed which is measured by the transient current at the moment when the twist is applied. One * of us found that the current due to twisting was opposite in direction in these two metals, and that it reached a maximum in moderate fields. As the magnetizing current was not very strong, no conclusive measurements were made as regards the nature of the transient current in strong fields. In order to clear this point and see if any intimate relation with the Wiedemann effect could be traced, fresh experiments were undertaken by the same method as before. We have to notice that the ferromagnetic wire was so placed in the axial line of the magnetizing coil that it lay in a nearly uniform field.

The measurements of the transient current for iron and nickel wires are shown graphically in fig. 14. The current for constant amount of twist increases with the strength of the longitudinal field; it, however, soon reaches a maximum, whence it gradually diminishes. In nickel the transient current attains asymptotic values in strong fields without changing its direction, while in iron it is reversed in a field of about 200 C.G.S. units, when the twist is small. The increase after the reversal is not pronounced, but becomes finally asymptotic.

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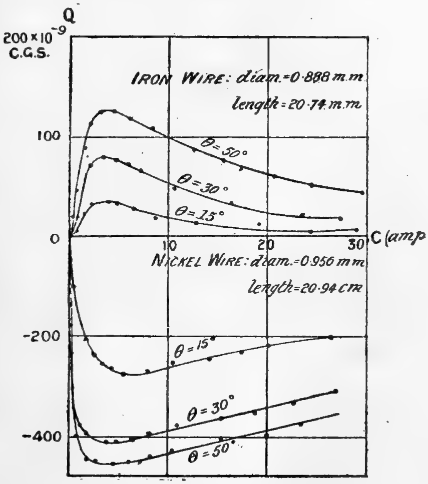
* Nagaoka, Phil. Mag. Feb., 1889.

(c) *Longitudinal magnetization produced by twisting a circularly magnetized wire.*

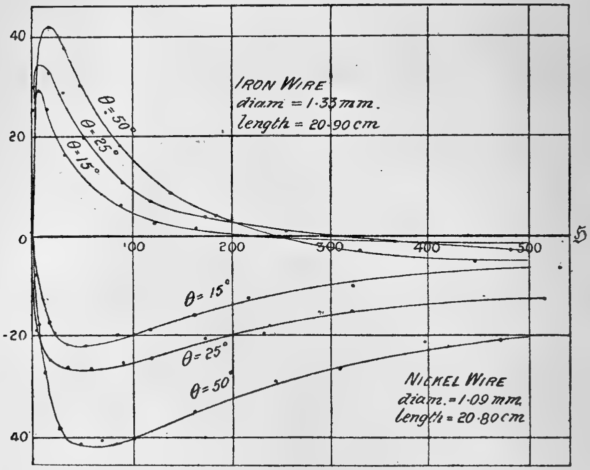
The longitudinal magnetization produced by twisting a circularly magnetized wire presents the same character as the transient current above described. The experiment is very difficult on account of the heating of the wires. To avoid the rise of temperature, the iron and the nickel wires were covered with *urushi* (Japan lac) which has the special property of being a very good insulator while, at the same time, the melting temperature is comparatively high. The wire thus insulated was stretched in the axial line of a secondary coil, whose diameter was 1·5 cm. and whose total number of turns was 540, and a current of cold water was kept flowing about it to keep the temperature of the wire uniform. Thus maintaining the electric current in the wire constant, it was twisted and the induced current in the secondary circuit due to the longitudinal magnetization thereby developed was measured by the ballistic method.

Fig. 14.



As will be seen from the curve (fig. 15, p. 66), the longitudinal magnetization developed by twisting a circularly magnetized iron wire attains a maximum when the mean circular field is about 10. It then decreases, but in spite of the constant stream of water, the heating due to electric current prevented the experiment from being pushed to the point where the direction of the current is reversed. To judge from the course of the curve, the tendency is such that there is a reversal. In nickel the direction of the induced current is opposite to that in iron, and the total quantity of the current attains a maximum, whence it continually diminishes, but not to such an extent that the current ultimately changes its direction.

Fig. 15.



These experiments show that the twist produced by the combined action of the longitudinal and circular magnetizations, the circular magnetization produced by twisting a longitudinally magnetized wire, and the longitudinal magnetization caused by twisting a circularly magnetized wire, are characterized by having various peculiarities, which are common to all of them. This cannot be a mere chance coincidence; we shall have to ascribe these allied phenomena to the same common cause.

In these experiments we were assisted by Mr. S. Shimizu, a post-graduate in physics, to whom our best thanks are due.

(d) *Application of Kirchhoff's Theory to Wiedemann Effect.*

In our last paper on magnetostriction, we noticed that Kirchhoff's theory can be extended to the study of the relation between torsion and magnetization, exactly in the same manner as was done by Maxwell and Chrystal to explain the Wiedemann effect. There we found that the *mean circular magnetization* called into play by twisting a ferromagnetic wire of radius R through an angle ω amounts to

$$-\tfrac{1}{3}\omega k''\mathfrak{H}R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

in field $\mathfrak{H}$, and that the *mean longitudinal magnetization* caused by twisting a ferromagnetic wire carrying an electric current C amounts to

$$-\tfrac{1}{2}\omega k''\mathrm{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(B)}$$

The reciprocal relation between these two phenomena is thus apparent at a glance. We shall next show how the same phenomena are reciprocally related with torsion produced by the interaction of the longitudinal and circular magnetizations.

The stress-components in a magnetic medium as given by Kirchhoff are as follows:—

$$\mathrm{X}_x = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\alpha^2+\frac{1}{2}\left(\frac{1}{4\pi}+k-k'\right)(\alpha^2+\beta^2+\gamma^2),$$

$$\mathrm{Y}_y = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\beta^2+\frac{1}{2}\left(\frac{1}{4\pi}+k-k'\right)(\alpha^2+\beta^2+\gamma^2),$$

$$\mathrm{Z}_z = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\gamma^2+\frac{1}{2}\left(\frac{1}{4\pi}+k-k'\right)(\alpha^2+\beta^2+\gamma^2),$$

$$\mathrm{Y}_z=\mathrm{Z}_y = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\beta\gamma,$$

$$\mathrm{Z}_x=\mathrm{X}_z = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\gamma\alpha,$$

$$\mathrm{X}_y=\mathrm{Y}_x = -\left(\frac{1}{4\pi}+k+\frac{k''}{2}\right)\alpha\beta.$$

Taking the axis of z in the axial line of the wire, and two other axes in the plane perpendicular to it, we see that the component magnetic forces in a longitudinally magnetized wire traversed by an electric current are

$$\alpha=-h\sin\theta\,, \qquad \beta=h\cos\theta\,, \qquad \gamma=\mathfrak{H}\,,$$

where h denotes circular field given by

$$h=\frac{2\mathrm{C}r}{\mathrm{R}}\,,$$

C being the current, r the distance of the point from the axis of the wire, R the radius, and θ the angle between r and the axis of x.

The stress-components in a ferromagnetic medium acted upon by the forces above specified are given by

$$X_x = -\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h^2 \sin^2\theta + \frac{1}{2}\left(\frac{1}{4\pi} + k - k'\right)(\mathfrak{H}^2 + h^2),$$

$$Y_y = -\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h^2 \cos^2\theta + \frac{1}{2}\left(\frac{1}{4\pi} + k - k'\right)(\mathfrak{H}^2 + h^2),$$

$$Z_z = -\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) \mathfrak{H}^2 + \frac{1}{2}\left(\frac{1}{4\pi} + k - k'\right)(\mathfrak{H}^2 + h^2),$$

$$Y_z = Z_y = -\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h\mathfrak{H} \cos\theta,$$

$$Z_x = X_z = \left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h\mathfrak{H} \sin\theta,$$

$$X_y = Y_x = \left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h^2 \sin\theta \cos\theta.$$

The moment about the axis of the wire is given by

$$N = \iint (Z_{yx} - Z_{xy})\, dx\, dy,$$

$$= -\iint \left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) h\mathfrak{H} r\, dx\, dy,$$

$$= -\frac{2}{R^2}\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) C\mathfrak{H} \int_0^R \int_0^{2\pi} r^3 dr\, d\theta,$$

$$= -\pi\left(\frac{1}{4\pi} + k + \frac{k''}{2}\right) C\mathfrak{H} R^2.$$

The moment just outside the wire amounts to

$$N_0 = -\pi\left(\frac{1}{4\pi} + k\right) C\mathfrak{H} R^2.$$

Thus the effective couple is equal to

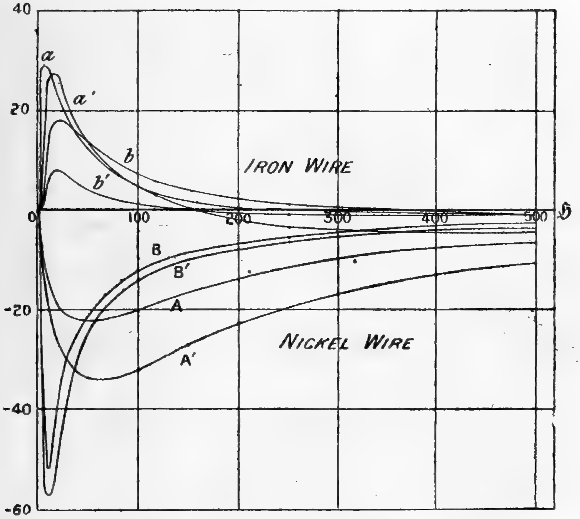
$$-\frac{\pi k''}{2} C\mathfrak{H} R^2 = -\frac{k'' C\mathfrak{H}}{2} \times \text{Cross section.} \quad . \quad . \quad . \quad (C)$$

Since the amount of torsion of a cylindrical wire by a given couple is inversely proportional to the fourth power of its radius, it is evident that for given longitudinal current and field the angle of twist is inversely proportional to the square of the radius. This inference was approximately verified in the present experiments.

In deducing the three formulæ (A), (B), (C), we cannot, strictly speaking, put k'' outside the sign of integration, because the strain coefficient depends on the field strength, which is not uniform in a wire traversed by an electric current. Hence we shall have to use a mean value to obtain a close approximation.

In order to test the consequences of the theory as regards the twist produced by the joint action of circular and longitudinal magnetizations, we have calculated the twist by assuming the values of k'' calculated from the changes of volume and of length in iron and nickel ovoids. Graphically represented (fig. 16), the fields of maximum twist by

Fig. 16.



a & *a′* : obs. & calc. transient currents in 10^{-8} C.G.S. units for iron.
A & *A′* : „ „ „ „ „ for nickel.
b & *b′* : obs. & calc. Wiedemann effect for iron.
B & *B′* : „ „ „ for nickel.

calculation coincide nearly with those given by experiments, and the reversal of twist in iron takes place in low fields as actually found by observation. The quantitative differences are, however, tolerably large in iron, but in nickel the amount of twist is nearly coincident with the experimental values. Calculating in the same manner the quantity of the transient current produced by twisting longitudinally magnetized wires, we find a close coincidence between the experimental and theoretical values in nickel, but the difference is tolerably large in iron. In using the strain coefficients, we must always bear in mind that these values are widely different according to the nature of the specimen; especially with wires, we are not sure of its being magnetically isotropic. The remarkable qualitative coincidence as regards the existence of maximum twist and its reversal in iron are proofs that the theory, so far as we know at present, admits of connecting various experimental facts in a common bond.

The reciprocal relations between the strain caused by magnetization, and the effects of stress on magnetization, as found by actual experiments, will be found to be of paramount importance in arriving at a correct theory of magnetostriction. The strain accompanying the magnetization of ferromagnetic metal will be determined, when we know the effects of stress on magnetization and *vice versâ*. As regards the relations between twist and magnetization in iron and nickel, we may conveniently place them under the following parallel statements:—

Strain produced by magnetization.	*Effects of stress on magnetization.*
(1) A longitudinally (or circularly) magnetized wire is twisted by circular (or longitudinal) magnetization.	(1′) Twisting a longitudinally (or circularly) magnetized wire gives rise to circular (or longitudinal) magnetization.
(2) Up to moderate fields, the twist produced by the longitudinal and circular magnetizations of an iron wire is opposite to that in nickel. In strong fields, the sense of twist is reversed in iron. The twist due to longitudinal magnetization of a circularly magnetized iron or nickel wire reaches a maximum in low fields.	(2′) Up to moderate fields, the transient current (or the longitudinal magnetization) produced by twisting a longitudinally (or circularly) magnetized wire, is opposite to that in nickel. In strong fields, the direction of the transient current is reversed in iron. The transient current in iron or nickel wire reaches a maximum in low fields.

§ 7. SUMMARY.

The results obtained in the present investigation can be summarized in the following statements:—

Magnetization.

(1) The magnetization of cast cobalt is nearly double that of the annealed metal. The magnetization of annealed cobalt is characterized by its high differential susceptibility.

(2) The magnetization of 46 per cent. reversible nickel-steel is between iron and cobalt (cast), while that of 36 per cent. Ni is nearly the same as in cobalt. The 29 per cent. Ni is nearly half as magnetizable as nickel, and 25 per cent. Ni is

only feebly magnetic. The course of the magnetization curve of nickel-steel resembles that of nickel.

(3) (*a*) In cast cobalt, mechanical elongation in the direction of magnetization produces diminution of magnetization in low fields, which gradually lessens as the field strength is increased. Ultimately there is increase of magnetization by elongation. Thus, there is a critical point in cobalt which is opposite in character to the Villari point in iron.

(*b*) In annealed cobalt, mechanical elongation in the direction of magnetization produces diminution of magnetization, which increases with the field.

(4) Mechanical elongation in the direction of magnetization produces increase of magnetization in nickel-steel.

Change of Length by Magnetization.

1. In cobalt, the character of the change is different in the cast and in the annealed state.

(*a*) Cast cobalt contracts in low fields and assumes minimum length in $\mathfrak{H}=130$, whence it returns to its former length in $\mathfrak{H}=740$, and goes on elongating at a slower rate as the field is increased (result already obtained by Bidwell with cobalt rod). This stands in reciprocal relation with the effect of mechanically elongating cast cobalt on its magnetization.

(*b*) Annealed cobalt contracts without showing maximum up to $\mathfrak{H}=1800$. The character of the change is similar to that in iron (after passing the maximum elongation). The effect of mechanically elongating annealed cobalt is reciprocal to the change of length by magnetization.

2. Nickel-steel elongates by magnetization. The character of the change is similar to that in nickel, but the sense is different. The rate of change $\left(\dfrac{d\left(\frac{\delta l}{l}\right)}{d\mathfrak{H}}\right)$ in high fields is greater in 29 per cent. Ni than in 36 per cent. Ni, in which it is again greater than in 46 per cent. Ni. Nickel-steel elongates to a greater degree in the annealed than in the hard-drawn state.

The elongation of nickel-steel in very low fields (comparable with the terrestrial magnetic field) is generally less than 10^{-7}.

Change of Volume by Magnetization.

1. Iron, steel, nickel, and nickel-steel increase in volume by magnetization, but cobalt shows contraction.

2. (*a*) Cast cobalt contracts at a rapid rate in low fields,

but above $\mathfrak{H}=100$ the rate becomes less and the contraction reaches a maximum in $\mathfrak{H}=900$, whence to return gradually with further increase of the field.

(*b*) Annealed cobalt contracts at a steady rate as the field is increased. The contraction becomes ultimately greater than in cast cobalt.

3. The increase of volume in 46 per cent. Ni, 36 per cent. Ni, 29 per cent. Ni steels takes place almost in proportion to the strength of the field. The amount of the increase becomes greater as the percentage of nickel becomes less. The volume change in 29 per cent. Ni is the greatest that has ever been observed, and is nearly 40 times that in iron, in strong fields.

Wiedemann Effect.

The twist produced by the combined action of circular and longitudinal magnetization in iron, nickel, and nickel-steel increases with the longitudinal field-strength, and reaches a maximum whence it decreases gradually as the field is further increased. The sense of twist in iron and nickel-steel is opposite to that in nickel. The transient current produced by twisting a longitudinally magnetized wire and the longitudinal magnetization caused by twisting a circularly magnetized wire are reciprocally related to the twist produced by longitudinal and circular magnetizations.

Physical Laboratory, Imperial University,
Tōkyō, March 1902.

V. *On the Hall Effect in Gold for Weak Magnetic Fields.* *By* Will. C. Baker, *M.A.*, 1851 *Exhibition Scholar from Queen's University, Kingston, Ontario, Canada, Non-Collegiate Student, Cambridge* [*].

VON ETTINGSHAUSEN and Nernst [†] found that the Hall coefficient in certain bismuth-tin alloys depended on the strength of the magnetic field employed. This change extending, in some cases, even to a reversal of the sign of the effect. Kundt [‡], in his work on the Hall effect in iron, cobalt, and nickel, showed incidentally that the coefficients for gold and silver remained constant even to fields of 21500 C.G.S. units.

In view of the above, Professor J. J. Thomson suggested that it would be of interest to examine the behaviour of pure

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[*] Communicated by Prof. J. J. Thomson.

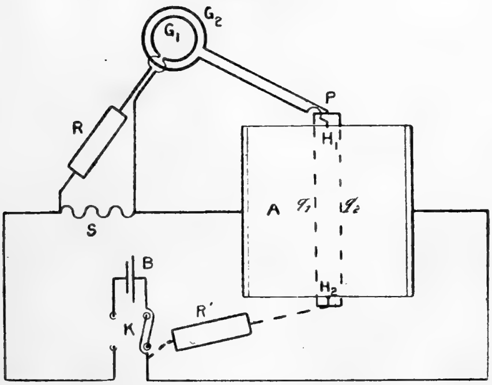
[†] Wied. *Ann.* xxxiii. p. 474 (1886).

[‡] *Ibid.* xlix. p. 264 (1893).

metals in very weak magnetic fields, to see if there existed, in that region, any change similar to the one quoted above for bismuth-tin alloys.

The method employed in this investigation was a slight modification of that given by Dr. A. Lebret*. It is represented diagrammatically in fig. 1. The current from a storage-cell B passed in turn through the reversing key K; a small resistance S (about 0·02 ohm), and through the plate of metal to be experimented upon, shown at A. This current is spoken of below as the primary current. From the ends of the small resistance S a shunt current was led through the resistance-box R, and then through one set of coils (G_1) of the differential galvanometer. This circuit is referred to below as the shunt circuit. The current from the "Hall electrodes" H_1 and H_2 was sent through the second set of coils (G_2) of the galvanometer, and is called the secondary current. In order to prevent changes in the strength of the magnetic field from acting inductively on that part of the secondary circuit that lay between the magnet poles, the device of S. Bidwell† was adopted. This consists in branching part of the circuit as shown at H_2P. Now as a change in the magnetic field acts in opposite senses on the partial circuits $H_1\ H_2\ q_1\ P$ and $H_1\ H_2\ q_2\ P$, these effects may be made to neutralize one another simply by bending one of the wires (q_1 or q_2) so as to equalize the magnetic flux through the two

Fig. 1.



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* Dr. A. Lebret: "A New Method of Measuring the Hall Effect, especially with reference to Variation of Temperature." Communications from the Physical Laboratory of the University of Leiden, No. 19. (Translated from *Verslagen en Medeelingen van die Kon. Acad. van Wetenschappen* van 18 April, 1895, p. 284.)

† Phil. Mag. vol. xvii. (April 1884); see also Lebret (*loc. cit.*).

"areas." A was placed between the poles of a magnet and the current set up in the secondary circuit, due to the action of the magnet on the primary current, was balanced against the current in the shunt-circuit, by altering the resistance R until the galvanometer spot remained at rest on closing the key K.

The advantage of this arrangement is that as the key K is closed only for a small fraction of a second, it permits the galvanometer to indicate at once whether the shunt current is greater or less than that in the secondary, but the primary current is stopped again before the complicated thermo-magnetic effects of von Ettingshausen and Nernst * have had time to rise to significant proportions. By thus obtaining the value of the compensating current in the shunt-circuit for both directions of the primary current and for both directions of the magnetic flux in each case, all effects but the one here sought are eliminated in the mean †.

Gold was chosen to work with chiefly because it could be obtained of a standard purity, in thin sheets, much more readily than other metals. The foil was procured from a local dentist, and its thickness was determined from its mass, area, and the density of beaten gold (19·367, Watts' 'Dictionary of Chemistry'). These sheets were found to vary in thickness, even for different parts of the same piece ; so in the final determination of the absolute value of the effect, the portion extending from one secondary electrode to the other was cut out, and its thickness determined after it had been thoroughly cleaned, first in alcohol, to remove the shellac, and then in strong nitric acid.

Much trouble was experienced in obtaining a successful connexion to the gold. Attempts to solder it to brass strips failed completely, as the thin foil dissolved in the hot solder, and, by its surface-tension, the alloy drew away from the gold, leaving absolutely no contact. Systems of clamps, such as Hall ‡ used in his original investigation, and the various modifications that were tried, all proved to be too variable to be used with the small resistances employed.

The method finally adopted is shown in fig. 2. Two comb-shaped bits of copper (D D) were screwed to a piece of ebonite about 12 cms. square and 5 mms. thick, the copper "teeth" being previously well tinned. The gold-foil A (10 cms. square) could just lie flat on the ebonite between

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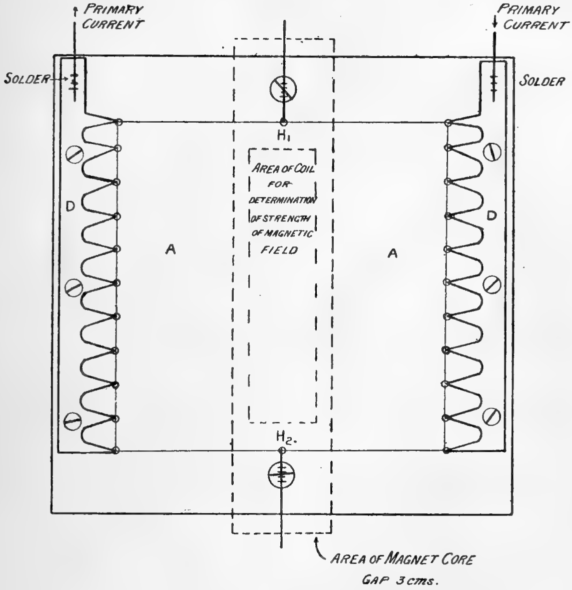
* Wied. *Ann.* xxix. p. 344.

† For a full discussion of how each separate effect is eliminated by taking the mean of these four readings, see Lebret's paper, *loc. cit.*

‡ Phil. Mag. vol. x. p. 301 (1880).

the two rows of teeth. Small drops of solder were let fall from a hot soldering-bolt so that they formed a connexion between the gold and the copper points. The solder dissolved some of the gold as before, but as the hot drops were already more or less spherical they did not draw away from the gold before they were cooled by conduction of heat into the copper. This gave a perfect connexion. The secondary electrodes—wires soldered to screws driven into the ebonite—were similarly attached to the gold. A very thin coat of shellac was now spread over the surface of the foil, to prevent its being torn by the circulating kerosene in the constant-temperature bath in which the measurements were made.

Fig. 2.



To measure the magnetic field, a coil of 18 turns*, fixed to a sheet of mica, was held by clamps just in front of the central portion of the gold plate. Its area was $2{\cdot}05 \times 8{\cdot}30$ sq.cms., so that it nearly covered the active portion of the gold. This was put in series with a ballistic galvanometer, of the D'Arsonval type, an earth-inductor, and a resistance-box.

The ebonite plate-support, with its attached foil and coil,

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* One of 100 turns was necessary at the lowest fields.

was placed between the poles of a small ring electromagnet. The cross-section of the laminated core of this magnet was 3 × 15 sq.cms. The space between the pole-faces was 3 cms. The winding was in two sections, one of 368 turns and the other of 519 turns. These could be used separately or in series. The exciting currents were drawn from a battery of storage-cells.

The magnet and the ebonite plate, with its attachments, were immersed in a bath of kerosene, so arranged that a constant circulation was maintained past the gold, by means of a small pump driven from a water-motor. This was found to keep the temperature practically constant, and to prevent thermoelectric changes at the secondary terminals.

The differential galvanometer I built specially for this investigation. It was of the Thomson reflecting type—four double coils of 50 turns each, No. 20 d.c.c. wire well insulated in paraffin—and a light astatic suspended system of parts of the finest cambric needles * on a fine glass staff, suspended on a single silk fibre 30 cms. long—magnetic control.

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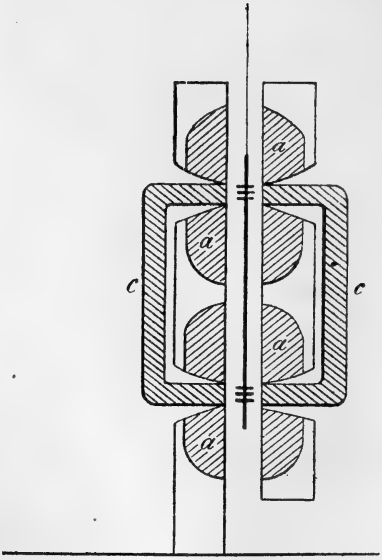
* These were magnetized in place by making use of the galvanometer itself. Soft iron cores (*c c*) were made so as to fit into the galvanometer coils (*a a a a*) and the needle-system was set between, as shown in the



sketch. All the coils were put in series so as to drive the magnetic flux across the two gaps in opposite directions. A current of eight amperes was put on for a second at a time, twice or three times, and this was found to saturate the needles. See also Wadsworth, Phil. Mag. xxxviii. p. 482 (1894).

The resistance of either set of four coils was a half an ohm. With a period of 15 seconds it gave a deflexion of 1 mm. scale-division at a little over a metre's distance, for a difference of current of 10^{-9} ampere. The ratio of the galvanometer constants of the coils $\frac{g_1}{g_2}$ was 0·96.

Leads from the secondary electrodes of the plate were soldered to the terminals of one set of coils of the galvanometer, so that all joints in the secondary circuit were soldered. Each joint was well wrapped in cotton-wool to prevent rapid changes of temperature from draughts &c. All wiring was tested as it was set up to ensure that there was no effect on the galvanometer from the primary or magnetizing currents. The entire secondary circuit, including the galvanometer, was set on paraffin.

As it is not practically possible to solder the secondary electrodes to points that shall be the ends of one and the same equipotential line when the primary current is passing through the plate, there being no magnetic field through the gold, the first operation was to cut notches in the top or bottom edges of the foil (as described in Hall's original paper, *loc. cit.*), to bring the potential at the upper electrode to, as nearly as possible, the same value as that at the lower electrode. This adjustment could never be carried out exactly. The current passing through the circuit due to this was always somewhat greater than that due to the effect sought. To overcome this difficulty Lebret (*loc. cit.*) used a "by-current," shown in fig. 1 as the dotted connexion between K and H_2. By adjusting the value of the resistance R′ the potential at H_2 could be brought exactly to that of H_1. It seemed to me that this was more open to objection than the method of omitting the "by-current" entirely, and measuring merely the change of the current in the secondary due to the assisting or opposing transverse electromotive force in the plate. Accordingly, after H_1 and H_2 were brought to be as nearly as possible at the same potential (when the primary current was flowing), and after the divided part of the secondary circuit had been adjusted so that even a reversal of the magnetic field left no resultant current through the galvanometer,—the order of operations was as follows:—

(*a*) Measurement of the magnetic field by reversing it through the coil carried in front of the gold plate, and comparing the throw obtained in the ballistic galvanometer with that due to the quick turning of an earth-inductor* through 180°.

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* The earth-inductor was standardized in place by comparison with the induced current obtained by reversing a known current through a set of coils of known dimensions.

(*b*) The current through the secondary circuit was balanced against the current in the shunt circuit by altering the value of the resistance R until there was no movement of the galvanometer-spot on closing the key. This was done for both directions of the primary current.

It was found that when a balance had been obtained the primary circuit might be left closed for about one minute before the thermomagnetic effects in the plate were sufficient to cause the spot to move from its zero. Now as in actual work this current was never left closed for more than a few seconds at most, it is easily seen how absolutely negligible are errors from these sources.

(*c*) The direction of the magnetic field was reversed, and balances again obtained for both directions of the primary current.

These balances for the two directions of the primary current differed at the very lowest fields. In such cases the value of the transverse current was calculated separately for each direction of the primary current and the mean taken. In the case of the lowest field—of 12 lines per sq.cm.—this difference was 6 per cent. for two cases, and 14 per cent. in the third; but the values obtained as above do not differ by more than 3 per cent. For fields above 100 lines per sq.cm. this difference is less than 1 per cent., and it vanishes entirely above 300 lines per sq.cm.

As the readings were taken on different nights, I think it is most likely due to some mechanical strain in the plate caused by a difference in the temperature of the whole bath—the coefficients of expansion of the gold and the ebonite or the copper distributing bars being different. At all events, an examination of the plotted results shows that the apparent lowering of the Hall coefficient at very low fields is in all probability due wholly to errors of experiment as the quantities observed were so small as to lie but very little within the limit of sensibility of the apparatus.

(*d*) The magnetic field was again measured as above. If any *small* difference from the previous value was found, the mean was taken to be the strength of field during the experiment. If the difference were large, due to the cells running down or other cause, the whole measurement was rejected.

The couple on the suspended system of the galvanometer is given by

$$\left(C+\frac{\beta H i}{t R_{II}}\right)g_2 m\,;$$

where C is the current in the secondary system when the magnetic field is zero: due to the inexact setting of H_1 and H_2. β is the Hall coefficient*. H is the magnetic field-strength in C.G.S. units. i is the current flowing through the primary. t is the thickness of the foil. R_{II} is the resistance of the entire secondary circuit. g_2 is the constant of the coil of the galvanometer included in the secondary circuit; and m is the equivalent magnetic moment of the suspended system.

This for the case of balance is equal and opposite to the effect of the shunt-current, which is given by

$$\frac{iS}{R_I}\,g_1 m \text{ (approximately)},$$

where S is the resistance of the shunt included in the primary current; R_I is the resistance of the box R when adjusted to balance; and g_1 is the constant of those coils of the galvanometer that are included in the shunt-circuit.

We have now

$$\left(C+\frac{\beta H i}{t R_{II}}\right)g_2=\frac{iS}{R_1}g_1.$$

When we reverse the magnetic field and readjust the resistance in the shunt-circuit (to say R_2) for a second balance, we have similarly

$$\left(C-\frac{\beta H i}{t R_{II}}\right)g_2=\frac{iS}{R_2}g_1,$$

whence

$$\beta=\frac{R_{II}S}{2}\left(\frac{1}{R_1}-\frac{1}{R_2}\right)\frac{t}{H}\cdot\frac{g_1}{g_2},$$

the value of i being eliminated. A series of tests showed that i might be as great as ⅓ ampere without bringing in error from thermal effects; this, of course, is largely in consequence of the method of leaving the primary current closed for short periods only.

The quantities employed were:—$i=0{\cdot}33$ ampere. R_1 and R_2 were of the order 1000 to 1500 ohms. $R_{II}=0{\cdot}801$ ohm. $S=0{\cdot}0178$ ohm. $\frac{g_1}{g_2}=0{\cdot}96$. $t=2{\cdot}05\times10^{-4}$ cms.

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* *I. e.* the transverse potential gradient for unit magnetic field and unit current density in a plate of unit thickness. This reduces directly to the "Rotary coefficient" definition given in Wiedemann's *Electricität*, iii. p. 202, *et seqq.* (edition of 1898).

Another sheet of similar dimensions with $t=1{\cdot}13\times10^{-4}$ * gave the same values for the Hall coefficient.

The results of a series of measurements on a sheet of dentists' gold, from a "book" marked "Chemically Pure Gold, soft extracohesive No. 4," are given in the following table, where, in the first column, is recorded the date of the observation. In the second column, marked H, is given the magnetic field-strength in C.G.S. units. The third column, marked β', gives numbers proportional to the Hall coefficient †, and the fourth column gives the strength of the current (in amperes) that flowed through the secondary system due to the Hall effect. These latter values are calculated from the formula

$$\frac{iS}{2}\left(\frac{1}{R_1}-\frac{1}{R_2}\right)\frac{g_2}{g_1},$$

and are used in the diagram (fig. 3, p. 82), where they are plotted against the corresponding field-strengths.

TABLE I.

Date, 1901.	H. (C.G.S.)	β'.	Current in Secondary due to Hall effect (amperes).
May 6	12·6	$4{\cdot}9\times10^{-4}$	$12{\cdot}8\times10^{-9}$
8	12·8	4·9	12·8
7	13·1	4·8	12·8
6	24·5	5·0	25·2
7	24·6	5·4	26·2
8	25·0	5·4	27·9
6	69·5	5·4	77·3
8	70·0	5·2	74·9
7	71·7	5·2	77·2
6	94·5	5·2	102
8	95·0	5·2	102
7	97·0	5·1	103
30	151	5·7	172
23	151	5·6	174
23	151	5·6	173
31	153	5·3	168

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* The thickness of these sheets of dentists' gold varies from point to point. For instance, the average value of t for the sheet used was $1{\cdot}51\times10^{-4}$ cms., but the active central part, when cut out, thoroughly cleaned and weighed, gave $t=2{\cdot}05\times10^{-4}$.

† See explanation below.

Table I. (*continued*).

Date, 1901.	H. (C.G.S.)	β'.	Current in Secondary due to Hall effect (amperes).
May 22	155	$5{\cdot}7\times10^{-4}$	182×10^{-9}
22	155	5·7	181
29	155	5·5	173
June 6	162	5·3	175
May 9	220	5·5	247
10	308	5·7	359
30	364	5·8	436
22	369	5·8	436
10	372	5·6	430
23	375	5·6	427
29	380	5·4	425
31	380	5 6	436
29	381	5·6	436
June 6	391	5·5	439
May 15	406	5·8	482
17	419	5·8	496
10	450	5·7	527
17	500	5·7	598
30	586	5·8	701
30	588	5·8	698
22	594	5·7	701
22	597	5·8	707
23	601	5·5	681
31	604	5·5	687
31	606	5·5	678
29	607	5·5	681
29	611	5·6	704
15	612	5·7	721
17	613	5·6	710
14	615	5·8	727
June 6	626	5·5	701
6	627	5·5	714
12	1173	5·9	1411
10	1175	5 5	1337
12	1190	5·4	1311
10	1247	5·4	1394
		Mean $5{\cdot}5\times10^{-4}$	

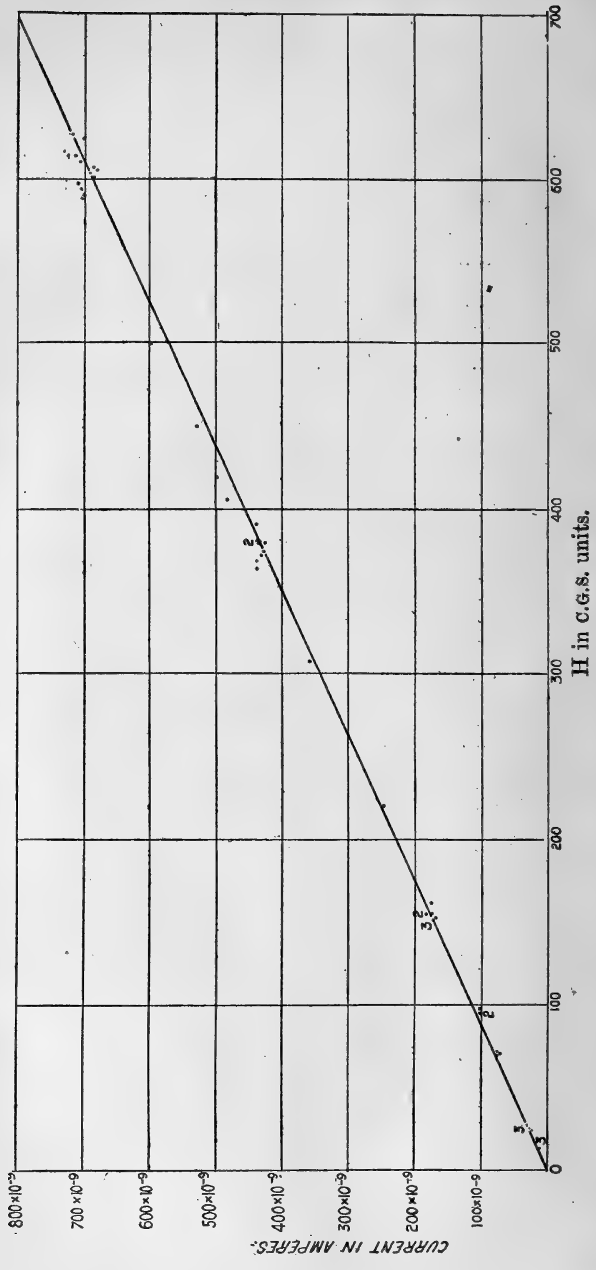

Fig. 3.—Showing relation between the "Hall current" and the magnetic field.

The reason why the values β' differ from the absolute value β by a constant factor is to be found in the following:—v. Ettingshausen and Nernst*, in their researches on the influence of the shape of the specimen on its Hall coefficient, showed that if the length of the plate (direction of primary current) were not at least double the breadth (direction of secondary current), the value obtained for the Hall coefficient was too small; but that it rose to a limiting value as the above-mentioned proportions were approached. This they showed to be due to the fact that all the current arising from the transverse electromotive force does not flow through the secondary leads, but that part of it leaks back through the plate and the primary distributing bars. This effect only becomes negligible at the secondary electrodes when the distance between them is less than half that between the primary bars.

The numbers given in column β' of the table were obtained with a *square* plate. The above given consideration shows that these are a constant fraction of the absolute value β.

In fig. 3 the values of the transverse current (from the fourth column of the table) are plotted against the corresponding magnetic fields. The line represents the value $\beta'=5{\cdot}5$, the mean of all the determinations made. The four highest points are omitted in order that the others may be shown on a larger scale. The omitted points fall on or near the same line as is shown by the values of β' obtained from them. In certain cases two or even three points fall so close together on the diagram as to be undistinguishable from single points. All such cases have a small numeral, 2 or 3, written near the point in question to indicate its double or triple character. The diagram shows that the relation of the transverse current (and hence the transverse E.M.F. in the plate) is linear to the field strength. That is, that the Hall coefficient is a constant over the range dealt with. The apparent diminution of β' at the lowest fields is probably due entirely to errors of experiment.

After the above given measurements were complete, the plate was cut down by half in breadth, but the values of the Hall coefficient were still found lower than the absolute, as the part of the plate *in the magnetic field* was not of the required proportions, and current was leaking back around the edges. Slits were next cut in the foil so as to prevent this, a strip one centimetre wide being left intact up the

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* *Wien. Ber.* xciv. (2) p. 560 (1886); *Beibl.* xi. 69, p. 352 (1887).

centre of the plate. Readings with this in a field of 459 C.G.S. units gave exactly Hall's (corrected) value for gold—obtained in his case in a field of 1600 units.

The above experiments, taken in connexion with Kundt's work (*loc. cit.*), show that the Hall coefficient for gold is a constant, at least for all fields between 12 and 21,500 units (C.G.S.).

During the whole of the above investigation I have been greatly assisted by the encouragement and advice of Professor J. J. Thomson, to whom I desire to express my gratitude.

Cavendish Laboratory, Cambridge,
July 30, 1901.

VI. *An Investigation into the Composition of Brittle Platinum.* *By* W. N. Hartley, *D.Sc., F.R.S.*[*]

THREE years ago a small packet containing ten pin-points of brittle platinum wire which had been in use for dental purposes, with a similar number of points in another packet labelled "tough Platinum" were submitted to me with a request that I should examine the brittle platinum for impurities of a metallic nature which it was supposed might be present. Full details of the chemical investigation have not been published, and as many points of interest have arisen in connexion with the unusual method of examination employed, I venture to present an account of it. Only a very small quantity of defective material could be placed at my disposal, the largest fragment of wire being only 1/25th of an inch or 1 millimetre in length. Their average weight was under 20 mlgrs., and the whole parcel of them did not weigh more than 0·2274 grs. When examined with the microscope they were seen to possess a crystalline fracture[†]. The pins broke readily on bending, and though they did not break under the hammer the flattened wires had ragged edges which was evidence of very imperfect malleability. It was desirable, if possible, to examine each fragment separately as there might be a difference in composition in pins which were supplied by different makers, or which had come from different sources. The very small quantity of material available would have rendered any attempt to separate the constituent substances by chemical means entirely futile, even if the whole quantity of the metal were employed in a single

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[*] Communicated by the Author.

[†] Andrews has investigated the microcrystalline structure of platinum by etching plane surfaces, but pure platinum has not a marked crystalline fracture. (Proc. Roy. Soc. vol. lxix. p. 433, 1902.)

analysis. It was decided to rely upon the spectrographic method, but considerable difficulties were encountered in operating on fragments of metal of such very small dimensions that it was almost impossible to make use of any form of clip to hold them in. Between thirty and forty photographs of spark-spectra were obtained and carefully examined.

It was proved beyond doubt that the following metals were most certainly completely absent, namely:—zinc, cadmium, copper, silver, mercury, tin, lead, arsenic, antimony, bismuth, tellurium, nickel, cobalt, aluminium, gold, chromium, and also the metals which would scarcely be expected to be found in platinum, namely indium and thallium. In no case could there have been 1/10th of a per cent. present, and in some instances even 1/1000th of a per cent. was excluded. A very careful examination was made for iron as this element is difficult to remove entirely from platinum, and for this purpose a spectrum of the purest platinum obtainable from Messrs. Johnson and Matthey was photographed. The photographs were also compared with those of the iron-spectrum and the platinum-spectrum published in the Trans. Chem. Soc. 1882. It was found that the pure platinum electrodes gave spectra identical line for line with the spectrum of two fragments of brittle platinum. It was therefore concluded that any metallic impurity in the brittle platinum must be in so very minute a proportion that it was impossible for it to impair its toughness. It was thought that the platinum might perhaps contain iridium, but a comparison of the platinum-spectrum with that of iridium showed that the *strong lines* of the latter element were absent from the platinum. There remain now certain non-metallic elements such as phosphorus, carbon, and silicon to be considered as possible impurities. In the United States, phosphorus has been added to native iridio-platinum for the purpose of rendering it fusible. It is said that the phosphorus is entirely eliminated from the iridio-platinum alloys by long continued heating. There appears to be no possibility of more than a very minute trace of iridium in the metal and the brittleness is not caused by that because, if it were, melting would not improve its malleability. Proof of melting having this effect occurs later.

It is, however, very possible that phosphorus may be present, and as the effect of phosphorus in minute proportions is to render platinum brittle and crystalline, the properties seen in the pins from this point of view are quite what might be expected and even predicted. Phosphorus would not be detected by the method of spectrum analysis, and it is extremely doubtful if any chemical method of separation would afford satisfactory proof of its presence when so small a quantity of material is available for analysis. Carbon also renders platinum brittle. The platinum cones or caps used in the ignition of the mixture of gas and air, or petroline vapour, which is used in gas and motor-car engines, become so brittle that they may be broken up between the fingers.

The final conclusion was that some non-metallic impurity, either carbon or phosphorus, is the cause of the brittle and markedly crystalline character of these pins, as observed in their fractures. It appeared possible that either of the substances might be introduced in the working up of old platinum. Both phosphorus and carbon can be eliminated by prolonged fusion of platinum under the oxy-hydrogen blowpipe flame; accordingly a number of the brittle pins were fused, and under this treatment the metal became greatly improved in malleability, which fact affords a strong confirmation of the correctness of the conclusion arrived at. I have been informed that when this matter was communicated to the International Congress at Paris in the year 1900, by the Dublin Branch of the Dental Association, it elicited a statement to the effect that the electric furnace has latterly been used for fusing platinum. This method of fusion would unquestionably lead to the introduction of phosphorus, and probably also of carbon and silicon, from the metal being in contact with carbon electrodes. We know that phosphorus is introduced into calcium carbide by the ash of the powdered coke used; and from the carbon electrodes in which silicon is always present, this element may possibly enter into platinum.

Experimental Details.

There were difficulties encountered in the examination of the spark-spectra emitted by these small fragments of metal. In the first place they could not be submitted to fusion lest they might be altered in composition, and secondly, it was very desirable that they should be examined separately. The largest fragment as already mentioned was only 1 mm. long, and some of them were no more than half this length. Conceive the difficulty of getting a pure spectrum from this. If held in a screw clip, the metal of the clip would contribute extraneous matter to the spark, steel for instance would furnish iron, while graphite or silver would at once constitute itself an electrode in place of the platinum because either of them is a much superior conductor.

The usual spring or screw clips were in fact found to be useless. Mounting was accomplished in two ways, first by fixing the pin in a clip of platinum-wire which, however, was rather a difficult operation, secondly by soldering the platinum points on to similar gold wires with pure gold. A photograph of each point was taken side by side with the spectrum of the pure platinum electrodes.

A careful examination of photographic enlargements up to a scale of 10 diameters showed that with the exception of thirty-five *gold lines* the two spectra were practically identical, or in other words that the lines unmistakeably due to iron did not appear, namely, the group of five very strong lines about 2743·4.

The thirty-five gold lines which appear when gold wires are used are here given, the wave-length quoted being according to Eder and Valenta's measurements (*K. Akad. der Wissenschaft*. vol. lxiii. Vienna, 1896).

Gold Lines.

4488·43
4065·20
4053·00
4016·27
3898·03
3804·22
3635·21
3633·40
3586·66
3230·73
3204·75
3122·88
3029·32
2995·13
2990·38
2954·64
2932·33
2918·48
2913·63
2907·16
2906·07
2893·51
2885·69
2883·60
2838·15
2825·59
2822·87
2820·09
2802·39
2748·35
2676·05
2641·70
2503·42
2428·10
2364·80

The following are the prominent iron lines seen when the pins were held in steel clips, the ends of which were covered with thin platinum foil. These wave-lengths are taken from Liveing and Dewar's measurements of the spark-spectrum of iron.

Iron Lines.

2755·5		2742·8	
2753·0		2739·2	Also arc.
2749·0	Also arc.	2736·5	Also in arc, weak.
2746·6 2746·1	Also arc.	2630·7 2631·0	

The lines bracketed appear as separated lines on my photographs. Two strong lines, however, seemed to be common to all four spectra, that is to say to iron, brittle platinum, tough platinum, and the two specimens of pure platinum. Here then is a fresh difficulty of a different character to contend with. This is scarcely a matter for surprise because of the very large number of iron lines and the manner in which they are very closely grouped together at a part of the spectrum where the lines of platinum are somewhat numerous.

The lines which appear as if common to the iron and the platinum-spectrum, namely, 2627·9 and 2625·2 in Liveing and Dewar's spark-spectrum of iron, are both very strong in the arc as well as in the spark. They are seen in the spectrum of pure platinum equal in strength to the lines in the brittle platinum, but not so strong as in the iron. Two lines, apparently the same, appear nearly as strong in the rhodium-spectrum as in that of iron. Taking Exner and Haschek's spectra of the platinum metals as a guide (*K. Akad. der Wissenschaft, Wien, Druckschriften*, Mittheilung vi. 1897), but disregarding the measurements in Mittheilung i. 1895, which are inaccurate, we have the following measurements closely approximating to those just mentioned.

Platinum.	*Palladium.*	*Rhodium.*
2628·13	2628·38	2628·34
2625·41		2625·55

As Exner and Haschek's photographs were not taken in such a manner as to show any marked features in the lines, I availed myself of a series of photographs taken by Dr. Adeney with the Rowland spectrometer in the Royal University of Ireland, which he kindly allowed me to examine. The characteristic features of the lines are the same as those seen on the photographs taken from prism spectra, already mentioned as having been published in the Transactions of the Chemical Society in 1882. They can therefore be identified with comparative ease, and when they differ in character it may safely be concluded that they are different lines. Both lines in the iron-spectrum are common to the arc and spark, and they have the same intensity. Liveing & Dewar's numbers differ from those of Kayser and Runge, and also from the later and more exact measurements made by Kayser (*Ann. der Physik*, ser. 4, vol. iii. 1900) which for these lines are given below.

	Wave-lengths.	Character.
IRON LINES (Kayser)	2628·383	Thin in the middle but broad at each end.
	2625·754	The same but the ends are broader.
RHODIUM LINES (Exner & Haschek)	2628·34.........	The same as the iron lines.
	2625·55.........	,, ,, ,,
PLATINUM LINES (Exner & Haschek)	2628·13.........	Of the same thickness throughout, weak compared with the iron lines, but stronger than the more refrangible platinum line.
	2625·41.........	Thin in the middle, nearly discontinuous, but thicker at either end. A weaker line than the one less refrangible.

Measurements made by Dr. Adeney have been communicated to me prior to publication. The iron lines are very closely in agreement with Kayser's wave-lengths while the numbers for the platinum lines prove their identity with those quoted above.

Adeney's Measurements.

Iron lines............	2628·396	and	2625·724
Platinum lines	2628·172	„	2625·400

I conclude that the lines have not a common origin, but are different lines with only approximately the same wave-lengths. Some trouble was taken to prove the presence or absence of silicon. The strongest lines of silicon, namely 2881·6, 2516·0, and 2506·7, have been sought for, but they appear to be absent from all the platinum-spectra. This does not, however, quite dispose of the question, because there are two lines on Adeney's spectrum of platinum with wave-lengths approximately 2514·20 and 2515·65, the former and more refrangible line being the stronger of the two, the former comes very near to one of the weaker lines of silicon 2514·4, and the latter near to the stronger line 2516·0. Exner and Haschek give two corresponding lines in platinum with wave-lengths 2513·8 and 2515·4.

In a subsequently published list of wave-lengths determined with greater accuracy (Mittheilung vi.), the former line alone is given as being a strong line with the wave-length 2513·98. The order of the relative intensities of the two silicon lines is the reverse of that of the platinum lines, and it is only the weaker line of the silicon spectrum that approximates in wave-length the stronger line of the platinum. There can be no doubt whatever that silicon is absent.

This investigation has proved in a forcible manner, 1st the utility for practical purposes of spectrographic analysis by means of the spark ; 2nd, the importance of determining the wave-lengths of arc and spark lines of pure elements with extreme accuracy; and 3rd, the advantage of being able to distinguish between two spark lines of very nearly the same wave-length by the difference in their characters. In conclusion I desire to express my thanks to Dr. Adeney for his courtesy in communicating his measurements of the platinum and iron lines.

Royal College of Science, Dublin,
April 9th, 1902.

VII. *On the Behaviour of Pleochroitic Crystals along Directions in the Neighbourhood of an Optic Axis**. *By* Professor W. Voigt, *of Göttingen*†.

1. ALL theories regarding the absorption of light in crystals agree in recognizing the fact that on account of absorption there is added to the characteristic triplet of directed quantities corresponding to each colour in transparent crystals a *second* triplet of analogous properties. The first triplet may conveniently, though not quite correctly, be regarded as forming the system of the three mutually perpendicular axes of symmetry for the *conservative* forces, while the second corresponds to the *absorptive* forces. To each of these axes there corresponds a certain number, which in transparent crystals represents, as is well known, the velocity of all those plane waves for which Fresnel's vibration-vector is parallel to the corresponding axis. If we use the term *tensor-triplet*, proposed by myself, to denote a system of three two-sided mutually normal directed quantities, then an absorbing crystal will have to be characterized, for a given colour, by *two* tensor-triplets. These two triplets may be denoted by the symbols a_1, a_2, a_3 and b_1, b_2, b_3, and we shall suppose that

$$a_1 > a_2 > a_3 \quad \text{and} \quad b_1 > b_2 > b_3 \,. \quad . \quad . \quad . \quad . \qquad (1)$$

2. It is known that in the case of transparent crystals most characteristic properties correspond to those two directions A_1 and A_2 which, lying in the plane of the greatest and the least tensors a_1 and a_3, make an angle ϑ with the latter defined by the equations

$$\sin^2\vartheta = \frac{a_1 - a_2}{a_1 - a_3}, \qquad \cos^2\vartheta = \frac{a_2 - a_3}{a_1 - a_3}. \quad . \quad . \quad . \qquad (2)$$

These directions are also of special importance in absorbing crystals, and are also called *optic axes* in this case, although on account of their altered properties they would be more correctly denoted by some other term (*e. g.* polarization axes).

Corresponding to the optic axes, we may conveniently consider as *absorption axes* the directions B_1, B_2 which, lying in the plane of the greatest and least tensors b_1 and b_3, make an angle δ with the latter defined by the equations

$$\sin^2\delta = \frac{b_1 - b_2}{b_1 - b_3}, \qquad \cos^2\delta = \frac{b_2 - b_3}{b_1 - b_3}. \quad . \quad . \quad . \quad . \qquad (3)$$

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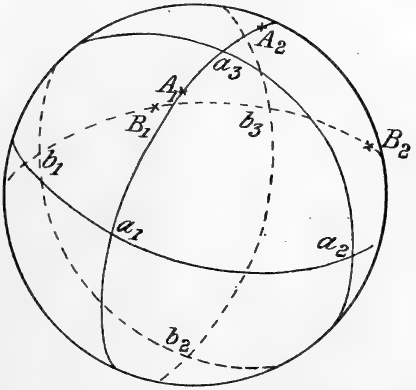
* A summary of the results contained in a paper presented on Feb. 8, 1902, to the Kgl. Gesellschaft der Wissenschaften zu Göttingen (*Gött. Nachr*. 1902, Heft 1).

† Communicated by Lord Kelvin.

The relative position of the two pairs A_1, A_2 and B_1, B_2 of axes is in general as impossible to assign as that of the tensor-triplets a_1, a_2, a_3 and b_1, b_2, b_3. It is only when the crystal possesses special symmetry that it becomes possible to say something more or less definite. Fig. 1 gives some idea regarding the general position of these axes; all the characteristic lines are drawn through the centre of a sphere, and their intersections with the spherical surface indicated.

Fig. 1.



3. The fundamental formulæ in the theory of plane wave propagation are obtained most simply by introducing a system of coordinate axes x, y, z, of which z coincides with the direction of propagation. If, then, we denote the components of the two tensor-triplets along these axes by a_{11}, a_{22}, a_{33}, a_{23}, a_{31}, a_{12} and b_{11}, b_{22}, b_{33}, b_{23}, b_{31}, b_{12}*, and if we write shortly

$$a_{hk}+ib_{hk}=c_{hk}, \quad \ldots \ldots \quad (4)$$

where $i=\sqrt{-1}$, then

$$(c_{11}-v^2)(c_{22}-v^2)=c_{12}^2, \quad \ldots \quad (5)$$

$$\frac{g^2}{f^2}+\frac{c_{11}-c_{22}}{c_{12}}\cdot\frac{g}{f}=1, \quad \ldots \quad (6)$$

where v stands for the so-called complex velocity, g/f for the ratio of the complex amplitudes for Neumann's vibration-vector along the y and x axes respectively. Expressed in

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* If α_h, β_h, γ_h are the direction-cosines of the triplet a_1, a_2, a_3 relatively to the axes x, y, z, then

$$a_{11}=a_1\alpha_1^2+a_2\alpha_2^2+a_3\alpha_3^2, \ldots$$
$$a_{23}=a_1\beta_1\gamma_1+a_2\beta_2\gamma_2+a_3\beta_3\gamma_3, \ldots$$

terms of the real velocity ω and the absorption-index κ,

$$v=\frac{\omega}{1-i\kappa}, \quad \ldots \ldots \ldots \quad (7)$$

and if G, F denote the real amplitudes, and R their relative retardation,

$$\frac{g}{f}=\frac{G}{F}e^{-iR}. \quad \ldots \ldots \ldots \quad (8)$$

The formulæ (5) and (6) express the fact that in every direction there are propagated two elliptically polarized waves with, in general, different velocities and different rates of damping.

4. Of special interest are those crystals in which absorption is so weak that κ^2 may be neglected in comparison with unity, so that we may write

$$v^2=\omega^2(1+2i\kappa). \quad \ldots \ldots \ldots \quad (9)$$

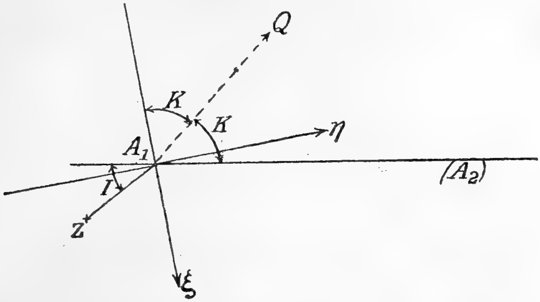
Such crystals produce no appreciable absorption in a thickness corresponding to a few wave-lengths, and are the only ones exhibiting the remarkable phenomena whose explanation forms the subject of the present paper. We have in the first place to consider the effects obtained within a small region in the neighbourhood of the optic axes defined by equations (2) ; in this region the variation of ω is, as may be shown, very slight, and the quantity $2\kappa\omega^2=k$ has a variation corresponding almost exactly to that of the analogous function κ/ω characteristic for absorption.

The two complex equations (5) and (6) thus define, within the region now considered, the real and imaginary parts of the two unknown quantities v and g/f, as well as the real velocity of propagation ω, the parameter of absorption k, the ratio G/F of the real amplitudes, and the relative retardation R.

5. Regarding these four quantities it must here suffice to state four propositions which, though only qualitative, are easily understood and extremely helpful towards an explanation of the effects considered. These propositions follow from the equations (5) and (6). In order to arrive at them, consider once more all the directions as passing through the centre of a sphere, and defined by their intersections with the spherical surface. The region surrounding an optic axis A_1 may then be approximately represented by a plane, as shown in fig. 2. We here have, besides the direction of the optic axis, represented by the point A_1, and that of the wave normal, represented by the point Z, also the plane $A_1 A_2$ of the optic axes ; A_2 being inclosed in brackets in order to

indicate the fact that the direction A_2 is not capable of being represented in the figure itself. The straight line $A_1 Q$ further represents a plane through the optic axis A_1 obtained

Fig. 2.



as follows:—Let a plane be drawn through the axes $A_1 B_1$, and another through the axes $A_1 B_2$; let the angle between them be J_1. Then $A_1 Q$ is the trace of the plane bisecting the angle J_1; let the angle made by this plane with the direction $A_1 A_2$ be denoted by K.

6. From the formulæ (5) and (6) it follows that the phenomena under consideration in the neighbourhood of the axis A_1 are symmetrical with respect to the $\xi\eta$ system of coordinates (also shown in the figure), the angle made by the $-\xi$-axis with the direction $A_1 A_2$ being equal to 2K.

Such being the case, the plane $A_1\eta$ contains two directions, C_1 and C_1' (see fig. 3), making the same angle θ with A_1, and which are highly characteristic of the behaviour of the crystal, and may be termed *singular axes*. The angle θ is determined by the tensors a_1, a_2, a_3 and b_1, b_2, b_3 which are characteristic of the crystal, and is most simply expressed in the form

$$\theta = \frac{(b_1 - b_3) \sin V_{11} \sin V_{21}}{2\sqrt{(a_1 - a_2)(a_2 - a_3)}}, \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

wherein V_{11} stands for the angle between A_1 and B_1, and V_{21} for that between A_1 and B_2. The angle θ thus determined is in all practically important cases *extraordinarily small.*

7. The four propositions referred to above follow from the formulæ (5) and (6), and, using the representation in the $\xi\eta$ plane, may be stated as follows:—

(*a*) The difference of the squares of the velocities of propagation, $\omega_1^2 - \omega_2^2$, of the two waves (corresponding to each direction Z)—and hence also, on account of the small difference between ω_1 and ω_2 in the region considered, the difference itself $\omega_1 - \omega_2$ approximately—is constant over ellipses having the points C_1 and C_1' for foci. This difference vanishes along the straight line C_1C_1', and increases as the ellipse opens out. (The mean square of the velocity, $\frac{1}{2}(\omega_1{}^2 + \omega_2{}^2)$, on the other hand, is constant along straight lines perpendicular to the direction $A_1 A_2$.)

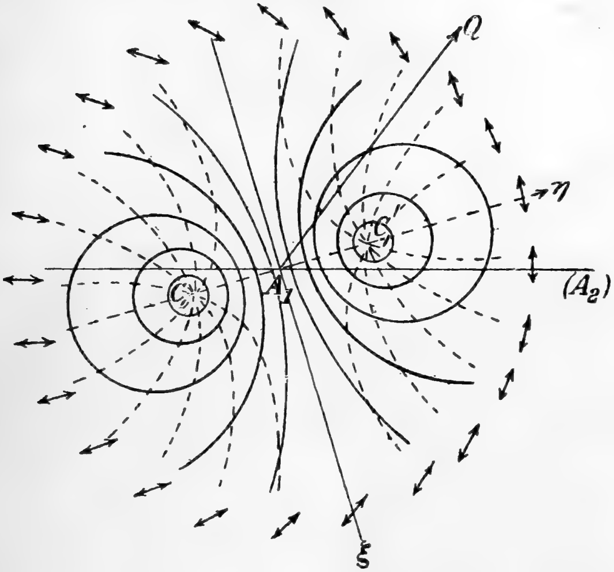
(*b*) The parameters k_1 and k_2, which determine the absorption of the two waves (corresponding to the same direction Z), are constant along hyperbolas having their foci at C_1 and C_1'. They have the same value k_0 along the straight lines obtained by producing C_1 C_1' both ways, and along any hyperbola have values which differ from k_0 by equal amounts of opposite sign, the maximum difference occurring along the ξ-axis.

(*c*) The vibration-ellipses of the two waves (corresponding to the same direction Z) have constant ratios of axes along circles whose centres lie on the straight lines obtained by producing C_1 C_1' both ways, and whose radii are such that all the circles cut the circle described on C_1 C_1' as diameter orthogonally. The ellipses degenerate into circles at the points C_1 and C_1', and become straight lines in the ξ-axis. The direction of vibration is of opposite sense on the two sides of the ξ-axis, but is everywhere the same for the two waves.

(*d*) The principal axes of the vibration-ellipses of the two waves are crossed; their position is constant along equilateral hyperbolas whose vertices lie on the lemniscate having C_1 C_1' for axis, and which pass through the points C_1 and C_1'. The coordinate-axes ξ and η are special cases of these hyperbolas. In order to determine the positions of the axes of the ellipses corresponding to these hyperbolas, it is most convenient to use the well-known theoretical result according to which in the case of *weak* absorption the vibrations, within a certain distance from the optic axes, differ only imperceptibly from those taking place in transparent crystals, and are therefore nearly rectilinear along directions determined by the famous construction due to Fresnel. According to this construction we have to draw planes through the axes Z and A_1, and Z and A_2, and to bisect the angle I between them; the ordinary wave is then polarized in a direction parallel, and the extraordinary one in a direction normal, to this bisecting plane.

In fig. 3 are shown the curves corresponding to propositions (*c*) and (*d*); in addition to this the double-headed arrows arranged round the circumference of a circle indicate the directions of polarization of the ordinary waves when the absorption is vanishingly small. In accordance with what has been said above, these arrows also give the directions of the axes *majores* for the ordinary, and of the axes *minores* for the extraordinary waves on the neighbouring branches of the hyperbolas. It will be seen that these directions are not constant along the entire hyperbolic branches, but that they become rotated through 45° during the passage through the points C_1 and C_1' of circular polarization.

Fig. 3.



It is evident that in all these propositions the singular axes play an extremely important part—they uniquely determine, from the qualitative point of view, the effects considered.

8. Now as regards the appearances which may be noticed in the neighbourhood of an optic axis, these present themselves in looking through a plate which has been cut in a direction approximately normal to an optic axis. It is easy to deduce the formulæ for the intensities with a degree of approximation corresponding to that of the experimental observations—for a given incident light—made either with the naked eye or by means of an inserted analyser. The formulæ are without exception very complicated, but may be simplified for distances from the singular axes C_1 and C_1' such that the terms containing the squares of the ratios ϵ of

the minor to the major axis of the vibration-ellipse as factors may be neglected. The region within which the simplified formulæ are not applicable is in general extraordinarily small.

In this way an explanation is very easily obtained of the dark pencils—first noticed by Brewster—which make their appearance when a natural source of light of sufficient dimensions is viewed through the crystal, without the use of any polarizer. The distribution of intensity is such that the hyperbolas mentioned in proposition (*b*) represent curves of constant absorption. The ellipticity of the vibrations in the plate need not in the case of this phenomenon—to the degree of approximation considered—be taken into account. According to the *strictly correct* formulæ the distribution of the intensity is somewhat modified in the neighbourhood of the singular axes.

9. The ellipticity of the vibrations has, on the other hand, a marked effect on the appearances presented when a *single* polarizer is used—whether it be that natural light is allowed to fall on the plate and is examined by means of an analyser, or that plane polarized light is after transmission examined by the unaided eye. Here an opportunity presents itself for testing in a simple manner one of the most remarkable consequences of theory.

If the experiment be carried out in the manner indicated with a plate of an ordinary or an active transparent crystal, whereby two linear or two elliptic similar but crossed vibrations of *oppositely directed* sense are propagated through the crystal, then according to theory there should be no interference-rings visible around the optic axis. Should, on the other hand, the vibrations be propagated through a pleochroitic crystal whereby the two elliptic vibrations have the *same sense* of rotation, then theory demands the presence of such rings. Experiment is completely in accord with this, and thus proves the existence, hitherto not established, of these pairs of waves with vibrations of the kind described.

The existence of the rings is easily proved in many pleochroitic crystals. Frequently it is possible to see them by looking with the unaided eye through the crystal plate at the sky when the light from the latter is strongly polarized; they have in this case been known for some time, but only now has a theoretical explanation been furnished. That the explanation given above, which is based on the peculiar nature of the vibrations in the waves traversing the plate, is the correct one, follows especially from the changes which come over the appearance presented when the plane of polarization of the incident light is rotated—changes which take place precisely in the manner indicated by the formulæ. When natural incident light is used, then according to the strictly correct formulæ, the rings are not entirely absent, but, depending as they do on ϵ^2, are faintly outlined only in the immediate neighbourhood of the singular axes. As a matter of fact there is in this case visible nothing beyond a mere trace, which appears as a dark spot, of the first minimum within the Brewster's pencils.

10. Although, in accordance with what has been said above, the interference rings observable with only a single polarizer (idiophanic rings) prove the propagation of two similarly rotating elliptic waves, they do not exhibit the change in the direction of rotation during the passage through the ξ-axis, referred to in the fourth proposition. A supplementary experiment thus appears desirable, and the following arrangement would appear to meet all requirements.

If instead of plane polarized we use elliptically polarized incident light, and view it with the naked eye, then according to theory, and as is otherwise evident, the phenomenon to be observed must assume a certain dissymmetry, which was nonexistent with plane polarized incident light. Now this want of symmetry is, as a matter of fact, very marked.

If we use, say, a plate of rhombic andalusite (whereby the plane $A_1\xi$ coincides with the plane of optic axes $A_1\ A_2$) in white or, perhaps better, blue light, and if the plane of the polarizer be normal to that of the optic axes of the crystal, then we obtain a nearly circular system of rings, crossed by a dark band which lies in the plane of the optic axes, a phenomenon with two mutually normal lines of symmetry. If between the polarizer and the crystal we insert a quarter-wave plate, then as the latter is rotated from the position of vanishing effect, the appearance becomes entirely asymmetric, and in a manner which agrees with the predictions of theory.

The dissymmetry is particularly striking when the light incident on the plate is right or left-handed *circularly* polarized light. In this case there appears on one side of the plane of the optic axis (the ξ-axis in fig. 3) a strongly marked dark spot, and on the other a bright spot, and these spots change places if the direction of rotation is reversed.

This observation proves in the simplest manner possible that the waves propagated through the crystal on the two sides of the ξ-axis have opposite directions of rotation, thus furnishing the desired and necessary completion of the proof of the theory.

Göttingen, March 1902.

VIII. *The Discharge of Positive Electrification by Hot Metals.*

By the Hon. R. J. STRUTT, *Fellow of Trinity College, Cambridge* *.

IT was first observed by Guthrie (Phil. Mag. [4] xlvi. p. 273) that red-hot metals were able to discharge positive electrification, and that white-hot metals were able, in addition, to discharge negative electrification.

The experiments described in the present paper were undertaken with a view to determine at what temperature the discharge of positive electrification became sensible, and how far this temperature was dependent on the conditions of the experiment, namely, the state of the metallic surface and the nature and condition of the surrounding gas.

It may be well to say at once that I have been able to detect the effect at temperatures of about 270° C., and that it increases with extraordinary rapidity when the temperature is raised.

The temperature at which the effect becomes sensible does not appear to depend very largely on the nature of the metallic surface, or on the surrounding gas, but it alters nearly as much from slight changes in the condition of the surface of the metal, produced by continued heating, as it does when an entirely different metal is substituted.

With this preface I will explain the method of experimenting adopted.

When it is desired to measure a very small electrostatic leakage there are two alternative methods. Either a very sensitive instrument must be used, the time of leakage being short, or, on the other hand, a less sensitive instrument may be employed, the leakage being allowed to proceed for a longer period.

The quadrant electrometer may be arranged so that it will detect a very small electromotive force ; on the other hand, its capacity is large, and its zero seldom remains so fixed in position as not to wander very appreciably in, say, one hour. Further, it is necessary to use long connecting wires to the instrument, and these in any case involve loss of insulation, owing to the conductivity existing normally in air (C. T. R. Wilson, Proc. Roy. Soc. lxviii. p. 151). If gas flames are in use at the same time there is all the more chance of leakage from the high-potential connecting wires, because of the conductivity of the gases from the flame.

A gold-leaf electroscope, read by a microscope with a micrometer eyepiece, is free from the objections of large

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* Communicated by the Author.

capacity and shifting of the zero, and can be arranged for the proposed experiment (as I shall explain) so that no connecting wires need be exposed to the air. It can be insulated by means of fused quartz in the form of rod and tube. In this way there is practically no limit to the time during which the leak may be allowed to proceed. It would be quite practicable, if desired, to measure a leakage from a charged wire at 100 volts not exceeding 10^{-18} ampere.

Fig. 1 (p. 100) represents the apparatus. *a* is the high-potential wire carried by the brass cap *b*, which in its turn is cemented into the quartz tube *d*. *d* forms a prolongation of the neck of the glass vessel *c*, which incloses the high-potential wire *a* and the thermometer *k*. The further end of *a* is supported by a quartz rod *g*, carrying a cup on the end in which the wire rests.

The glass vessel *c* is silvered inside, and connected to earth through a platinum wire *f*. The brass cap *b* presses against the brass strip *p*, which carries the gold-leaf *o*. This strip and gold-leaf are inclosed in a glass vessel very thinly silvered inside to make it conducting, and dried by phosphoric anhydride contained in *m*. This vessel can be exhausted, as shown in the figure.

The arrangement of the electroscope is very similar to that employed by Wilson (*loc. cit.*). The brass strip *p* is supported by a quartz rod *q*, and this quartz by a brass rod *s* passing out through the indiarubber cork *t*. *p* and *s* can be brought into temporary metallic contact by means of the iron wire *r*, movable by an external magnet. To charge the wire *a* and the electroscope it is merely necessary to give a suitable charge to *s* (this charge being adjusted to a convenient value by means of an auxiliary electroscope), and then to make contact with *p* by means of the iron wire *r*. When a suitable charge has been given the magnet is removed and the contact thus broken. *s* is then touched to discharge it. When *c* and the electroscope were exhausted insulation was so good that the potential of the system did not sink more than a fraction of a volt in 24 hours when initially charged to about 100 volts.

In order to raise the temperature of the wire *a*, the vessel *c* was inclosed in a metal oven heated by a gas-burner. In this oven was also placed an elongated glass bulb containing air. This worked a temperature-regulator in the ordinary way, cutting off the gas by its expansion when the temperature rose too high.

The neck *f* of the vessel was long enough to prevent the electroscope getting seriously heated by the radiation from the gas-burner when screens were interposed. As, however, the electroscope was exhausted, to improve the insulation, the gold-leaf was liable to show radiometer effects. These could be greatly mitigated by not pushing the exhaustion of the electroscope too far.

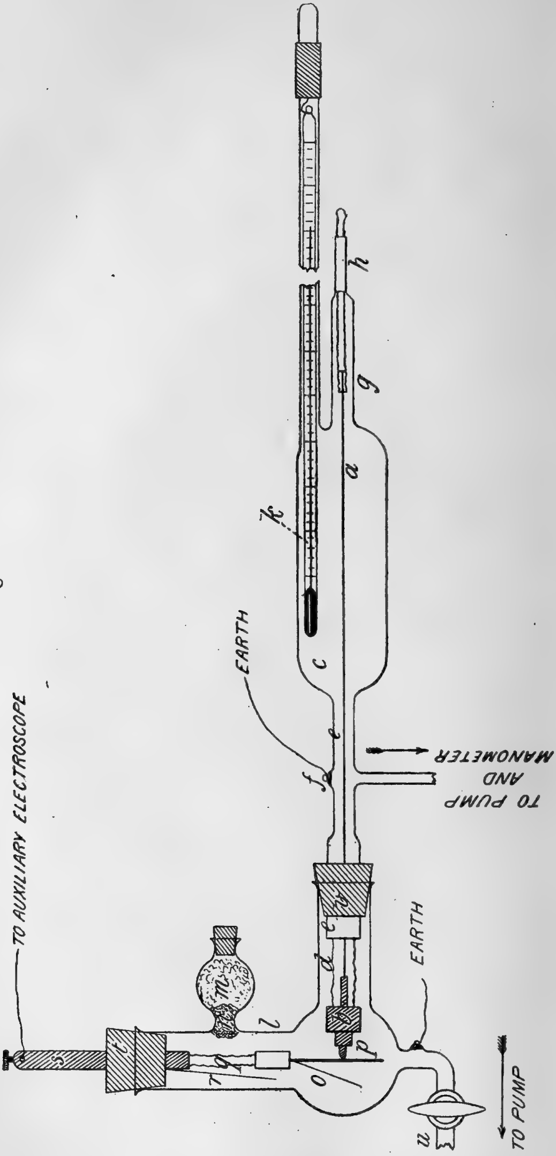


Fig. 1.

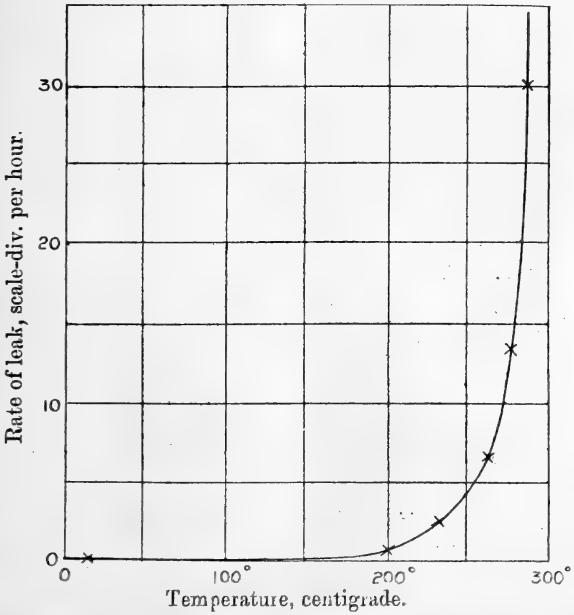
The electroscope was observed with a microscope provided with a scale in its eyepiece. It was found, on comparing the scale of the electroscope with a multicellular voltmeter, that the divisions were of approximately equal value throughout the scale, very nearly one volt per division. The scale had 50 divisions.

When the apparatus was filled with air at atmospheric pressure a leak was observed at ordinary temperatures. This effect is quite distinct from the effect discovered by Guthrie, since it is observed equally whether the charge is + or − (Wilson, *loc. cit.*), whereas Guthrie's effect is only obtained with a + charge, unless the temperature is above a red heat. To make this effect insensible the pressure was reduced to 1 cm. of mercury. The Guthrie effect is not apparently much affected by moderate reduction of pressure, whereas the effect investigated by Wilson is diminished nearly in the same proportion as the pressure.

The first experiments were made with a pure silver wire in air at 1 cm. pressure. This was heated to successively increasing temperatures, and the corresponding rates of leak determined. These were practically uniform for different parts of the electroscope scale. The results were:—

Temperature..	15°	202°	236°	265°	277°	287°
Leak........	·14	·59	2·70	6·5	13·5	30·0

Fig. 2.



These results are plotted on the appended diagram (fig. 2).

The temperatures are given in degrees centigrade, the rates of leak in scale-divisions per hour.

By interpolation it was found that the rate of 10 div. per hour was attained at 270°. The same wire was again taken up the scale of temperature without removing it from the apparatus.

Temperature..	13°	194°	210°	217°	227°	240°	258°
Leak........	·5	·7	1·34	1·96	5·5	6·7	45·6

The rate was 10 div. per hour at 250°, 20 degrees lower than before.

This change in the temperature at which an assigned rate of leak (10 per hour) was attained is, of course, far beyond the uncertainties of experiment, and must be attributed to a change in the state of the silver surface. Further heating did not alter it much more.

The apparatus was exhausted, filled with pure hydrogen, and the pressure reduced to 1 cm.

Temperature..	15°	175°	183°	210°	225°	233°
Leak........	·2	·6	1·0	2·5	6·1	14·8

10 div. per hour at 228°.

Thus the leakage set in in hydrogen at a somewhat lower temperature than in air.

The next experiments were made with a copper wire substituted for a silver one. This wire was cleaned with emery paper before it was put in; in the course of the experiment it became oxidized. This oxidizing process did not apparently facilitate the escape of positive electrification since the leakage was not so soon apparent as in the case of the silver wire.

The results were:—

Temperature..	167°	226°	253°	271°	289°	308°	325°	331°
Rate of Leak .	·1	·3	·55	2·9	12·0	38·0	204·0	340·0

Thus the rate of leak was 10 div. per hour at about 287°.

A repetition of the experiment gave a very similar result.

The copper wire was taken out and thoroughly oxidized in a blowpipe flame. It was then replaced. The rates of leak were as follows:—

Temperature	255°	259°	272°	283
Rate of Leak	·7	3·11	15·0	83·2

Here the rate of leak was 10 div. per hour at 266°.

Finally, a well oxidized copper wire was tried in hydrogen.

Temperature	267°	287°	307°	316°
Rate of Leak	1·05	1·4	6·0	21·4

10 div. per hour at 310°.

These experiments fall into two classes.

(1) Those cases where chemical action was occurring between the electrified surface and the surrounding gas.

(2) Those cases where there was no such action.

To summarize the results: under the first head we have—

Copper in air . . .	10 div. of leak per hour	at 287°
Copper oxide in hydrogen	„ „ „	at 310°

under the second—

Silver in air. .	10 div. leak per hour at	250°
Silver in hydrogen	„ „ „	228°
Copper oxide in air	„ „ „	266°

So far as the experiments go they suggest that chemical action is rather unfavourable than otherwise to the escape of positive electrification.

The result of most interest in the present investigation is that the discharge of positive electrification by hot metals can be detected at much lower temperature than has hitherto been supposed, becoming apparent very far below a red heat, and increasing rapidly with the temperature.

IX. *On a General Numerical Connexion between the Atomic Weights.* *By* J. H. Vincent, *D.Sc., B.A.*[*]

[Plates I. & II.]

Historical.

MANY relationships have been made out between the atomic weights of the elements when these are considered in small groups: and there are a few formulæ which have been proposed to express the connexion between the atomic weight of an element and the order in which it stands in a list of elements of ascending atomic weights.

Mills (Phil. Mag. [5] xviii. p. 393 & xxi. p. 151) states that "it is probable that the equation

$$y = p \, . \, 15 - 15(\cdot 9375)^x$$

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[*] Communicated by Prof. J. J. Thomson, F.R.S.

includes the numerics of all known elements excepting hydrogen," a numeric being an atomic weight y. He arranged all the atomic weights in ascending order of magnitude, and without altering the order, these were divided into sixteen groups by trial. The number p is the same integer for each group. The value of x was obtained by arithmetic for each element. Mills restricted himself only by having x always either an integer or infinity, and then chose its value so that the calculated atomic weight should be as near as possible to the experimental value. An example of a group is given below to illustrate the method.

Group III.

$$y=45-15(\cdot9375)^x.$$

	x.	y.	y calc.
P	1	30·96	30·94
S	2	31·98	31·82
Cl	7	35·37	35·45
K	14	39·02	38·92
Ca	17	39·90	39·99
Sc	42	43·98	44·00

When we consider the large amount of choice involved in the compilation of such a table, it is not at all surprising that the numbers in the last two columns of the above table agree closely; indeed there seems no reason to doubt that by some such arbitrary process the numbers in the last two columns could be made to agree to any required degree of accuracy.

To find the atomic weight of an element by this method one would require to know the group in which the element had been placed, the value of x assigned to the element, as well as the constants occurring in the equation.

While regarding the work as leading to the conclusion that there might be an infinite number of elements having atomic weights less than about 240, Mills considered that this value was the upper limit.

The formulæ are subsequently derived by the contemplation of a hot nebular mass of primitive substance which, while cooling freely in space, gives birth to polymers of this primitive material. "But on account of the evolution of heat when a polymer is formed, there will ensue, as a physical consequence, the inversion of more or less of the cooling, and therefore of the polymerization." Incidentally this theory is used to explain the phenomena of variable stars.

The important point about Mills' work is that it may be considered as indicating the existence of an upper limit for atomic weights. The weak point is that the number of elements below this limit may be infinite. On this latter question Mendeléeff ('Principles of Chemistry,' English translation, 1891 ed. p. 19) expresses himself with great clearness. "The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weights—in a word it does not express an uninterrupted function."

In conclusion, Mills uses his formulæ to classify the elements with some degree of success.

Stoney (Proc. Roy. Soc. 1888, p. 115, and Circular issued to members of B. A. at Bath, 1888) plots as ordinates the cube roots of the atomic weights referred to hydrogen as unit, the abscissæ being successive integers. "A curve

$$y_m = k \log (m\alpha),$$

where

$$\log k = 0{\cdot}785,$$

and

$$\log \alpha = \bar{1}{\cdot}986,$$

threads its way through the positions plotted down from the observations."

Having obtained an expression of this form, Stoney investigated subsequent terms which should include deviations from the formula. Finally a spiral was constructed and so arranged that it not only showed the periodic classification of the elements, but also gave by inspection the atomic weights.

It should be noted that according to Stoney's formula elements of less atomic weight than hydrogen and also of greater atomic weight than uranium may exist. Three elements lighter than hydrogen and six between hydrogen and lithium were predicted; a vacant "sesqui-radius" in the spiral was left, across which the transition from electro-positive to electro-negative elements was abrupt. This "is not arbitrarily introduced into the diagram, but has a real existence in nature." This "sesqui-radius" is now occupied by the new gases, and thus the prophecy of Stoney has been fulfilled in a most remarkable way.

This is a very strong argument in favour of the formula with which Stoney worked, but it is perhaps a stronger argument in favour of the treatment of the periodic law by graphic methods. The prejudice against such methods entertained by Mendeléeff is very surprising. In his book already referred to, he says he has never expressed, "and will never express, the periodic relations of the elements by any geometrical figures."

Carnelley (Phil. Mag. [5] xxix. p. 97) founded his method of computing the atomic weights on the periodic law. He mentions that he had made frequent attempts to find a simple numerical expression for the periodic law during seventeen years previous to the publication of this paper, but without marked success.

The atomic weight A is given by the formula

$$A=6{\cdot}6(m+\sqrt{v}),$$

where m is a constant for each of Mendeléeff's "series," while v is equal to the order of each element in its series. The values chosen for m were 0, $2\frac{1}{2}$, 5, $8\frac{1}{2}$, and thence by differences of $3\frac{1}{2}$ to 33, for the successive series II., III., ... XII. Thus "for any element in series IV. or upwards

$$A=6{\cdot}6(3{\cdot}5a-9+\sqrt{v}),$$

where a = the number of series to which the element belongs, and v the numerical order of the element in its own series." A table of determined and computed atomic weights with their differences is given, from which it is at once evident that the rule is capable of calculating the atomic weights with a considerable degree of accuracy. The greatest variation is for iodine, in which the computed atomic weight falls short of the real atomic weight by 6·7 units. The difference in the same direction for tellurium is given as 6·5; but if we substitute the value now accepted for the atomic weight of tellurium, the difference becomes greater. The mean difference for the 54 elements considered is only 1·9.

If, on the other hand, we examine the results from a percentage point of view, they do not appear so satisfactory. Thus the computed value for the atomic weight of carbon is 10 per cent. too high, that of selenium is 8·2 per cent. too low, that of lithium is 5·7 per cent. too low, and that of nitrogen is 5·7 per cent. too high.

The nearness of the constant 6·6 to the 6·4 of Dulong and

Petit's law suggested to Carnelley the trial of the rule

$$\text{Specific heat} = \frac{1}{m+\sqrt{v}};$$

and he found "that in almost all cases the numbers agree very closely with the experimental specific heats."

A NEW RULE FOR COMPUTING ATOMIC WEIGHTS.

If a list of all the atomic weights in ascending order of magnitude be taken and the order in this list be called n, then the nth atomic weight, from $n=3$ to $n=60$, is given by the equation

$$W=(n+2)^{1\cdot21}.$$

In the table (p. 108) headed "Augmented List of the Elements," the numbers standing under n give the actual order of the elements in such a list as the above. The determined atomic weights are given under w, the computed atomic weights under W.

The atomic weights are Clarke's with hydrogen as unit (Journ. Am. Chem. Soc. March 1902).

The difference between the determined and the calculated atomic weight is given in another column. Confining our attention for the present to that part of the table from lithium to samarium inclosed by the large bracket, we see that for the 58 elements considered, the difference between the experimentally determined atomic weight and that calculated by the rule is less than unity in 36 cases. It is greater than 1 and less than 2 in 13 cases; is between 2 and 3 in 7 cases; while in only two cases does the computed value differ from the determined value by more than three units, in both of which the difference is less than 4. The mean difference for the whole of the 58 elements with which we are now dealing is about 1·01.

The percentage differences are given also in the table. In 19 instances the difference is less than 1 per cent., in 19 it is either 1 per cent. or greater than 1 per cent. and less than 2 per cent.; in 11 cases it is greater than 2 but less than 3, and in 6 it is either equal to or greater than 3 and less than 4, in two instances the percentage difference exceeds 4, and in one case the error is 5·8 per cent. The mean percentage error for the 58 elements is about 1·6.

AUGMENTED LIST OF THE ELEMENTS.

n.		N.	*w.*	W.	*w*−W.	$\frac{(w-W)}{w}\times 100$.
1. Hydrogen		1	1 (by definition)	1	0·00	0·0
…………		2	……	2·313	……	…
2. Helium		3	3·93	3·780	+0·15	+3·8
…………		4	……	5·352	……	…
3. Lithium		5	6·97	7·012	−0·04	−0·6
4. Glucinum		6	9·0	8·746	+0·25	+2·8
5. Boron		7	10·9	10·54	+0·36	+3·3
6. Carbon		8	11·9	12·38	−0·48	−4·0
7. Nitrogen		9	13·93	14·28	−0·35	−2·5
8. Oxygen		10	15·88	16·22	−0·34	−2·1
9. Fluorine		11	18·9	18·20	+0·70	+3·7
10. Neon		12	19·8	20·24	−0·44	−2·2
11. Sodium		13	22·88	22·28	+0·60	+2·6
12. Magnesium		14	24·1	24·37	−0·27	−1·1
13. Aluminium		15	26·9	26·49	+0·41	+1·5
14. Silicon		16	28·2	28·64	−0·44	−1·6
15. Phosphorus		17	30·75	30·82	−0·07	−0·2
16. Sulphur		18	31·83	33·03	−1·20	−3·8
17. Chlorine		19	35·18	35·26	−0·08	−0·2
18. Potassium		20	38·82	37·53	+1·29	+3·3
19. Argon		21	39·6	39·80	−0·20	−0·5
20. Calcium		22	39·8	42·10	−2·30	−5·8
21. Scandium		23	43·8	44·43	−0·63	−1·4
22. Titanium		24	47·8	46·78	+1·02	+2·1
23. Vanadium		25	51·0	49·15	+1·85	+3·6
24. Chromium		26	51·7	51·55	+0·15	+0·3
25. Manganese		27	54·6	53·94	+0·66	+1·2
26. Iron		28	55·5	56·37	−0·87	−1·6
27. Nickel		29	58·25	58·82	−0·57	−1·0
28. Cobalt		30	58·55	61·28	−2·73	−4·7
29. Copper	$N=n+2$	31	63·1	63·76	−0·66	−1·0
30. Zinc		32	64·9	66·26	−1·36	−2·1
31. Gallium		33	69·5	68·78	+0·72	+1·0
32. Germanium		34	71·9	71·30	+0·60	+0·8
33. Arsenic		35	74·45	73·85	+0·60	+0·8
34. Selenium		36	78·6	76·41	+2·19	+2·8
35. Bromine		37	79·35	78·98	+0·37	+0·5
36. Krypton		38	81·15	81·57	−0·42	−0·5
37. Rubidium		39	84·75	84·17	+0·57	+0·7
38. Strontium		40	86·95	86·79	+0·16	+0·2
39. Yttrium		41	88·3	89·43	−1·13	−1·3
40. Zirconium		42	89·7	92·07	−2·37	−2·6
41. Columbium		43	93·0	94·74	−1·74	−1·9
42. Molybdenum		44	95·3	97·40	−2·10	−2·1
43. Ruthenium		45	100·9	100·1	+0·8	+0·8
44. Rhodium		46	102·2	102·8	−0·6	−0·6
45. Palladium		47	106·2	105·5	+0·7	+0·7
46. Silver		48	107·11	108·2	−1·1	−1·0
47. Cadmium		49	111·55	110·9	+0·7	+0·6
48. Indium		50	113·1	113·7	−0·6	−0·5
49. Tin		51	118·1	116·5	+1·6	+1·4

TABLE (*continued*).

n.		N.	w.	W.	$w-$W.	$\frac{(w-\text{W})}{w}\times 100$.
50. Antimony	N = n + 2.	52	119·5	119·2	+0·3	+0·3
51. Iodine		53	125·89	122·0	+3·9	+3·1
52. Tellurium		54	126·1	124·8	+1·3	+1·0
53. Xenon		55	127	127·6	−0·6	−0·5
54. Cæsium		56	131·9	130·4	+1·5	+1·1
55. Barium		57	136·4	133·2	+3·2	+2·3
56. Lanthanum		58	137·6	136·1	+1·5	+1·1
57. Cerium		59	138·0	138·9	−0·9	−0·7
58. Praseodymium		60	139·4	141·8	−2·4	−1·7
59. Neodymium		61	142·5	144·6	−2·1	−1·5
60. Samarium		62	149·2?	147·5	+1·7	+1·1
……		63	……	150·4	…	…
……		64	……	153·3	…	…
61. Gadolinium		65	155·2	156·2	−1·0	−0·6
62. Terbium		66	158·8	159·1	−0·3	−0·2
……		67	……	162·0	…	…
63. Erbium		68	164·7	164·9	−0·2	−0·1
……		69	……	167·9	…	…
64. Thulium		70	169·4	170·8	−1·4	−0·8
65. Ytterbium		71	171·9	173·8	−1·9	−1·1
……		72	……	176·8	…	…
66. Tantalum		73	181·5	179·7	+1·8	+1·0
67. Tungsten		74	182·6	182·7	−0·1	0·1
……		75	……	185·7	…	…
68. Osmium		76	189·6	188·8	+0·8	+0·4
69. Iridium		77	191·7	191·7	0·0	0·0
70. Platinum		78	193·4	194·7	−1·3	−0·7
71. Gold		79	195·7	197·8	−2·1	−1·1
72. Mercury		80	198·50	200·8	−2·3	−1·2
73. Thallium		81	202·61	203·8	−1·2	−0·6
74. Lead		82	205·36	206·9	−1·5	−0·7
75. Bismuth		83	206·5	209·9	−3·4	−1·6
……		84	……	213·0	…	…
……		85	……	216·1	…	…
……		86	……	219·2	…	…
……		87	……	222·2	…	…
……		88	……	225·3	…	…
……		89	……	228·4	…	…
76. Thorium		90	230·8 ?	231·5	−0·7	−0·3
……		91	……	234·7	…	…
77. Uranium		92	237·8	237·8	0·0	0·0

We may add this statement to the rule: that if the atomic weights are from Clarke's 1902 list with hydrogen as unit, then the greatest difference between the computed and the determined value will not exceed 4 units, nor will the percentage difference be greater than 6; while in 36 cases the result will not be a unit wrong, and in 19 cases will not be 1 per cent. wrong.

Deviations from the Formula.

The elements deviating most from the formula, judging from the differences between the computed and experimental values, are:—

	$w-W$.
Iodine	+3·9
Barium	+3·2
Cobalt	−2·73
Praseodidymium	−2·4
Zirconium	−2·37
Calcium	−2·30
Selenium	+2·19
Molybdenum	−2·1
Neodidymium	−2·1

Iodine is thus a very marked exception to a rule which holds fairly correctly for 57 other elements. This may be explained by assuming either (1) that the real atomic weight of iodine is less than that accepted, or (2) that the order in the table is too low; and thus the suspicion of error in the atomic weight falls upon its next highest neighbour tellurium. The atomic weight of tellurium is a matter of some uncertainty owing to two causes. One of these is that successive attempts to determine its atomic weight do not yield concordant results, and the other is that unless the atomic weight of tellurium is below that of iodine these two elements constitute a serious exception to the periodic law. If we assume that its atomic weight is less than that of iodine, then iodine would have

$$n=52.$$

Its computed value would be 124·8, which differs from the determined value by 1·09, a quantity little greater than the mean deviation. The most probable atomic weight for tellurium on this view is 122.

The fact that the greatest variation of the rule leads to the same conclusion as the periodic law may be taken as tending to confirm the legitimacy of the former. No general relation has been found to connect the deviations, but a term could be inserted in the formula whose magnitude depended on whether n were odd or even, which would make the errors less.

It may be noted that iodine, molybdenum, and selenium are exceptions to Dulong and Petit's law.

Judged from the percentage standpoint, the elements deviating most from the formula are:—

	$\frac{w-W}{w}100.$
Calcium	$-5{\cdot}8$
Cobalt	$-4{\cdot}7$
Carbon	$-4{\cdot}0$
Sulphur	$-3{\cdot}8$
Fluorine	$+3{\cdot}7$
Vanadium	$+3{\cdot}6$
Potassium	$+3{\cdot}3$
Boron	$+3{\cdot}3$
Iodine	$+3{\cdot}1$

Of these, calcium, carbon, fluorine, sulphur, boron, and iodine are exceptions to Dulong and Petit's law.

Argon is an exception to the periodic law, which would lead one to expect its atomic weight to be between those of chlorine and potassium. If, however, its atomic weight should be proved to be greater than that of calcium, the atomic weight of the latter would be given correctly by the rule. The value to be then expected for argon would be 42·1.

Extension of the Formula to all the Elements.

The evidence which has been adduced in favour of the formula

$$W = (n+2)_{1{\cdot}21}$$

warrants an attempt being made to apply it to the remaining elements.

The plan adopted has been to replace the $(n+2)$ of the above formula by N, where N is the order in what will be called for short the augmented list. This augmented list is one in which, though the real order of arrangement is never reversed, a value for N is taken so that the particular element shall have its atomic weight given as nearly as possible by the formula. Thus the augmented list is a list of the elements in ascending order of magnitude, with gaps left in it so as to make the experimental results fit the formula.

The justice of this process may be tested by seeing whether the necessary gaps are too numerous, or are in any other way improbable; or whether the gaps can be reconciled with acknowledged chemical principles.

Over the range from lithium to samarium the change is simply to replace $n+2$ by N. That is, instead of regarding lithium as the third heaviest atom, it is taken as the fifth in the augmented list, germanium as the sixth instead of the fourth, and so on up to samarium. For hydrogen N=1, and for helium N=3. The formula is of such a type as to give the atomic weight of hydrogen correctly; the calculated weight of helium is only ·15 of a unit wrong, which, however, is a percentage error of 3·8. The most probable value for helium is 3·78.

These two gaps near the beginning of the augmented list have no chemical evidence in their favour. There is no room in the periodic table for an element between helium and lithium, and any theory based on the periodic law which would predict any elements between hydrogen and helium would predict several and not merely one.

It is necessary to assume thirteen other gaps in order to complete the augmented list. The table gives the positions and also the atomic weights which they would have on this theory.

The periodic table leaves five gaps between samarium and gadolinium. This table also shows that if there are not five missing elements then there are two. In the latter case elements analogous to rhodium, ruthenium, and palladium would not be represented. The augmented list agrees with this second view. The periodic law would lead us to expect a maximum of seven elements between gadolinium and terbium. The augmented list indicates that five only are to be expected. Their exact positions in the periodic table cannot be predicted until the positions occupied by terbium, erbium, and thulium are known. An element is predicted by the periodic law between ytterbium and tantalum, and between tungsten and osmium. These are also predicted by the augmented list, which agrees also in predicting only one element in each of these positions. An unbroken line of elements occurs from osmium to bismuth in both the periodic table and in the augmented list. Between bismuth and thorium both leave six elements to be discovered, while the last gap between thorium and uranium occurs in both the periodic table and the augmented list.

The results given in the table are shown graphically in Plates I. and II., in which + indicates the atomic weight given by the formula and ● shows the actual atomic weight. The sign ∗ marks the most probable atomic weight of a predicted element.

Pl. I. is drawn on ordinary squared paper, and is thus suited to show the differences between the computed and the experimentally found numbers.

Pl. II. is drawn on paper ruled logarithmically. The graph of an equation of the form $y=x^m$ is a straight line on this paper, so that all the computed points lie on a straight line. The actual distances of the points (●) showing the experimentally determined values above or below the straight line, are proportional to the percentage differences between the computed and the experimental numbers.

It will be seen that the actual values of the atomic weights lie very close to the straight line in Pl. II.

An equally good straight line would of course be obtained by plotting the cube roots of w instead of w.

Thus the formula is of a different type to Stoney's, from which it would follow that the actual values (not the logarithms) of the cube roots of the atomic weights plotted against the logarithm of the order would give a straight line.

On the Determination of the Power Constant and the Use of the Rule.

The whole of the preceding leads to the conclusion that a relationship of the form

$$W=N^q$$

expresses to a close degree of accuracy some fundamental connexion which exists between the masses of different kinds of atoms.

The equation has been thrown into the form

$$W=N^{1\cdot21}$$

in the previous pages so as to render the whole as definite as possible. But no claim is made as to 1·21 being the best value to give to q. The value of q should be obtained from the list of elements from lithium to samarium, augmented or not as may appear most just to anyone who wishes to redetermine the value of q. If there is any truth in the views explained in this paper, the constant q is of primary importance, and its exact determination becomes a matter of interest. The value which will be obtained depends on whether or not an element analogous to manganese is to be assumed between molybdenum and ruthenium; q will be slightly less or greater according as a gap is or is not left.

The method might, however, be used to test this point. By considering only elements as far as molybdenum the best value of q could be found, and then the sum of the deviations with this value of q could be found 1st when no gap was left, 2nd with the gap.

If the second arrangement gave a smaller mean difference than the first, then this would justify the prediction of an element in the place under discussion.

It may well be, however, that the result of such an investigation would be different according as one regarded percentage differences or the differences themselves as of more importance. If the latter, then the mean error is less when no gap is left between molybdenum and ruthenium.

Thus if we regard any atomic weight w_N as giving us a value of q, we have a series of equations like

$$w_N = N^q,$$

or

$$\log w_N = q \log N.$$

Using the atomic weights of all the elements up to and including molybdenum, we have

$$\begin{aligned} \log 3{\cdot}93 &= q \log 3, \\ \log 6{\cdot}97 &= q \log 5, \\ \log 9{\cdot}0 \ &= q \log 6, \\ \cdot\ \cdot\ \cdot\ &\cdot\ \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ &\cdot\ \cdot\ \cdot \\ \log 95{\cdot}3 &= q \log 44. \end{aligned}$$

The value of q given by

$$q = \frac{\Sigma \log w}{\Sigma \log N}$$

will be such that the percentage errors will be least. This equation may be written

$$q = \frac{\Sigma \log w}{\log \underline{|44} - \log 8},$$

from which q may be found readily by using a table of the logarithms of factorials. The value obtained is

$$q = 1{\cdot}209.$$

Similarly q may be computed, when no gap is left between molybdenum and ruthenium, from the atomic weights of the elements from ruthenium to samarium. In this case

$$q=\frac{\Sigma \log w}{\log \underline{|62}-\log \underline{|44}}$$
$$=1{\cdot}211.$$

If, however, we leave the gap, we have

$$q=\frac{\Sigma \log w}{\log \underline{|63}-\log \underline{|45}}$$
$$=1{\cdot}205.$$

Thus the q when we leave no gap is nearer to the first value ($q=1{\cdot}209$) than is the value of q obtained when we leave the gap. This leads to the conclusion that no element of atomic weight about 101 with properties analogous to manganese is to be predicted.

The mean value of q can now be calculated from

$$q=\frac{\Sigma \log w}{\log \underline{|62}-\log \underline{|8}},$$

which gives

$$q=1{\cdot}210.$$

When the value of q has been determined as accurately as possible, then the formula may be employed to determine what empty places in the periodic table are to be filled by predicted elements, in the same way as has been already done above on the assumption that $q=1{\cdot}21$.

CONCLUSION.

The consequence which follows from the assumption that

$$W=N^q,$$

where N is a + integer and q a positive number whose actual value approximates to 1·21, is that the list of atomic weights starts abruptly at hydrogen but has no end.

The fact that for many years all the elements that have been discovered have atomic weights greater than that of hydrogen and less than that of uranium would point to the conclusion that any law for the connexion between the masses of different kinds of atoms should lead to the list of elements being limited at both the beginning and end.

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X. *Observations on Mixtures with Maximum or Minimum Vapour-Pressure.* *By* J. P. Kuenen *and* W. G. Robson*.

IN previous papers † an account was given of the properties of certain mixtures which have a maximum in their vapour-pressures at a given temperature and a minimum in their critical temperatures; and more recently ‡ a case was investigated in which a minimum in the vapour-pressures went hand in hand with a maximum critical temperature.

This combination of corresponding properties follows as a result from van der Waals' theory of mixtures, if the mixtures are assumed to have the simple characteristic equation similar to van der Waals' well-known equation for simple substances. This assumption involves the more general one that the mixtures are normal, *i. e.* without association of molecules, although the two suppositions are by no means identical; a simple substance may disobey van der Waals' law (as it invariably does) and still be normal, as testified by its obeying the law of corresponding states.

It will be convenient to briefly restate the theoretical conclusions on the above assumption.

For mixtures which have a maximum vapour-pressure for a given composition at a low temperature, the maximum shifts towards the component with the higher vapour-pressures, and may either disappear or remain up to the critical condition. These mixtures have at the same time a minimum in their "hypothetical" critical temperatures—*i. e.* the critical temperatures which they would have if they did not split up into mixtures of different composition but remained homogeneous,—at a composition coinciding with the composition of maximum vapour-pressure at low temperatures, and have accordingly a tendency towards a minimum in their real critical temperatures.

If there is a minimum vapour-pressure at a low temperature, the minimum shifts towards the component with the lower vapour-pressures, and may disappear or remain up to the critical point. These mixtures have a maximum critical temperature at a composition near that of the minimum vapour-pressure at low temperatures.

If the mixtures are abnormal either because one or both the components are so, or because of mutual association of the two kinds of molecules, the above rules cannot be expected to hold good. A maximum vapour-pressure may be due not to the low mutual attraction of the two substances,

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* Communicated by the Authors.

† Phil. Mag. [5] xl. p. 173; xliv. p. 174.

‡ Ibid. [6] i. p. 593.

as is the cause of a maximum with normal mixtures, but to the association at low temperatures of the molecules of the component which has the higher vapour-pressures at high temperatures, and the abnormally low vapour-pressure exerted by this substance in consequence. This abnormality naturally makes the vapour-pressures of the mixtures appear relatively high, and may even produce a maximum. In that case there would be no reason to expect a minimum critical temperature.

Other exceptional cases due to association will naturally suggest themselves, and instances will be discussed below.

The above conclusions for normal substances are, to a certain extent, confirmed by the results contained in former papers, to which the reader may here be referred. The experiments described in this paper were undertaken with a view to completing the comparison with theory, and obtaining further information on the behaviour of similar mixtures. Three different combinations were examined and will be taken up successively.

1. *Propyl Alcohol and Water.*

In this mixture it was our object to follow the maximum in the vapour-pressure discovered by Konowalow [*] up to the critical point, to ascertain whether the maximum shifts to any extent to mixtures of different composition, whether it disappears or not, and finally whether the critical temperatures showed a minimum or not.

The propyl alcohol obtained from Kahlbaum was found to be sufficiently pure to be used without further purification. Three mixtures were investigated, the first containing approximately 2½ per cent. of water (mixture 1); the second and third both approximately 25 per cent. (mixtures 2 and 3). This is approximately the maximum mixture at the boiling-point. Some of our results are shown in Tables I.–V. (p. 118), and the diagram (fig. 1). As we could not observe the beginning of the condensation of the mixtures in our tubes, we always took the pressure at a small volume near the end of condensation: the figure thus gives condensation *lines* instead of narrow *loops*.

The vapour-pressures of water used in the figure are due to Batelli [†]; at temperatures above 250° the values are somewhat higher than those found by Cailletet and Colardeau [‡].

Our value for the critical temperature of propyl alcohol agrees well with that found by Ramsay and Young [§], viz.,

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[*] Wied. *Ann.* xiv. p. 34.

[†] *Ann. Chimie et Phys.* [7] iii. p. 412.

[‡] *Ibid.* [6] xxv. p. 527.

[§] Phil. Trans. clxxx. p. 137.

TABLE I.—Vapour-pressures of Propyl Alcohol.

Temperature.	Pressure.
96·0	0·96
98·45	1·06
105·1	1·37
128·3	2·97
131·1	3·23
149·9	5·63
160·2	7·21
166·9	8·47
183·3	12·20
228·3	28·71
242·1	36·35
248·2	39·76
250·6	41·36
264·0	51·51 Critical point.

TABLE II.—Vapour-pressures of Mixture 1.

Temperature.	Pressure.
95·15	1·04
98·0	1·17
105·05	1·52
116·8	2·25
130·8	3·54
145·4	5·57
160·2	7·99
183·1	13·35
216·8	25·12
227·8	30·61
245·1	40·14
254·6	47·42
264·9	55·94 Plait-point.

TABLE III.

Vapour-pressures of Mixture 2.

Temperature.	Pressure.
166·9	11·20 read after the higher temperatures.
179·1	14·56
182·7	15·76
215·7	30·57
224·6	35·85
241·35	47·98
250·2	56·2
261·8	67·33
275·85	83·81 Plaitpoint.

TABLE IV.

Vapour-pressures of Mixture 3.

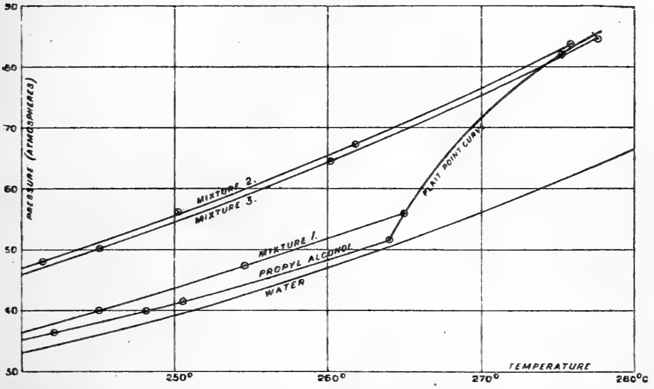
Temperature.	Pressure.
85·2	0·91
87·6	1·00
92·2	1·17
94·15	1·26
105·1	1·89
116·8	2·81
123·65	3·50
131·1	4·37
145·3	6·74
160·15	9·88
170·9	12·43
183·4	16·34
245·15	50·16
260·1	64·42
275·1	82·04
277·5	84·6 Plait-point.

TABLE V.—Critical Constants.

	Temperature.	Pressure.
Propyl alcohol	264·0	51·5
Mixture 1	264·9	55·9
Mixture 2	275·85	83·8
Mixture 3	277·5	84·6

262°·7, but our pressures are all a little higher than theirs, the difference increasing with the temperature up to the critical point, where we find 51·51, their value being 50·16.

Fig. 1.



This difference is probably due to a trace of water in our alcohol (see below). It will be seen (1) that the maximum vapour-pressure remains up to the critical point, and (2) that the critical temperatures have no minimum.

The very small difference in the critical temperatures of pure propyl alcohol and of the first mixture leaves some doubt as to whether there might not actually be a small minimum close to propyl alcohol (especially since readings were taken with different thermometers, one having been broken). But even if it did exist, which is very unlikely, the minimum would be very little pronounced, and would not belong to the mixture of maximum vapour-pressure at low temperatures. The fact that Ramsay and Young found a lower critical temperature for water-free propyl alcohol supports the conclusion that there is no minimum.

This deviation from the normal case, as deduced from the theory and as realized by mixtures of ethane and carbon dioxide (see above), makes it probable that the maximum vapour-pressure in the combination of propyl alcohol and water is not due to a small attraction between the two kinds of molecules, but to association of molecules. The chief cause is probably the very high association of the water molecules amongst themselves. That this association has begun even at high temperatures appears from the fact that the vapour-pressure curve of water, which is considerably below the curve of propyl alcohol at low temperatures, approaches the latter as the temperature rises, so that it looks as if they would intersect, if the propyl-alcohol curve were a little longer. This irregularity would not occur with normal substances, and is due to the very high abnormality of water, which reduces its pressure abnormally as the temperature falls. This low vapour-pressure of the water makes those of the mixtures appear relatively high.

In a somewhat crude form our explanation is this: if the water molecules did not associate, water would have higher vapour-pressures than propyl alcohol. Adding water to propyl alcohol, therefore, raises the vapour-pressure until, when the density of the water in the mixture becomes sufficiently high, the association begins to make itself felt, and the vapour-pressure passes through a maximum and falls towards the pressure of water itself. It is thus unnecessary to assume a specially small mutual attraction between the two kinds of molecules, and there is no reason to expect the critical temperature to fall when water is added to propyl alcohol.

As regards the shifting of the maximum, our experiments, as far as they go, do not seem to show a considerable change in the composition of the maximum mixture. On the contrary, the almost perfect parallelism of the vapour-pressure curves for the two mixtures, 2 and 3, seems to show that the change is very small, and it looks altogether as if the 25 per cent. mixture was still approximately the maximum mixture in the critical region *.

It follows, from the position of the critical curve in the diagram, that all the mixtures between propyl alcohol and the maximum mixture ought to show retrograde condensation of the second kind. It was impossible to confirm this completely in the experiments, but what was observed is in accordance with the theoretical conclusion. When the mixture 1 was in the critical condition, *i. e.* at its plaitpoint, compression invariably brought back the liquid surface, and made the liquid increase until it filled the tube. This phenomenon shows that the plaitpoint in the volume-composition diagram is placed on the side of the large volumes; and this agrees with the theory and with the existence of retrograde condensation of the second kind, which, owing to gravitation and slight impurities, could not itself be observed.

We did not consider it worth while repeating our experiments with purified alcohol, as a special experimental difficulty prevented us from obtaining accurate results or going into the various questions more thoroughly. We refer to the action of water on glass, which we observed in 1898 †, and

* Compare Ramsay and Young, Phil. Trans. clxxx. p. 157.

† Phil. Mag. [5] xlviii. p. 188.

which has been fully investigated by Barus*. A mixture kept at a temperature above 200° C. is constantly losing water which is absorbed by the glass; the tube gradually becomes quite opaque. The composition of the mixture is thus always changing, and it is obviously impossible, under these circumstances, to make accurate measurements about the relation between vapour-pressure and composition. We had, therefore, to content ourselves with the results obtained.

2. *Acetone and Chloroform.*

According to v. Zawidski † mixtures of these two substances have a minimum vapour-pressure at ordinary and low pressures. As our success with mixtures of hydrochloric acid and methyl ether ‡, which also have a minimum vapour-pressure, had been only partial, owing to chemical action at high temperatures, we resolved to undertake the investigation of these mixtures in the neighbourhood of the critical point.

We began by testing v. Zawidski's observations, and found them confirmed. In our first experiments at high temperatures, we inclosed the substances in the usual way in a high-pressure tube of a Ducretet apparatus above mercury §, but unfortunately it appeared that at high temperatures a chemical action takes place between the chloroform and the mercury. We then carefully dried the chloroform (Schering's chloral chloroform) with calcium chloride, but were unable to reduce the action to any extent. The nature of the action is such as to generate a gas which reduces the critical temperature and raises the pressure. It is so rapid, that in a short time the tube becomes opaque and useless. The acetone (obtained from Kahlbaum, made from the bisulphite compound) gave no difficulty.

The results obtained by this method are contained in the following table (VI.) (p. 122).

The table only contains the earlier observations of each series, which are naturally more trustworthy than the later ones, although even these show that the chloroform is gradually changing into a mixture. From the vapour-pressures at 251°·3 and the critical data, we find by interpolation the following vapour-pressures:—

Temperature.	Pressure.	
	Chloroform.	Mixture.
257°·6	50·1	51·4
259·6	51·5	53·3

Comparing these, it appears that the pressure of the mixture

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* Phil. Mag. xlvii. pp. 104, 461.

† *Zeitschr. physik. Chemie,* xxxv. p. 129.

‡ Phil. Mag. [6] i. p. 593.

§ Phil. Mag. [5] xlviii. p. 187.

TABLE VI.—Vapour-pressures of Chloroform, Acetone, and Mixture.

Temperature.	Pressure.
	Chloroform.
244·5	42·7
251·3	45·0
—	45·6 Later.
—	48·4 After prolonged heating.
262·9	53·8 Critical point.
262·55	54·6 „ „ later.
	Acetone.
195·0	25·44
204·9	29·97
214·8	35·11
224·75	40·79 At different volumes.
—	40·84
—	40·80
233·65	46·76 Critical point.
233·7	46·78 „ „
	Mixture.
251·3	46·3 At different volumes.
—	49·5
257·6	51·4
259·6	53·3 Plaitpoint.
259·4	54·6 „ „ later.

is higher than the pressure of the chloroform at the same temperature. Again, drawing a straight line between the critical points of acetone and chloroform in the pressure-temperature diagram, it appears that the critical pressure of the mixture, 53·26, is slightly higher than the pressure on this straight line at the same temperature, 53·03. With a tolerable degree of certainty we may therefore consider the following facts to have been established :—

(1) The minimum vapour-pressure which exists at low temperatures has disappeared at the critical point; and (2) There is no maximum critical temperature, and the critical curve connects the two critical points in the normal manner, with a slight convexity towards the high pressures.

In order to confirm the results obtained, as far as possible, by a better method we repeated the determination of the critical temperatures of chloroform and of two mixtures—one containing a very small and the other a somewhat larger quantity of acetone, in a closed tube without mercury. These tubes were closed at one end, provided with a small bulb at the top and drawn out. They were filled by exhaustion and boiling at the air-pump, and then sealed. In order to obtain the critical phenomena about the middle of the tube, we found that the tubes had to contain as nearly as possible two-fifths of their volume of liquid at the ordinary temperature*. The following values were obtained:—

Chloroform . . .	262°·65
1st mixture . . .	260·5
2nd mixture . . .	258·4

Our previous results were thus confirmed as regards the temperatures, and there is no reason to doubt the accuracy of the above conclusions.

In chloroform and acetone we have therefore a combination which has no maximum or minimum in the critical temperature or in the vapour-pressures in the critical region, but in which a minimum vapour-pressure appears at low temperatures. This cannot be accounted for by the probable but certainly only slight abnormality of acetone. On the contrary, this abnormality would tend to make the vapour-pressures of the mixtures appear higher. The low pressures of the mixtures might indicate a strong attraction of the two substances; but according to theory this attraction would have produced a maximum in the critical temperatures. As such a maximum does not appear, we are led to the conclusion that the low vapour-pressures at low temperatures are due to an abnormal increase in the mutual attraction of the two substances at lower temperatures, and therefore probably to mutual association of the two kinds of molecules. Of course this conclusion is only legitimate on the assumption that the equation used by van der Waals is a sufficiently correct test of normality or abnormality.

The non-existence of a maximum critical temperature thus suggests the probability of mutual association. With methyl ether and hydrochloric acid, where a maximum critical temperature exists, as pointed out in the paper on these mixtures †, we had no means of distinguishing between association and mutual attraction. But a great deal more evidence will be required before this distinction is capable of being clearly drawn.

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* In Ostwald's 'Physico-chemical Measurements' (1894, p. 114) the prescription is to fill the tubes to two-thirds of their volume. This quantity is much too large, at least with an air-free liquid. The correct amount is given by Nadejdine, *Exner's Repertorium*, xxiii. (1887) p. 617.

† Phil. Mag. [6] i. p. 597.

3. *Carbon Dioxide and Ethane at Low Temperatures.*

These mixtures, as was discovered before *, have a minimum critical temperature and a maximum vapour-pressure, but had only been examined at temperatures above 0° C.

In extending the investigation towards low temperatures, we wanted to trace the maximum vapour-pressure more fully than could be done in the small range between 0° C. and the critical region, and to ascertain whether the maximum was in any way connected with a splitting into two liquids at low temperatures. We have found that no such separation takes place up to the region where solidification sets in. This solidification of the carbon dioxide afforded an opportunity for the study of the influence of the second substance on the phenomenon.

The minimum critical temperature belongs to a mixture containing 45 per cent. of ethane; the maximum vapour-pressure, near the critical point, to a mixture containing 30 per cent. According to the theory, the maximum at low temperatures ought to belong to the 45 per cent. mixtures.

This point was tested in the following manner:—Two strong glass tubes closed at the bottom were connected with each other at the top by means of flexible high-pressure piping, and with the two supply vessels containing the purified carbon dioxide and ethane. A mixture was let into one of the tubes cooled for the purpose to −50° C., and then distilled into the second tube, and so on backwards and forwards. The last portion in every distillation was not caught in the glass tube, but was blown off and collected over mercury and analysed. From the theory of mixtures of maximum vapour-pressure, it follows that the mixture coming over must gradually approach the maximum mixture at the temperature of the liquid. The pressure will therefore gradually increase. This appeared to be actually the case. The initial pressure was 7·8 atmospheres, and after successive distillations the readings were 8·5, 8·8, 8·5, 8·6, the temperature being kept roughly constant. The analysis of two samples after the third and the last distillations gave as the compositions 42 and 44 per cent. ethane respectively. The mixture has approached and practically reached the theoretical value of 45 per cent. The predictions of the theory had thus been completely verified.

We then proceeded to measure vapour-pressures of two different mixtures by the accurate method described for pure carbon dioxide and ethane in a former paper †. The change of the vapour-pressure with volume is comparatively small for both mixtures, owing to the narrowness of the conden-

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* Phil. Mag. [5] xliv. p. 187.

† Ibid. [6] iii. p. 149.

sation loops*, so that we could with safety apply the method. The vapour-pressures contained in the table are thus intermediate values between the smallest and largest, but much nearer the latter, as the greater part of the mixture was liquid.

One of the mixtures selected is the maximum mixture at the critical point, mixture A (30 per cent.); the other one, B, we had intended to be the 45 per cent. mixture, but by mistake we prepared a 50 per cent. one. It will be seen from the tables (VII. & VIII.) that the pressures of mixture A are

Table VII.—Vapour-pressures of mixture of equal volumes of Carbon Dioxide and Ethane.

Temperature.	Pressure.	
+17·8	56·17	
14·8	52·71	
0	37·21	
− 9·48	29·42	
20·83	21·85	
32·22	15·75	
32·90	15·29	Larger Volume.
—	15·39	Small „
40·94	11·66	
47·48	9·60	
56·80	6·90	
58·61	6·44	
60·54	5·97	
62·69	5·488	
65·17	4·950	
68·11	4·332	Solid and Liquid.
69·39	4·066	„ „
78·38	2·721	„ „

Table VIII.—Vapour-pressures of mixture of three volumes of Ethane to seven volumes of Carbon Dioxide.

Temperature.	Pressure.	
+18·85	60·54	
0	38·93	
9·26	30·76	
20·80	22·41	
32·15	16·02	
32·75	15·37	
41·15	11·92	
47·60	9·56	
56·32	6·95	
60·54	5·97	
62·65	5·426	
62·79	5·25	Solid & Liquid (large volume).
64·63	5·058	„ „ (small volume).
68·07	4·337	„ „ „ „
78·17	2·657	„ „ „ „

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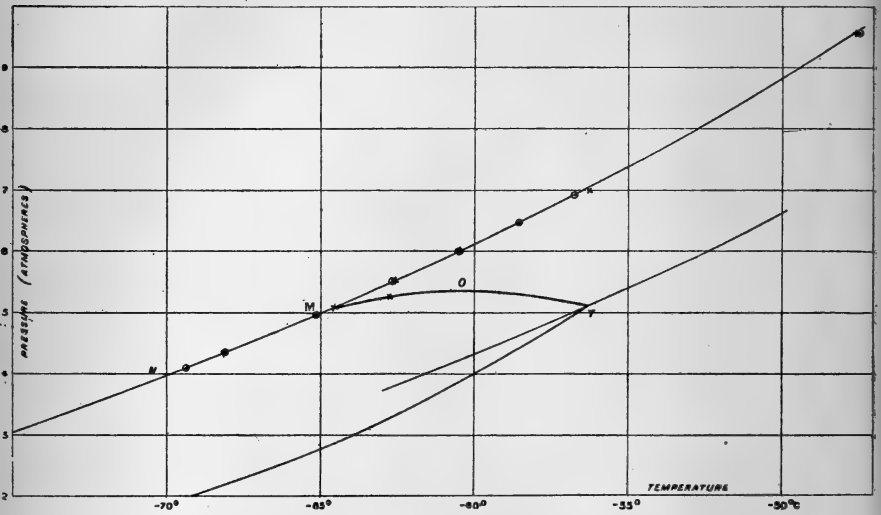
* Phil. Mag. [5] xliv. p. 188.

considerably higher than those of mixture B at ordinary temperatures; as the temperature falls in accordance with the previous experiments, the two curves approach each other (fig. 2), and ultimately the pressures of B are higher than those of A. This would naturally have shown even better if we had used the maximum mixture of 45 per cent. ethane instead of 50 per cent.

Fig. 2.



The plaitpoint of mixture A appeared to be at 18°·85 C. and 60·54 atmospheres, as against 18°·77 C. and 61·3 atmospheres obtained before for the same mixture*. The other mixture B had its plaitpoint at 17°·8 C. and 56·17 atmospheres, as compared with 17°·75 C. and 57·2 found before. The temperatures agree very well: the difference in the pressures is due to the uncertainty of the high-pressure gauges used in the earlier experiments, as explained in our paper on the vapour-pressures of carbon dioxide and ethane.

The two curves (fig. 2) practically coincide for such a long distance that the exact point of intersection cannot be ascertained; but this is of minor importance. The curve TOMN is the solidification or three-phase curve: starting from T the triple point of carbon dioxide it rises slightly, attains a maximum at O, and then gradually falls, passing through M, where the curve for the maximum mixture reaches and touches the three-phase curve. From the point of view of the separation of solid carbon dioxide, the mixtures fall into two groups. The mixtures of one group contain less ethane

* Phil. Mag. [5] xliv. p. 187.

than the maximum mixture (45 per cent.), and solidify at points between M and T; the mixtures of the second group contain more than 45 per cent. of ethane, and solidify at points beyond M. It will be seen from Table VII. that the 50 per cent. mixture belongs to the second group, as it has not solidified at $-65°\cdot17$ C.: its pressure is at this temperature a little below the three-phase pressure, although the scale of the diagram is too small to show this. The 30 per cent. mixture, on the other hand, belongs to the first group, and the maximum mixture must lie between the two as we we have seen it actually does. The difference between the pressures on the three-phase curve obtained with the two mixtures at the lowest temperature, the boiling-point of solid carbon dioxide, is due to the considerable slowness with which the proper equilibrium sets in; the stirrer which we had inside the tube having become quite immovable in the solid.

In figs. 3 and 4 (p. 128) we give on a larger scale diagrams of the relative positions of the three-phase curve and the condensation curves for mixtures belonging to the first and second groups respectively. These diagrams can only be properly understood by simultaneous consultation of figs. 5 and 6, which are intended to give an idea of the nature of the volume-composition diagram at two different temperatures, fig. 5 above and fig. 6 below the temperature corresponding to the point M in fig. 2.

Figs. 5 and 6 contain the projection of the vapour-liquid plait with the maximum M. A part of this plait is cut off (*i. e.* is made metastable) by the solidification figure. This figure consists of (1) the vapour-solid plait which reduces to a fan-shaped projection owing to the very small change of volume of the solid; (2) the three-phase triangle SLV; and (3) the solid-liquid plait, beyond SL, the properties of which are unknown. The three-phase triangle leaves the maximum free in fig. 5, and covers it in fig. 6, so that in this latter case the maximum belongs to the unrealizable (metastable) part. The metastable curves, as far as shown, are dotted.

It is now easily seen what condensation phenomena may be expected at the various temperatures with the various mixtures. As an instance, we point out that the mixture x in fig. 5 will, on compression, first begin to solidify at a, then liquid will appear at b: there are now three phases, and the pressure becomes constant. On further diminution of volume the solid will diminish and disappear at c, and ultimately the vapour will all go at d, and the mixture will be completely liquid. The corresponding points a, b, c, and d are also shown in fig. 3. We were able to confirm this somewhat complex series of changes with the 30 per cent. mixture at a temperature of about −63° C. We may leave it to the reader to deduce the phenomena in other cases from the figures, and to ascertain that the p–t figures (3 and 4) are in accordance with the v–x figures (5 and 6).

Fig. 3.

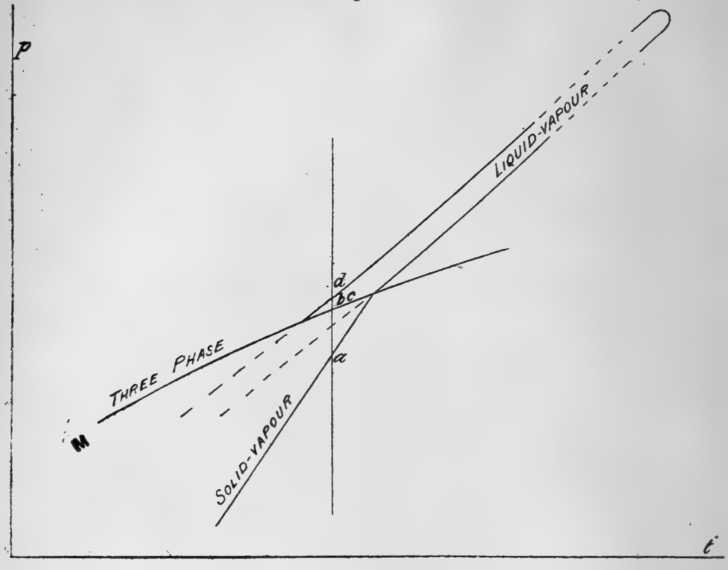
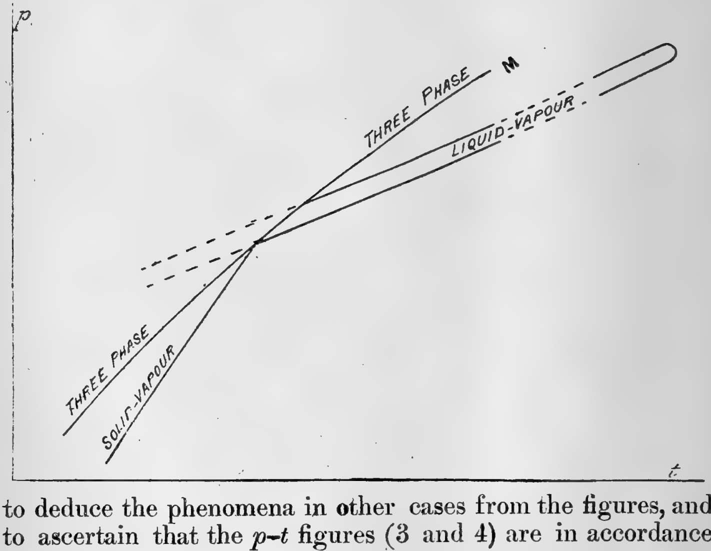


Fig. 4.



Further consideration of the pressure-temperature diagram leads to some important results. On the three-phase curve the gaseous mixture is in equilibrium both with the liquid mixture and with the solid phase; *i.e.* with pure solid carbon dioxide. It follows that the partial pressure of carbon dioxide in the vapour must be approximately the vapour-pressure of the solid at each temperature. As this quantity is known, the composition of the vapour-phase may be deduced from the pressures. We may test this conclusion at the point M, where the maximum curve reaches the three-phase curve, considering that for the maximum mixture the composition of the vapour is the same as for the liquid, and thus the same as the composition of the mixture as a whole. The pressure at M is 4·94 atmospheres; the pressure of solid carbon dioxide at the same temperature ($-65^\circ{\cdot}15$) being 2·72 atmospheres: the maximum mixture thus contains $2{\cdot}72/4{\cdot}94 = {\cdot}55$ parts of carbon dioxide, which is in exact accordance with our former results.

We are thus enabled to determine by the same method the composition of the gas-phase all along the three-phase curve. In this manner we find at O, the top of the curve, $3{\cdot}85/5{\cdot}33 = {\cdot}72$ parts of carbon dioxide and ·28 parts of ethane. In our experiments we were not able to observe the temperature and pressure at which the gas was in equilibrium with a trace of liquid and of solid, so that we do not know where the gas curve for the mixture ·30 cuts the three-phase curve. We cannot therefore compare the result about the point O with experiment.

An approximate value for the volume of the vapour may now be found from the composition and the pressure by applying the gas laws, and we are thus enabled to determine the heat of transformation of the mixture on the three-phase curve from the formula

$$\mathrm{H} = \mathrm{T}\frac{dp}{d\mathrm{T}}\mathrm{V}, \quad \ldots \ldots \quad (1)$$

where V represents the change of volume of the transformation corresponding to the heat H.

The value of H is of special interest at M, where, as we saw, vapour and liquid have the same composition; the transformation at this point thus consists of the evaporation of the liquid mixture as a whole, the solid taking no part in the transformation. H in this case is simply the latent heat of evaporation of the mixture, and V the difference between vapour and liquid volumes, precisely as with pure substances. It is clear that we might apply the same calculation to any other point of the maximum curve.

For $\frac{dp}{dT}$ at M we find ·209: the volume of one gramme of the gas calculated by the gas laws is 91 c. c.: subtracting from this the approximate volume of the liquid, and allowing for a small deviation from the gas law we find for H per gramme of the mixture 89 calories; the latent heat of carbon dioxide and of ethane at the same temperature being 95 and 114 respectively.

If we subtract from the latent heat the external work, we obtain the internal latent heat which should give us a more accurate measure of the relative values of the internal energies. The value of this quantity for the mixture is 79 calories, and for the components 86 and 100. Moreover, we ought to compare not a gramme of the mixture with a gramme of the components, but with the sum of the quantities actually contained in the mixture; in this way we find 91 calories compared with 79 for the mixture.

In whichever way we make the comparison, the latent heat of the mixture appears to be small, as might have been expected: for the maximum mixture is characterized by a comparatively small mutual attraction between the component substances, on which attraction the latent heat doubtlessly to a large extent depends. On the theory of van der Waals the internal latent heat is equal to $a\left(\frac{1}{v_l}-\frac{1}{v_v}\right)$ where a is the attraction-constant and v_l and v_v are the volumes of liquid and vapour *. As v_l, the volume to which the vapour contracts on condensation, depends on the volume-constant b in the equation of condition, we see that in general the latent heat depends on both constants, but we know from previous results † that b for mixtures of carbon dioxide and ethane has the normal value, and that the maximum vapour-pressure is due to a small a_{12} the mutual attraction constant.

Without actually calculating the value of the heat of transformation at other points on the three-phase curve, we can see how the value of H/V gradually diminishes at temperatures beyond M, becomes zero at O where $dp/dt=0$, and is negative between O and T where $dp/dt<0$.

The meaning of these changes is the following:—If we take V positive, *i. e.* if we increase the volume in which the mixture in its three phases is contained, the transformation (fig. 5) consists in an evaporation of the liquid mixture, L. This mixture contains more carbon dioxide than the vapour

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* Bakker, *Dissertation*, Schiedam 1888.

† Kuenen, Phil. Mag. [5] xliv. p. 195.

V, and during the transformation part of its carbon dioxide will thus be condensed into solid. The evaporation requires heat, but the formation of solid yields heat. As the difference in composition between liquid and vapour increases, the heat of solidification also increases, and at O the two have become equal. Beyond O up to T the heat developed is larger than the heat absorbed, and H becomes negative.

Fig. 5.

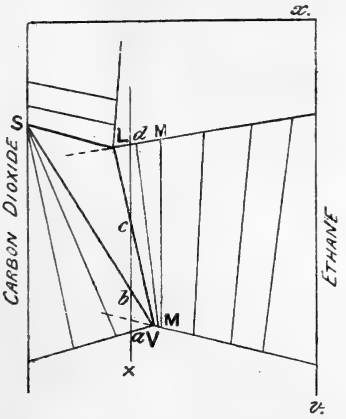
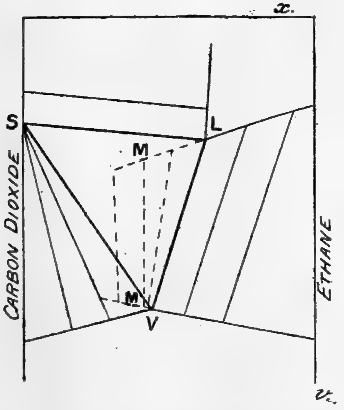


Fig. 6.



The following gives an answer to the question, on what conditions the sign of the heat of transformation at and near the triple point depends. If x_1 and x_2 are the amounts of ethane contained in a gramme of the liquid and the vapour respectively, the evaporation of one gramme of the liquid gives x_1 grammes of gaseous ethane: this quantity requires $\frac{x_1}{x_2}(1-x_2)$ grammes of carbon dioxide, so that

$$1-x_1-\frac{x_1}{x_2}(1-x_2)=\frac{x_2-x_1}{x_2}$$

grammes will be solidified. We thus find for the heat absorbed, and the corresponding increase of volume near T,

$$\mathrm{H}=\mathrm{L}_{lv}-\frac{x_2-x_1}{x_2}\mathrm{L}_{sv}=\frac{x_1}{x_2}\mathrm{L}_{sv}-\mathrm{L}_{sv}+\mathrm{L}_{lv}, \quad . \quad . \quad . \qquad (2)$$

$$\mathrm{V}=v_v-v_l-\frac{x_2-x_1}{x_2}(v_v-v_s)=\frac{x_1}{x_2}(v_v-v_s)-v_l+v_s. \qquad (3)$$

At T itself we must take for L_{sv} the heat of sublimation, and for L_{lv} the heat of evaporation of carbon dioxide, and the sign of H thus depends upon whether $\frac{x_1}{x_2}\gtrless\frac{\mathrm{L}_{sl}}{\mathrm{L}_{sv}}$. The value of this fraction for carbon dioxide is 43·8/129·9 = ·34. The amount of ethane in the vapour is thus found to be more than three times the amount in the liquid. The value of $\frac{dp}{d\mathrm{T}}$ at T is about −·10 atmosphere per degree. By means of the expression for H (1) combined with (2) and (3) we can now calculate both x_1/x_2 and H. The result is $x_1/x_2=\cdot 26$, and H = −9·9 calories.

If we apply the above formula (2) for H to the condition at O where H = 0, we can obtain an approximate value for the ratio x_1/x_2 at that point. Taking for L_{sv} 129 calories, and L_{lv} 88 calories, we find $x_1/x_2=\cdot 32$. According to this calculation, which however is only very approximate, the ratio of the compositions of the liquid and vapour, which according to Henry's law would be a constant within certain limits, has only come up from ·26 at T to ·32 at O. At M, as we saw before, its value reaches unity.

The direction of the three-phase curve at T agrees with that found by Stortenbeker* for mixtures of iodine and chlorine. Bakhuis Roozeboom and van der Waals† were the first to discuss the properties of such curves from a general thermodynamical point of view. We hope that the above will be found to contain a not unimportant addition to our knowledge of the subject.

University College,
Dundee.

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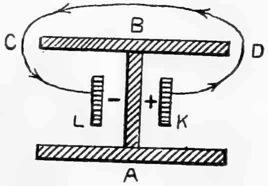
* Stortenbeker, *Zeit. phys. Chem.* iii. p. 19.

† Roozeboom, *Zeit. phys. Chem.* ii. p. 462.

XI. *On a New Reaction between Electrostatic Tubes and Insulators, and on the Electrostatic Field round an Electric Current, and the Theory of* Professor Poynting. *By* M. W. de Nicolaiève*.

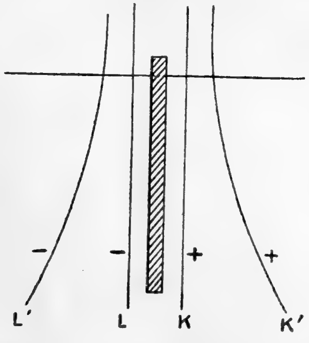
On a new reaction between electrostatic tubes and insulators.—This special reaction is observed in the electrostatic field which the author has shown to exist in electrolysis during the passage of the current. The tubes of force of this field coincide with the lines of current, and so insulating matter which is dielectric for tubes of the ordinary field behaves in an electrolyte like a perfect dia-electric deprived of electric permeability.

Fig, 1.



First Experiment.—Place in distilled water a system of two vertical plates perpendicular to a third, AB, fig. 1, all insulating, the horizontal section having an **H**-form. In the compartments formed by this plate immerse two strips of tin 15 to 20 cms. long with horizontal sections represented by K and L. When the strips are connected up to a source of current they diverge under the influence of tubes of the kind represented by K D B C L, as represented in elevation in fig. 2. If they are connected up to the terminals of a 300-volt transformer their extremities are displaced as much as 20 mms. outwards. The set of tubes like K D B C L can only exist through the action of the diaphragm

Fig. 2.



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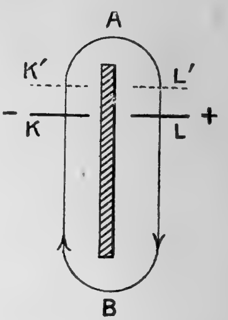
* From the *Comptes Rendus*, 30th December, 1901, and 6th January, 1902, with some additions by the Author. Communicated by Prof. J. H. Poynting.

upon them, and these tubes will have a reaction tending to compress the diaphragm.

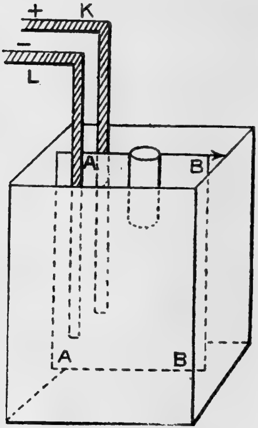
Second Experiment—Two strips K and L (fig. 3) are suspended in water and separated from each other by a glass partition, A B. The electrostatic tubes of the kind L A K displace the strips into the positions K′ and L′, so that the two bodies under their mutual actions are displaced in the same direction, which is contrary to the fundamental law of Action and Reaction. The only plausible explanation is that the edge A reacts upon the tubes L A K which act like stretched elastic threads pressing against the edge and pulling the strips.

Fig. 3.



Third Experiment.—Metallic wires or strips K and L (fig. 4) are immersed in water and are fixed. The mica partition, A B, floated by a cork, is movable. When in the position A B it moves from A towards B, in the opposite direction to the movement of the strips in the second experiment. The moving force is the difference of the pulls of the tubes L A K and L B K (fig. 3). When the edge A has passed the line of the electrodes K L the tubes issuing from the other faces of the electrodes act still in the same direction. When the mica is parallel to the plane through K L it retreats from them, a movement which is produced by the pressures

Fig 4.



of the tubes. Such pressures should be experienced by the walls of vessels containing electrolytes. To confirm the experiment and to be assured that the movements are not due to currents of liquid, two electrolytes were placed in series, both consisting of distilled water. After the mica had moved in one, a small quantity of chloride of sodium was dissolved in it. The current became stronger, but the electrostatic field became weaker and the mica showed hardly any trace of movement. Tinfoil floating in the water and replacing the mica behaved in the opposite way. The author intends to make the third experiment in rarefied gases, where by ionization the electrostatic tubes may also coincide with the tubes of current, but where the influence of the statical lines upon the walls will also come into account.

Fourth Experiment.—A mica pendulum (fig. 5) movable round a light axis of glass is placed between the terminals of a Holtz machine with the axis parallel to the line joining the terminals. If this line passes through the plate and the spark is obliged to turn from the most direct route, the pendulum retreats from the terminals. If the air is ionized by the discharges the effect may be attributed to the reactions of the electrostatic tubes on the edge of the mica, but if not, we cannot so explain the motion. The two faces of the mica may perhaps be electrified by charges of the same sign respectively as those in the points A and B, and the displacement to the right may be due to repulsion of like charges. It would be necessary to put a flame under the points and

Fig 5.

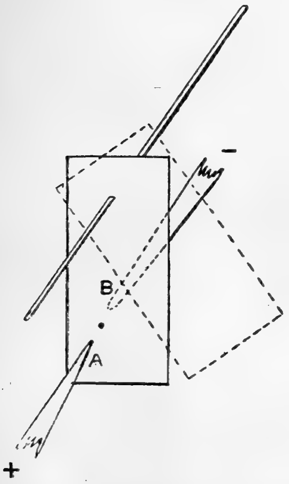
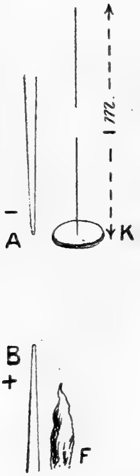


Fig. 6.

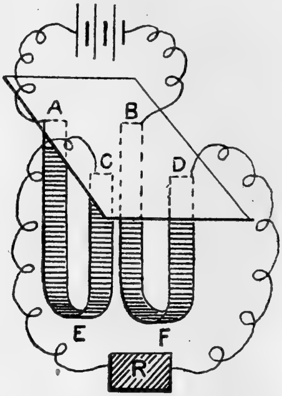


the mica to take away the charges from the latter and to facilitate the ionization of the air, but the illness of the author has interrupted this experiment. He has made the following experiment. A disk of mica K (fig. 6) is suspended excentrically to one side of the line of two-pointed terminals connected to a Holtz machine. When the flame F is lighted the disk K is displaced to the right by the current of hot air. But when the electric machine is in action, the disk is displaced at least twice as much.

On the Electrostatic Field round an Electric Current.

Apparatus.—In a large glass tube placed vertically are suspended two loops, A E C and B F D (fig. 7), parallel to each other, 4 to 5 mm. apart, and consisting of two strips of tinfoil, 3 mm. wide, hanging down to a depth of 50 cm. The greater this depth the more marked is the effect. The free ends, A B C D, are fixed in a card placed on the top of the tube.

Fig. 7.



The points A and B of the loops are connected up to the terminals of a battery of 100 volts. The points C and D are either insulated or are connected through a rheostat of glow-lamps. In the first case the loops are charged to the potentials of the battery terminals; in the second case a constant current flows through the two loops in opposite directions so that the electromagnetic forces tend to make them repel each other.

First Experiment.—The battery is unconnected, and the loops are at rest. Then the battery is joined up and the loops move towards each other. The attraction is produced by the system of electrostatic tubes from the one loop to the other.

Second Experiment.—The battery circuit is completed by a rheostat of 900 ohms. The movement towards each other persists and differs little from that on open circuit. The repulsive electromagnetic action exists, but does not manifest itself owing to the feebleness of the current (0·11 amp.). There is only one probable explanation. The electrostatic tubes join the two loops in the same way as in the statical case, and the mechanical effect remains nearly the same, because on the one hand through the small fall of potential the tubes have nearly the same strength, and on the other the electromagnetic repulsion is very small.

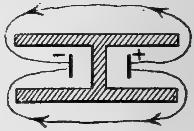
In the statical condition the difference of potential between the two ends of each tube is the same and the system of tubes is in equilibrium. In the dynamical condition the differences of potential diminish from 100 volts to zero, and the equilibrium of the tubes is disturbed. The transversal pressures diminish gradually, and the tubes are displaced perpendicularly to their axes, sliding along the conductors and sweeping through the dielectric medium. The fall of potential along the circuit shows that each tube, after an infinitely small displacement, will have a less difference of potential between its ends, an effect which may be set down to the destructive discharge of the end-cellules in the body of the conductors. We see that the experiment leads to results exactly agreeing with the theory of Professor Poynting, and that it confirms that theory. When the inserted resistance is diminished to 200 ohms the attraction changes to electromagnetic repulsion. As the electrostatic action is inversely proportional to the squares of the distances, and the electromagnetic action is inversely proportional to the distances, we can make either prevail by varying the distance.

Third Experiment.—In naphtha the attraction increases.

Fourth Experiment.—Cutting out the rheostat and immersing the loops in distilled water the attraction becomes very powerful and is manifested at a distance of 4 or 5 cm. To get rid of the small liquid currents, and to be sure of the electric character of the attraction, the author put on an alternating current from a transformer and observed the attraction while he dissolved larger and larger quantities of some salt: the current and the electrolysis went on gradually increasing, but the difference of potential between the loops decreased, and at the same time the attraction decreased down to zero. In this experiment the electrostatic tubes are propagated in the water transversely to the conducting loop; they are destroyed in the liquid itself by means of an intermolecular discharge (by the aid of ions), and the lines of current are directed along the electrostatic tubes. As the tensions of these tubes are, before destruction, several times greater than in air, a more powerful attraction is observed than in air.

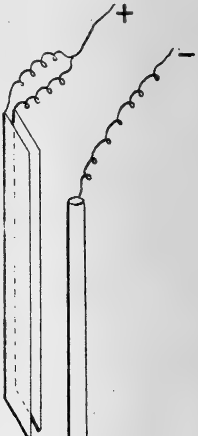
Fifth Experiment.—Two vertical strips of tinfoil, parallel to each other 4 or 5 mm. apart, are immersed in water, a plate of glass or of mica a little wider than the strips is interposed, and while the current is on, a repulsion of the strips is observed. The electrostatic tubes coincide with the lines of electrolytic current, and as the plate deviates the tubes uniting the interior and opposite faces, the resultant of the attractions becomes smaller than that of the repulsions due to the tubes applied to the exterior faces. To direct the Faraday tubes so as to give preponderance to those which pull the strips apart, it is necessary to arrange as in fig. 8, that is, to fix to the diaphragm two perpendicular plates which do not allow the tubes (and lines of current) to scatter laterally; the divergence of the leaves is thus increased several fold.

Fig. 8.



Sixth Experiment.—Two vertical strips of tinfoil are immersed in water (fig. 9). They are parallel, and as near each other as is possible consistent with not being drawn together by capillarity. The pair of strips constitutes one electrode, while the other is a vertical metallic wire, placed in the plane of the first electrode, and 3 cm. distant from it. On the passage of the current, the strips move a little towards the wire, and at the same time diverge from each other just as if they were in air before an electrified conductor.

Fig. 9.



The 4th, 5th, and 6th experiments show the existence of the electrostatic field inside an electrolyte.

Seventh Experiment.—If the two linear conductors in Herz's experiment are replaced by two flexible loops 15 or 20 cm. apart, they attract each other powerfully. Here the tubes are in motion between the linear conductors along which they slide by their extremities, and this is the cause of the equality of velocity of propagation in the medium and in conductors.

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XII. *Molecular Dynamics of a Crystal.* *By* Lord KELVIN [*].

§ 1. THE object of this communication is to partially realise the hope expressed at the end of my paper of July 1 and July 15, 1889, on the "Molecular Constitution of Matter [†]":—"The mathematical investigation must be deferred for a future communication, when I hope to give it *with some further developments.*" The italics are of present date.

Following the ideas and principles suggested in §§ 14–20 of that paper (referred to henceforth for brevity as M. C. M.), let us first find the work required to separate all the atoms of a homogeneous assemblage of a great number n of molecules to infinite distances from one another. Each molecule may be a single atom, or it may be a group of i atoms (similar to one another or dissimilar, as the case may be) which makes the whole assemblage a group of i assemblages, each of n single atoms.

§ 2. Remove now one molecule from its place in the assemblage to an infinite distance, keeping unchanged the configuration of its constituent atoms, and keeping unmoved every atom remaining in the assemblage. Let W be the work required to do so. This is the same for all the molecules within the assemblage, except the negligible number of those (§ 30 below) which are within influential distance of the surface. Hence $\frac{1}{2}n\mathrm{W}$ is the total work required to separate all the n molecules of the assemblage to infinite distances from one another. Add to this n times the work required to separate the i atoms of one of the molecules to infinite distances from one another, and we have the whole work required to separate all the in atoms of the given assemblage.

Another procedure, sometimes more convenient, is as follows:—Remove any one atom from the assemblage, keeping all the others unmoved. Let w be the work required to do so, and let Σw denote the sum of the amounts of work required to do this for every atom separately of the whole assemblage. The total amount of work required to separate all the atoms to infinite distances from one another is $\frac{1}{2}\Sigma w$. This (not subject to any limitation such as that stated for the former procedure) is rigorously true for any assemblage whatever of any number of atoms, small or large. It is, in fact, the well-known theorem of potential energy in the

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[*] From the Proceedings of the Royal Society of Edinburgh for 1901–2, communicated by the Author.

[†] Proc. Roy. Soc. Edin., and vol. iii. of Mathematical and Physical Papers, art. xcvii.

dynamics of a system of mutually attracting or repelling particles; and from it we easily demonstrate the item $\frac{1}{2}n\mathrm{W}$ in the former procedure.

§ 3. In the present communication we shall consider only atoms of identical quality, and only two kinds of assemblage.

I. A homogeneous assemblage of N single atoms, in which the twelve nearest neighbours of each atom are equidistant from it. This, for brevity, I call an equilateral assemblage. It is fully described in M. C. M., §§ 46, 50 . . . 57.

II. Two simple homogeneous assemblages of $\frac{1}{2}\mathrm{N}$ single atoms, placed together so that one atom of each assemblage is at the centre of a quartet of nearest neighbours of the others.

For assemblage II., as well as for assemblage I., w is the same for all the atoms, except the negligible number of those within influential distance of the boundary. Neglecting these, we therefore have $\Sigma w = \mathrm{N}w$, and therefore the whole work required to separate all the atoms to infinite distances is—

$$\tfrac{1}{2}\mathrm{N}w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

§ 4. Let $\phi(\mathrm{D})$ be the work required to increase the distance between two atoms from D to ∞; and let $f(\mathrm{D})$ be the attraction between them at distance D. We have

$$f(\mathrm{D}) = -\frac{d}{d\mathrm{D}}\phi(\mathrm{D}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

For either assemblage I. or assemblage II. we have

$$w = \phi(\mathrm{D}) + \phi(\mathrm{D}') + \phi(\mathrm{D}'') + \text{etc.} \quad . \quad . \quad . \quad (3);$$

where D, D′, D″, etc., denote the distances from any one atom of all neighbours, including the farthest in the assemblage, which exercise any force upon it.

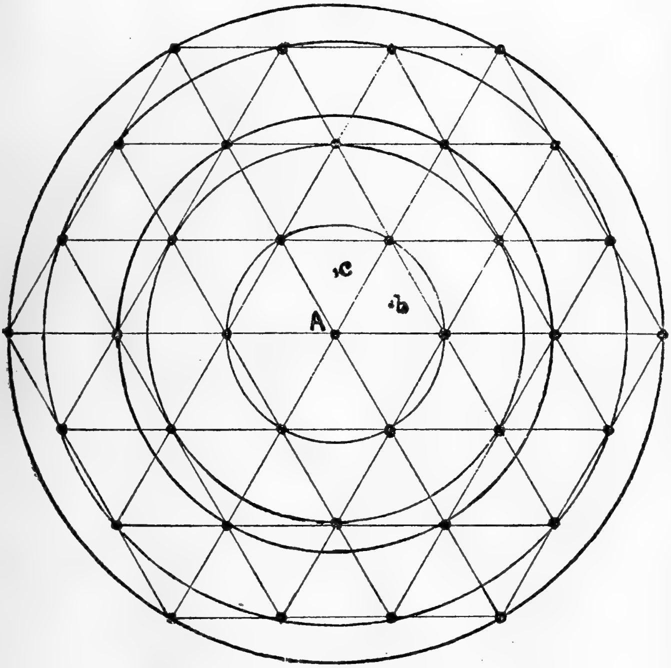
§ 5. To find as many as we desire of these distances for assemblage I. look at figs. 1 and 2. Fig. 1 shows an atom A, and neighbours in one plane in circles of nearest, next-nearest, next-next-nearest, etc. Fig. 2 shows an equilateral triangle of three nearest neighbours, and concentric circles of neighbours in the same plane round it. The circles corresponding to r_4 and r_8 of § 7 below, are not drawn in fig. 2. In all that follows the side of each of the equilateral triangles is denoted by λ.

§ 6. All the neighbours in assemblage I. are found by aid of the diagrams as follows:—

(*a*) The atoms of the net shown in fig. 1. The plane of this net we shall call our "middle plane." Let lines be drawn perpendicular to it through the atom A, and the points marked *b*, *c*, to guide the placing of nets of atoms in parallel planes on its two sides.

(*b*) Two nets of atoms at equal distances $\lambda\sqrt{\frac{2}{3}}$ on the two sides of the "middle plane." These nets are so placed that an atom of one of them, say the near one as we look at the diagram, is in the guide line *b*; and an atom of the far one is in the guide line *c*.

Fig. 1.



(*c*) Two parallel nets of atoms at equal distances, $2\lambda\sqrt{\frac{2}{3}}$, on the two sides of the "middle plane," so placed that an atom of the near one is in the guide line *c*, and an atom of the far one is in the guide line *b*.

(*d*) A third pair of parallel planes at equal distances, $3\lambda\sqrt{\frac{2}{3}}$, from the "middle plane," and each of them having an atom in guide line A.

(*e*) Successive triplets of parallel nets with their atoms cyclically arranged Abc Abc . . at greater and greater distances from A on the near side of the paper, and Acb Acb . . at greater and greater distances on the far side.

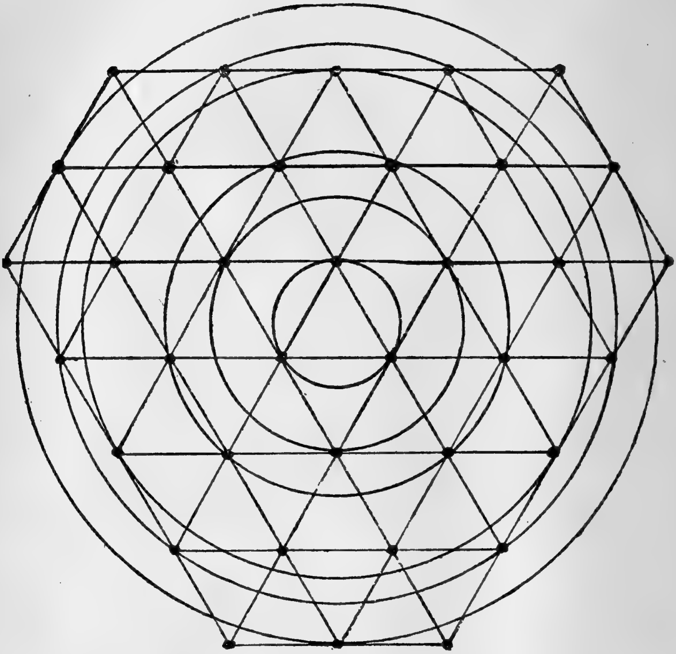
§ 7. Let q_1, q_2, q_3 . . . be the radii of the circles shown in fig. 1, and r_1, r_2, r_3 . . . be the radii of the circles shown in fig. 2; and for brevity denote $\lambda\sqrt{\frac{2}{3}}$ by κ. The distances from A of all the neighbours around it are:—

In our "middle plane": 6 each equal to q_1; 6, q_2; 6, q_3; 12, q_4; 6, q_5; . . . .

In the two parallel nets at distances κ from middle: 6 each equal to $\sqrt{(\kappa^2+r_1^2)}$; 6, $\sqrt{(\kappa^2+r_2^2)}$; 12, $\sqrt{(\kappa^2+r_3^2)}$; 12, $\sqrt{(\kappa^2+r_4^2)}$; 6, $\sqrt{(\kappa^2+r_5^2)}$; 12, $\sqrt{(\kappa^2+r_6^2)}$; 6, $\sqrt{(\kappa^2+r_7^2)}$.

In the two parallel nets at distances 2κ from middle: the same as (B) altered by taking 2κ everywhere in place of κ.

Fig. 2.



In the two parallel nets at distances 3κ from centre: the same as (A) altered by taking $\sqrt{(9\kappa^2+q_1^2)}$, $\sqrt{(9\kappa^2+q_2^2)}$, etc., in place of q_1, q_2, etc.

In nets at distances on each side greater than 3κ: distances of atoms from A, found as above, according to the cycle of atomic configuration described in (*e*) of § 6.

§ 8. By geometry we find

$$\left.\begin{array}{l} q_1=\lambda;\ q_2=\sqrt{3}\lambda=1{\cdot}732\lambda;\ q_3=2\lambda;\ q_4=\sqrt{7}\lambda=2{\cdot}646\lambda;\ q_5=3\lambda: \\ r_1=\sqrt{\tfrac{1}{3}}\lambda={\cdot}577\lambda;\ r_2=2\sqrt{\tfrac{1}{3}}\lambda=1{\cdot}154\lambda;\ r_3=\sqrt{\tfrac{7}{3}}\lambda=1{\cdot}527\lambda;\ r_4=\sqrt{\tfrac{13}{3}}\lambda=2{\cdot}082\lambda; \\ r_5=4\sqrt{\tfrac{1}{3}}\lambda=2{\cdot}308\lambda;\ r_6=\sqrt{\tfrac{19}{3}}\lambda=2{\cdot}517\lambda;\ r_7=5\sqrt{\tfrac{1}{3}}\lambda=2{\cdot}887\lambda. \end{array}\right\}\ (4).$$

§ 9. Denoting now, for assemblage I., distances from atom A of its nearest neighbours, its next-nearests, its next-next-nearests, etc., by D_1, D_2, D_3, etc., and their numbers by j_1, j_2, j_3, etc., we find by §§ 7, 8 for distances up to 2λ, for use in § 12 below,

$$D_1=\lambda,\quad D_2=1{\cdot}414\lambda,\quad D_3=1{\cdot}732\lambda,\quad D_4=2\lambda,$$

$$j_1=12\,;\quad j_2=6\,;\qquad j_3=18\,;\qquad j_4=6.$$

§ 10. Look back now to § 5, and proceed similarly in respect to assemblage II., to find distances from any atom A to a limited number of its neighbours. Consider first only the neighbours forming with A a single equilateral assemblage: we have the same set of distances as we had in § 9. Consider next the neighbours which belong to the other equilateral assemblage. Of these, the four nearest (being the corners of a tetrahedron having A at its centre) are each at distance $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda$, and these are A's nearest neighbours of all the double assemblage II. Three of these four are situated in a net whose plane is at the distance $\frac{1}{4}\sqrt{\frac{2}{3}}\lambda$ on one side of our "middle plane" through A, and having one of its atoms on either of the guide lines *b* or *c*. The distances from A of all the atoms in this net are, according to fig. 2,

$$\sqrt{(\tfrac{1}{16}\kappa^2+r_1^2)},\ \sqrt{(\tfrac{1}{16}\kappa^2+r_2^2)},\ \text{etc.}\quad .\quad .\quad .\quad (5).$$

The remaining one of the four nearests is on a net at distance $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda$ from our "middle plane," having one of its atoms on the guide line through A. The distances from A of all the atoms in this net are, according to fig. 1,

$$\tfrac{3}{4}\sqrt{\tfrac{2}{3}}\lambda,\ \sqrt{(\tfrac{9}{16}\kappa^2+q_1^2)},\ \sqrt{\tfrac{9}{16}\kappa^2+q_2^2)},\ \text{etc.}\quad .\quad .\quad (6).$$

All the other atoms of the equilateral assemblage to which A does not belong lie in nets at successive distances κ, 2κ, 3κ, etc., beyond the two nets we have already considered on the two sides of our "middle plane"; the atoms of each net placed of course according to the cyclical law described in (*e*) of § 6.

§ 11. Working out for the double assemblage II. for A's nearest neighbours according to § 10, we find four nearest neighbours at equal distances $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda={\cdot}613\lambda$; twelve next-nearests at equal distances λ; and twelve next-next-nearests at equal distances $\sqrt{\frac{11}{8}}\lambda=1{\cdot}173\lambda$. These suffice for § 12 below. It is easy and tedious, and not at present useful, to work out for D_4, D_5, D_6, etc.

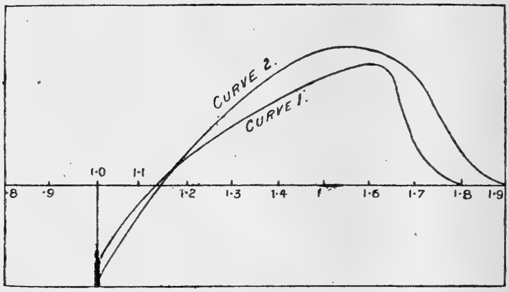
§ 12. Using now §§ 9, 11 in (3) of § 4 we find,—

$$\left.\begin{aligned}&\text{for assemblage I.,}\\&w=12\phi(\lambda)+6\phi(1{\cdot}414\lambda)+18\phi(1{\cdot}732\lambda)+6\phi(2\lambda)+\,.\\&\text{for assemblage II.}\\&w=4\phi({\cdot}613\lambda)+12\phi(\lambda)+12\phi(1{\cdot}173\lambda)+\;\;.\;\;.\;\;.\;\;.\end{aligned}\right\}(7).$$

These formulas prepare us for working out in detail the practical dynamics of each assemblage, guided by the following statements taken from §§ 18, 16 of M. C. M.

§ 13. Every infinite homogeneous assemblage of Boscovich atoms is in equilibrium. So, therefore, is every finite homogeneous assemblage, provided that extraneous forces be applied to all within influential distance of the frontier, equal to the forces which a homogeneous continuation of the assemblage through influential distance beyond the frontier would exert on them. The investigation of these extraneous forces for any given homogeneous assemblage of single atoms—or groups of atoms as explained above (§ 1)—constitutes the Boscovich equilibrium-theory of elastic solids.

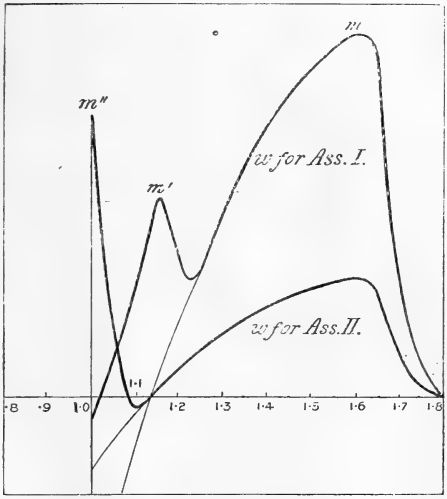
Fig. 3.



It is wonderful how much towards explaining the crystallography and elasticity of solids, and the thermo-elastic properties of solids, liquids, and gases, we find; without assuming, in the Boscovichian law of force, more than one transition from attraction to repulsion. Suppose, for instance, that the mutual force between two atoms is zero for all distances exceeding a certain distance I, which we shall call the diameter of the sphere of influence; is repulsive when the distance between them is $<\zeta$; zero when the distance is $=\zeta$; and attractive when the distance is $>\zeta$ and $<$ I.

§ 14. Two different examples are represented on the two curves of fig. 3, drawn arbitrarily to obtain markedly diverse conditions of equilibrium for the monatomic equilateral assemblage (I.), and also for the diatomic assemblage (II.). The abscissa (x) of each diagram, reckoned from a zero outside the diagram on the left, represents the distance between centres of two atoms; the ordinates (y) represent the work required to separate them from this distance to ∞. Hence $-\frac{dy}{dx}$ represents the mutual attraction at distance x. This we see by each curve is $-\infty$ (infinite repulsion) at distance 1·0, which means that the atom is an ideal hard ball of diameter 1·0. For distances increasing from 1·0 the force is repulsive as far as 1·61 in curve 1, and 1·55 in curve 2. At these distances the mutual force is zero; and at greater distances up to 1·8 in curve 1, and 1·9 in curve 2, the force is attractive. The force is zero for all greater distances than the last mentioned in the two examples respectively. Thus, according to my old notation, we have $\zeta=1·61$, $I=1·8$ in curve 1; and $\zeta=1·55$, $I=1·9$ in curve 2. The distances for maximum attractive force (as shown by the points of inflection of the two curves) are 1·68 for curve 1, and 1·76 for curve 2.

Fig. 4.

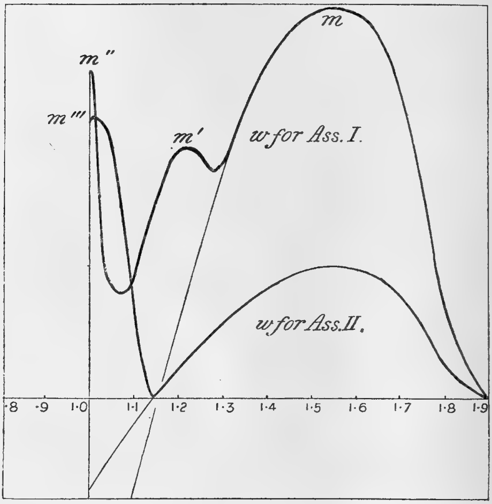


Law of Force according to Curve 1.

According to our notation of § 4 we have $y=\phi(\mathrm{D})$, if $x=\mathrm{D}$ in each curve.

§ 15. The two formulas (7), § 12, are represented in fig. 4 for curve 1. and in fig. 5 for curve 2; with $x=\lambda$ for Ass. I. and $x=·613\lambda$ for Ass. II. In each diagram the abscissa, x, is distance between nearest atoms of the assemblage. The heavy portions of the curves represent the values of w calculated from (7). The light portions of the curves, and their continuations in heavy curves, represent $4\phi(x)$ and $12\phi(x)$ respectively in each diagram. The point where the light curve passes into the heavy curve in each case corresponds to the least distance between neighbours at which next-nearests are beyond range of mutual force. All the diagrams here reproduced were drawn first on a large scale on squared paper for use in the calculations from (7); which included accurate determinations of the maximum and minimum values of w and the corresponding distances between nearest neighbours in each assemblage. The corresponding densities, given in the last column of the following table of results,

Fig. 5.



Law of Force according to Curve 2.

are calculated by the formula $\sqrt{2}/\lambda^3$ for assemblage I., and $2\sqrt{2}/\lambda^3$ for assemblage II.; "density" being in each case number of atoms per cube of the unit of abscissas of the diagram. This unit is (§ 14) equal to the diameter of the atom. For simplicity we assume the atom to be an infinitely hard ball exerting (§ 13) on neighbouring atoms, not in contact with it, repulsion at distance between centres less than ζ and attraction at any distance between ζ and I.

§ 16. To interpret these results, suppose all the atoms of the assemblage to be subjected to guidance constraining them either to the equilateral homogeneousness of assemblage I., or to the diatomic homogeneousness of assemblage II., with each atom of one constituent assemblage at the centre of an equilateral quartet of the other constituent assemblage. It is easy to construct ideally mechanism by which this may be done; and we need not occupy our minds with it at present. It is enough to know that it can be done. If the system, subject to the prescribed constraining guidance, be left to itself at any given density, the condition for equilibrium without extraneous force is that w is either a maximum or a minimum; the equilibrium is stable when w is a maximum, unstable when a minimum. It is interesting to see the two stable equilibriums of assemblage I. according to law of force 1, and the three according to law of force 2; and the two stable equilibriums for assemblage II. with each of these laws of force.

Assemblage I.			Assemblage II.		
Distances between centres of nearest atoms for maximum and minimum values of w.	Maximum and minimum values of w.	Densities.	Distances between centres of nearest atoms for maximum and minimum values of w.	Maximum and minimum values of w.	Densities.
Law of Force according to Curve 1.					
1·16	8·28 (max.)	·904	1·00	11·52 (max.)	·652
1·23	5·22 (min.)	·759	1·10	·76 (min.)	·490
1·61	14·76 (max.)	·338	1·61	4·92 (max.)	·158
Law of Force according to Curve 2.					
1·00	11·58 (max.)	1·414	1·00	12·36 (max.)	·652
1·07	3·78 (min.)	1·146	1·15	0·16 (min.)	·433
1·22	10·44 (max.)	·774	1·53	5·20 (max.)	·184
1·28	9·36 (min.)	·671			
1·53	15·60 (max.)	·393			

§ 17. But we must not forget that it is only with the specified constraining guidance (§ 16) that we are sure of these equilibriums being stable. It is quite certain, however, that without guidance the monatomic assemblage would be stable for the small density corresponding to the point m of each of the diagrams, because for infinitesimal deviations each atom experiences forces only from its twelve nearest neighbours, and these forces are each of them zero for equilibrium. It may conceivably be that each of the maximums of w, whether for the monatomic or the diatomic assemblage, is stable without guidance. But it seems more probable that, for assemblage I. and law of force 2, the intermediate maximum m' (close to a minimum) is unstable. If it is so, the assemblage left to itself in this configuration would fall away, and would (in virtue of energy lost by waves through ether, that is to say, radiation of heat) settle in stable equilibrium corresponding to the maximum m (single assemblage), or either of the maximums m'' (single assemblage), or m''' (double assemblage). It is also possible that for law of force 1 the maximum m' for the single assemblage is unstable. If so, the system left to itself in this configuration would fall away and settle in either of the configurations m (single assemblage) or m'' (double assemblage). Or it is possible that with either of our arbitrarily assumed laws of force there may be stable configurations of equilibrium with the atoms in simple cubic order (§ 21 below): and in double cubic order; that is to say, with each atom in the centre of a cube of which the eight corners are its nearest neighbours.

§ 18. It is important to remark further, that certainly a law of force fulfilling the conditions of § 13 may be found, according to which even the simple cubic order is a stable configuration; though perhaps not the only stable configuration. The double cubic order, which has hitherto not got as much consideration as it deserves in the molecular theory of crystals, is certainly stable for some laws of force which would render the simple cubic order unstable. Meantime it is exceedingly probable that there are in nature crystals of elementary substances, such as metals, or frozen oxygen or nitrogen or argon, of the simple cubic, and double cubic, and simple equilateral, and double equilateral, classes. It is also probable that the crystalline molecules in crystals of compound chemical substance are in many cases simply the chemical molecules, and in many cases are composed of groups of the chemical molecules. The crystalline molecules, however constituted, are, in crystals of the cubic class, probably arranged either in simple cubic, or double cubic, or in simple equilateral, or double equilateral, order.

§ 19. It will be an interesting further development of the molecular theory to find some illustrative cases of chemical compound molecules (that is to say, groups of atoms presenting different laws of force, whether between two atoms of the same kind or between atoms of different kinds), which are, and others which are not, in stable equilibrium at some density or densities of *equilateral* assemblage. In this last class of cases the molecules make up crystals not of the cubic class. This certainly can be arranged for by compound molecules with law of force between any two atoms fulfilling the condition of § 13; and it can be done even for a monatomic homogeneous assemblage very easily, if we leave the simplicity of § 13 in our assumption as to law of force.

§ 20. The mathematical theory wants development in respect to the conditions for stability. If, with the constraining guidance of § 16, w is either a maximum or a minimum, there is equilibrium with or without the guidance. For w a maximum the equilibrium is stable *with the guidance*; but may be stable or unstable without the guidance. A criterion of stability which will answer this last question is much wanted; and it seems to me that though the number of atoms is quasi infinite the wanted criterion may be finite in every case in which the number of atoms exerting force on any one atom is finite. To find it generally for the equilibrium of any homogeneous assemblage of homogeneous groups, each of a finite number of atoms, is a worthy object for mathematical consideration. Its difficulty and complexity is illustrated in §§ 21, 22 for the particularly simple case of similar atoms arranged in simple cubic order; and in §§ 23–29 for a still simpler case.

§ 21. Consider a group of eight particles at the eight corners of a cube (edge λ) mutually acting on one another with forces all varying according to the same law of distance. Let the magnitudes of the forces be such that there is equilibrium; and in the first place let the law of variation of the forces be such that the equilibrium is stable. Build up now a quasi infinite number of such cubes with coincident corners to form one large cube or a crystal of any other shape. Join ideally, to make one atom, each set of eight particles in contact which we find in this structure. The whole system is in stable equilibrium. The four forces in each set of four coincident edges of the primitive cubes become one force equal to the force between atom and atom at distance λ. The two forces in either diagonal of the coincident square faces of two cubes in contact make one force equal to the force between atoms at distance $\lambda\sqrt{2}$. The single force in each body-diagonal of any one of the cubes is the force between atom and atom at distance $\lambda\sqrt{3}$. The three moduluses of elasticity (compressibility-modulus, modulus with reference to change of angles of the square faces, and modulus with reference to change of angles between their diagonals) are all easily found by consideration of the dynamics of a single primitive cube, or they may be found by the general method given in "On the Elasticity of a Crystal according to Boscovich"*. (In passing, remark that neither in this nor in other cases is it to be assumed without proof that stability is ensured by positive values of the elasticity moduluses.)

§ 22. Now while it is obvious that our cubic system is in stable equilibrium if the eight particles constituting a detached primitive cube are in stable equilibrium, it is not obvious without proof that this condition, though sufficient, is necessary for the stability of the combined assemblage. It might be that though each primitive cube by itself is unstable, the combined assemblage is stable in virtue of mutual support given by the joinings of eight particles into one at the corners of the cubes which we have put together.

§ 23. The simplest possible illustration of the stability question of § 20 is presented by the exceedingly interesting problem of the equilibrium of an infinite row of similar particles, free to move only in a straight line. The consideration of this linear problem we shall find also useful (§§ 28, 29 below) for investigation of the disturbance from homogeneousness in the neighbourhood of the bounding surface, experienced by a three-dimensional homogeneous assemblage in equilibrium. First let us find a, the distance, or one of the distances, from atom to atom at which the atoms must be placed for equilibrium; and after that try to find whether the equilibrium is stable or unstable.

§ 24. Calling $f(\mathrm{D})$ (as in § 4) the attraction between atom and atom at distance D, we have for the sum, P, of attractions between all the atoms on one side of any point in their line, and all the atoms on the other side, the following finite expression having essentially a finite number of terms, greater the smaller is a:

$$f(a)+2f(2a)+3f(3a)+\ldots\ldots=\mathrm{P} \quad . \quad . \quad . \quad (8).$$

Hence a, for equilibrium with no extraneous force, is given by the functional equation

$$f(a)+2f(2a)+3f(3a)+\ldots\ldots=0 \quad . \quad . \quad . \quad (9);$$

which, according to the law of force, may give one or two or any number of values for a: or may even give no value (all roots imaginary) if the force at greatest distance for which there is force at all, is repulsive. The solution or all the solutions of this equation are readily found by calculating

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* Proc. R.S.L., vol. 54, June 8, 1893.

from the Boscovich curve representative of $f(D)$ a table of values of P, and plotting them on a curve, by formula (8), for values of a from $a=I$ (the limit above which the force is zero for all distances) downwards to the value which makes $P=-\infty$, or to zero if there is no infinite repulsion. The accompanying diagram, fig. 6, copied from fig. 1 of Boscovich's great book *, with slight modifications (including positive instead of negative ordinates to indicate attraction) to suit

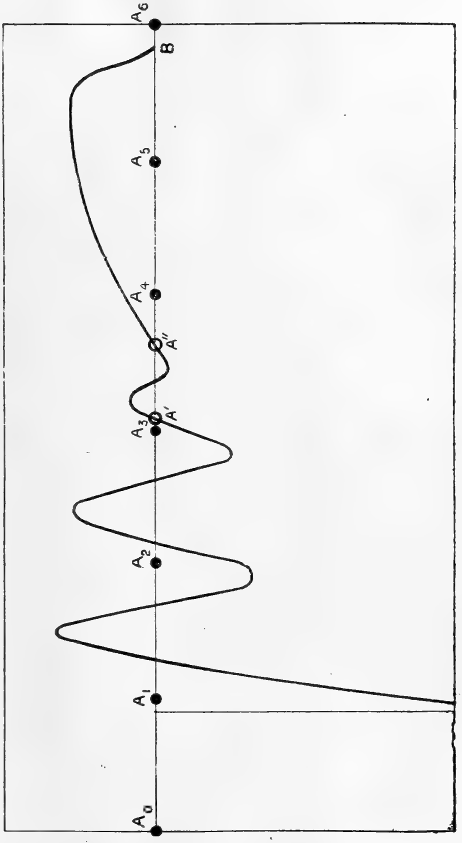

Fig. 6.

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* Theoria Philosophiæ Naturalis redacta ad unicam legem virium in natura existentium, auctore P. Rogerio Josepho Boscovich, Societatis Jesu, nunc ab ipso perpolita, et aucta, ac a plurimis præcedentium editionum mendis expurgata. Editio Veneta prima ipso auctore præsente, et corrigente. Venetiis, MDCCLXIII. Ex Typographia Remondiniana superiorum permissu, ac privilegio.

our present purpose, shows for this particular curve three of the solutions of equation (8). (There are obviously several other solutions.) In two of the solutions, respectively, A_0, A', and A_0, A'', are consecutive atoms at distances at which the force between them is zero. These are configurations of equilibrium, because A_0B, the extreme distance at which there is mutual action, is less than twice A_0A', and less than twice A_0A''. In the other of the solutions shown, A_0, A_1, A_2, A_3, A_4, A_5, A_6 are seven equidistant consecutive atoms of an infinite row in equilibrium in which A_5 is within range of the force of A_0, and A_6 is beyond it. The algebraic sum of the ordinates with their proper multipliers is zero, and so the diagram represents a solution of equation (9).

§ 25. In the general linear problem to find whether the equilibrium is stable or not for equal consecutive distances, a, let (as in § 4) $\phi(D)$ be the work required to increase the distance between two atoms from D to ∞. Suppose now the atoms to be displaced from equal distances, a, to consecutive unequal distances—

$$\ldots\ldots a+u_{i-2},\ a+u_{i-1},\ a+u_i,\ a+u_{i+1},\ a+u_{i+2},\ \ldots \quad (10).$$

The equilibrium will be stable or unstable according as the work required to produce this displacement is, or is not, positive for all infinitely small values of $\ldots\ldots u_{i-1}, u_i, u_{i+1}, \ldots\ldots$ Its amount is W_0-W; where W denotes the total amount of work required to separate all the atoms from the configuration (10) to infinite mutual distances.

According to § 2 above W is given by

$$W=\tfrac{1}{2}(\ \ldots + w_{i-1}+w_i+w_{i+1}+\ \ldots\ ) \ . \quad (11);$$

where

$$\begin{aligned} w_i &= \phi(a+u_i) + \phi(2a+u_{i-1}+u_i) + \phi(3a+u_{i-2}+u_{i-1}+u_i) + \ldots \\ &\quad + \phi(a+u_{i+1}) + \phi(2a+u_{i+1}+u_{i+2}) + \phi(3a+u_{i+1}+u_{i+2}+u_{i+3}) + \ldots \\ &\quad + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12). \end{aligned}$$

Expanding each term by Taylor's theorem as far as terms of the second order, and remarking that the sum of terms of the first order is zero for equilibrium * at equal distances, a, and

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* It is interesting and instructive to verify this analytically by selecting all the terms in W which contain u_i, and thus finding $\dfrac{dW}{du_i}$. This equated to zero, for zero values of $\ldots u_{i-1},\ u_i,\ u_{i+1}, \ldots$ gives equation (9) of the text.

putting $\phi''(D)=-f'(D)$, we find

$$W_0-W=\tfrac{1}{4}\Sigma\{f'(a)(u_i^2+u^2_{i+1})$$
$$+f'(2a)[(u_{i-1}+u_i)^2+(u_{i+1}+u_{i+2})^2]$$
$$+f'(3a)[(u_{i-2}+u_{i-1}+u_i)^2+(u_{i+1}+u_{i+2}+u_{i+3})^2]$$
$$+\quad \text{etc.}\quad \text{etc.}\quad \text{etc.}\quad \text{etc.}\}\quad (13);$$

where Σ denotes summation for all values of i, except those corresponding to the small numbers of atoms (§§ 28, 29 below) within influential distances of the two ends of the row.

§ 26. Hence the equilibrium is stable if $f'(a)$, $f'(2a)$, $f'(3a)$, etc., are all positive; but it can be stable with some of them negative. Thus, according to the Boscovich diagram, a condition ensuring stability is that the position of each atom be on an up-slope of the curve showing attractions at increasing distances. We see that each of the atoms in each of our three equilibriums for fig. 6 fulfils this condition.

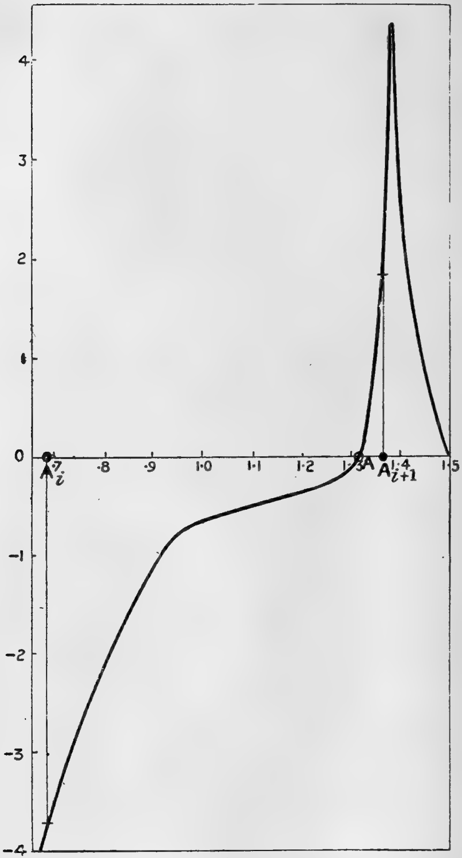
§ 27. Fig. 7 shows a simple Boscovich curve drawn arbitrarily to fulfil the condition of § 13 above, and with the further simplification for our present purpose, of limiting the sphere of influence so as not to extend beyond the next-nearest neighbours in a row of equidistant particles in equilibrium, with repulsions between nearests and attractions between next-nearests. The distance, a, between nearests is determined by

$$f(a)+2f(2a)=0 \quad . \; . \; . \; . \; . \quad (14),$$

being what (9) of § 24 becomes when there is no mutual force except between nearests and next-nearests. There is obviously one stable solution of this equation in which one atom is at the zero of the scale of abscissas (not shown in the diagram) and its nearest neighbour on the right is at A, the point of zero force with attraction for greater distances and repulsion for less distances. The only other configuration of stable equilibrium is found by solution of (14) according to the plan described in § 24, which gives $a=\cdot 680$. It is shown on fig. 7 by A_i, A_{i+1}, as consecutive atoms in the row.

§ 28. Consider now the equilibrium in the neighbourhood of either end of a rectilinear row of a very large number of atoms which, beyond influential distance from either end, are at equal consecutive distances a satisfying § 27 (14). We shall take for simplicity the case of equilibrium in which there is no extraneous force applied to any of the atoms, and no mutual force between any two atoms except the positive or negative attraction $f(D)$. But suppose first that ties or struts are placed between consecutive atoms near each end of the row so as to keep all their consecutive distances exactly equal to a. For brevity we shall call them ties, though in ordinary language any one of them would be called a strut if its force is push instead of pull on the atoms to which it is applied. Calling A_1, A_2, A_3, . . . the atoms at one end of the row, suppose the tie between A_1 and A_2 to be removed, and A_1 allowed to take its position of equilibrium. A single equation gives the altered distance A_1A_2, which we shall denote by $a+{}_1x_1$. Let an altered tie be placed between A_1 and A_2 to keep them at this altered distance during the operations which follow. Next remove the tie between A_2 and A_3, and find by a single equation the altered distance $a+{}_1x_2$. After that

Fig. 7.



remove the tie between A_3 and A_4 and find, still by a single equation, the altered distance $a + {}_1x_3$, and so on till we find ${}_1x_7$ or ${}_1x_8$ or ${}_1x_i$, small enough to be negligible. Thus found, ${}_1x_1$, ${}_1x_2$, ${}_1x_3$, ... ${}_1x_i$ give a first approximation to the deviations from equality of distance for complete equilibrium. Repeat the process of removing the ties in order and replacing each one by the altered length as in the first set of approximations, and we find a second set ${}_2x_1$, ${}_2x_2$, ${}_2x_3$ . . . . Go on similarly to a third, fourth, fifth, sixth . . . . approximation till we find no change by a repetition of the process. Thus, by a process essentially convergent if the equilibrium with which we started is stable, we find the deviations from equality of consecutive distances required for equilibrium when the system is left free in the neighbourhood of each end, and all through the row (except always the constraint to remain in a straight line). By this proceeding applied to the curve of fig. 7 and the case of equilibrium $a = \cdot 680$, the following successive approximations were found :—

	x_1	x_2	x_3	x_4	x_5	x_6	x_7
1st Approximation .	$+\cdot 018$	$-\cdot 009$	$+\cdot 004$	$-\cdot 002$	$+\cdot 001$	$-\cdot 001$	$\cdot 000$
2nd ,, .	$+\cdot 026$	$-\cdot 014$	$+\cdot 007$	$-\cdot 003$	$+\cdot 002$		
3rd ,, .	$+\cdot 031$	$-\cdot 018$	$+\cdot 009$	$-\cdot 005$	$+\cdot 003$		
4th ,, .	$+\cdot 034$	$-\cdot 020$	$+\cdot 011$	$-\cdot 006$			
5th ,, .	$+\cdot 036$	$-\cdot 022$	$+\cdot 012$	$-\cdot 007$			
6th ,, .	$+\cdot 037$	$-\cdot 023$	$+\cdot 013$				
7th ,, .	$+\cdot 038$	$-\cdot 024$					
8th ,, .	$+\cdot 039$						

Thus our final solution, with $a = \cdot 680$, is

$$x_1 = +\cdot 039,\ x_2 = -\cdot 024,\ x_3 = +\cdot 013,\ x_4 = -\cdot 007,\ x_5 = +\cdot 003,$$
$$x_6 = -\cdot 001,\ x_7 = \cdot 000.$$

§ 29. It is exceedingly interesting to remark that the deviations of the successive distances from a are alternately positive and negative, and that they only become less than one-seventh per cent. of a for the distance between A_7 and A_8. Thus, if we agree to neglect anything less than one-seventh per cent. in the distance between atom and atom, the influential distance from either end is $7a$, although the mutual force between atom and atom is null at all distances exceeding $2{\cdot}2a$.

§ 30. If, instead of $f(D)$ denoting the force between two atoms in a rectilinear row, it denotes the mutual force between two parallel plane nets in a Bravais homogeneous assemblage of single atoms, the work of §§ 27, 28 remains valid; and thus we arrive at the very important and interesting conclusion that when there is repulsion between nearest nets, attraction between next-nearests, and no force between next-next-nearests or any farther, the disturbance from homogeneousness in the neighbourhood of the bounding plane consists in alternate diminutions and augmentations of density becoming less and less as we travel inwards, but remaining sensible at distances from the boundary amounting to several times the distance from net to net.

XIII. *On Spectra arising from the Dissociation of Water Vapour and the Presence of Dark Lines in Gaseous Spectra.* *By* JOHN TROWBRIDGE *.

[Plate III.]

IN passing from the study of the light emitted by gases under the effect of electrical discharges to the investigation of the light produced by discharges of great quantity, one enters a new field of research. In previous papers on the spectra of hydrogen I have stated my convictions of the importance of the rôle played by water-vapour in glass spectrum-tubes. The results of further study emphasize these convictions. With powerful discharges in hydrogen, oxygen, and rarefied air, even when these gases are dried with the utmost care, I always obtain the same spectrum, which I regard as that arising from the dissociation of water-vapour which is always present in glass tubes. The bright-line spectrum, moreover, at high temperatures is accompanied by a faint continuous spectrum on which are dark lines which indicate a selective reversibility in the silver salt. This reversibility, it seems to me, is of great significance in the application of photography to astrophysics.

It has long been recognized that spectrum analysis is an extremely delicate method of recognizing the presence of a gas or the vapour of a metal under the excitation of heat; and when the improvements in photography enabled us to obtain permanent records of the spectra of gases, it was supposed that we had a means of escaping from the fallacies of eye-observations which arose from personal idiosyncracies. If the photographic plate were a perfect instrument for recording the infinite number of vibrations which light can communicate to atoms of matter, we should certainly feel that we had made a great advance in physical science. When

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* Communicated by the Author.

we reflect, however, on the supposition that emulsions containing silver salts are capable of responding and giving a permanent record of all waves of light, even in the portion of the spectrum considered most actinic, when the waves exceed a certain intensity, we are conscious that we rely without proof upon an infinite range of photochemical action; and indeed I show in this paper the existence of a selective reversibility produced on the photographic plate by powerful discharges producing light of great intensity.

Realizing the importance of studying the behaviour of gases under different forms of excitation, I have collected in the rooms devoted to spectrum analysis in this laboratory three forms of apparatus: an induction-coil actuated by a very efficient liquid break, giving a spark of 30 inches in air; a step-up transformer, excited by an alternating current, producing with glass condensers of about ·3 microfarad discharges of an inch in length of great body; and a storage-battery of twenty thousand cells. A plant of this nature I conceive to be necessary in the present stage of spectrum analysis; for molecular motions excited in rarefied gases vary greatly with the kind of electrical discharge. In the application of photography to spectrum analysis one is immediately confronted with the necessity of submitting the gas to a comparatively long electrical stimulus in order to obtain a negative. Even with a concave grating of short focus several discharges are necessary with a narrow slit. Each discharge is capable of modifying the condition of the gas. This fact is well recognized by taking successive photographs upon the same plate with different strengths of current. A simple form of plate-holder enables this to be done. One obtains a striking example of the instability of a spectrum-tube filled, apparently, with dry hydrogen when one subjects it first to very powerful discharges from a glass condenser of ·6 microfarad charged by a storage-battery of twenty thousand cells, with practically no self-induction in the circuit, and follows this excitation by an alternating current of much less quantity. The powerful discharge gives what I term the spectrum arising from the dissociation of water-vapour; and the alternating current gives the spectra of argon. This results, I suppose, from the oxidization of traces of air in the tube under the action of the dissociation of the water-vapour. The presence of hydrogen is concealed. On cooling, the tube again shows the four-line spectrum of hydrogen. The period of the condenser-discharges which I have employed varied from one five-hundred thousandth of a second to one millionth. The practically instantaneous current, therefore, varied from five thousand amperes to ten thousand. The revolving-mirror method showed that the pilot spark was mainly effective, and that the subsidiary oscillations were feeble. The spectrum-tube speedily became milk-white from the sodium set free from the glass. Lord Rayleigh has shown how to demonstrate the presence of argon from very small quantities of air (Phil. Mag. [6] vol. i. p. 108, 1901). My method is substantially his, except that I employ very powerful discharges which set free a sufficient amount of sodium-vapour from the glass: and the oxygen is supplied from the dissociation of water-vapour which is always in evidence when powerful discharges are employed. The production of argon under these circumstances I regard as a striking proof that I am dealing in this investigation with the spectra arising from the dissociation of water-vapour. From the same tube one can, by modifying the strength and character of the electrical discharges, obtain what is generally termed the four-line spectrum of hydrogen, the spectrum of sodium, the spectra of argon, and the spectrum arising from the dissociation of water-vapour. Doubtless one could recognize also the spectrum of helium; I am not yet sufficiently familiar with it.

In the course of the study of the water-vapour spectrum one is naturally led to photograph the spectrum of the electric spark under water. It is possible to obtain powerful discharges of any suitable length under distilled water by inclosing the spark terminals in glass tubes, allowing only a small portion of the platinum terminals to project from the ends of the tubes. If the terminals are immersed more than one inch under the water, the resulting explosion is apt to break the glass containing-vessel. The light of these discharges under distilled water is white and extraordinarily brilliant to the eye. When it is examined by the spectroscope one sees a continuous spectrum; and one obtains a continuous spectrum by photography even in the most actinic portion of the spectrum. On bringing the spark terminals to the surface of the water, one immediately obtains the four-line spectrum of hydrogen or water-vapour. To what is due the continuous spectrum under water? Does it result from the production of the dissociation-spectrum of water-vapour under great pressure? That there is great pressure is shown by the sudden explosion, which is sufficient to blow the small tamping of water out of both ends of the containing tube. If the water is covered with a thin film of oil, this oil is immediately disseminated through the water, making a milky white emulsion which remains for days.

When we turn to powerful discharges through Plücker or

Geissler tubes filled with hydrogen which has been dried with care, we also obtain a faint continuous spectrum on which are bright lines and dark lines. Moreover, what are apparently the strongest bright lines of the dissociation-spectrum of water-vapour are not reversed. There is a selective reversibility which arises at high temperatures.

This fact seems to me of great importance in the application of photography to the study of celestial phenomena. Reversal of spectrum-lines does not necessarily indicate reversing layers of cooler gases, and in certain cases may arise from photochemical action of the silver salt. One immediately thinks in this connexion of the phenomenon of dark lightning or the Clayden effect, and of the interesting experiments of Professor Nipher *. Spectrum analysis, however, reveals a selective reversibility which must be carefully studied before we can properly interpret the records of photography. There are doubtless many states of vibration, even in the actinic portion of the spectrum, which are not recorded by the silver salt: for this selective reversibility may obliterate or prevent a permanent record. I have obtained this reversing action with different emulsions on glass and also on celluloid films. The strongest reversals are approximately at wave-lengths 4227, 3930, 3965. There is also a faint reversal at wave-length 3953. Reversals are often seen on the negative which disappear in the fixing-bath.

In this investigation ten thousand cells were employed to charge a glass condenser of ·6 microfarad. The charge was sent through Geissler tubes with practically no self-induction in the discharge-circuit. The bore of the capillary tubes was 1 mm., and the tubes were filled with apparently dry hydrogen at a pressure of approximately ·1 mm. The tubes were also filled with oxygen and also with rarefied air at the same pressure. I have reached a limit in subjecting glass tubes to powerful discharges, and am now turning my attention to obtaining quartz tubes in the hope of securing a more resisting material.

In a previous paper † I expressed my conviction that the four-line spectrum observed in the protuberances of the sun is an evidence of the presence of water-vapour in the sun's atmosphere, and an evidence, therefore, of the presence of oxygen. In the spectrum (Plate III. fig. 7, B) one sees on the negative two reversed lines which coincide with the great H, H lines of the solar spectrum. These are seen bright in

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* "On Certain Properties of Light-Struck Plates," Trans. Academy of St. Louis, Mo. U. S. vol. x. No. 6.

† Phil. Mag. [5] vol. l. p. 338 (1900).

B, fig. 4. One also sees a strong reversed line at approximately wave-length 4227; and there is a reversed band coinciding with the solar region of reversed lines between wave-lengths 4315–4285. These regions in the sun are doubtless composite photographs of reversals of many elements. I believe that there is a basis of reversal due to the dissociation of water-vapour.

The nomenclature of the stars in regard to their types of spectra may need revision. The higher temperature I get the more dark lines I obtain.

An excess of dissociation of water-vapour may suffice to give at a comparatively low temperature the bright-line spectrum of hydrogen. At higher temperature the dissociation of this vapour in the presence of atmospheric air may give dark lines. The intense light due to the dissociation of water-vapour under the effect of powerful discharges is the nearest approach to sunlight which I have been able to produce. Its actinic effect is greater than that of magnesium, zinc, or aluminium. It may be that the variability of certain stars is due to a variability in the amount of water-vapour which is being dissociated; and one is led to conjecture whether the light of the sun's atmosphere may not be due to an electrical dissociation. The selective reversibility of the silver salts seems to me, therefore, of great interest in the subject of astrophysics; for we can have reversible effects on the photographic plates which are not due to the reversing effect of colder layers of gases. In other words, we have actions recorded which are on the plates and not in the heavens. The intense light due to the dissociation of water-vapour may entirely mask the fainter light of the metallic lines in stars which show only gaseous spectra, especially when we consider the varying distances of the stars. I have employed electrodes of platinum, copper, silver, aluminium, iron, and found no trace of the lines of their vapour in the spectrum of the dissociation of water-vapour. Even when caustic soda is present in the tubes, although it fills the tube with a brilliant yellow light with comparatively low discharges, no trace is seen of it when the tube is excited with powerful discharges. Then we have the brilliant white light of the water-vapour spectrum.

The silver salt, therefore, does not respond to all rates of vibration; or if it does respond, the molecular action is unstable and there is no resultant reaction which is evidenced by a photographic image. There may be spectra at very high instantaneous temperatures which we cannot photograph. It seems reasonable to suppose that the silver molecule is limited in its rate of vibrations, and that the photographic plate as well as the human eye is a limited instrument of research.

On Plate III., A represents the normal solar spectrum in the neighbourhood of the great H, H lines. B represents the gaseous spectra. The photographs were taken with a Rowland concave grating, and are not enlarged or touched in any way. Unfortunately the reproductions do not give many of the reversals, and some of the bright lines do not appear. This is especially the case in fig. 5. Figs. 1 and 2, B, are spectra of oxygen and traces of rarefied air taken with comparatively low current and voltage at a pressure of 1 millimetre. Fig. 3 is a spectrum of hydrogen under the same conditions. Fig. 4 is the spectrum arising from the dissociation of water-vapour with very powerful discharges. Fig. 5 shows a line of selective reversibility at wave-length 4227. On the negative the two brilliant lines (fig. 4) which closely coincide with the great H, H lines of the solar spectrum are seen to be reversed, and therefore appear as dark lines. This reversal is shown in fig. 7. The gaseous spectrum B of fig. 7 closely resembles in general features the solar spectrum photographed with a wide slit in order to give the general distribution of darkness and light.

My conclusions are as follows:—

Dissociation of water-vapour takes place in the atmosphere of the sun. Oxygen, therefore, must be present. From a careful study of my negatives I regard the evidence for the presence of this vapour as conclusive as that generally accepted for the presence of sodium in the sun.

The dissociation of water-vapour by powerful electric discharges in the presence of small amounts of atmospheric air results in the production of argon even in tubes presumably filled with hydrogen.

Dark lines occur in the spectra of gases which increase with the intensity of the light, and are photochemical in their origin.

The great brilliancy of the dissociation spectrum of water-vapour, which obscures the presence of metallic spectra, and the presence of dark lines due to photochemical reversals, makes one cautious in accepting photographic evidence in regard to the states of development of stars.

XIV. *A Problem in Conduction of Heat.* *By* H. S. Carslaw, *M.A., D.Sc.* (*Lecturer in Mathematics in the University of Glasgow*) *.

THE problem of the Linear Flow of Heat in a solid extending to infinity on one side of an infinite plane, while radiation takes place across that plane into a medium at zero temperature, was discussed by Riemann (*Partielle Differential-Gleichungen*, § 69). His solution depends upon that for the more general problem of the sphere, and is obtained by making the radius of the sphere increase indefinitely. Another solution was given by Bryan † by the synthetical method, and in Weber's new edition of Riemann's book ‡ a third discussion of this problem is to be found.

In the following pages another discussion of this problem is given, in which use is made of Cauchy's Theorem in Contour Integration.

The equations which the temperature has to satisfy are as follows :—

$$\left.\begin{aligned} \frac{\partial v}{\partial t} &= k\frac{\partial^2 v}{\partial x^2}, \quad x>0, & \quad \dots \dots \quad (1)\\ v &= f(x), \quad t=0, & \quad \dots \dots \quad (2)\\ -\frac{\partial v}{\partial x}+hv &= 0, \quad x=0, & \quad \dots \dots \quad (3) \end{aligned}\right\}$$

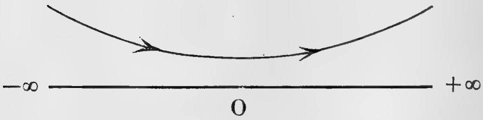
We begin with the solution for a source in an infinite solid,

$$v=\frac{1}{2\sqrt{\pi kt}}e^{-\frac{(x-x')^2}{4kt}}. \quad \dots \dots \quad (4)$$

This may be expressed by the integral,

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-k\alpha^2 t}e^{i\alpha(x-x')}d\alpha.$$

Fig. 1.



The path P in α-plane.

We transform this into the integral over the path (P) of

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* Communicated by Prof. A. Gray, F.R.S.

† "On an Application of the Method of Images to the Conduction of Heat," Proc. Lond. Math. Soc. vol. xxii.

‡ Weber-Riemann, *Partielle Differential-Gleichungen*, Bd. ii. § 38.

fig. 1, and we take the expressions

$$\frac{1}{2\pi}\int e^{-k\alpha^2 t}\, e^{i\alpha(x-x')}\, d\alpha,$$

and

$$\frac{1}{2\pi}\int e^{-k\alpha^2 t}\, e^{-i\alpha(x-x')}\, d\alpha,$$

according as $x \gtrless x'$.

The path (P) must have the argument of α at infinity on the right hand between 0 and $\frac{\pi}{4}$, and on the left between $\frac{3\pi}{4}$ and π, so that $e^{-k\alpha^2 t}$ may vanish there: and for the same reason we have chosen the different expressions for the integral as $x \gtrless x'$.

Associate with this solution

$$\frac{1}{2\pi}\int \mathrm{A} e^{i\alpha x}\, e^{-k\alpha^2 t}\, d\alpha,$$

over the same path (P).

The quantity A is determined by the surface condition (3), and is given by

$$\mathrm{A} = -\frac{h+i\alpha}{h-i\alpha} \cdot e^{i\alpha x'}. \qquad (5)$$

We have thus obtained a solution of (1) and (3) in the form of the sum of two complex integrals, and we proceed to show that this solution corresponds to a source at (x') in our solid.

Our solution is given by the equation

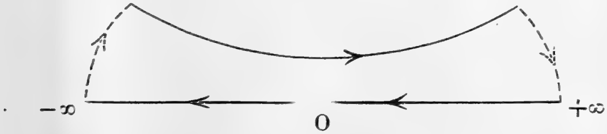
$$v = \frac{1}{2\pi}\left\{\int e^{-k\alpha^2 t}\, e^{-i\alpha(x-x')}\, d\alpha - \int e^{-k\alpha^2 t}\, e^{i\alpha(x+x')}\, \frac{h+i\alpha}{h-i\alpha}\, d\alpha\right\}, \qquad (6)$$

the integrals being taken over the path (P), and the first integral being altered when $x > x'$, as explained above.

This may be written

$$= \frac{1}{2\pi}\int e^{-k\alpha^2 t}\, e^{-i\alpha(x-x')}\, d\alpha + \frac{1}{2\pi}\int e^{-k\alpha^2 t}\, e^{i\alpha(x+x')}\, d\alpha - \frac{ih}{\pi}\int e^{-k\alpha^2 t}\, \frac{e^{i\alpha(x+x')}}{\alpha + ih}\, d\alpha. \qquad (7)$$

Fig. 2.



The α-plane.

Since there is no pole of any of these integrals within the closed circuit of fig. 2, and the parts contributed by the circular arcs vanish in the limit, these complex integrals may be replaced by integrals along the real axis of α.

The first two become

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-k\alpha^2 t}\, e^{-i\alpha(x-x')}\, d\alpha + \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-k\alpha^2 t}\, e^{i\alpha(x+x')}\, d\alpha,$$

whether x is greater or less than x'.

These may be replaced by

$$\frac{1}{2\sqrt{\pi k t}}\left[e^{-\frac{(x-x')^2}{4kt}} + e^{-\frac{(x+x')^2}{4kt}}\right].$$

We have therefore only to show that the third integral of (7) vanishes in the limit when t diminishes indefinitely.

This is best done by considering the complex integral

$$\int e^{-k\alpha^2 t}\frac{e^{i\alpha(x+x')}}{\alpha+ih}\, d\alpha$$

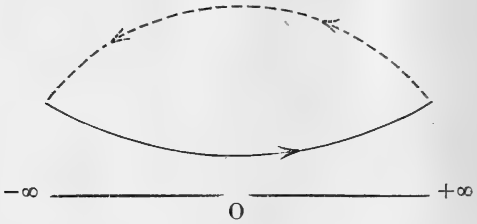
over the path (P).

This integral converges to its value for $t=0$, as t converges to zero. When we take the value for $t=0$, namely

$$\int \frac{e^{i\alpha(x+x')}}{\alpha+ih}\, d\alpha,$$

and consider the integral taken over the closed circuit of fig. 3, since the integrand vanishes at infinity in the upper part of the α-plane, and there are no poles inside the circuit, we see that

Fig. 3.



The α-plane.

$$\int \frac{e^{i\alpha(x+x')}}{\alpha+ih}\, d\alpha$$

over the path (P) is zero.

Our solution in (7) therefore satisfies the initial condition for the source at the point x', and the surface conditions were fulfilled by the choice of A in (5).

We now replace the third integral of (7) by the equivalent integral over the real axis in the α-plane, and obtain our solution for the source in the form

$$v=\frac{1}{2\sqrt{\pi kt}}\left[e^{-\frac{(x-x')^2}{4kt}}+e^{-\frac{(x+x')^2}{4kt}}\right]$$

$$-\frac{2h}{\pi}\int_0^\infty e^{-k\alpha^2t}\frac{h\cos\alpha(x+x')-\alpha\sin\alpha(x+x')}{\alpha^2+h^2}d\alpha. \quad (8)$$

Since

$$\int_0^\infty e^{-h\xi}\cos\alpha\xi d\xi=\frac{h}{\alpha^2+h^2},$$

and

$$\int_0^\infty e^{-h\xi}\sin\alpha\xi d\xi=\frac{\alpha}{\alpha^2+h^2},$$

this may be changed to its final form,

$$v=\frac{1}{2\sqrt{\pi kt}}\left[e^{-\frac{(x-x')^2}{4kt}}+e^{-\frac{(x+x')^2}{4kt}}-2h\int_0^\infty e^{-h\xi}\,.\,e^{-\frac{(x+x'+\xi)^2}{4kt}}d\xi\right] \quad (9)$$

which agrees with that given by Bryan.

The solution for the initial distribution $v=f(x)$ follows in the usual way by integration, and is given by the equation

$$v=\frac{1}{2\sqrt{\pi kt}}\left[\int_0^\infty f(x')\left(e^{-\frac{(x-x')^2}{4kt}}+e^{-\frac{(x+x')^2}{4kt}}\right)dx'\right.$$

$$\left.-2h\int_0^\infty\int_0^\infty e^{-h\xi}e^{-\frac{(x+x'+\xi)^2}{4kt}}f(x')d\xi dx'\right]. \quad (10)$$

The result for the case of constant initial temperature is of interest, as Riemann's original problem was to obtain the distribution in this case after a considerable time had elapsed.

Put $f(x)=v_0$ and integrate: the second integral of (10) simplifies after integration by parts and we obtain

$$v=\frac{1}{2\sqrt{\pi kt}}\left[\int_0^\infty e^{-\frac{(x-x')^2}{4kt}}dx'-\int_0^\infty e^{-\frac{(x+x')^2}{4kt}}dx'+2\int_0^\infty e^{-hx'}\,.\,e^{-\frac{(x+x')^2}{4kt}}dx'\right],$$

the form in which Weber gives the solution of this problem. Riemann's result may be at once deduced.

XV. *Contributions to the Theory of the Resolving Power of Objectives.* *By* Professor J. D. Everett, *F.R.S.*[*]

In high class objectives, both of telescopes and microscopes, the practical limit to the power of separating close points (called *resolving power* or *separating power*) depends upon the blurring due to diffraction. Owing to diffraction, the image formed of a bright point is not a point, but a spot, brightest in the central part, and falling off without any discontinuity from the centre to the margin. In favourable circumstances this spot is surrounded by a succession of bright rings. The phenomenon is seen in its greatest perfection when small aperture is combined with good definition. Blocking out the central portion of the objective makes the spot smaller and the surrounding rings relatively brighter.

Dawes (Mem. R. Ast. Soc. xxxv. p. 158) made very elaborate observations on double stars for the purpose of investigating the separating power of telescopes; and arrived at the conclusion that the angular distance between the two components, when they are nearly equal in magnitude, and are just separated, is given by the formula—

4·56 *seconds, divided by diameter of objective in inches.*

The first calculation of the relative brightness at different points of the spot and rings, which constitute the diffraction image of a point formed by a lens symmetrical round an axis, was published by Airy in 1836 (Camb. Trans. v. p. 283), in a very clear and readable paper. His basis of procedure is the very direct and intelligible one of considering the concave wave-front which advances from the objective to the focus, and computing, for its initial position, the "disturbance" which it produces (according to Huygens' principle) at any given small distance measured laterally from the geometrical focus.

Another principle of calculation, less obviously correct but leading to precisely the same result, is employed in Mascart's *Optique* and in Preston's Light.

Both methods of procedure lead to one and the same infinite series for the "disturbance" at given lateral distance from the geometrical focus; and this series is a Bessel's function of the first order. It is in fact $\frac{2J_1(m)}{m}$, m denoting $\frac{2\pi}{\lambda}\frac{R}{f}b$, where R is radius of aperture, f focal length, b lateral distance, and λ wave-length. The calculation assumes identity of disturbance both in degree and in kind at all points of the wave-front.

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[*] Communicated by the Physical Society; read Feb. 28, 1902.

A simple calculation (given at p. 277 of my *Deschanel*, Part iv.) shows that the extreme difference of optical path, for disturbances coming from different points of a concave wave-front to a point at lateral distance b from the geometrical focus (the centre of the sphere to which the wave-front belongs), is $2b \sin \alpha$, α denoting the angular radius of the wave-front as seen from the focus. When the extreme difference of path is λ, we have therefore

$$b = \frac{\lambda}{2 \sin \alpha}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Comparison with observation shows that this value of b represents with fair accuracy the limit of separation. The angle subtended by the distance b at the second nodal point of the objective, which is identical with the angle subtended by the corresponding distance in the object, as seen from the first nodal point, is

$$\frac{b}{f} = \frac{\lambda}{2f \sin \alpha} = \frac{\lambda}{D}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

f being the focal length, and D the diameter of the objective. This formula λ/D for the least distance between the components of a double star, agrees with Dawes's value above quoted, if we put $\lambda = {\cdot}000022$ inch $= {\cdot}56$ micron. The wave-length for the brightest rays is usually taken as ·55 micron, which is as good an agreement as could be desired.

Passing now to the case of the microscope, and supposing the same formula for the minimum distance b in the image to be still applicable, we may conveniently transform it by means of the equation (which we shall discuss later)

$$\mu_1 y_1 \sin \theta_1 = \mu_2 y_2 \sin \theta_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

applicable to any optical system which gives sharp flat images.

In this equation,

y_1 y_2 denote the distances of a point of the object, and the corresponding point of the image, from the axis of the system;

μ_1 μ_2 the indices of the first and last media;

θ_1 θ_2 the angles made with the axis by any incident ray and the corresponding emergent ray.

The ratio $(\mu_1 \sin \theta_1)/(\mu_2 \sin \theta_2)$ is equal to the magnification y_2/y_1, and is therefore the same for all values of θ. This constancy is called by Abbe the *sine condition*.

In the present case θ_2 is α, y_2 is b, μ_2 is 1; and if α_1 denote the obliquity of an extreme incident ray, the equation gives

$$\mu_1 \; y_1 \sin \alpha_1 = b \sin \alpha,$$

$$y_1 = \frac{\sin \alpha}{\mu_1 \sin \alpha_1} b = \frac{\sin \alpha}{\mu_1 \sin \alpha_1} \cdot \frac{\lambda}{2 \sin \alpha} = \frac{\lambda}{2\mu_1 \sin \alpha_1} = \frac{\lambda_1}{2 \sin \alpha_1}. \quad (4)$$

λ_1 denoting the wave-length in the first medium which corresponds to λ in air. This value for y_1, the distance between points or lines which can be barely separated, has been extensively adopted. Helmholtz in the *Jubelband* of Pogg. *Ann.* 1874, p. 557 adopts it in the form last written. Abbe calls $\mu_1 \sin \alpha_1$ the *numerical aperture* of the objective, and adopts the formula *wave-length divided by twice the numerical aperture.* Drude (*Lehrbuch der Optik*) adopts it as the limiting distance for oblique illumination, and its double as the limiting distance for direct illumination.

Microscopic test-objects are not self-luminous like double stars, but are viewed by transmitted light. If no condensing arrangement is employed, the pencil of light sent by a point of the object to the objective consists of rays from different parts of the source, that is, in effect, from different sources. An orthogonal section of such a pencil does not possess the characteristic properties of a wave-front. Different portions of it have no definite relation of phase, and are incapable of mutual interference. Our formulæ are therefore no longer applicable. Practically we may regard such an orthogonal section as made up of a number of small parts, each of which is a wave-front, giving by reason of its smallness a very large diffraction image of a point of the object. These separate images of the same point overlap without interference, and as they do not exactly coincide, compose a larger and more blurred image of the point represented.

The cure for this evil is furnished by employing a condenser of high quality, to throw upon the part of the object under examination a very sharp image of the source of illumination. If the image were perfectly sharp, each point of the object would get its light from its own special point of the source, and the effect would be to make the object act as if it were self-luminous. Each point of the object would send to the objective a pencil whose orthogonal sections would be true wave-fronts, to which our previous reasoning would be applicable ; so that the diffraction spot which represents a point would have the small size due to the largeness of the entire aperture.

This appears to me to be the chief benefit conferred by sharply focussing the source on the object ; but it has not so far as I am aware been pointed out by any writer on the microscope hitherto. Abbe in his great paper on microscopic perception (*Archiv für mikr. Anat.* ix. p. 413, 1873) regards the condenser merely from the point of view of geometrical optics, and recommends the use of one which is not achromatic. Microscopic observers long ago ascertained, as an empirical fact, that achromatic condensers gave better results than non-achromatic; while mathematicians refused to believe them, and maintained that achromatism could be of no advantage, seeing that the sole purpose of a condenser was to give wide pencils of strong light.

There is another advantage from sharp focussing by the condenser, which may be regarded as the complement of that above indicated. If the focussing were perfectly sharp, the waves from one point of the object could not interfere with waves from another point. Such interference gives rise to spurious diffraction patterns, liable to be mistaken for structures existing in the object. The two components of a double star exhibit no mutual interference in a telescope; and different points of a microscopic object cannot produce mutual interference if they send light which has come from completely distinct sources. Lord Rayleigh (Phil. Mag. xlii. 1896) was, I believe, the first to indicate this advantage. Abbe, in his paper on microscopic perception, makes no allusion either to the focussing of the source on the object, or to the finite size of the spot which (with its surrounding rings) is the diffraction image of a single isolated point.

The following explanation of the advantage of oblique illumination is, I believe, new.

Perfect sharpness of focussing by a condenser is unattainable; and two points of the object which are not further apart than twice the limiting distance of separability will inevitably have a portion of the source in common, as regards their illumination. Let β denote the obliquity of the illumination, the two object-points in question being supposed to be in a plane which contains the illuminating rays and the axis of the objective. The difference of optical path for rays coming from the same point of the source to the two object-points is $s \sin \beta$, s denoting the distance between the two points. The best condition for separation is, that this difference of path shall be half a wave-length in the medium in which the object is immersed (say $\frac{1}{2}\lambda_1$), for this gives the most complete extinction in the overlapping portion of the two diffraction spots which are the images of the two points. Putting then

$$s \sin \beta = \tfrac{1}{2}\lambda_1, \quad \ldots \ldots \quad (5)$$

and assigning to s the value $\lambda_1/\sin \alpha_1$, which being double of the accepted minimum value may be taken as representing an ordinary test, we deduce

$$\sin \beta = \tfrac{1}{2} \sin \alpha_1. \quad \ldots \ldots \quad (6)$$

If we put s equal to the accepted minimum itself, we obtain

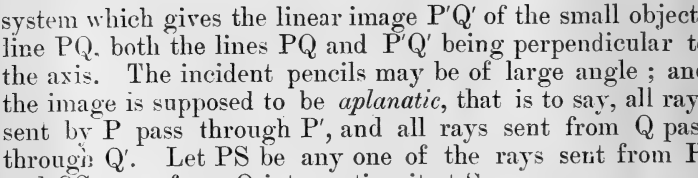
$$\sin \beta = \sin \alpha_1. \quad \ldots \ldots \quad (7)$$

These conclusions agree with the received view among microscopists, that the obliquity of illumination should be rather less than the obliquity of the extreme rays of the incident pencil.

Note on Hockin's proof of the Sine Condition.

Various proofs have been given of the sine condition expressed by equation (3), which must be fulfilled in every case in which a sharp image, in a plane perpendicular to the axis of the instrument, is formed of a small flat object whose plane is perpendicular to the axis. By far the simplest is that given in an article "On the Estimation of Aperture in the Microscope," published after the author's death in the Journal of the Royal Microscopical Society (1881, ser. 2, iv. p. 337), where he is described as the late Mr. Charles Hockin, junr., an electrician and mathematician of repute. Appreciative notes by Abbe are inserted in the article. Strange to say, the proof does not seem to have been reproduced in any English publication, though it is to be found, modified for the worse, in German optical treatises. In Müller-Pouillet it is erroneously described, and the author's name is given as John Hockin. These circumstances, in conjunction with the great importance of the theorem itself, are my reasons for reproducing it. I have corrected a clerical error of − for + in the two principal equations.

Let PP′ in the figure represent the axis of an optical system which gives the linear image P′Q′ of the small object-line PQ, both the lines PQ and P′Q′ being perpendicular to the axis. The incident pencils may be of large angle; and the image is supposed to be *aplanatic*, that is to say, all rays sent by P pass through P′, and all rays sent from Q pass through Q′. Let PS be any one of the rays sent from P, and QS a ray from Q intersecting it at S.



Since PQ is small, the angle PSQ is small, and the plane pencil bounded by PS, QS will give an emergent pencil bounded by P′S′, Q′S′, the optical path from S to S′ having the same value for all the rays of the pencil; denote this value by (SS′).

Then, if μ be the index of the first and μ' that of the last medium, the optical path from P to P′ is

$$\mu\,.\,\mathrm{PS}+(\mathrm{SS}')-\mu'\,.\,\mathrm{P'S'},$$

and is constant for all rays that go from P to P′. Similarly the optical path from Q to Q′ is

$$\mu \,.\, \mathrm{QS} + (\mathrm{SS}') - \mu' \,.\, \mathrm{Q'S'},$$

and is constant. Subtracting, and denoting the difference of the two constants by c, we have

$$\mu(\mathrm{PS}-\mathrm{QS}) - \mu'(\mathrm{P'S'}-\mathrm{Q'S'}) = c,$$

or (calling the obliquities θ, θ'),

$$\mu \,.\, \mathrm{PQ} \sin\theta - \mu' \mathrm{P'Q'} \sin\theta' = c.$$

But θ and θ' vanish together, therefore c is zero; and we have

$$\mu \,.\, \mathrm{PQ} \sin\theta = \mu' \,.\, \mathrm{P'Q'} \sin\theta'. \quad . \quad . \quad . \quad (3)$$

The ratio of $\mu \sin\theta$ to $\mu' \sin\theta'$ has therefore the constant value P′Q′/PQ for all the rays by which the image is formed.

The present paper has been framed with a view to supplementing two papers by Lord Rayleigh, one of them (in two parts) in the Phil. Mag. for the second half of 1879, and the other (which has been already quoted) in Phil. Mag. vol. xlii. 1896. They contain a much fuller treatment of the theory of resolution than I have met with elsewhere.

11 Leopold Road, Ealing, W.

XVI. *Notices respecting New Books.*

Histoire de l'Observatoire de Paris de sa fondation à 1793. *Par* C. Wolf, *Membre de l'Institut, Astronome Honoraire de l'Observatoire.* Paris: Gauthier-Villars, Imprimeur-Libraire.

THIS is the first part of a work in which it is proposed to give a history, not of the astronomical observations and results which have been accomplished at the famous Observatory of Paris, which was founded about eight years earlier than that at Greenwich, but of its buildings, instruments, and the *personnel* composing its staff, with the successive modifications and additions in these. It is well known that the Paris Observatory, for more than the first century and a quarter of its existence, was directed by four generations of the family of Cassini, the first of whom was invited from Italy by Colbert, and eventually appointed to take charge of the new establishment. The fourth, also J. D. Cassini, was in charge at the time when the great Revolution transformed not only the rule of the Observatory, but that of all France. Before leaving his post, Cassini formed the project of writing a complete history of the establishment, and requested of the Director of the royal buildings that a search should be made in the public archives for the documents relating to the foundation of the Observatory and its early annals. Though the answer gave him very little encouragement in his scheme, he took the trouble to gather together all the accessible papers which were left by his ancestors, particularly his great-grandfather: these he presented in 1811 to the Bureau des Longitudes, and they form one of the principal sources of information made use of in the work before us. As its title shows, it carries the history down to the year 1793: the subsequent period will form the subject of a second volume.

The foundation of the Observatory resulted directly and immediately from the creation of the Academy of Sciences in 1666. This was at first called the New Academy, and was installed in the buildings of a house in the Rue Vivien belonging to one of Colbert's sons. In the garden of this house, those members of the Academy who were astronomers—Picard, Auzout, and others—made observations of the stars. But long before this the idea of a regular observatory had been started. Morin in 1634 had proposed that one should be erected on Mont Valérien; and in 1665, Auzout, in dedicating to the King his ephemerides of the comet of 1664, strongly urged the desirability of establishing a building for the express purpose of astronomical observations. It was in 1667 that the observatory was commenced, the architect being Perrault; only the first story was completed when Cassini arrived in Paris in 1669. Although, as M. Wolf points out, it was impossible at that time to foresee what the progress of astronomy would shortly require in regard to methods of observation, Cassini did himself contend for considerable modifications in the original plan. M. Wolf takes a view of his appointment and work very different from that with which we are familiar in the pages of Delambre, and much more favourable to him. A native of the county of Nice when it was included in the dominions of Savoy, his first appointment was at Bologna; when Colbert invited him (and many other learned men) to Paris he came intending to make, like Huygens, only a temporary stay, but ultimately was induced to remain, and, though he never spoke the French language with fluency, became naturalized and married a French lady. When he died in 1712 (three years before Louis XIV., in whose name he had been invited to France) he was in the eighty-eighth year of his age, but had been for some time totally blind. His eldest son was killed at the battle of La Hogue in 1692; it was the second, Jacques, who succeeded his father at the Observatory, and during a visit to England become acquainted with Newton and Flamsteed. (Halley, it will be remembered, had visited Paris in 1680 and observed there, in company with the elder Cassini, the great comet of that year, in regard to which Newton first applied his principle of universal gravitation to comets.) The third Cassini (César François) took the title of de Thury from an estate acquired by his father; and *his* son the fourth (named like his great ancestor J. D. Cassini) is commonly called the Count de Thury. We have already mentioned his intention to write a history of the Observatory, and the trouble that he took to collect the documents which have so greatly aided our present author in the first part of his noble work, very interesting to all astronomers. Cassini IV. formed schemes for greatly improving the buildings and instruments of the Observatory; but the great Revolution in France upset scientific as well as all other arrangements, and led to his resignation in 1793, though he did not die till 1845, in the ninety-eighth year of his age. With his retirement M. Wolf's first volume ends: we shall look forward with interest to the appearance of the second, and its proposed account of the subsequent developments of the Paris Observatory, particularly under Le Verrier, whose directorship (during which the writer of this notice paid his only visit to the establishment) was interrupted and resumed after the death of Delaunay. Two directors, Arago and Mouchez, were natives of Spain. The present eminent head of the Paris Observatory M. Loewy, is a Viennese, and was invited to Paris by Le Verrier; he is also editor of the *Connaissance des Temps*. Astonishment has sometimes been expressed that Picard, its founder, was not, instead of Cassini, appointed the first director of the Paris Observatory, but M. Wolf gives reasons why the former preferred the arrangement actually made. The work is illustrated, and has for a frontispiece a representation of a visit by Louis XIV. to the Observatory. W. T. LYNN.

An Elementary Treatise on Alternating Currents. By W. G. RHODES, *M.Sc.* Pp. xii+212. London: Longmans, Green & Co. 1902.

THE literature of alternating currents is growing apace, and the next few years will probably witness a considerable number of additions to the text-books on this highly important subject. Since the recognition of the fact that alternating currents offer the only satisfactory solution of the problem of power transmission over very long distances, engineers have taken a keen interest in this branch of applied science, and the demand for suitable text-books appears to have been considerable.

The book before us is evidently intended for readers possessing a fair knowledge of elementary mathematics, including the elements of differentiation and integration, and should prove especially useful to students in technical colleges. We fully share the author's view that the elements of vector algebra should form part of the curriculum of every technical school.

In the first eight chapters, which contain a brief account of alternating-current theory, the author is at his best. The numerical examples given at the end of each chapter should prove of great assistance to the student. Chapter IX. calls for some criticism. In dealing with a Fourier series, most modern writers agree in calling the "fundamental" the *first* harmonic term, its "octave" the *second* harmonic, and so on (this, for instance, is the method adopted by J. J. Thomson and Poynting in their text-book on Sound). The author begins by adopting the old and now generally abandoned method of regarding the first term as the *fundamental*, and calling the remaining terms the 1st, 2nd, &c. *harmonics*. Immediately afterwards, however, he states (p. 67) that "even harmonics are generally absent from the curves representing alternating currents"—when it is clear that he means *odd* harmonics, if his own nomenclature be adopted. This point is likely to occasion considerable confusion in the mind of the student.

The account of methods of testing transformers given in

Chapter XII. deserves severe criticism. It seems a pity that the author did not make a more exhaustive study of this subject before proceeding to write on it. Many standard methods which have given excellent results are omitted, while Mr. Mordey's "thermometer" method is duly mentioned.

The section on polyphase induction motors appears capable of considerable improvements. The Heyland diagram for the induction motor, which is so freely used by almost every continental writer on the subject, is not even mentioned, and in place of it we have purely analytical investigations which are not likely to appeal to the reader.

Altogether, the second half of the book is much less satisfactory than the first, and we hope that in a future edition the blemishes which we have pointed out will be removed. There is ample room for a book of this kind, and we believe that, in spite of its defects, it will prove extremely useful to a large circle of readers.

XVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. iii. p. 554.]

January 8th, 1902.—J. J. H. Teall, Esq., M.A., V.P.R.S., President, in the Chair.

THE following communications were read:—

1. 'A System of Glacier-Lakes in the Cleveland Hills.' By Percy Fry Kendall, Esq., F.G.S., Lecturer in Geology at the Yorkshire College, Leeds.

After referring to existing 'extra-morainic' lakes, such as the Märjelen See and those of the Chaix Hills, the author proceeds to deal with the criteria for the recognition of such lakes. These include beaches, deltas, floor-deposits, and overflow-channels. Shore-scarps are common in Cleveland, but beaches are rare or absent, the reason being in part that stability was rarely secured owing to the overflows being over soft Jurassic strata. Deltas also are not common. The floor-deposit of lakes may be distinguished from river-alluvia by the fact that the lamination is close and regular, but, being parallel to the subjacent surface, it may be highly inclined. On the other hand, alluvia are laid down on horizontal surfaces, but rarely show good lamination. Overflow-channels are grouped into four main types: 'direct overflows,' which trench the main watershed of a country; 'severed spurs,' across the spurs of the main watershed; 'marginal overflows,' at first merely a shelf cut in the hillside, but subsequently developed into an actual gorge; and 'in-and-out channels,' or crescentic valleys excavated in the face of a hill by water flowing round a lobe of ice. Such overflows are independent of the natural drainage; they have at first a slight and then a steep fall, and in section they have steep sides and flat floors. The meanders of the valleys and the run of the contouring also possess special features, and the valleys rarely or never receive any considerable tributaries.

Evidence from borings and Drift-filled channels is given to show that during or before the Glacial Period the land was considerably above its present level. The Glacial deposits are described in detail from sections and borings, some of them carried out by the author, and the assemblages of boulders are identified and classified into three chief groups—a Western group, from the Solway, Vale of Eden, Stainmoor Pass, and the Tees; a Northern group, from the Tweed and Cheviots and from Eastern Durham; and an Eastern group, from the Christiania region, the Gulf of Bothnia, and Denmark or the North Sea.

The author has been unable to detect any signs of the presence of the sea in this area at any time during the Glacial Period. Three main ice-masses appear to have been concerned in producing the deposits: one from the Southern Uplands and the Solway, joined by the local ice of the Tees; a second originating in the Tweed Valley, and driven southward round the Cheviots by the pressure of the third, or Scandinavian, ice-mass. The general order of events is supposed to have been:—(1) the unobstructed passage of the Teesdale glacier to the coast, (2) the arrival of the Scandinavian ice, and (3) the invasion of the Scottish ice.

The first of the extra-morainic lakes described is that of the Vale of Pickering, the lowest of the sequence, which for a long period received all the drainage of the district except that of the western margin, and the outflow from which into Lake Humber was that now occupied by the River Derwent. Newton Dale was the outflow of the lake-series of the Eskdale country. The Eskdale system comprises a series of lakes connected by an 'aligned sequence' of overflows; and here it is possible to trace the consequences of the shrinkage of the ice-masses and to follow out the low-level phases of the lake. The ice pressing upon the northern face of the Cleveland Hills gave rise to a series of lakelets, connected with which are the following set of overflows:—Scugdale and Scarth Nick, Bilsdale, Kildale, Ewe Crag Beck, Tranmire, and Egton Moor. Iburndale contained a lakelet overflowing eastward. Behind a narrow coast-strip of country, extending from Robin Hood's Bay to Hunmanby, there runs a gorge which receives all the drainage of the 'hinterland' and carries it into the Vale of Pickering. In the production of this arrangement the effects of an ice-sheet shutting the seaward ends of the valleys is traceable; the position of the main overflows was stable, and the drainage was permanently deflected.

In dealing with the sequence of the ice-movements, evidence is brought forward to prove that the Teesdale ice was the first on the ground in question, but none of the lake-phenomena have been correlated with this first phase. The second phase was the complete diversion of this ice into the Vale of York, brought about by the growth of the Scandinavian ice-sheet. The third is the invasion of Scottish-Northumbrian ice, which may have passed out to sea and been driven inland again, carrying flints and smashed sea-shells with it, and may have extended as far as Lincolnshire on the south and Whorlton on the west.

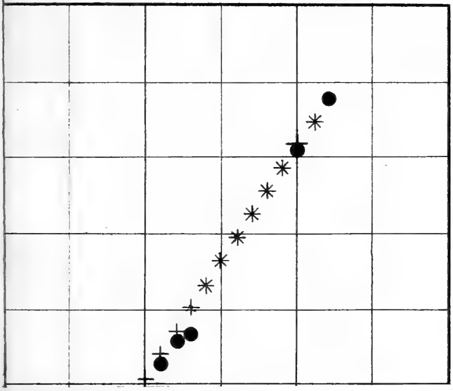
2. 'The Glaciation of Teesdale, Weardale, and the Tyne Valley, and their Tributary Valleys.' By Arthur Richard Dwerryhouse, Esq., B.Sc., F.G.S.

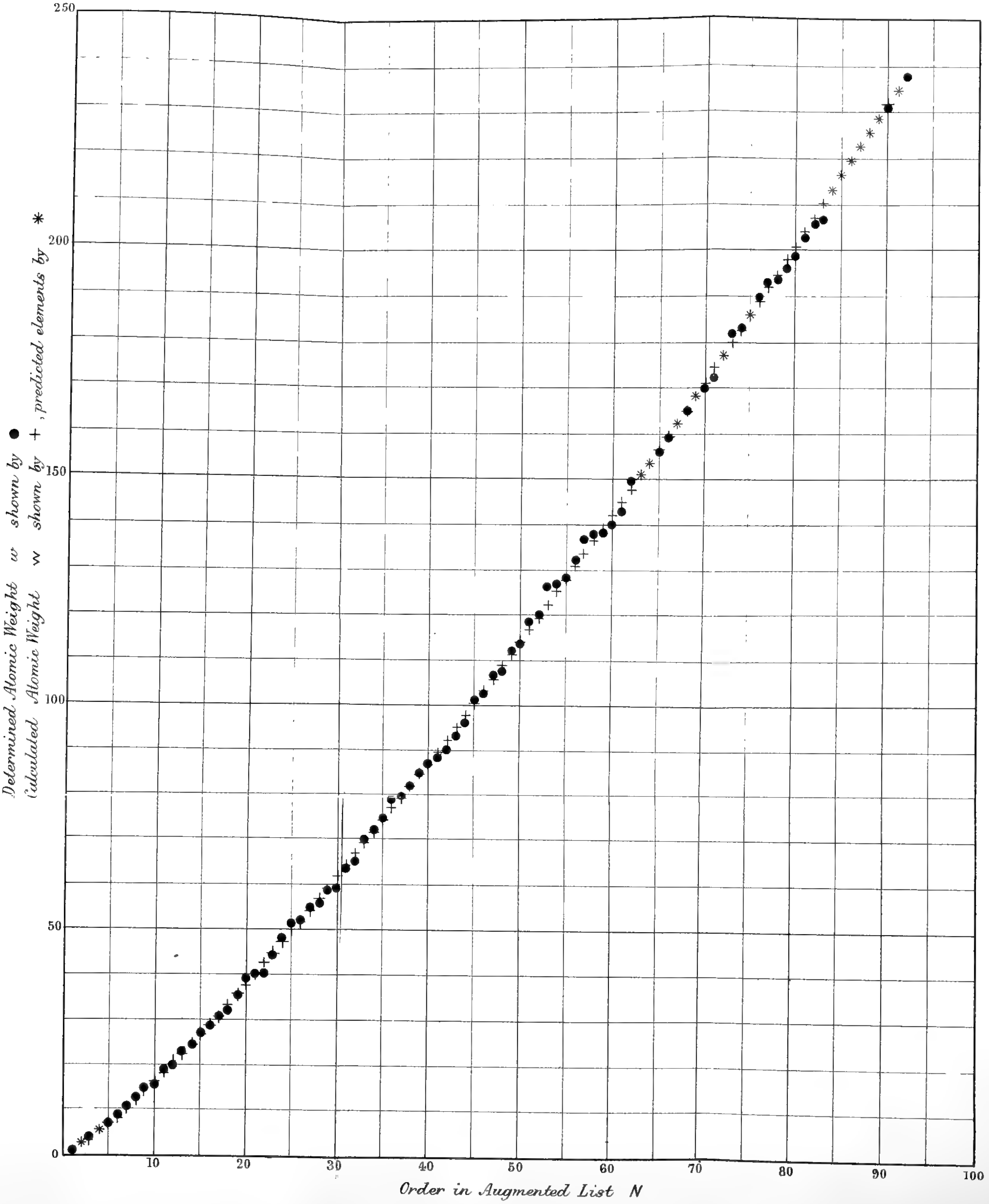
After an account of the topographical solid geology of Teesdale, the author describes the four distinct types of Drift in the area as follows:—

(*a*) A sandy reddish-brown clay, with a large number of well-scratched stones;
(*b*) A black loamy or peaty clay;
(*c*) A coarse gravelly deposit, with many waterworn and a few scratched stones;
(*d*) A stiff blue Boulder-Clay.

The first class is the most widely distributed; it occurs in elongated ridges, and is the direct product of ice-action on the rocks of the upper part of the Dale. The black loamy clay is characteristic of areas occupied by ice-dammed lakes. The third class occurs in long esker-like ridges, and is particularly plentiful in the country formerly occupied by the Stainmoor glacier. The dark-blue clay is mainly derived from Carboniferous rocks. A detailed description of the Glacial deposits, boulders, and striæ is next given; and from this the following conclusions are deduced:—Upper Teesdale was heavily glaciated by local ice from the eastern slope of the Cross Fell Range; this part of the Dale was not invaded by any other ice, and the higher peaks stood out as nunataks. At the period of maximum glaciation a number of lakes were formed, owing to the obstruction of the drainage of lateral tributary-valleys by the ice of the main glaciers. Lunedale was occupied by ice (the Stainmoor glacier) which came from the drainage-basin of the Irish Sea, joined the Teesdale glacier about Middleton-in-Teesdale, and by its thrust deflected the Teesdale ice into the Valley of the Wear. During the retreat of the ice there was a lengthened period of 'constant level,' when well-marked drainage-channels were formed, and after this the ice was removed with great rapidity. A tongue of ice flowed from Upper Teesdale by Yad Moss to the Valley of the South Tyne.

Similar evidence with regard to Weardale and the Tyne Valley is given, and the following conclusions are drawn among others:—Ice from Teesdale and the tributaries of the South Tyne occupied the valley of the latter nearly as far as Lambley, where it was joined by a large glacier which crossed the northern end of the Pennine Chain. This glacier was continuous in a northerly direction with the ice of the Southern Uplands and the glacier of the North Tyne, and, when at its maximum, deflected the last north-eastward, causing a movement in that direction along the southern flanks of the Cheviot Range. But at the beginning and end of the glaciation the ice in the Valley of the North Tyne flowed south-eastward. The southern margin of the South Tyne glacier passed across the heads of Allendale and Devil's Water into the Wear Valley; and along this margin were a series of ice-dammed lakes with a corresponding series of overflow-channels, many of which are now streamless. Weardale was mainly occupied by its own ice, but the lower part of the valley was invaded by the Tyne ice from the north and that of the Tees from the south. There were no lakes strictly connected with the last system.





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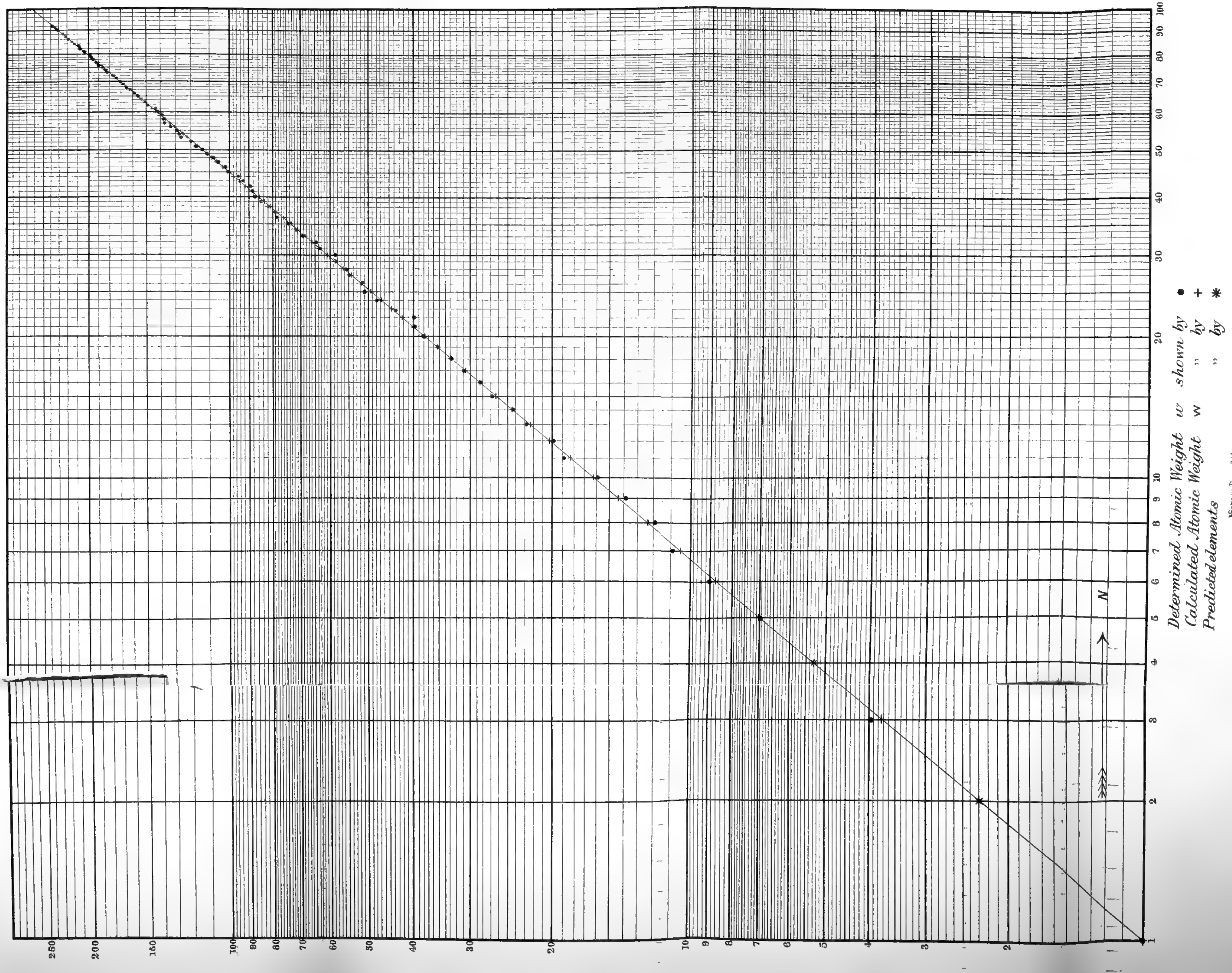
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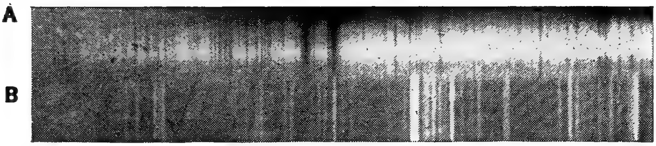


Fig. 1.

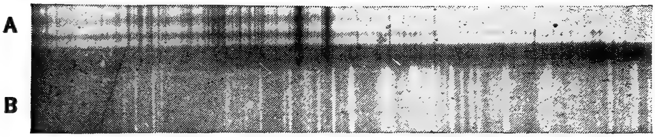


Fig. 2.

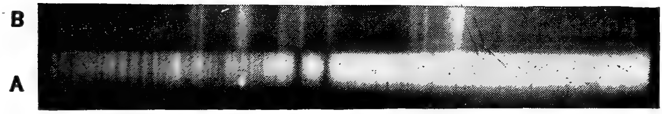


Fig. 3.

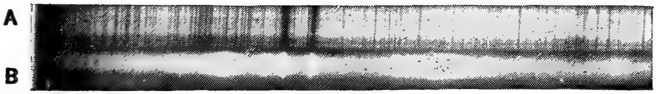


Fig. 4.

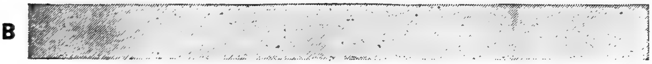


Fig. 5.

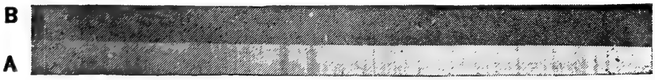


Fig. 6.

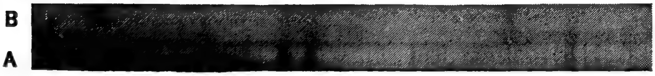
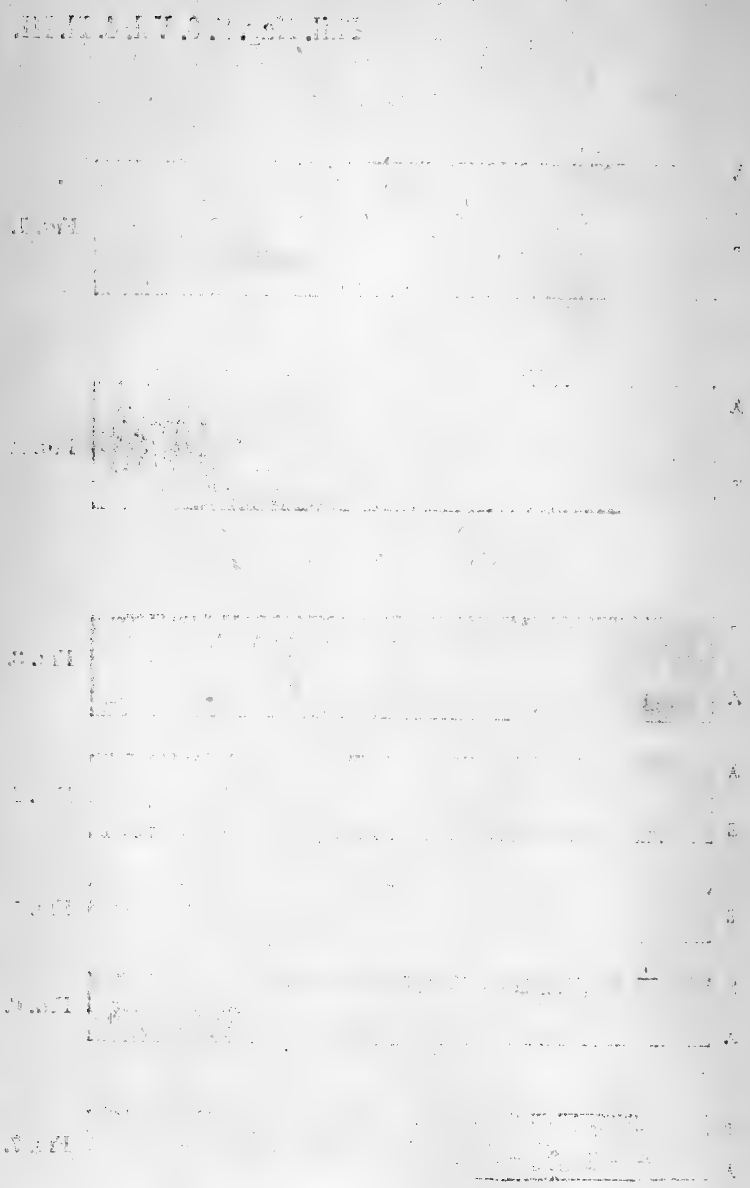


Fig. 7.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

AUGUST 1902.

XVIII. *On the Weights of Atoms**.

By Lord KELVIN, *G.C.V.O.*†

§ 23. HITHERTO in all our views we have seen nothing of absolute dimensions in molecular structure, and have been satisfied to consider the distance between neighbouring molecules in gases, or liquids, or crystals, or non-crystalline solids to be very small in comparison with the shortest wave-length of light with which we have been concerned. Even in respect to dispersion, that is to say, difference of propagational velocity for different wave-lengths, it has not been necessary for us to accept Cauchy's doctrine that the spheres of molecular action are comparable with the wave-length. We have seen that dispersion can be, and probably in fact is, truly explained by the periods of our waves of light being not infinitely great in comparison with some of the periods of molecular vibration; and, with this view, the dimensions of molecular structure might, so far as dispersion is concerned, be as small as we please to imagine them, in comparison with wave-lengths of light. Nevertheless it is exceedingly interesting and important for intelligent study of molecular structures and the dynamics of light, to have some well-founded understanding in respect to probable distances between centres of neighbouring molecules in all kinds of ponderable matter, while for the present at all

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* This is Lecture XVII. of my Baltimore Lectures, as now extended and prepared for press. For convenience of reference the sectional numbers have been retained as in the volume of Lectures.

† Communicated by the Author.

events we regard ether as utterly continuous and structureless. It may be found in some future time that ether too has a molecular structure, perhaps much finer than any structure of ponderable matter; but at present we neither see nor imagine any reason for believing ether to be other than continuous and homogeneous through infinitely small contiguous portions of space void of other matter than ether.

§ 24. The first suggestion, so far as we now know, for estimating the dimensions of molecular structure in ordinary matter was given in 1805 by Thomas Young *, as derived from his own and Laplace's substantially identical theories of capillary attraction. In this purely dynamical theory he found that the range of the attractive force of cohesion is equal to $3T/K$; where T denotes the now well-known Young's tension of the free surface of a liquid, and K denotes a multiple integral which appears in Laplace's formulas and is commonly now referred to as Laplace's K, as to the meaning of which there has been much controversy in the columns of 'Nature' and elsewhere. Lord Rayleigh in his article of 1890, "On the Theory of Surface Forces †," gives the following very interesting statement in respect to Young's estimate of molecular dimensions:—

§ 25. "One of the most remarkable features of Young's "treatise is his estimate of the range a of the attractive force "on the basis of the relation $T=\frac{1}{3}aK$. Never once have "I seen it alluded to; and it is, I believe, generally supposed "that the first attempt of the kind is not more than twenty "years old. Estimating K at 23000 atmospheres, and T at "3 grains per inch, Young finds that 'the extent of the "'cohesive force must be limited to about the 250 millionth "'of an inch [10^{-8} cm.]'; and he continues, 'nor is it very "'probable that any error in the suppositions adopted can "'possibly have so far invalidated this result as to have made "'it very many times greater or less than the truth' . . . . "Young continues:—'Within similar limits of uncertainty, "'we may obtain something like a conjectural estimate of "'the mutual distance of the particles of vapours, and even "'of the actual magnitude of the elementary atoms of liquids, "'as supposed to be nearly in contact with each other; for "'if the distance at which the force of cohesion begins is "'constant at the same temperature, and if the particles of

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[*] "On the Cohesion of Fluids," Phil. Trans. 1805; Collected Works, vol. i. p. 461.

[†] Phil. Mag. vol. xxx. 1890, p. 474.

"'steam are condensed when they approach within this "'distance, it follows that at 60° of Fahrenheit the distance "'of the particles of pure aqueous vapour is about the 250 "'millionth of an inch; and since the density of this vapour "'is about one sixty thousandth of that of water, the distance "'of the particles must be about forty times as great; "'consequently the mutual distance of the particles of water "'must be about the ten thousand millionth of an inch * "'[$\cdot025 \times 10^{-8}$ cm.]. It is true that the result of this calcu- "'lation will differ considerably according to the temperature "'of the substances compared. . . . This discordance does not "'however wholly invalidate the general tenour of the con- "'clusion . . . and on the whole it appears tolerably safe to "'conclude that, whatever errors may have affected the "'determination, the diameter or distance of the particles of "'water is between the two thousand and the ten thousand "'millionth of an inch' [between $\cdot125 \times 10^{-8}$ and $\cdot025 \times 10^{-8}$ "of a cm.]. This passage, in spite of its great interest, has "been so completely overlooked that I have ventured briefly "to quote it, although the question of the size of atoms lies "outside the scope of the present paper."

§ 26. The next suggestion, so far as I know, for estimating the dimensions of molecular structure in ordinary matter, is to be found in an extract from a letter of my own to Joule on the contact electricity of metals, published in the 'Proceedings' of the Manchester Literary and Philosophical Society †, Jan. 21, 1862, which contains the following passage:—"Zinc and copper connected by a metallic arc "attract one another from any distance. So do platinum "plates coated with oxygen and hydrogen respectively. "I can now tell the amount of the force, and calculate how "great a proportion of chemical affinity is used up electrically, "before two such discs come within 1/1000 of an inch of "one another, or any less distance down to a limit within "which molecular heterogeneousness becomes sensible. This "of course will give a definite limit for the sizes of atoms, or "rather, as I do not believe in atoms, for the dimensions of "molecular structures." The theory thus presented is somewhat more fully developed in a communication to 'Nature'

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* Young here, curiously insensible to the kinetic theory of gases, supposes the molecules of vapour of water at 60° Fahr. to be within touch (or direct mutual action) of one another; and thus arrives at a much finer-grainedness for liquid water than he would have found if he had given long enough free paths to molecules of the vapour to account for its approximate fulfilment of Boyle's law.

† Reproduced as Art. 22 of my 'Electrostatics and Magnetism.'

in March 1870, on "The Size of Atoms"*, and in a Friday evening lecture † to the Royal Institution on the same subject on February 3, 1883; but to illustrate it, information was wanted regarding the heat of combination of copper and zinc. Experiments by Professor Roberts-Austen and by Dr. A. Galt, made within the last four years, have supplied this want; and in a postscript of February 1898 to a Friday evening lecture on "Contact Electricity," which I gave at the Royal Institution on May 21, 1897, I was able to say "We cannot avoid seeing molecular structures beginning to "be perceptible at distances of the hundred-millionth of a "centimetre, and we may consider it as highly probable that "the distance from any point in a molecule of copper or zinc "to the nearest corresponding point of a neighbouring "molecule is less than one one-hundred-millionth, and greater "than one one-thousand-millionth of a centimetre"; and also to confirm amply the following definite statement which I had given in my 'Nature' article (1870) already referred to:—"Plates of zinc and copper of a three-hundred-millionth "of a centimetre thick, placed close together alternately, form "a near approximation to a chemical combination, if indeed "such thin plates could be made without splitting atoms."

§ 27. In that same article thermodynamic considerations in stretching a fluid film against surface tension led to the following result:—"The conclusion is unavoidable, that a "water-film falls off greatly in its contractile force before it "is reduced to a thickness of a two hundred-millionth of a "centimetre. It is scarcely possible, upon any conceivable "molecular theory, that there can be any considerable falling "off in the contractile force as long as there are several "molecules in the thickness. It is therefore probable that "there are not several molecules in a thickness of a two-"hundred-millionth of a centimetre of water." More detailed consideration of the work done in stretching a water-film led me in my Royal Institution Lecture of 1883 to substitute one one-hundred-millionth of a centimetre for one two-hundred-millionth in this statement. On the other hand a consideration of the large black spots which we now all know in a soap-bubble or soap-film before it bursts, and which were described in a most interesting manner by Newton ‡, gave

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* Republished as Appendix (F) in Thomson and Tait's 'Natural Philosophy, part ii. second edition.

† Republished in 'Popular Lectures and Addresses,' vol. i.

‡ Newton's 'Optics,' pp. 187, 191, Edition 1721, Second Book, Part i.: quoted in my Royal Institution Lecture, 'Pop. Lectures and Addresses,' vol. i. p. 175.

absolute demonstration that the film retains its tensile strength in the black spot "where the thickness is clearly much less "than 1/60000 of a centimetre, this being the thickness of "the dusky white" with which the black spot is bordered. And further in 1883 Reinold and Rücker's * admirable application of optical and electrical methods of measurement proved that the thickness of the black film in Plateau's "liquide glycérique" and in ordinary soap solution is between one eight-hundred-thousandth of a centimetre and one millionth of a centimetre. Thus it was certain that the soap-film has full tensile strength at a thickness of about a millionth of a centimetre, and that between one millionth and one one-hundred-millionth the tensile strength falls off enormously.

§ 28. Extremely interesting in connection with this is the investigation, carried on independently by Röntgen † and Rayleigh ‡, and published by each in 1890, of the quantity of oil spreading over water per unit area required to produce a sensible disturbance of its capillary tension. Both experimenters expressed results in terms of thickness of the film, calculated as if oil were infinitely homogeneous and therefore structureless, but with very distinct reference to the certainty that their films were molecular structures not approximately homogeneous. Rayleigh found that olive oil, spreading out rapidly all round on a previously cleaned surface of water from a little store carried by a short length of platinum wire, produced a perceptible effect on little floating fragments of camphor at places where the thickness of the oil was $10{\cdot}6 \times 10^{-8}$ cm., and no perceptible effect where the thickness was $8{\cdot}1 \times 10^{-3}$ cm. It will be highly interesting to find, if possible, other tests (optical or dynamical or electrical or chemical) for the presence of a film of oil over water, or of films of various liquids over solids such as glass or metals, demonstrating by definite effects smaller and smaller thicknesses. Röntgen, using ether instead of camphor, found analogous evidence of layers $5{\cdot}6 \times 10^{-8}$ cm. thick. It will be very interesting for example to make a thorough investigation of the electric conductance of a clean rod of white glass of highest insulating quality surrounded by an atmosphere containing measured quantities of vapour of water. When the glass is at any temperature above the dew-point of

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* "On the Limiting Thickness of Liquid Films," Roy. Soc. Proc. April 19, 1883; Phil. Trans. 1883, part ii. p. 645.

† Wied. *Ann.* vol. xli. 1890, p. 321.

‡ Proc. Roy. Soc. vol. xlvii. 1890, p. 364

the vapour, it presents, so far as we know, no optical appearance to demonstrate the pressure of condensed vapour of water upon it: but enormous differences of electric conductance, according to the density of the vapour surrounding it, prove the presence of water upon the surface of the glass, or among the interstices between its molecules, of which electric conductance is the only evidence. Rayleigh has himself expressed this view in a recent article, "Investigations on Capillarity," in the Philosophical Magazine*. From the estimates of the sizes of molecules of argon, hydrogen, oxygen, carbonic oxide, carbonic acid, ethylene (C_2H_4), and other gases, which we shall have to consider (§ 47 below), we may judge that in all probability if we had eyes microscopic enough to see atoms and molecules, we should see in those thin films of Rayleigh and Röntgen merely molecules of oil lying at greater and less distances from one another, but at no part of the film one molecule of oil lying above another or resting on others.

§ 29. A very important and interesting method of estimating the size of atoms, founded on the kinetic theory of gases, was first, so far as I know, thought of by Loschmidt† in Austria and Johnstone Stoney in Ireland. Substantially the same method occurred to myself later and was described in 'Nature,' March 1870, in an article‡ on the "Size of Atoms" already referred to, § 26 above, from which the quotations in §§ 29, 30 are taken.

"The kinetic theory of gases suggested a hundred years "ago by Daniel Bernoulli has, during the last quarter of a "century, been worked out by Herapath, Joule, Clausius, and "Maxwell to so great perfection that we now find in it "satisfactory explanations of all non-chemical" and non-electrical "properties of gases. However difficult it may be "to even imagine what kind of thing the molecule is, we "may regard it as an established truth of science that a gas "consists of moving molecules disturbed from rectilinear paths "and constant velocities by collisions or mutual influences, so "rare that the mean length of nearly rectilinear portions of "the path of each molecule is many times greater than the "average distance from the centre of each molecule to the "centre of the molecule nearest it at any time. If, for "a moment, we suppose the molecules to be hard elastic

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* Phil. Mag., Oct. 1899, p. 337.

† *Sitzungsberichte* of the Vienna Academy, Oct. 12, 1865, p. 395.

‡ Reprinted as Appendix (F) in Thomson and Tait's 'Natural Philosophy,' part. ii. p. 499.

" globes all of one size, influencing one another only through " actual contact, we have for each molecule simply a zigzag " path composed of rectilinear portions, with abrupt changes " of direction . . . . But we cannot believe that the individual " molecules of gases in general, or even of any one gas, are " hard elastic globes. Any two of the moving particles or " molecules must act upon one another somehow, so that " when they pass very near one another they shall produce " considerable deflexion of the path and change in the velocity " of each. This mutual action (called force) is different at " different distances, and must vary, according to variations " of the distance, so as to fulfil some definite law. If the " particles were hard elastic globes acting upon one another " only by contact, the law of force would be . . . zero force " when the distance from centre to centre exceeds the sum of " the radii, and infinite repulsion for any distance less than " the sum of the radii. This hypothesis, with its ' hard and " ' fast ' demarcation between no force and infinite force, " seems to require mitigation." Boscovich's theory supplies clearly the needed mitigation.

§ 30. To fix the ideas we shall still suppose the force absolutely zero when the distance between centres exceeds a definite limit, λ; but when the distance is less than λ, we shall suppose the force to begin either attractive or repulsive, and to come gradually to a repulsion of very great magnitude, with diminution of distance towards zero. Particles thus defined I call Boscovich atoms. We thus call $\frac{1}{2}\lambda$ the radius of the atom, and λ its diameter. We shall say that two atoms are in collision when the distance between their centres is less than λ. Thus " two molecules in collision will exercise " a mutual repulsion in virtue of which the distance between " their centres, after being diminished to a minimum, will " begin to increase as the molecules leave one another. " This minimum distance would be equal to the sum of the " radii, if the molecules were infinitely hard elastic spheres; " but in reality we must suppose it to be very different in " different collisions."

§ 31. The essential quality of a gas is that the straight line of uniform motion of each molecule between collisions, called the free path, is long in comparison with distances between centres during collision. In an ideal perfect gas the free path would be infinitely long in comparison with distances between centres during collision, but infinitely short in comparison with any length directly perceptible to our senses; a condition which requires the number of molecules in any perceptible volume to be exceedingly great. We shall see that in gases which at ordinary pressures and temperatures approximate most closely, in respect to compressibility, expansion by heat, and specific heats, to the ideal perfect gas, as, for example, hydrogen, oxygen, nitrogen, carbon-monoxide, the free path is probably not more than about one hundred times the distance between centres during collisions, and is little short of 10^{-5} cm. in absolute magnitude. Although these moderate proportions suffice for the well-known exceedingly close agreement with the ideal gaseous laws presented by those real gases, we shall see that large deviations from the gaseous laws are presented with condensations sufficient to reduce the free paths to two or three times the diameter of the molecule, or to annul the free paths altogether.

§ 32. It is by experimental determinations of diffusivity that the kinetic theory of gases affords its best means for estimating the sizes of atoms or molecules and the number of molecules in a cubic centimetre of gas at any stated density. Let us therefore now consider carefully the kinetic theory of these actions, and with them also, the properties of thermal conductivity and viscosity closely related to them, as first discovered and splendidly developed by Clausius and Clerk Maxwell.

§ 33. According to their beautiful theory, we have three kinds of diffusion; diffusion of molecules, diffusion of energy, and diffusion of momentum. Even in solids, such as gold and lead, Roberts-Austen has discovered molecular diffusion of gold into lead and lead into gold between two pieces of the metals when pressed together. But the rate of diffusion shown by this admirable discovery is so excessively slow that for most purposes, scientific and practical, we may disregard wandering of any molecule in any ordinary solid to places beyond direct influence of its immediate neighbours. In an elastic solid we have diffusion of momentum by wave motion, and diffusion of energy constituting the conduction of heat through it. These diffusions are effected solely by the communication of energy from molecule to molecule and are practically not helped at all by the diffusion of molecules. In liquids also, although there is thorough molecular diffusivity, it is excessively slow in comparison with the two other diffusivities, so slow that the conduction of heat and the diffusion of momentum according to viscosity are not practically helped by molecular diffusion. Thus, for example, the thermal diffusivity * of water (·002, according to J. T. Bottomley's first investigation, or about ·0015 † according to later experimenters) is several hundred times, and the diffusivity for momentum is from one to two thousand times, the diffusivity of water for common salt, and other salts such as sulphates, chlorides, bromides, and iodides.

§ 34. We may regard the two motional diffusivities of a liquid as being each almost entirely due to communication of motion from one molecule to another. This is because every molecule is always under the influence of its neighbours and has no free path. When a liquid is rarefied, either gradually as in Andrews' experiments showing the continuity of the liquid and gaseous states, or suddenly as in evaporation, the molecules become less crowded and each molecule gains more and more of freedom. When the density is so small that the straight free paths are great in comparison with the diameters of molecules, the two motional diffusivities are certainly due, one of them to carriage of energy, and the other to carriage of momentum, chiefly by the free rectilinear motion of the molecules between collisions. Interchange of energy or of momentum between two molecules during collision will undoubtedly to some degree modify the results of mere transport; and we might expect on this account the motional diffusivities to be approximately equal to, but each somewhat greater than, the molecular diffusivity. If this view were correct, it would follow that, in a homogeneous gas when the free paths are long in comparison with the diameters of molecules, the viscosity is equal to the molecular diffusivity multiplied by the density, and the thermal conductivity is equal to the molecular diffusivity multiplied by the thermal capacity per unit bulk, pressure constant: and that whatever deviation from exactness of these equalities there may be, would be in the direction of the motional diffusivities being somewhat greater than the molecular diffusivity. But alas, we shall see, § 45 below, that hitherto experiment does not confirm these conclusions: on the contrary the laminar diffusivities (or diffusivities of momentum) of the only four gases of which molecular diffusivities have been determined by experiment, instead of being greater than, or at least equal to, the density multiplied by the molecular diffusivity, are each somewhat less than three-fourths of the amount thus calculated.

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* 'Math. and Phys. Papers,' vol. iii. p. 226. For explanation regarding diffusivity and viscosity see same volume, pp. 428–435.

† See a paper by Milner and Chattock, Phil. Mag. vol. xlviii. 1899.

§ 35. I see no explanation of this deviation from what seems thoroughly correct theory. Accurate experimental determinations of viscosities, whether of gases or liquids, are easy by Graham's transpirational method. On the other hand even roughly approximate experimental determinations of thermal diffusivities are exceedingly difficult, and I believe none, on correct experimental principles, have really been made *; certainly none unvitiated by currents of the gas experimented upon, or accurate enough to give any good test of the theoretical relation between thermal and material diffusivities, expressed by the following equation, derived from the preceding verbal statement regarding the three diffusivities of a gas,

$$\theta = K\rho\frac{\mu}{\rho} = K\mu = kc\mu.$$

where θ denotes the thermal conductivity, μ the viscosity, ρ the density, $K\rho$ the thermal capacity per unit bulk pressure constant, K the thermal capacity per unit mass pressure constant, c the thermal capacity per unit mass volume constant, and k the ratio of the thermal capacity pressure constant to the thermal capacity volume constant. It is interesting to remark how nearly theoretical investigators † have come to the relation $\theta = kc\mu$; Clausius gave $\theta = \frac{5}{4}c\mu$; O. E. Meyer, $\theta = 1{\cdot}6027\,c\mu$, and Maxwell, $\theta = \frac{5}{3}\,c\mu$. Maxwell's in fact is $\theta = kc\mu$ for the case of a monatomic gas.

§ 36. To understand exactly what is meant by molecular diffusivity consider a homogeneous gas between two infinite parallel planes, GGG and RRR, distance a apart, and let it be initially given in equilibrium; that is to say, with equal numbers of molecules and equal total kinetic energies in equal volumes, and with integral of component momentum in any and every direction, null. Let N be the number of molecules per unit volume. Let every one of the molecules be marked either green or red, and whenever a red molecule strikes the plane GGG, let its marking be altered to green, and, whenever a green molecule strikes RRR, let its marking be altered to red. These markings are not to alter in the slightest

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* So far as I know, all attempts hitherto made to determine the thermal conductivities of gases have been founded on observations of rate of communication of heat between a thermometer-bulb, or a stretched metallic wire constituting an electric resistance thermometer, and the walls of the vessel enclosing it and the gas experimented upon. See Wiedemann's *Annalen* (1888), vol. xxxiv. p. 623, and 1891, vol. xliv. p. 177. For other references, see O. E. Meyer, § 107.

† See the last ten lines of O. E. Meyer's book.

degree the mass or shape or elastic quality of the molecules, and they do not disturb the equilibrium of the gas or alter the motion of any one of its particles; they are merely to give us a means of tracing ideally the history of any one molecule, or set of molecules, moving about and colliding with other molecules according to the kinetic nature of a gas.

§ 37. Whatever may have been the initial distribution of the greens and reds, it is clear that ultimately there must be a regular transition from all greens at the plane GGG and all reds at the plane RRR, according to the law

$$g=N\frac{x}{a};\ r=N\frac{a-x}{a} \quad . \quad . \quad . \quad . \quad (1),$$

where g and r denote respectively the number of green molecules and of red molecules per unit volume at distance x from the plane RRR. In this condition of statistical equilibrium, the total number of molecules crossing any intermediate parallel plane from the direction GGG towards RRR will be equal to the number crossing from RRR towards GGG in the same time; but a larger number of green molecules will cross towards RRR than towards GGG, and, by an equal difference, a larger number of red molecules will cross towards GGG than towards RRR. If we denote this difference per unit area per unit time by QN, we have for what I call the material diffusivity (called by Maxwell, "coefficient of diffusion"),

$$D=Qa \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

We may regard this equation as the definition of diffusivity. Remark that Q is of dimensions LT^{-1}, because it is a number per unit of area per unit of time (which is of dimensions $L^{-2}T^{-1}$) divided by N, a number per unit of bulk (dimensions L^{-3}). Hence the dimensions of a diffusivity are L^2T^{-1}; and practically we reckon it in square centimetres per second.

§ 38. Hitherto we have supposed the G and the R particles to be of exactly the same quality in every respect, and the diffusivity which we have denoted by D is the inter-diffusivity of the molecules of a homogeneous gas. But we may suppose G and R to be molecules of different qualities; and assemblages of G molecules and of R molecules to be two different gases. Everything described above will apply to the inter-diffusions of these two gases; except that the two differences which are equal when the red and green molecules are of the same quality are now not equal or, at all events, must not without proof be assumed to be equal. Let us therefore denote by Q_gN the excess of the number of G molecules crossing any intermediate plane towards RRR over the number crossing towards GGG, and by Q_rN the excess of the number of R molecules crossing towards GGG above that crossing towards RRR. We have now two different diffusivities of which the mean values through the whole range between the bounding planes are given by the equations

$$D_g = Q_g a\ ;\ D_r = Q_r a\ ;$$

one of them, D_g, the diffusivity of the green molecules, and the other, D_r, the diffusivity of the red molecules through the heterogeneous mixture in the circumstances explained in § 37. We must not now assume the gradients of density of the two gases to be uniform as expressed by (1) of § 37, because the homogeneousness on which these equations depend no longer exists.

§ 39. To explain all this practically*, let in the diagram the planes GGG, and RRR, be exceedingly thin plates of dry porous material such as the fine unglazed earthenware of Graham's experiments. Instead of our green and red marked molecules of the same kind, let us have two gases, which we shall call G and R, supplied in abundance at the middles of the two ends of a non-porous tube of glass or metal, and guided to flow away radially in contact with the end-plates as indicated in the diagram. If the two axial supply-streams of the two pure gases are sufficiently abundant, the spaces GGG, RRR, close to the inner sides of the porous end-plates will be occupied by the gases G and R, somewhat nearly pure. They could not be rigorously pure even if the velocities of the scouring gases on the outer sides of the porous end-plates were comparable with the molecular velocities in the gases, and if the porous plates were so thin as to have only two or three

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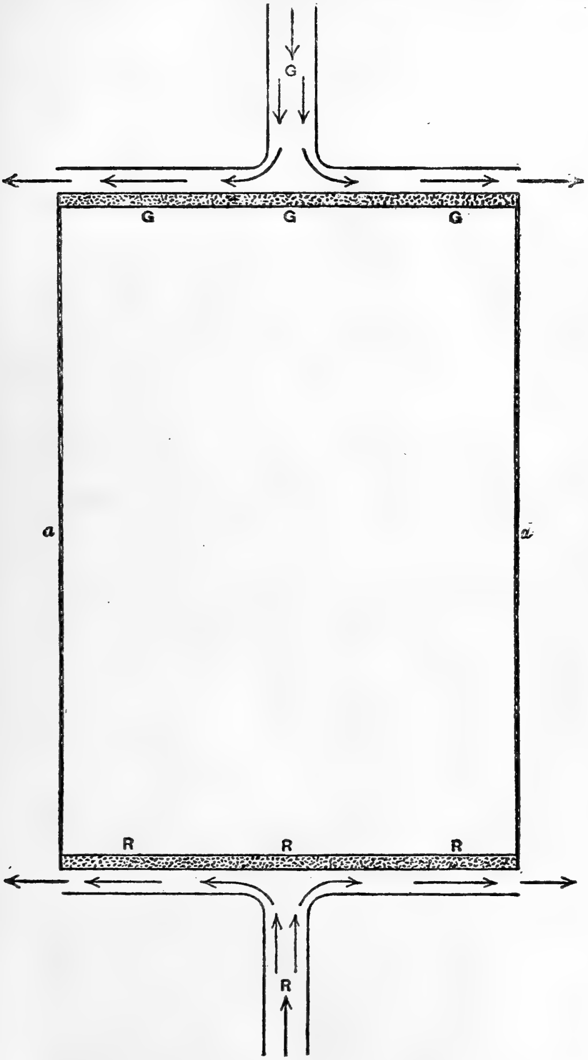
* For a practical experiment it might be necessary to allow for the difference of the proportions of the G gas on the two sides of the RRR plate and of the R gas on the two sides of the GGG plate. This would be exceedingly difficult, though not impossible, in practice. The difficulty is analogous to that of allowing for the electric resistances of the connexions at the ends of a stout bar of metal of which it is desired to measure the electric resistance. But the simple and accurate "potential method" by which the difficulty is easily and thoroughly overcome in the electric case is not available here. I do not, however, put forward the arrangement described in the text as an eligible plan for measuring the inter-diffusivity of two gases. Even if there were no other difficulty, the quantities of the two pure gases required to realize it would be impracticably great.

molecules of solid matter in their thickness. The gases in contact with the near faces of the porous plates would however, probably be somewhat approximately pure in practice with a practically realisable thinness of the porous plates, if *a*, the distance between the two plates, is not less than five or six centimetres and the scouring velocities moderately, but not impracticably, great. According to the notation of § 37,



Q_g is the quantity of the G gas entering across GGG and leaving across RRR per sec. of time per sq. cm. of area; Q_r is the quantity of the R gas entering across RRR and leaving across GGG per sec. of time per sq. cm. of area; the unit quantity of either gas being that which occupies a cubic centimetre in its entry tube. The equations

$$D_g = Q_g \frac{a}{(1-g-r)}, \quad D_r = Q_r \frac{a}{(1-g-r)},$$

where g and r are the proportions of the G gas at R and of the R gas at G, define the average diffusivities of the two gases in the circumstances in which they exist in the different parts of the length a between the end-plates. This statement is cautiously worded to avoid assuming either equal values of the diffusivities of the two gases or equality of the diffusivity of either gas throughout the space between the end-plates. So far as I know difference of diffusivity of the two gases has not been hitherto suggested by any writer on the subject. What is really given by Loschmidt's experiments, § 43 below, is the arithmetic mean of the two diffusivities D_g and D_r.

§ 40. In 1877 O. E. Meyer expressed the opinion on theoretical grounds, which seem to me perfectly valid, that the inter-diffusivity of two gases varies according to the proportions of the two gases in the mixture. In the 1899 edition of his 'Kinetic Theory of Gases'[*] he recalls attention to this view and quotes results of various experimenters, Loschmidt, Obermayer, Waitz, seeming to support it, but, as he says, not quite conclusively. On the other hand, Maxwell's theory (§ 41 below) gives inter-diffusivity as independent of the proportions of the two gases; and only a single expression for diffusivity, which seems to imply that the two diffusivities are equal according to his theory. The subject is of extreme difficulty and of extreme interest, theoretical and practical; and thorough experimental investigation is greatly to be desired.

§ 41. In 1873 Maxwell[†] gave, as a result of a theoretical investigation, the following formula which expresses the inter-diffusivity (D_{12}) of two gases independently of the proportion of the two gases in any part of the mixture: each gas being supposed to consist of spherical Boscovich atoms mutually acting according to the law, force zero for all distances exceeding the sum of the radii (denoted by s_{12}) and infinite repulsion when the distance between their centres is infinitely

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[*] Baynes' translation, p. 264.

[†] "On Loschmidt's Experiments on Diffusion in relation to the Kinetic Theory of Gases," Nature, Aug. 1873; Scientific Papers, vol. ii. pp. 343–350.

little less than this distance:

$$D_{12}=\frac{1}{2\sqrt{6\pi}}\frac{V}{N}\sqrt{\left(\frac{1}{w_1}+\frac{1}{w_2}\right)}\frac{1}{s_{12}^2}\quad .\ .\ .\ .\quad (1),$$

where w_1, w_2 are the masses of the molecules in the two gases in terms of that of hydrogen called unity; V is the square root of the mean of the squares of the velocities of the molecules in hydrogen at 0° C.; and N is the number of molecules in a cubic centimetre of a gas (the same for all gases according to Avogadro's law) at 0° C. and standard atmospheric pressure. I find the following simpler formula more convenient

$$D_{12}=\frac{1}{2\sqrt{6\pi}Ns_{12}^2}\sqrt{(V_1^2+V_2^2)}\quad .\ .\ .\quad (2),$$

where V_1^2, V_2^2 are the mean squares of the molecular velocities of the two gases at 0° C., being the values of $3\,p/\rho$ for the two gases, or three times the squares of their Newtonian velocities of sound, at that temperature. For brevity, we shall call mean molecular velocity the square root of the mean of the squares of the velocities of the molecules. The same formula is, of course, applicable to the molecular diffusivity of a single gas by taking $V_1=V_2=V$ its mean molecular velocity, and $s_{12}=s$ the diameter of its molecules; so that we have

$$D=\frac{1}{2\sqrt{3\pi}}\frac{V}{Ns^2}\quad .\ .\ .\ .\ .\ .\ .\quad (3).$$

§ 42. It is impossible by any direct experiment to find the molecular diffusivity of a single gas as we have no means of marking its particles in the manner explained in § 37 above; but Maxwell's theory gives us, in a most interesting manner, the means of calculating the diffusivity of each of three separate gases from three experiments determining the inter-diffusivities of their pairs. From the inter-diffusivity of each pair determined by experiment we find, by (2) § 41, a value of $s_{12}\sqrt{(2\sqrt{3\pi N})}$ for each pair, and we have $s_{12}=\frac{1}{2}(s_1+s_2)$*, whence

$$s_1=s_{12}+s_{13}-s_{23};\ s_2=s_{12}+s_{23}-s_{13};\ s_3=s_{13}+s_{23}-s_{12}\quad .\ (1).$$

Calculating thus the three values of $s\sqrt{(2\sqrt{3\pi N})}$, and using them in (3) § 41, we find the molecular diffusivities of the three separate gases.

§ 43. In two communications† to the Academy of Science

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* This agrees with Maxwell's equation (4), but shows his equation (6) to be incorrect.

† "Experimental-Untersuchungen über die Diffusion von Gasen ohne poröse Scheidewände," *Sitz. d. k. Akad. d. Wissensch.*, March 10 and May 12, 1870.

of Vienna in 1870, Loschmidt describes experimental determinations of the inter-diffusivities of ten pairs of gases made, by a well-devised method, with great care to secure accuracy. In each case the inter-diffusivity determined by the experiment would be, at all events, somewhat approximately the mean of the two diffusivities, § 39 above, if these are unequal. The results reduced to 0° C. and standard atmospheric pressure, and multiplied by 2·78 to reduce from Loschmidt's square metres per hour to the now usual square centimetres per second, are as follows:—

TABLE OF INTER-DIFFUSIVITIES D.

Pairs of Gases.	D in sq. cms. per sec.
H_2, O_2	·7214
H_2, CO	·6422
H_2, CO_2	·5558
O_2, CO	·1802
O_2, CO_2	·1409
CO, CO_2	·1406
CO_2, Air	·1423
CO_2, NO	·0984
CO_2, CH_4	·1587
SO_2, H_2	·4809

In the first six of these, each of the four gases H_2, O_2, CO, CO_2 occurs three times and we have four sets of three inter-diffusivities giving in all three determinations of the diffusivity of each gas as follows:—

Gases.
H_2 ......(1)
O_2 ......(2)
CO ......(3)
CO_2......(4)

Pairs of gases.	D_1.	Pairs of gases.	D_2.
(12, 13, 23)	1·31	(12, 13, 23)	·193
(12, 14, 24)	1·44	(12, 14, 24)	·190
(13, 14, 34)	1·22	(23, 24, 34)	·182
	Mean 1·32		Mean ·188
	D_3.		D_4.
(12, 13, 23)	·168	(12, 14, 24)	·107
(13, 14, 34)	·175	(13, 14, 34)	·112
(23, 24, 34)	·172	(23, 24, 34)	·110
	Mean ·172		Mean ·110

Considering the great difficulty of the experimental investigation, we may regard the agreements of the three results for each separate gas as, on the whole, very satisfactory, both in respect to the accuracy of Loschmidt's experiments and the correctness of Maxwell's theory. It certainly is a very remarkable achievement of theory and experiment to have found in the four means of the sets of three determinations, what must certainly be somewhat close approximations to the absolute values for the four gases, hydrogen, oxygen, carbon-monoxide, and carbon-dioxide, of something seemingly so much outside the range of experimental observation as the inter-diffusivity of the molecules of a separate gas.

§ 44. Maxwell, in his theoretical writings of different dates, gave two very distinct views of the inner dynamics of viscosity in a single gas, both interesting, and each, no doubt, valid. In one*, viscous action is shown as a subsidence from an "instantaneous rigidity of a gas." In the other †, viscosity is shown as a diffusion of momentum: and in p. 347 of his article quoted in § 41 above he gives as from "the theory," but without demonstration, a formula (5), which, taken in conjunction with (1), makes

$$\frac{\mu}{\rho}=D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1);$$

ρ denoting the density, μ the viscosity, and D the molecular diffusivity, of any single gas. On the other hand, in his 1866 paper he had given formulas making ‡

$$\frac{\mu}{\rho}=\cdot 648D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

§ 45. Viewing viscosity as explained by diffusion of momentum we may, it has always seemed to me (§ 34 above), regard (1) as approximately true for any gas, monatomic, diatomic, or polyatomic, provided only that the mean free

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* Trans. Roy. Soc., May 1866; Scientific Papers, vol. ii. p. 70.

† "Molecules," a lecture delivered before the Brit. Assoc. at Bradford, Scientific Papers, vol. ii. p. 378. See also O. E. Meyer's 'Kinetic Theory of Gases,' (Baynes' trans. 1899), §§ 74–76.

‡ The formula for viscosity (Sci. Papers, vol. ii. p. 68) taken with the formula for molecular diffusivity of a single gas, derived from the formula of inter-diffusivity of two gases of equal densities, gives $\frac{\mu}{\rho D}=\frac{A_1}{3A_2}$, which is equal to ·648 according to the values of A_1 and A_2 shown in p. 42 of vol. ii. Sci. Papers.

path is large in comparison with the sum of the durations of the collisions. Unfortunately for this view, however, comparisons of Loschmidt's excellent experimental determinations of diffusivity with undoubtedly accurate determinations of viscosity from Graham's original experiments on transpiration, and more recent experiments of Obermeyer and other accurate observers, show large deviations from (1) and are much more nearly in agreement with (2). Thus taking ·0000900, ·001430, ·001234, ·001974 as the standard densities of the four gases, hydrogen, oxygen, carbon-monoxide, and carbon-dioxide, and multiplying these respectively by the diffusivities from Loschmidt's experiments and Maxwell's theory, we have the following comparison with Obermeyer's viscosities at 0° C. and standard pressure, which shows the discrepance from experiment and seeming theory referred to in § 34.

Col. 1.	Col. 2.	Col. 3.	Col. 4.
Gas.	Viscosity calculated by Maxwell's theory from Loschmidt's diffusivities $\mu=\rho D$.	Viscosities according to Obermeyer.	Ratio of values in Col. 3 to those in Col. 2.
H_2	·000119	·0000822	·691
O_2	·000269	·0001873	·695
CO	·000212	·0001630	·769
CO_2	·000218	·0001414	·649

§ 46. Leaving this discrepance unexplained, and eliminating *D* between (1) of § 44 and (3) of § 41, we find as Maxwell's latest expression of the theoretical relation between number of molecules per cubic centimetre, diameter of the molecules, molecular velocity, density, and viscosity of a single gas,

$$Ns^2 = \frac{1}{2\sqrt{3\pi}}\frac{V\rho}{\mu} = \cdot 1629\,\frac{V\rho}{\mu} \quad . \quad . \quad . \quad . \quad (1).$$

The number of grammes and the number of molecules in a cubic centimetre being respectively ρ and N, ρ/N is the mass of one molecule in grammes; and therefore, denoting this by m, we have

$$m = 2\sqrt{3\pi}\,\frac{\mu}{V}s^2 = 6\cdot 140\,\frac{\mu}{V}s^2 \quad . \quad . \quad . \quad . \quad (2).$$

In these formulas, as originally investigated by Maxwell for the case of an ideal gas composed of hard spherical atoms, s is definitely the diameter of the atom, and is the same at all temperatures and densities of the gas. When we apply the formulas to diatomic or polyatomic gases, or to a monatomic gas consisting of spherical atoms whose spheres of action may overlap more or less in collision according to the severity of the impact, s may be defined as the diameter which an ideal hard spherical atom, equal in mass to the actual molecule, must have to give the same viscosity as the real gas, at any particular temperature. This being the rigorous definition of s, we may call it the proper mean shortest distance of inertial centres of the molecules in collision to give the true viscosity; a name or expression which helps us to understand the thing defined.

§ 47. For the ideal gas of hard spherical atoms, remembering that V is independent of the density and varies as $t^{\frac{1}{2}}$ (t denoting absolute temperature), § 46 (2) proves that the viscosity is independent of the density and varies approximately as $t^{\frac{1}{2}}$. Rayleigh's experimental determinations of the viscosity of argon at different temperatures show that for this monatomic gas the viscosity varies as $t^{\cdot 815}$; hence § 46 (2) shows that s^2 varies as $t^{-\cdot 315}$, and therefore s varies as $t^{-\cdot 16}$. Experimental determinations by Obermayer* of viscosities and their rates of variation with temperature for carbonic acid, ethylene, ethylene-chloride, and nitrous oxide, show that for these the viscosity is somewhat nearly in simple proportion to the absolute temperature: hence for them s^2 varies nearly as $t^{-\cdot 5}$. His determinations for the five molecularly simpler gases, air, hydrogen, carbonic oxide, nitrogen, and oxygen show that the increases of μ, and therefore of s^{-2}, with temperature are, as might be expected, considerably smaller than for the more complex of the gases on which he experimented. Taking his viscosities at 0° Cent., for carbonic acid and for the four other simple gases named above, and Rayleigh's for argon, with the known densities of all the six gases at 0° C. and standard atmospheric pressure, we have the following table (p. 196) of the values concerned in § 46 (1).

§ 48. The meaning of "s," the diameter, as defined in § 46, is simpler for the monatomic gas, argon, than for any of the others; and happily we know for argon the density,

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* Obermayer, Wien. Akad. 1876, Mar. 16th, vol. 73, p. 433.

not only in the gaseous state (·001781) but also in the liquid state (1·212)*. The latter of these is 681 times the former. Now, all things considered, it seems probable that the crowd of atoms in the liquid may be slightly less dense than an assemblage of globes of diameter s just touching one another in cubic order; but, to make no hypothesis in the first place, let qs be the distance from centre to centre of a cubic arrangement of the molecules 681 times denser than the gas at 0° C. and standard atmospheric pressure; q will be greater than unity if the liquid is less dense, or less than unity if the liquid is denser, than the cubic arrangement with molecules, regarded as spherical of diameter s, just touching. We have

Col. 1.	Col. 2.	Col. 3.	Col. 4.	Col. 5.	Col. 6.	Col. 7.	Col. 8.	Col. 9.
Gas.	ρ in terms of grammes per cubic centimetre.	μ in terms of dynes per square centimetre.	V in terms of centimetres per second.	Ns^2 in terms of (centimetre)$^{-1}$.	Hence taking $N=10^{20}$ (§ 50) we have s at 0° Cent. in terms of centimetres.	Taking $N=10^{20}$, m in terms of grammes.	Mean free paths according to Maxwell's formula † $l=\frac{1}{\sqrt{2}\,.\,\pi N s^2}$ in terms of centimetres.	Ratio of volume occupied by molecules tc whole volum $N\frac{\pi}{6}s^3$.
CO_2	·001974	·0001414	39200	89500	2·99 . 10^{-8}	19·74 . 10^{-24}	2·52 . 10^{-6}	1·340 . 10^{-}
H_2	·0000900	·0000822	184200	32900	1·81 ,,	0·90 ,,	6·84 ,,	·311 ,,
CO	·001234	·0001630	49600	61300	2·48 ,,	12·34 ,,	3·62 ,,	·799 ,,
N_2	·001257	·0001635	49000	61600	2·48 ,,	12·57 ,,	3·64 ,,	·799 ,,
O_2	·00143	·0001873	46100	57500	2·40 ,,	14·3 ,,	3·91 ,,	·724 ,,
Argon	·001781	·0002083	41400	57700	2·40 ,,	17·81 ,,	3·89 ,,	·724 ,,

$$681N = 1/(qs)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

and for argon we have by § 46 (1),

$$Ns^2 = 57700 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Eliminating s between these equations we find

$$N = 681^2\,.\,57700^3 q^6 = 8{\cdot}9\,.\,10^{19}\,.\,q^6 \quad . \quad . \quad . \quad (5).$$

If the atoms of argon were ideal hard globes, acting on one another with no force except at contact, we should almost certainly have $q \geqq 1$ (because with closer packing than that of

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* See Ramsay and Travers, Proc. R. S., Nov. 1900, p. 331.

† Maxwell's Collected Papers, vol. ii. p. 348, eqn. (7). The formula as printed in this paper contains a very embarrassing mistake, $\sqrt{2\pi}$ for $\sqrt{2}\,.\,\pi$.

cubic order it seems not possible that the assemblage could have sufficient relative mobility of its parts to give it fluidity) and therefore N would be $\geqq 8{\cdot}9 \,.\, 10^{19}$.

§ 49. For carbonic acid, hydrogen, nitrogen, and oxygen, we have experimental determinations of their densities in the solid or liquid state; and dealing with them as we have dealt with argon, irrespectively of their not being monatomic gases, we find results for the five gases as shown in the following table:

Col. 1.	Col. 2.		Col. 3.	Col. 4.	Col. 5.
Gas.	Solid or liquid density.		Ratio of solid or liquid density to standard gaseous density.	Number of molecules per cubic centimetre of gas at standard density.	Values of q (§ 48) according to $q^{-6} = {\cdot}89$ for argon (liquid compared with gas at 0° and atmospheric pressure).
				N	
CO_2	Solid..........	1·58	800	$45{\cdot}9 \,.\, 10^{19} \,.\, q^6$	·776
H_2	liquid at 17° absolute...	·090	1000	3·56 ,,	1·188
N_2	liquid	1·047	833	16·2 ,,	·923
	solid	1·400	1114	29·0 ,,	·837
O_2	liquid at its freezing pt.	1·27	888	15·0 ,,	·935
Argon	liquid	1·212	681	8·9 ,,	1·020
	solid at 86° absolute ...	1·396*	784	12·8 ,,	·960

In this table, q denotes the ratio to s of the distance from centre to centre of nearest molecules in an ideal cubic assemblage of the same density as the solid or liquid, as indicated in cols. 3 and 2.

§ 50. According to Avogadro's doctrine, the number of molecules per cubic centimetre is the same for all "perfect" gases at the same temperature and pressure; and even carbonic acid is nearly enough a "perfect gas" for our present considerations. Hence the actual values of q^6 are inversely proportional to the numbers by which they are multiplied in col. 3 of the preceding table. Now, as said in § 48, all things considered, it seems probable that for argon, liquid at density 1·212, q may be somewhat greater, but not much greater, than unity. If it were exactly unity, N would be $8{\cdot}9 \,.\, 10^{19}$; and I have chosen $q = ({\cdot}89)^{-\frac{1}{6}}$ or 1·020, to make N the round number 10^{20}. Col. 6, in the table of § 47

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* From information communicated by Prof. W. Ramsay, July 23, 1901.

above, is calculated with this value of N; but it is not improbable that the true value of N may be considerably greater than 10^{20} *.

§ 51. As compared with the value for argon, monatomic, the smaller values of q for the diatomic gases, nitrogen and oxygen, and the still smaller values for carbonic acid, triatomic, are quite as might be expected without any special consideration of law of force at different distances between atoms. It seems that the diatomic molecules of nitrogen and oxygen and still more so the triatomic molecule of carbonic acid, are effectively larger when moving freely in the gaseous condition, than when closely packed in liquid or solid assemblage. But the largeness of q for the diatomic hydrogen is not so easily explained: and is a most interesting subject for molecular speculation, though it or any other truth in nature is to be explained by a proper law of force according to the Boscovichian doctrine which we all now accept (many of us without knowing that we do so) as the fundamental hypothesis of physics and chemistry. I hope to return to this question as to hydrogen in a crystallographic appendix.

I am deeply indebted to Professor Dewar for information regarding the density of liquid hydrogen, and the densities of other gases, liquefied or frozen, which he has given me at various times within the last three years.

[To be continued.]

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* Maxwell, judging from "molecular volumes" of chemical elements estimated by Lorentz, Meyer and Kopp, unguided by what we now know of the densities of liquid oxygen and liquid hydrogen and of the liquid of the then undiscovered gas argon, estimated $N = \cdot 19 \,.\, 10^{20}$ (Maxwell's Collected Papers, vol. ii. p. 350) which is rather less than one-fifth of my estimate 10^{20}. On the same page of his paper is given a table of estimated diameters of molecules which are about 3·2 or 3·3 times larger than my estimates in col. 6 of the table in § 47. In a previous part of his paper (p. 348) Maxwell gives estimates of free paths for the same gases, from which by his formula (7), corrected as in col. 8 of my table in § 47, I find values of N ranging from $6\cdot 05 \,.\, 10^{18}$ to $6\cdot 96 \,.\, 10^{13}$ or about one-third of $\cdot 19 \,.\, 20^{20}$. His uncorrected formula $\sqrt{2\pi}$ (instead of $\sqrt{2} \,.\, \pi$) gives values of N which are $\sqrt{\pi}$ times, or 1·77 times as great, which are still far short of his final estimate. The discrepance is therefore not accounted for by the error in the formula as printed, and I see no explanation of it. The free paths as given by Maxwell are about 1·3 or 1·4 times as large as mine.

XIX. *Researches on the Blue Colour of the Sky.* Extracts from a Thesis for the Doctor of Science degree of the University of Rome. *By* GIUSEPPE ZETTWUCH[*].

DR. ZETTWUCH'S paper, from which the extracts given below are selected, is divided into three parts. In Part I. the author gives a connected historical account of the various theories which have been propounded to account for the blue colour of the sky; Part II. deals with the present state of the problem; and Part III. contains an account of the author's experimental researches on the subject. These researches were directed mainly towards the verification of Lord Rayleigh's theory, according to which the intensity of the various radiations due to particles small in comparison with wave-lengths which constitute part of the light of the sky is inversely proportional to the fourth power of the wave-length. The apparatus consisted of a Krüss spectroscope fitted with a Vierordt double-slit collimator, which enabled it to be used as a spectrophotometer.

"*Results of the Observations.*—The observations are referred to the true mean time at which they were taken, and to the distance of the sun from the zenith at the same time. Moreover, as the results calculated as explained in an earlier part of the paper varied with the hour at which the observations were taken and according to local conditions, it was thought more instructive to calculate the value of n which would satisfy an assumed law $\frac{1}{\lambda^n}$ instead of $\frac{1}{\lambda^4}$, and all the series of observations are accompanied by a brief description of the state of the sky."

The author next gives a long table of results, and then follow his

"*Conclusions.*—1. From the general nature of the observations and the table of results it is clearly evident that we have to deal with a highly variable phenomenon, as the light reflected from the sky, and coming from the same point of it, is of variable composition. All the observations, no matter what the state of the sky, show that the predominant radiations are those of short wave-length. But their proportion is not even approximately constant.

"The divergence presented by the different series of observations is not surprising, as it occurs even in the same series of observations when taken with a variable state of the sky.

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[*] Communicated by Lord Kelvin. Translated from the Italian.

It is thus easy to understand how under such circumstances no general law is capable of representing the phenomenon.

"I wish further to draw attention to the fact that even with an apparently serene and immutable sky different values have been obtained for n in the same set of observations, and the differences appear to exceed the limits of errors of observation.

"2. Considering merely the results obtained on clear days, such as those on July 11, 16, and 17, and on October 6, it is seen that the value of n increases continuously with the zenithal distance of the sun; its minimum appears to coincide with the minimum daily zenithal distance. The variations are best seen by constructing a curve whose abscissæ represent zenithal distances and ordinates the calculated values of n. [Two such curves, corresponding to July 17 and October 6, are given.]

"3. These curves show that for large zenithal distances, between 70° and 90°, n increases fairly rapidly.

"4. The composition of the zenithal light cannot be represented by a single general formula. In rare instances the results approximate to Rayleigh's law; however, it is clearly seen that, for zenithal distances in the neighbourhood of 90°, they show no great divergence from it, and tend towards it rapidly. It is further also seen at a glance that it is not at the zenith that the blue has the maximum degree of saturation; but that this always occurs at an angular distance of 90° from the sun, a result which also follows from Wild's observations.

"I have as yet been unable to take observations with a very deep-blue sky; even on the days when the highest values of n were obtained, the sky did not appear to me to be of an intense and deep blue.

"According to my results it appears that the blue of the sky at Rome is less pronounced than in England, Germany, and France.

"This conclusion may, however, be somewhat premature. It is necessary to wait for the collection of a larger number of observations, made at a more favourable time than was possible to myself—since the past year has been an exceptionally rainy one. Moreover, it becomes necessary to consider the small altitude of the observation-station above sea-level (60 m.), and its surroundings.

"5. The perturbing cause which in most cases produces variations in the composition of the diffused light is undoubtedly to be found in the clouds; which, though small in numbers and very thin, disturbed the relative intensity of the two spectra in a surprising manner as they approached the zenith; as they passed the zenith, they rendered any adjustment impossible by reason of the variations in the intensity which occurred while the observations were being taken. When the movement of the clouds took place between the horizon and the zenith, the values found for *n* from different readings of the same series of observations were markedly discordant, as is shown by the table.

"6. A curious result is obtained by comparing the values found for *n* with the relative humidity *u*. This comparison shows that to a high value of *u* there also corresponds in general a high value of *n*. This parallelism does not appear to me to have any clear significance, since *n* has a larger value in the morning than evening, and the relative humidity in the neighbourhood of the soil is then also greater than at any other time in the course of a fine day. The conclusion, therefore, cannot be regarded as reliable.

"When ultimately analysed, the results obtained do not admit of an absolutely definite conclusion that at no time does the composition of the diffuse light of the sky coming from the zenith satisfy Rayleigh's law. It must be stated that under certain circumstances, in a perfectly transparent atmosphere and at a suitable angular distance from the sun, the value corresponding to Rayleigh's law is undoubtedly continuously approached, and in certain cases surpassed.

"But if the observations on the diffuse light of the sky have in the case of every observer given variable and complex results, those on the blue light emitted laterally by a suitable turbid medium, and in particular on the artificial sky-blue of Bock, have yielded reliable and uniform results. This will be clearly seen from the values which I have calculated for *n* from the observations of Bock [referred to above]; the calculation being conducted in a manner similar to that used in my own experiments.

Blue of the Sky.	Blue of Vapour Jet.
$n_{\text{yellow}} = 2{\cdot}45$	3·99
$n_{\text{green}} = 4{\cdot}08$	3·99
$n_{\text{blue}} = 3{\cdot}69$	3·99
$n_{\text{violet}} = 4{\cdot}26$	4·00

"On the one hand, for the blue of the sky the values of *n* corresponding to the same series of observations exhibit a considerable amount of divergence; on the other, the values found for the vapour-jet are in perfect accord, and yield the value for *n* required by Rayleigh's theory.

"From the fact that, on account of the variations taking place at different times of the day and under different atmospheric conditions, and thus escaping the notice of even an expert observer, Rayleigh's formula regarding the composition of the diffuse light of the sky is not verified numerically, it does not follow that Rayleigh's theory is not to be retained as furnishing the best explanation of the colour of the atmosphere. Variations in the number and size of the particles which give rise to the turbidity of the atmosphere, and in what is still more irregular—equally invisible strata of water-vapour in the lower regions—explain sufficiently, in accordance with Rayleigh's theory, the discrepancies among the complex results which have been obtained in the strata just above the surface of the soil—strata forming 'atmospheric mud.'

"At the present time, the controversial choice lies between the colour proper of the air and Rayleigh's theory. This theory has an energetic and staunch supporter in Prof. Pernter, who, as we have seen, has several times replied to Spring, combating the latter's views. In the present state of science, Rayleigh's theory is the only one capable of explaining satisfactorily certain observed facts of special importance in connexion with the colour of the atmosphere, of which the principal one is that at an angle of 90° we get the maximum of polarization by the atmosphere, and of light reflected by a turbid medium—a fact which, according to Pernter, 'is the *experimentum crucis* with regard to the theory of the blue colour of the sky.'

"I shall conclude by quoting Pernter:—

" 'The turbid medium called air is that which gives rise to the blue colour of the sky. The weak colour proper of the air—if it exists—contributes nothing towards it.' "

XX. *The Effect of the Presence of Hydrogen on the Intensity of the Lines of the Carbon Spectrum. By* Arthur M. Herbert, *B.A.**

In a paper "On the Spectra of some of the Chemical Elements," in the Philosophical Transactions for 1864, Sir William Huggins remarks that "when carbon is subjected to the induction-spark in the presence of hydrogen the strong line in the red (a little less refrangible than the hydrogen red line corresponding to Fraunhofer's C in the solar spectrum) is not seen." This peculiarity is referred to by him once again in connexion with certain cometary spectra

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* Communicated by Prof. Arthur Schuster, F.R.S.

in a later paper (Phil. Trans. 1868), so that apparently he considered the result to be unquestioned.

As no details of the experiments were given, and in fact no further reference to this particular question could be found anywhere, the following experiments were undertaken at Professor Schuster's suggestion, whose constant advice I had the advantage of in the conduct of them.

The red line of carbon is a double one $\left(\lambda \begin{matrix} 6583 \\ 6577 \end{matrix}\right)$, the more refrangible one being the stronger. When the slightest trace of hydrogen was present along with the carbonic acid gas, in which the spark was taken in the first instance, the red line of hydrogen (λ 6562) appeared; as more and more hydrogen was admitted it was found that the carbon red line very rapidly diminished in brightness, so that with a comparatively small proportion of hydrogen in the mixture the carbon line appeared very faint.

The other principal line of carbon seen when the spark is taken in carbonic acid is a broad one in the violet (λ 4266). The behaviour of this line in the presence of hydrogen was quite different; as the relative proportion of hydrogen was increased this line merely suffered a gradual diminution in brightness (along with several oxygen lines in its neighbourhood), but it never disappeared, being quite distinct when the amount of hydrogen present was far in excess of the carbonic acid; indeed it was quite recognizable with an exceedingly small proportion of carbonic acid in the mixture, and seemed, if anything, to be more persistent than the oxygen lines near it in the violet.

Two other carbon lines were examined (λ 5640 and λ 5145); they apparently suffered merely a gradual weakening as the proportion of hydrogen was increased, but as they are much fainter than the two principal lines they were not attended to in the subsequent experiments, which were directed solely to investigating the difference in behaviour of the two strong lines. Thus it appeared from these initial experiments that the red line of carbon seen under these conditions is affected by the presence of hydrogen in a totally different way from the other carbon lines.

After these few preliminary experiments, in which Sir William Huggins's observations were generally confirmed, several series of experiments were made with mixtures of carbonic acid and hydrogen in known proportions by volume. The gases, supplied by two Kipp's apparatus, were passed into an aspirator which was graduated so that definite volumes of each gas could be admitted; from the aspirator the gas, or mixed gases, was forced through the discharge-tube, after bubbling through strong sulphuric acid to get rid of most of the moisture present. A slow current of gas was maintained so as to prevent the accumulation in the discharge-tube of any products of chemical decomposition due to the passage of the spark.

The spark passed between platinum-iridium electrodes which were about 3 mm. apart; these were fused into the bulb of the discharge-tube, the diameter of the bulb being about 4 cm. One of Apps's induction-coils was used which gave a spark of about 3 inches between its terminals in air, when four Tudor cells (2 volts each) supplied the primary current.

A small leyden-jar, the outer tinfoil area being about 280 sq. cm., was included in the circuit. In all the experiments the spark was taken at atmospheric pressure.

The following results were obtained, each set of experiments being repeated several times with similar results; the effects upon the two red lines are noted:—

A. *Spark in mixture of Carbonic Acid Gas and Hydrogen.*

(i.)	2½	parts H in	25	parts mixture	=10 per cent. H.	[Hydrogen line stronger than carbon line.]
(ii.)	5	,,	25	,,	=20 per cent. H.	[Hydrogen line strong, carbon line faint.]
(iii.)	5	,,	17	,,	=30 per cent. H. (approx.)	[Hydrogen line very strong, carbon line very faint.]
(iv.)	7	,,	14	,,	=50 per cent. H.	[Carbon line hardly distinguishable.]
(v.)	1	,,	20	,,	= 5 per cent. H.	[Lines about equally strong; hydrogen, if anything, slightly stronger.]

A second set of experiments gave the following results:—

(i.)	2½	parts H in	25	parts mixture	=10 per cent. H.	[Hydrogen line slightly the stronger.]
(ii.)	6	,,	20	,,	=30 per cent. H.	[Hydrogen line very strong, carbon line very faint.]
(iii.)	10	,,	25	,,	=40 per cent. H.	[Carbon line hardly distinguishable.]
(iv.)	12½	,,	25	,,	=50 per cent. H.	[Carbon line hardly visible.]
(v.)	½	,,	50	,,	= 1 per cent. H.	[Carbon line very strong; hydrogen line very faint, but quite distinct.]
(vi.)	1	,,	20	,,	= 5 per cent. H.	[Lines about equally strong; carbon, if anything, slightly stronger.]

The percentages given do not, of course, pretend to any great accuracy; thus there did not seem to be much difference in the effects between 40 per cent. and 50 per cent. of hydrogen.

It will be noticed that in the first set of experiments the hydrogen line appeared slightly the stronger with 5 per cent. hydrogen in the mixture, whereas in the second set the carbon line was slightly the stronger with the same percentage. This is probably due to the fact that the vessel containing sulphuric acid through which the gas bubbled was, after each experiment, left full of the mixture just used, so that this contaminated, especially at first, the next mixture. In the first case 5 per cent. hydrogen was tried immediately after 50 per cent. hydrogen, so that probably the hydrogen was somewhat in excess of 5 per cent. during most of the time. In the second case the preceding mixture contained mostly carbonic acid, so that in this case the hydrogen would probably be slightly less than 5 per cent. in the mixture during most of the time. It is likely, therefore, that with 5 per cent. hydrogen in the mixture the two lines are about equally strong.

As before stated, the violet strong line of carbon is not affected to this extent; it was examined in each experiment, and it merely suffered a natural weakening as the proportion of carbonic acid diminished, but it was quite distinct with 90 per cent. of hydrogen in the mixture, and easily visible with still more hydrogen.

Before proceeding any further the effect of nitrogen (or rather, air) was tried; this simply weakened both carbon lines more or less equally; with 80 per cent. of air, for example, both carbon lines were quite distinct and fairly bright.

The experiments were now repeated, using higher dispersion so as to separate the two red lines still further. Two prisms of dense glass were used, and a small screen was fixed in the eyepiece, which could be moved along horizontally by means of a screw-head so as to cover up the hydrogen line, and hence to eliminate all possibility of optical illusion due to contrast effects. The results were substantially the same as before; it appeared that with 50 per cent. of hydrogen the carbon red line is still faintly visible but not readily distinguishable—it seemed to flash in and out faintly rather than to be faintly persistent. At times I thought it was present, at other times I was sure it was not, so that its presence seemed to depend upon very unstable conditions.

B. *Spark in mixture of Carbon Monoxide and Hydrogen.*

(i.) 19 parts H in 38 parts mixture = 50 per cent. H. [Hydrogen line very strong; carbon line hardly visible.]
(ii.) 1 ,, 20 ,, = 5 per cent. H. [Lines about equal.]
(iii.) 9 ,, 32 ,, = 28 per cent. H. [Hydrogen line strong, carbon line faint.]
(iv.) 22 ,, 44 ,, = 50 per cent. H. [Carbon line hardly distinguishable.]

Several other series of experiments with mixtures of carbonic oxide and hydrogen were made, and the results agreed together, and with the corresponding results obtained with mixtures of carbonic acid and hydrogen so far as could be estimated by the conditions of the experiments.

C. *Spark in Coal-gas.*

The spark in coal-gas showed the red hydrogen line strongly—the other hydrogen lines were not attended to—the violet carbon line well, but the red carbon line was hardly visible. Taken as a whole, the appearance of these three lines was much the same as in a mixture of carbonic acid and hydrogen containing 50 per cent. of hydrogen.

The effect of mixing coal-gas with carbonic acid was then tried with the following results:—

(i.)	5 per cent. coal-gas in the mixture.	[Carbon red line slightly the stronger.]
(ii.)	10 ,, ,,	[Hydrogen line slightly the stronger.]
(iii.)	33 ,, ,,	[Carbon red line faint, but quite distinguishable.]
(iv.)	50 ,, ,,	[Carbon line very faint, but more readily seen than with 50 per cent. hydrogen.]

It will be seen that the red line of carbon is more persistent than in the case of corresponding mixtures of carbonic acid and hydrogen; this is only to be expected, as the coal-gas brings carbon as well as hydrogen into the mixture.

From these experiments the conclusion seems certain that though the red carbon line may not be completely destroyed by the presence of hydrogen—at any rate when the proportion of hydrogen does not exceed 50 per cent.—yet it is influenced in a way totally different from the other strong line of carbon in the violet, whereby it suffers a very rapid quenching, as the proportion of hydrogen is increased, to which the violet line is not subject.

It might, perhaps, be thought that the effects observed are due to the faint carbon line being rendered invisible owing to the strong glare of the hydrogen red line in its neighbourhood. But this possible objection is, I think, completely met by the consideration of the following facts.

Firstly, the two lines were well separated by the instrument used, and the screen fixed in the eyepiece enabled either one of them to be covered up; secondly, when a mixture containing a mere trace of hydrogen was examined the very faint persistent hydrogen line was seen without any difficulty by the side of the very bright carbon line; and, lastly, when, with 50 per cent. hydrogen, the carbon red line appeared to flash in and out, it was quite distinctly seen when it flashed in, and its flashing out was equally distinct.

It has been suggested to me by Professor Schuster that the experiments seem to show that the red and violet carbon lines must belong to different spectra of carbon, the particular molecular combination which gives rise to the red line being destroyed by the presence of hydrogen. The fact that the two interfering lines lie near each other in the spectrum is probably accidental. I have to thank Professor Schuster also for many other suggestions made during the course of the experiments.

XXI. *The Laws of Electrolysis of Alkali Salt-Vapours.* By HAROLD A. WILSON, *D.Sc., M.Sc., B.A., Clerk-Maxwell Student, Fellow of Trinity College, Cambridge*[*].

IN 1891 Arrhenius (Wied. *Ann.* xlii. p. 18, 1891) published the results of an investigation on the passage of electricity through flames containing salt-vapours, and proposed the theory that the salts dissociate into ions in the flame in the same way that salts are ionized in aqueous solutions.

Arrhenius' results were confirmed and extended in 1899 in a research initiated by Prof. A. Smithells and carried out in conjunction with Dr. H. M. Dawson and the writer (Phil. Trans. A. 1899). Since then the writer has published (Phil. Trans. A. 1899 and 1901) the results of further work which seem to show conclusively that conduction through salt-vapours is accomplished by means of ions of some kind, and is therefore to this extent at least analogous to conduction through solutions.

The experiments now to be described were undertaken with the object of determining the relative conductivities of different alkali salt-vapours at various temperatures. Many of the results obtained have been published in a paper on the "Electrical Conductivity of Air and of Salt-Vapours," read to the Royal Society this year.

In aqueous solutions a salt such as KCl dissociates into two ions +K and −Cl, so that the most likely supposition is that in salt-vapours the ions are of the same nature.

However, determinations of the velocities of the various ions in salt-vapours show that the ions generally behave as if they were much heavier than single atoms, and that the positive ion always moves more slowly than the negative ion.

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[*] Communicated by the Author. (A paper read to the British Association, Glasgow, 1901.)

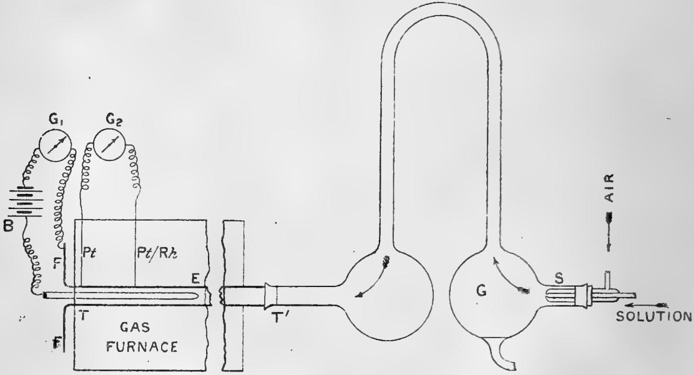
Under these circumstances it does not seem to be justifiable to make the simple supposition mentioned above, at least not without further experimental evidence in its favour.

The experiments now to be described show conclusively that above 1300° C. there is a very close analogy between salt-vapours and liquid electrolytes. In fact it is shown that Faraday's laws of electrolysis are strictly applicable to salt-vapours just as to salt-solutions.

It is probable that the gaseous ions attract neutral molecules to themselves, which accounts for their small velocities; and apparently the positive ions condense many more molecules in this way than the negative ions, so that the negative ions move much the faster. But this condensation, which appears to be peculiar to ions in the gaseous state, need not affect the number of ions produced by the dissociation of one salt molecule or the charges which they carry. It will be shown below that a salt in the state of vapour gives rise to the same number of ions carrying the same charges as a salt in an aqueous solution, in other words, the capacity of a salt-vapour for transporting electricity is the same as the capacity of an equal amount of salt in the state of solution.

The apparatus used is shown in the accompanying figure.

Fig. 1.



It consisted of a platinum tube TT′ 40 centims. long and 0·75 centim. in diameter, having a flange FF 6 centims. in diameter joined on at one end. This tube was supported horizontally in a Fletcher's tube furnace. The flange served to keep the furnace gases from the open end of the tube. An electrode EE, consisting of a platinum tube 12 centims. long and 0·3 centim. in diameter, was supported, on an adjustable insulating stand, along the axis of the tube TT′.

The end of this electrode was closed by a conical platinum cap which was about 9 centims. down the tube TT′.

At T′ the platinum tube was fitted tightly into a glass tube through which air charged with spray of a salt-solution entered. The spray was produced by a Gouy sprayer S, which projected the spray into a glass bulb G, about 8 centims. in diameter, from which the air and spray were led through an inverted U-tube, in which the coarser spray settled. The salt-solution was contained in a reservoir, the level of the surface being 30 centims. above the nozzle of the sprayer. The greater part of the spray settled in the bulb and first half of the U-tube, and was returned to the reservoir through a tube up which the liquid was forced by compressed air.

The supply of compressed air used was obtained by means of two water-injector pumps similar to the one used in the previous work on the conductivity of flames. Some of the air was allowed to escape by bubbling through mercury which served to keep its pressure nearly constant, and the rest was passed through a large carboy to smooth out small oscillations in the pressure.

The air-pressure at the sprayer was measured by means of a water manometer, and was kept constant at 50 centims. This arrangement gave enough air to work the sprayer and also the furnace, except at temperatures above about 1100° C., when the air-supply to the furnace was supplemented by oxygen from a cylinder, by means of which a temperature of 1400° C. could be obtained.

The temperature of the tube was measured by means of a platinum platinum-rhodium thermo-couple, which was simply connected through a resistance-box and commutator to an Ayrton-Mather dead-beat galvanometer G_2 of about 500 ohms resistance.

The platinum wire served to support the tube, and the Pt/Rh wire was fused on to the tube at a point on its upper surface so that the tube itself formed one of the elements of the couple. The couple was standardized by determining the galvanometer deflexion corresponding to the melting-point of K_2SO_4, which melts, according to Heycock and Neville, at 1066° C. The K_2SO_4 was introduced into the tube on a small platinum spatula, and the temperature gradually increased until it was seen to melt, and the corresponding deflexion noted. Then by maintaining the tube at a series of constant temperatures near the M.Pt. and finding at which the K_2SO_4 melted, it was possible to obtain two temperatures very near together, at one of which the K_2SO_4 melted and at the other remained solid. The mean of the two galvanometer deflexions was taken as corresponding to 1066° C., and the temperature corresponding to any other deflexion was first calculated on the assumption that the deflexion was proportional to the difference between the temperatures of the two junctions. The "platinum temperatures" thus obtained have been corrected to the centigrade scale by means of the table of corrections given by Callendar (Phil. Mag. Dec. 1899, p. 534).

This method of getting the temperature was quite sufficiently accurate for the purposes of the present investigation, for which it was useless to aim at a greater accuracy than 5 or 10 degrees, and according to Callendar the corrections are much more accurate than this near 1000°, while even at 300° the error is not more than 10°.

The Pt and Pt/Rh wires dipped into mercury cups kept in a water-bath at a known temperature from which copper wires led to the galvanometer.

The gas supplied to the furnace was kept at a constant pressure by means of a gasometer, and the air and oxygen supply-tube was provided with a water manometer, by means of which the pressure of the supply could be maintained constant, if necessary, for any length of time. In this way the tube could be maintained constantly at any desired temperature within 5° C. without difficulty.

The current through the air and salt between the electrode EE and the tube TT′ due to various potential-differences between them was measured by means of an Ayrton-Mather galvanometer G_1. The P.D. was obtained from a battery of small accumulators B, and was measured by means of a Braun's electrostatic voltmeter reading from 50 to 1500 volts. Two commutators served to reverse the current through the galvanometer only or through the whole apparatus.

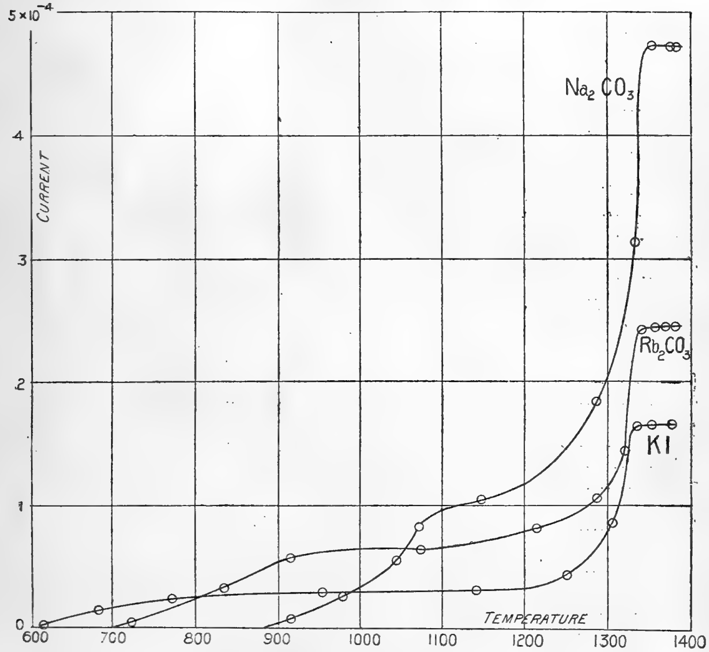
Fig. 2 shows the way in which the current with a constant E.M.F. (840 volts) varies with the temperature when solutions of one gram in a litre are sprayed.

It will be seen that in each case the current at first rises rapidly to a nearly constant value which in the case of KI is maintained over a wide range of temperature. Near 1200° the current again begins to rise rapidly, and then somewhere above 1300° suddenly attains a nearly constant value. It is this nearly constant value with which the present paper is mainly concerned. It appears to be the maximum current which the amount of salt passing through the tube can carry, for it is very little affected by increasing either the temperature or E.M.F.

Of course it is possible that with higher temperatures and

E.M.F.'s than those which it was possible to use in these experiments a further increase in the current might occur;

Fig. 2.



but in the absence of any evidence to the contrary, this approximately constant value of the current will be regarded in what follows as the maximum current which the amount of salt used can carry. This current may be conveniently termed the "saturation" current for the particular salt used.

In the following table (p. 212) the values of this maximum current observed with a number of different salt-solutions are given under the heading current (C). The electrochemical equivalent (E) and the value of the product EC are also given for each solution.

The temperature in each case was about 1350° C., and the E.M.F. used 840 volts.

It is clear from these results that the saturation current is inversely proportional to the electrochemical equivalent of the salt. The mean value $2{\cdot}67 \times 10^{-2}$ of the product EC for solutions of 1 gram in a litre is also very approximately one-tenth of the value $2{\cdot}65 \times 10^{-1}$ obtained with solutions containing 10 grams in a litre, which shows that the saturation current is proportional to the concentration of the solution sprayed.

Salt.	Grams per litre.	Electro-chemical Equivalent. E.	Current. C.	EC.
CsCl	10	168	$15{\cdot}1\times10^{-4}$	$2{\cdot}54\times10^{-1}$
RbI	10	212	13·5 „	2·86 „
KI	10	166	16·4 „	2·72 „
NaI	10	150	16·4 „	2·46 „
CsCl	1	168	1·61 „	$2{\cdot}70\times10^{-2}$
Cs_2CO_3	1	163	1·61 „	2·62 „
RbI...	1	212	1·25 „	2·65 „
RbCl	1	121	2·24 „	2·71 „
Rb_2CO_3	1	115	2·44 „	2·80 „
KI	1	166	1·66 „	2·75 „
KBr	1	119	2·13 „	2·53 „
KF	1	58	4·42 „	2·57 „
K_2CO_3	1	69	4·00 „	2·76 „
NaI............	1	150	1·82 „	2·73 „
NaBr	1	103	2·44 „	2·52 „
NaCl	1	59	4·73 „	2·79 „
Na_2CO_3	1	53	4·73 „	2·51 „
LiI...	1	134	2·03 „	2·72 „
LiBr	1	87	3·12 „	2·72 „
LiCl	1	43	6·25 „	2·69 „
Li_2CO_3	1	37	7·48 „	2·77 „

When an electrolyte is decomposed by the passage of a current, then according to Faraday's well-known laws of electrolysis the amount of salt decomposed is proportional (1) to the amount of electricity carried, and (2) to the chemical equivalent of the salt. Thus we see that the above results, which show (1) that the maximum amount of electricity transported by a salt-vapour is proportional to the amount of salt passing between the electrodes, and (2) that the saturation current with a definite amount of any salt passing between the electrodes is inversely as the chemical equivalent of the salt, amount to a proof that Faraday's laws of electrolysis apply also to the saturation current carried by a salt-vapour.

To show that the analogy between salt-vapours and electrolytes is complete, it remains to show that the factor of proportionality in the second law is the same for both. To decide this it was necessary to make an estimate of the amount of salt passing between the electrodes when a solution of known strength was being sprayed.

The amount of salt passing through the tube was determined by a modification of the method originally employed by Arrhenius to determine the amount of salt supplied by a sprayer to a flame.

A solution containing 40 grams of lithium chloride per litre was sprayed and the air and spray mixed with coal-gas and the mixture then burnt from a brass tube so as to form a Bunsen flame. A Bunsen burner was adjusted so as to give another sensibly equal and similar flame which was placed close beside the first. A weighed bead of fused LiCl was held in the axis of the second flame on a platinum-wire loop and its height in the flame adjusted till the tips of the two flames appeared equally brightly coloured.

Under these circumstances the rate of supply of salt to the two flames must be nearly the same, so that the loss of weight of the bead of LiCl measures the rate at which LiCl is supplied by the sprayer.

The loss of weight of the LiCl bead was found to be 7 milligrams in ten minutes in one experiment, and 6 milligrams in ten minutes in another experiment. This gives for the number of milligrams of salt passing through the platinum tube per second when a solution containing 1 gram in a litre is being sprayed:—

$$\frac{6{\cdot}5}{600 \times 40} = 2{\cdot}7 \times 10^{-4}.$$

For this amount of any salt we have found experimentally

$$EC = 2{\cdot}67 \times 10^{-2}.$$

Hence the amount of salt per second of electrochemical equivalent unity which would correspond to a current of 1 ampere is

$$\frac{2{\cdot}7 \times 10^{-4}}{2{\cdot}67 \times 10^{-2}} = 1{\cdot}01 \times 10^{-2} \text{ milligram.}$$

Now 1 ampere in one second liberates in electrolysis $1{\cdot}04 \times 10^{-2}$ milligram of hydrogen, so that it appears that the factor of proportionality is nearly the same for salt-vapours as for electrolytes.

It is evident that these results prove that Faraday's laws for the passage of electricity through liquids apply also to alkali salts in the state of vapour. This must be regarded as very conclusive evidence in favour of the theory that the passage of electricity through salt-vapours is a process very analogous to the electrolysis of salt-solutions.

In a dilute solution of such a salt as KCl each molecule of the salt is believed to dissociate into two ions $+\mathrm{K}$ and $-\mathrm{Cl}$. According to the corpuscular theory of electricity, if we denote a corpuscle by α, then these ions are $\mathrm{K}-\alpha$ and $\mathrm{Cl}+\alpha$.

The results described in this paper prove that the amount of electricity which can be transported by salt in the form of vapour is equal to the amount required to electrolyse the same amount of salt in a solution.

This can be explained on the corpuscular theory in two ways, the first of which involves electrolysis of the salt, whereas the second does not. According to the first the molecules of the salt-vapour dissociate into ions $\mathrm{K}-\alpha$ and $\mathrm{Cl}+\alpha$ exactly as in a solution. These ions then move to the electrodes and give up their charges, so becoming K and Cl, the K being at the negative electrode and the Cl at the positive electrode.

According to the other explanation a molecule of the salt-vapour loses a corpuscle, thus forming two ions,

$$\mathrm{KCl}-\alpha \text{ and } \alpha.$$

Then the $\mathrm{KCl}-\alpha$ goes to the negative electrode and only corpuscles go to the positive electrode, so that no separation of the two constituent atoms of the molecule takes place.

The high velocity of the negative ions compared with that of the positive ions seems to favour the latter view; but the known cases in which separation of the elements of a compound by electrolysis in gases appears to take place strongly support the view that the ions are similar to those existing in solutions.

The present experiments do not show what happens to the ions after they have discharged on the electrodes, except that apparently they do not participate any further in the transport of the electricity. It is hoped that future experiments will throw more light on this question.

These experiments were done in the Cavendish Laboratory, and I am greatly indebted to Prof. J. J. Thomson for his advice and encouragement throughout the course of the work.

XXII. *Is Rotatory Polarization influenced by the Earth's Motion?* *By* Lord RAYLEIGH, *F.R.S.*[*]

THE question whether the rotation of the plane of polarization of light propagated along the axis of a quartz crystal is affected by the direction of this axis relatively to that of the earth's orbital motion, is of considerable theoretical importance. According to an investigation of Lorentz, an effect of the first order might be looked for. Such an effect would be rendered apparent by comparing the rotations when the direction of propagation of the light is parallel to that of the earth's motion and in the reverse direction, and it might amount to $\frac{1}{10,000}$ of the whole rotation[†]. According to Larmor's theory[‡] there should be no effect of the first order.

The question was examined experimentally many years ago by Mascart[§], who came to the conclusion that the reversal of the ray left the rotation unchanged to $\frac{1}{20,000}$ part. In most of the experiments, however, the accuracy was insufficient to lend support to the above conclusion.

Dr. Larmor (*l. c.* p. 220) having expressed the opinion that it might be desirable to re-examine the question, I have made some observations which carry the test as far as can readily be done. It appears that the rotation is certainly not altered by $\frac{1}{100,000}$ part, and probably not by the half of this, when the direction of propagation of the light is altered from that of the earth's motion to the opposite direction.

I should scarcely have been able to carry the test to so satisfactory a point, had it not been for the kindness of Prof. MacGregor, who allowed me the use of certain valuable quartz crystals belonging to the Edinburgh collection of apparatus. These crystals, five in number, are all right-handed, and measure about 50 mm. each in the direction of the optical axis, to which the polished faces are approximately perpendicular. They were prepared for Prof. Tait, and were employed by him for his "rotatory polarization spectroscope of great dispersion"[||]. For the most part they are nearly free from blemish, and well adapted to the purpose in view.

In principle the experiment is very simple, scarcely differing

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[*] Communicated by the Author.

[†] This fraction representing approximately the ratio of the velocity of the earth in its orbit to the velocity of light.

[‡] 'Æther and Matter,' Cambridge, 1900.

[§] *Annales de l'Ecole Normale*, vol. i. p. 157 (1872).

[||] Nature, vol. xxii. 1880; Tait's 'Scientific Papers,' vol. i. p. 423.

from ordinary polarimetry, as, for example, in determining the rotation due to sugar and other active bodies. But the apparatus needs to be specially mounted upon a long stiff board, itself supported upon a point, so that the absolute direction of the light may be reversed without danger of even the slightest relative displacement of the parts. The board swings round in the horizontal plane; and if its length is directed from east to west, or from west to east, observations taken at noon (in June) correspond pretty accurately to propagation of the light with or against the earth's motion in its orbit. Similar comparisons at 6 o'clock are nearly independent of the earth's motion.

In another respect the experiment is peculiar on account of the enormous amount of the rotation to be dealt with. For sodium light the rotation is 22° per millimetre of quartz, so that the whole rotation is 5500°, or more than 15 complete revolutions. In the preliminary experiments, with one of the crystals only, sodium light was employed; but the observations were unsatisfactory, even although the light was resolved into a spectrum. If the flame was well supplied with salt, the extinction of the D-line by suitable adjustment of the nicol still left the *neighbouring* region of the spectrum so bright as to prejudice the observation by lessening the sensitiveness of the eye. This effect, which is quite distinct from what is ordinarily called the broadening of the D-lines and can be made still more pronounced by stimulating the flame with oxygen, does not appear to present itself in any other method of observation, and is of interest in connexion with the theory of luminous emission. A very moderate rotation of the nicol revives the D-lines sufficiently to extinguish the neighbouring spectrum, just as the first glimpse of the limb of the sun after a total eclipse extinguishes the corona *.

When all five quartzes were brought into use it was hopeless to expect good results from a soda-flame. From the fact that the rotation is as λ^{-2} we see that there must be 11° difference of rotation for the two D-lines, so that a satisfactory extinction is out of the question. For the observations about to be recorded a so-called vacuum-tube, charged with *helium*, was employed, the yellow line (situated close to the D-lines)

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* *July* 6.—A doubt having suggested itself as to whether this effect might not be due to an actual whitening of the Bunsen flame, such as sometimes occurs rather unexpectedly, the experiment was repeated with a flame of pure *hydrogen*. The region of the spectrum in the neighbourhood of D was even brighter than before. An attempt to produce an analogous effect with *lithium* was a failure, apparently in consequence of insufficient brightness of the flame.

being chosen. It was actuated by a Ruhmkorff coil and four Grove cells, situated at some distance away.

The various parts, all mounted upon the pivoted board, will now be specified in order. First came the helium tube with capillary vertical, then at a distance of 25 cm. a collimating spectacle-lens, followed by the polarizing nicol. The field of view presented by this nicol was contracted to a circular aperture 7 mm. in diameter, and was further divided into two parts by a "sugar-cell." This cell was the same as that formerly used in a cognate research on the rotation of the plane of polarization in bisulphide of carbon under magnetic force *. "The polarimeter employed is on the principle of Laurent, but according to a suggestion of Poynting (Phil. Mag. July 1880) the half-wave plate of quartz is replaced by a cell containing syrup, so arranged that the two halves of the field of view are subjected to small rotations differing by about 2°. The difference of thickness necessary is best obtained by introducing into the cell a piece of thick glass, the upper edge of which divides the field into two parts. The upper half of the field is then rotated by a thickness of syrup equal to the entire width of the cell (say $\frac{1}{2}$ inch), but in the lower half of the field part of the thickness of syrup is replaced by glass, and the rotation is correspondingly less. With a pretty strong syrup a difference of 2° may be obtained with a glass $\frac{3}{16}$ inch [inch $=2{\cdot}54$ cm.] thick. For the best results the operating boundary should be a true plane perpendicular to the face. The pieces used by me, however, were not worked, being simply cut with a diamond from thick plate glass; and there was usually no difficulty in finding a part of the edge sufficiently flat for the purpose, *i. e.* capable of exhibiting a field of view sharply divided into two parts .... By this use of sugar, half-shade polarimeters may be made of large dimensions at short notice and at very little cost. The syrup should be filtered (hot) through paper, and the cell must be closed to prevent evaporation."

The light next traversed the quartz crystals, each mounted upon a small stand admitting of adjustment in azimuth and level so as to bring the optical axis into parallelism with the line of vision. The analysing nicol, mounted near the end of the board, was distant 102 cm. from the polarizer. After passing the nicol the light traversed in succession a direct-vision prism of sufficient aperture and a small opera-glass focussed upon the sugar-cell. The aperture limiting the field had been so chosen that, as seen through the spectroscope, the

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* Phil. Trans. clxxvi. p. 343 (1885); 'Scientific Papers,' vol. ii. p. 363.

yellow image under observation was sufficiently separated from the neighbouring red and green images corresponding to other spectral lines of helium. The position of the analysing nicol was read with a vernier to tenths of a degree—an accuracy which just sufficed, and the setting could be made by causing the two halves of the field of view afforded by the sugar-cell to appear *equally* dark.

A good deal of time was spent in preliminary experiment before the best procedure was hit upon. It is necessary that the optic axes of the crystals be adjusted pretty accurately to the line of vision, and this in several cases involved considerable obliquity of the terminal faces. In these adjustments the sugar-cell and its diaphragm are best dispensed with, the crystals being turned until the rotation required to darken the field is a minimum and the darkness itself satisfactory. When the first crystal has been adjusted, a second is introduced and adjusted in its turn, and so on. In some cases a further shift of the crystal parallel to itself was required in order to remove an imperfection from the part of the field to be utilized. In the end a fairly satisfactory darkness was attained, but decidedly inferior to that obtainable when the quartzes were removed. Part of the residual light may have been due to want of adjustment; but more seemed to originate in imperfections in the quartzes themselves.

In my former experiments upon bisulphide of carbon advantage was found from a device for rocking the plane of polarization through a small constant angle*. During the observations now under discussion this effect was obtained by the introduction of a second sugar-cell, not divided into two parts or seen in focus, just in front of the analysing nicol. The cell was mounted so that it could slide horizontally in and out up to fixed stops. The thickness of the cell being sufficient, the strength of the syrup was adjusted to the desired point. Thus when the nicol was correctly set, the upper half of the field was *just distinctly* the brighter when the cell was *in*, and the lower half with *equal distinctness* the brighter when the cell was *out*, the object to be aimed at in the setting of the nicol being the *equality* of these small *differences*. For the results now to be given the setting of the nicol was by myself and the reading of the vernier was by Mr. Gordon. A second observer is a distinct advantage.

As a specimen, chosen at random, I will give in full all the

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* *Loc. cit.*; 'Scientific Papers,' vol. ii. p. 366.

readings made in the neighbourhood of noon on June 19. Five readings were taken in each position and then the board was reversed. The headings "East" and "West" indicate the end at which the observer was sitting; "East" therefore meaning that the course of the light was from West to East.

Table I.

Time $11^{h}\,30^{m}$. Temp. 17°·4. East.	Time $11^{h}\,50^{m}$. Temp. 17°·7. West.	Time $12^{h}\,5^{m}$. Temp. 17°·9. East.	Time $12^{h}\,15^{m}$. Temp. 17°·9. West.	Time $12^{h}\,25^{m}$. Temp. 17°·9. East.
45°·7	45°·4	45°·6	45°·9	46°·0
45·5	45·9	45·8	45·7	46·1
45·5	45·4	45·5	45·9	46·1
45·6	45·7	45·6	45·7	46·0
45·6	45·7	45·7	45·8	46·0
45·58	45·62	45·64	45·80	46·04

The mean of the three "Easts" is 45·75, and of the two "Wests" is 45·71; so that

$$E-W=+\cdot 04^{\circ}.$$

All these numbers are in decimals of a degree. The progressive alteration in the readings corresponds to the rise of temperature. It would appear that, as was natural, the quartzes lagged somewhat behind the thermometer.

Table II.—Noon.

Date.	E−W.
June 17	+·03°
„ 18	−·05
„ 19	+·04
Mean	+·007

Three sets of observations were taken at noon, and the results are recorded in Table II. In two other sets taken about 6^h the differences E—W were even less. The comparison of the two hours serves to check possible errors, *e. g.* of a magnetic character, such as might be caused by the magnetism of the Ruhmkorff coil, if insufficiently distant.

It seems certain that at neither hour does the difference E—W actually amount to $\frac{1}{20}$ of a degree, *i. e.* to $\frac{1}{100,000}$ of the whole rotation. In all probability the influence of the reversal is much less, if indeed it exists at all.

P.S.—Since the above observations were made, I see from the Amsterdam Proceedings (May 28, 1902) that Lorentz maintains his opinion against the criticism of Larmor. Lorentz's theoretical result contains an unknown quantity which might be adjusted so as to make the influence of the earth's motion evanescent; but for this special adjustment there appears to be no theoretical reason. I hope that the above experimental demonstration of the absence of effect, to a high order of accuracy, will be found all the more interesting.

XXIII. *Experiments on the Electro-thermal Effect in Tourmaline.* *By* R. Straubel*.

As was first shown by W. Thomson in 1877, from thermodynamical considerations, there corresponds to the pyro-electric phenomenon—*i. e.* the electrification produced by a uniform rise of temperature—a reverse effect, namely, a temperature change due to a variation of the electric state. If a pyro-electric crystal be brought into an electric field so that the lines of force run from the analogous to the antilogous pole, it will be heated; if the orientation of the crystal in the field is reversed, a cooling will take place.

On the effect so predicted by theory I carried out some experiments about two years ago, using a Brazilian tourmaline. These experiments, though only qualitative, will be briefly described in what follows.

Four plates, each 0·2 cm. thick, were cut from the tourmaline crystal in a direction normal to its axis. The plates were then arranged in two pairs, in one of which the analogous poles, and in the other the antilogous poles, were uppermost. Between the plates of each pair was introduced one set of junctions of a home-made thermopile of ten elements, made of fine wires of constantan and iron. The

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* Translated from the *Nachrichten der K. Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-physikalische Klasse.* 1902. Heft 2.

thermopile was flattened by being placed between two plane hardened steel plates which were subjected to hydraulic pressure; it was coated with a thin layer of shellac to obtain insulation between neighbouring wires. The plates and thermopile were fitted between the two horizontal plates of a condenser in a vulcanite box 1 cm. high and 12 cm. in diameter, the end-wires of the thermopile being brought out through the curved surface of the box.

With the d'Arsonval galvanometer employed, one scale-division corresponded to $1 \cdot 83 \times 10^{-8}$ ampere, or, since the resistance of the galvanometer and thermopile amounted to 8·59 ohms, to $1 \cdot 57 \times 10^{-7}$ volt. If we take the thermoelectric power of the iron-constantan combination to be 53×10^{-6} volt, then one scale-division represents a temperature-difference between the two sets of junctions of $0 \cdot 3 \times 10^{-3}$ degree C.

The small single-plate influence-machine used in the experiments had its circuit either open or closed by a cylinder of wood. Between the influence-machine and the plates of the condenser was inserted a paraffin commutator, which also allowed of the short-circuiting of the condenser. The potential-difference between the plates of the condenser—which were placed 1·35 cm. apart—was maintained as high as was consistent with steadiness; in the majority of the experiments it was estimated at some 30,000 volts; it might, however, have departed appreciably from this value, as the estimate was based on the spark-length between spheres of 2 cm. diameter, and determinations of this could only be made before and after the actual observations.

The observations were made as follows:—As soon as the electric field was established, the galvanometer gave a deflexion whose direction depended on that of the field. This deflexion reached a maximum in about half a minute, and then fell to zero in about four minutes. As soon as this happened, *i. e.* as soon as no appreciable movement of the spot of light could be noticed, the field was reversed, the maximum deflexion to the other side of zero observed, and so on. The following is such a series of observations; the scale-divisions were 2 mm. ones (p. 222).

The extreme two columns on the right are obtained by subtracting the immediately preceding zero reading from the maximum elongation.

Such a set of observations having been obtained, one or other of the two pairs of plates was reversed, so that now all the plates had their analogous poles pointing in the same direction. Under these conditions no deflexion was observable

Elongation.	Zero reading.	Elongation.	Maximum deflexion, in scale-divisions.	
	239·4			
		245		+5·6
	239·4			
235			−4·4	
	239			
		243·6		+4·6
232·7			−5·3	
	236·3			
		240·6		+4·3
	236·6			
231·7			−4·9	
	235			+5·7
		240·7		
	237		−4·9	
232·1				+4·3
	237			
		241·4		
			Mean −4·9	+4·9

on establishing a field, since the same temperature change occurred at both sets of junctions. The following set of observations was obtained immediately after the set given above:—

Elongation.	Zero reading.	Elongation.	Maximum deflexion, in scale-divisions.	
	234			
		234·4		+0·4
	233·7			
234			+0·3	
	234			
		234·2		+0·2
	234			
233·7			−0·3	
	234			
		234·5		+0·5
	234·4			
234·6			+0·2	
	234·8			
		234·8		+0·0
	234			
234			0·0	
	234·8			
		234·3		−0·5
	234·6			
235			+0·4	
			Mean +0·1	+0·1

Similar results were obtained by inclining the vulcanite box, thereby displacing the plates so that the junctions of the thermopile were no longer between the plates. This was more convenient, as it did away with the necessity of touching the plates, and it was unnecessary to wait a long time before thermal equilibrium was established.

As regards the interpretation of the observations, I should like to offer the following remarks:—There seems to me to be no doubt that we really have to deal here with the electrothermal effect sought for. In support of this view we have in the first place the regularity with which the effect changes its sign with a reversal of the field. In none of the observations has this change of sign failed to take place. Further, where no effects were to be expected, none occurred, or only insignificant and irregular ones. Lastly, the magnitudes are, for fields of approximately equal intensity, equal. Three more extended series of observations, which were comparatively free from disturbance—*i. e.* from considerable changes in the zero—gave the mean values 4·3, 4·5, and 4·1 scale-divisions (2 mm. ones).

The slow falling-off in the deflexion which takes place with a constant P.D. between the condenser-plates is evidently to be accounted for in the following way, which is also in accord with other considerations. With the establishment of an electric field there occur the temperature changes in the two pairs of plates, there being a rise of temperature in one pair and a fall in the other. The junctions begin to respond to the temperature changes in their surroundings, and the galvanometer gives a deflexion. But the electrical conduction along the tourmaline surface comes into play the instant the field is established, and by the formation of surface charges neutralizes the electrical action of the field on the tourmaline. In proportion to the amount of this action, however, the temperature-change will, of course, be reversed. The greater part of the actually occurring temperature-equalization is thus probably brought about by a decrease of electrical excitation rather than by radiation or conduction (although the metallic connexion of the two pairs of plates by the thermopile might produce a perceptible effect).

As regards the amount of the observed electric change of temperature, it may be remarked, in conclusion, that since the d'Arsonval galvanometer was damped so as to be aperiodic, it will be sufficient for the purpose in hand to multiply its deflexions by half the value of the constant given above for the degree value of a scale-division. This gives, in the example considered, a temperature change of $0{\cdot}74 \times 10^{-3}$ deg. C. for each pair of plates, a number which, so far as the order of magnitude is concerned, is in sufficiently good agreement with the value demanded by theory.

Jena, February 20, 1902.

XXIV. *A High Pressure Spark-Gap used in connexion with the Tesla Coil.* *By* F. J. Jervis-Smith, *M.A., F.R.S.**

In October 1896 I showed that an *x*-ray-photo could be produced by means of an exhausted bulb having no terminals, and in January 1897 the relationship between the position of maximum activity at the bulb and the discharge from a Tesla inductor was described. The references are p. 594, vol. liv. and p. 294, vol. lv. 'Nature.' Again returning to experiments with exhausted bulbs having no terminals, I wished to improve the Tesla inductor formerly used by me. When a spark-gap is employed in air at normal or less than normal pressure, the sparks often leap from ball to ball, not by the nearest path, but through a rather long one of curved form [the ends of the curved path often terminating in the equatorial regions of the two balls], the discharge from the secondary coil at the same time being somewhat reduced. With this before one it seemed highly probable that far better results would be obtained if the spark-gap were subjected to pressure.

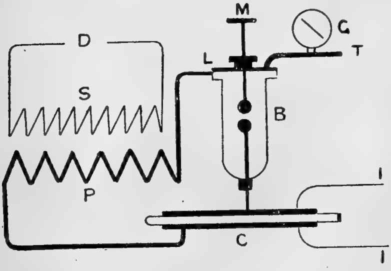

Fig. 1.

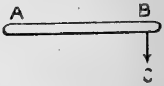

Fig. 4.

Fig. 2.

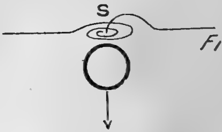

Fig. 3.

In order to put this to the test a spark-gap was constructed as shown in fig. 1, where B is a glass vessel closed with a metal lid L, provided with a stuffing-box through which a screwed rod can be moved by means of a micrometer head M; the rod carries the upper ball, the lower ball is attached to a rod which passes through a plug in the bottom of the vessel; a tube T and a pressure-gauge G are attached to the lid, and also to an air force-pump (not shown) ; one end of the primary coil P is attached to the lid and the other end to the condenser C. The two sides of the condenser are connected to the secondary of an induction-coil, by the wires I, I. S is

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* Communicated by the Author.

the secondary of the Tesla inductor, and the discharge takes place at D. In one experiment the balls in B were placed 0·3 cm. apart, and the distance between the terminals at D was 7·0 cm. The pressure was normal.

When the induction-coil was started only a luminous brush of very thin sparks crossed at D. The distances remaining the same in B and at D the pressure in B was raised to 75 cm. of mercury; shortly before this pressure was reached, a torrent of thick sparks passed at D, at the same time the sparks in B became compact and exceedingly bright. On removing the pressure the discharge returned to its former condition. Some of the effects produced by the discharge, though by no means of great length in air, were as follows:—

A vulcanite tube 0·45 cm. thick in the wall was placed in paraffin oil, a wire from one terminal being placed within it, and outside it was placed a wire from the other terminal; on putting on the current the vulcanite was instantly perforated by the discharge.

Next a piece of plate-glass 0·4 cm. thick was placed in the oil, the terminals being placed face to face on either side of it.

The instant the current was put on the glass was perforated without being cracked. On replacing the thick glass by a sheet of half the thickness, and repeating the experiment, a nearly round hole (0·2 cm. in diameter) was made by the discharge.

In each case the conductor in contact with the glass was pointed. A thick piece of plate-glass was also cut through and divided into two parts by means of the discharge. The sheet of glass was placed on a sheet of tinfoil in a flat vessel, such as a photographic developing dish, and covered to the depth of about 2 cm. with oil, the foil was connected to one terminal, then on ruling a line with the other terminal on the plate-glass as rapidly as the hand could move it, the glass was found to be cut through under along the path of the terminal.

The discharge so produced, by the addition of the high pressure spark-gap, is very effective when used to excite the Röntgen effects in exhausted tubes and bulbs having no terminals. A bulb (fig. 2) was placed in the line of discharge, the distance between B and C being so arranged that but little discharge passed before the introduction of the bulb; when the apparatus was in action a vivid green glow was produced on the lower side of the bulb at A. In my early experiments in 1896 I used bulbs of about 4 cm. in diameter. The pictures were fairly good. I now find that in order to obtain sharp definition the bulb should be small, about 1·5 cm.

in diameter, and placed about 17 cm. above the object to be x-ray-graphed. [Time of exposure two to three minutes.]

Another way (fig. 3) of exciting the effects is to place a flat spiral of wire S above the bulb, the spiral forming a portion of the secondary circuit of the Tesla inductor, provided with a spark-gap having spherical terminals.

If a long exhausted tube (fig. 4) (30 cm. long, 1·5 cm. diam.) be excited in any of the ways mentioned, at A, and a conductor be placed close to or in contact with the tube at B, then the x-ray effect will be found opposite to B, acting approximately in the direction C.

The apparatus here described is now being reconstructed so that much greater pressures may be used in the spark-gap vessel, but even with the pressures already reached the discharge from the secondary of the Tesla-coil is enormously increased.

June 18, 1902.

P.S.—I also find that the high-pressure spark-gap, when placed in the secondary of an ordinary induction-coil, increases its effects considerably when used as a generator of Hertz waves. A pressure of one atmosphere alters the length of a spark between brass balls from 2·5 cm. to 0·75 cm.

July 12, 1902.

XXV. *The Steady Temperatures of a Thin Rod.* *By* JAMES W. PECK, *M.A., Arnott and Thomson Demonstrator in Physics in the University of Glasgow* [*].

THE well-known Fourier problem referred to in this paper may be briefly stated as follows:—A homogeneous rod of small cross-section and great length has one end maintained at a constant temperature greater than that of the medium in which the rod is placed. By lateral radiation into this medium (also kept at a constant temperature) the rod acquires a steady distribution of temperature, diminishing as we go along the bar from the heated end. If V denote the temperature of the hot end (that of the medium being taken as zero), e the emissivity (*conducibilité extérieure*) of the surface of the bar, k the conductivity of the material, s the cross-section (uniform), p the perimeter, then v the temperature at the distance x from the hot end is given by [†]

$$v = \mathrm{V} \exp\left(-x\sqrt{\frac{ep}{ks}}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[*] Communicated by Prof. A. Gray, F.R.S.

[†] Fourier, *Théorie Analytique de la Chaleur*, p. 55, Darboux's edition.

An inconsistency seems to arise when this result is regarded from the point of view of the isothermal surfaces and the tubes of flow. For the above solution gives

$$x=\mathrm{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as the family of isothermal surfaces (where A is a parameter), *i. e.* a series of planes transverse to the axis of the rod. Consequently the tubes of flow are rectilinear filaments parallel to that axis. This, however, contradicts the initial hypothesis of emission of heat at the lateral surface; and it therefore becomes of interest to trace the cause of this discrepancy. The difficulty is not avoided by supposing that the lateral radiation is negligible; for it is this radiation alone that is responsible for the drop of temperature along the rod. If the lateral radiation were entirely negligible the equation

$$\frac{\partial^2 v}{\partial x^2}=\frac{ep}{ks}v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

on which the above solution is founded would fail altogether, and would in fact reduce to

$$\frac{\partial^2 v}{\partial x^2}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

giving a solution of the type

$$v=\mathrm{A}x+\mathrm{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

thus giving isothermals the same as in (2).

If, therefore, we are to retain the drop in geometrical progression as opposed to that in arithmetical progression, a further consideration is necessary.

The physical explanation is that the tubes are not rigidly parallel and rectilinear; they bend slightly away from the axis and increase in cross-section as we proceed along the rod; so that all the heat which is delivered at the hot end where they start parallel to the axis is ultimately sent out at the lateral surface. The amount of this bending is very small for good conductors, but is considerable for the badly conducting metals and for the non-metals. This will be shown below by deriving the Fourier result as a first approximation from the rigorous solution in Bessel functions; and in the same way a second approximation will be arrived at which will give as the isothermals co-axial paraboloids of revolution, and as the lines of flow logarithmic curves (the rod having a circular cross-section). With this result the difficulty mentioned above is avoided, and the position of the Fourier solution in the series from large lateral emission of heat to complete thermal insulation at the surface, is more clearly seen.

Fourier of course recognizes the approximate nature of his solution when he states that as a consequence of the small cross-section of the rod the temperature may be supposed the same over any such section. But though this is one condition of the approximation, it is also necessary to take account of the relative values of the conductivity and the emissivity. It will be shown below that for a rod of circular cross-section of radius a the criterion of the approximation is that $ea/2k$ (a quantity of zero dimensions) should be small. Fourier takes account of the a part but makes no mention of the value of e/k and its relationships to the other linear dimensions of the rod. In his time there were no exact measurements of emissivity, although a rough appreciation of the smallness of e relative to k, for metals must be evident to any observer. This consideration is probably implicitly recognized when the temperature is assumed the same over any cross-section. As to the isothermals and tubes of flow, the difficulty would only arise with the vogue of graphical methods. It seems desirable, however, to recognize the complete criteria of applicability of the solution, especially in view of the fact that Despretz[*] applied the result to rods of marble, porcelain, sandstone, firebrick, pine-wood; Helmersen[†] to quartz, granite, marble, serpentine, mica, calcspar; von Littrow[‡] to a variety of badly conducting substances; while Wiedemann and Franz[§], going to the other extreme, used lengths of rods which gave for good conductors a temperature drop in arithmetical progression. It will be shown that two important conditions must be satisfied if the result

$$v = \mathrm{V} \exp\left(-x\sqrt{\frac{ep}{ks}}\right),$$

and its well-known dependent formulæ

$$\frac{k_1}{l_1^2} = \frac{k_2}{l_2^2} = \ldots; \quad \frac{v_1 + v_3}{v_2} = 2n; \quad \frac{k_1}{k_2} = \frac{\log\left(n_2 + \sqrt{n_2^2 - 1}\right)}{\log\left(n_1 + \sqrt{n_1^2 - 1}\right)}, \quad (6)$$

are to be valid; or if the experimental methods of Ingenhausz, Despretz, Wiedemann, and Franz are to be applicable.

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[*] *Ann. de Chimie et de Physique* (1) xxxvi. p. 422 (1827); *Comptes Rendus*, xxxv. p. 540 (1852).

[†] Pogg. *Ann.* lxxxviii. p. 461 (1853).

[‡] *Wien. Sitzungsberichte* (2) lxxi. p. 99 (1875).

[§] Pogg. *Ann.* lxxxix. p. 497 (1853); *Ann. de Chimie et de Physique*, xli. p. 107 (1854).

We may arrive at these results by employing the well-known solution in Bessel functions, of the problem of the steady temperatures of an infinitely long cylinder whose base is kept at a fixed temperature, and whose surface radiates to a medium at a lower fixed temperature. This solution was given in essence by Fourier [*], although the Bessel functions were not then so named. If x denote the distance along the axis of the cylinder measured from the hot end, r the radial coordinate, then v the temperature at the point x, r, must satisfy

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right)+\frac{\partial^2 v}{\partial x^2}=0 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

at all points in the interior, and

$$k\frac{\partial v}{\partial r}+ev=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

at all points of the surface where $r=a$.

The solution satisfying (7) and (8) is

$$v=\Sigma\,A_s\exp\left(-\lambda_s x\right)J_0(\lambda_s r), \quad . \quad . \quad . \qquad (9)$$

where the constants A_s must satisfy the equation

$$V=\Sigma\,A_s J_0(\lambda_s r), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

V being the constant temperature of the hot end, and λ_s a root of the transcendental equation

$$k\left.\frac{\partial J_0(\lambda r)}{\partial r}\right|_{r=a}+eJ_0(\lambda a)=0. \quad . \quad . \qquad (11)$$

Now

$$J_0(\lambda r)=1-\frac{\lambda^2 r^2}{2^2}+\frac{\lambda^4 r^4}{2^2 4^2}-\ldots; \quad . \quad . \qquad (12)$$

and hence to approximate, suppose λr so small that second and higher powers may be neglected. The justification of this hypothesis will be shown later. We have therefore

$$J_0(\lambda r)=1\,; \qquad \left.\frac{\partial J_0(\lambda r)}{\partial r}\right|_{r=a}=-\frac{\lambda^2 a}{2}. \quad . \quad . \qquad (13)$$

The surface equation therefore becomes

$$-k\frac{\lambda^2 a}{2}+e=0,$$

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[*] *Théorie Analytique*, chapter vi.

giving

$$\lambda = \pm\sqrt{\frac{2e}{ka}}. \quad \text{(14)}$$

If we put this value of λ in the solution, take $J_0(\lambda r)=1$, and choose the negative sign so as to make v finite when x is infinite, we get

$$v = V\exp\left(-x\sqrt{\frac{2e}{ka}}\right) \quad \text{(15)}$$

as a first approximation. This result is the same as the Fourier solution.

The condition of this approximation is that λa (and hence λr) should be so small that $\frac{\lambda^2 a^2}{4}$ and higher powers may be neglected. By (14) we therefore must have $\frac{ea}{2k}$ or $\frac{a}{2} : \frac{k}{e}$ small. From this, or from a consideration of the dimensions of the quantities, it is evident that the ratio k/e has the dimensions of a length. This length has of course no connexion with the dimensions of any particular piece of the substance under consideration, but is a quantity characterizing the thermal properties of the material so far as conduction and radiation are concerned. To this length a definite physical meaning may be given which is of importance in the problem under consideration. In the first place let a large homogeneous slab of the substance have its parallel plane faces maintained permanently at unit temperature difference. Steady flow of heat will take place along straight lines perpendicular to these faces, and the temperature gradient will be uniform, *i. e.* the decreasing temperatures form, for equal space steps, an arithmetical progression. Let the quantity of heat that passes per sq. cm. per sec. across any isothermal (a plane) be noted. In the second place, let heat radiate from the surface of the substance and let definite conditions as to the coating of the surface, the pressure and nature of the surrounding medium be specified. Let also the temperature difference between the surface (supposed an isothermal if more than an elementary part is considered) and the medium be unity, *i. e.* the same as that between the faces of the slab in the first case. If now the thickness of the slab in the first case be so adjusted that the quantity of heat conducted per sq. cm. per sec. in the first case is the same as that radiated in the second case, then that particular thickness which gives this equality is the length k/e. This can be easily proved by a consideration of the elementary equations of conduction and emission, viz.:—

$$Q=k\,\frac{v_1-v_2}{a}\,.\,A\,.\,t\,;\qquad Q=e(v_3-v_4)\,.\,A\,.\,t\,;\quad . \quad (16)$$

subject to the conditions above specified. The number thus obtained is a constant for a substance of given conductivity with its radiating surface under definite conditions; and by its means is expressed the relationship of the conducting and radiating powers necessary in the present problem. This thermal constant will be called, for convenience of reference in this paper, the thermal length modulus of the substance.

If we symbolize this length by L, the Fourier result may be stated in the form

$$v=V\exp\left(-x\Big/\sqrt{\frac{La}{2}}\right),\quad . \quad . \quad . \quad . \quad (17)$$

with the following two restrictions:—(1) the semi-radius of the rod must be small in comparison with the thermal length modulus; (2) the geometric mean of these two lengths must be small in comparison with the length of the rod. The first restriction is the condition of the approximation from the rigorous solution for the cylinder referred to in equation (9) above. The second is evident if we consider that the practical realization of the infinitely long bar of the problem is that the radiation at the cold end should be a negligible quantity.

The following table gives approximate values of the thermal length modulus, in centimetres, for various substances. Two values are given in each case, corresponding to the extreme

Substance.	Conductivity.	Thermal Length Modulus.	
Silver	1·09	3630	5450
Copper	·98	3270	4900
Zinc	·30	1000	1500
Brass	·26	870	1300
Iron	·15	500	750
German silver	·11	370	550
Lead	·083	280	415
Antimony	·042	140	210
Rose's Metal	·038	130	190
Wood's Metal	·027	90	135
Bismuth	·018	60	90
Granite	·007	23	35
Marble	·005	17	25
Oak	·004	13	20
Glass	·002	7	10
Paraffin	·0006	2	3
Sulphur	·0004	1	2

values of the emissivity 0·0003 and 0·0002 respectively. The temperature difference of radiating surface and medium is here supposed not to exceed a few degrees, so that the Newtonian law of cooling is applicable.

Thus for any substance to which it is proposed to apply the Fourier solution there are four lengths to be taken account of, viz. the semiradius $(a/2)$, the thermal length modulus (L), the geometric mean of these two, and the length of the bar (l). In experiments on a series of these substances a proper proportioning of the bars so as to give the ratios $a/2 : \mathrm{L}$, and $\sqrt{a\mathrm{L}/2} : l$, the same for all will give the same degree of approximation in all the cases. Of course it is to be noted that the equations (6) above would not now be applicable, inasmuch as they assume equality of radius of the bars under comparison. But the modified forms are easily arrived at and are not much more complicated.

The next point is the numerical values which should be assigned to these two characteristic ratios. According to Lord Kelvin (*Encyc. Britann.* Article "Heat," § 78), for an iron bar the Fourier solution may be applied with safety for all radii up to 5 cms. Beyond this the radial temperature-gradient would become perceptible, and therefore the solution inapplicable. Taking this as a basis, the characteristic fraction $a/2 : \mathrm{L}$ is 1/224. With the refined thermoelectric measure of temperature now available, this value should certainly not be exceeded. As to the second ratio a value of 1/5 is sufficient; for if the length of the rod is five times the value of $\sqrt{\mathrm{L}a/2}$, the ratio of the cold end temperature to the hot end temperature is 1/148, and therefore the end radiation is negligible for all ordinary experimental methods of heating.

It will be seen from the above table that the first criterion is satisfied for most of the metals for bars say up to 5 cms. in radius, though for the metals of inferior conducting power the point would become of importance with refined measure of temperature. It is moreover impossible to diminish the radii of the bars in the same proportion as their thermal length moduli, so that the error becomes increasingly great as we descend the list, and when we come to the non-metals is sufficiently large to vitiate the method altogether. For example, Despretz[*], in the account of his experiments, states that the law of the drop of temperature in geometrical progression is not well satisfied for lead and the inferior metals. He used square bars of edge 2·4 cms., and blackened or varnished the surfaces; so that for bismuth, say (assuming

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[*] *Ann. de Chimie et de Physique,* t. xxxvi. p. 422 (1827).

that some characteristic fraction of about the same order of magnitude holds for a square bar), we have the first ratio about 1/100. Despretz also employed the method to determine the conductivity of marble, porcelain, and other nonconductors, but got completely discordant results. The fraction $(v_1+v_3)/v_2$, which should be constant for the same bar, varied from 10·83 to 3·87 for marble. From the table we see that the characteristic ratio for marble is for the size of bar employed by Despretz about 1/30, a value much too large for the solution to be applicable.

The experiments of Wiedemann and Franz* illustrate the need for the second criterion. They used much thinner bars (0·4 to 0·6 cm. in diameter), and the observations were confined to metals only, so that for both these reasons the first condition is satisfied. But no attempt seems to have been made to choose appropriate lengths for the different substances. All the bars were made 50 cms. long, so that the second condition is not satisfied. In the account of the experiments they state that the expression $(v_1+v_3)/v_2$ does not, for the highly conducting substances, vary appreciably from 2, and that therefore the values of the conductivity for these substances are not very reliable. This value 2 implies that the curve of temperatures is not logarithmic but rectilinear, the arithmetical progression has taken the place of the geometrical progression ; in other words, the lateral radiation is non-effective, and the end radiation is effective in producing the temperature drop, so that the conditions of the problem are not satisfied. If we work out for the length employed (50 cms.) and for the case of copper (taking the larger value of the thermal length modulus since in these experiments the bars were plated) we find the characteristic fraction $\sqrt{\frac{La}{2}} : l$ to be about 1/2, *i. e.* the condition is not satisfied. The same holds true in a worse degree for the silver bars employed in these experiments.

Of course this method is not now regarded as satisfactory except for the highly conducting substances, and in several places † we find it stated that the conductivity should be large and the cross-section of the bar small. But so far as I can find these two relationships of the four lengths are not given. To say that k is to be large and a small gives an approach to the conditions ; but to get an exact idea of the

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* *Ann. de Chimie et de Physique*, t. xli. p. 107 (1854).

† Kelvin, Article "Heat," in *Encyc. Britann.* § 78 ; Tait, Text-book on Heat, p. 213.

approximation it is necessary to have a comparison of quantities of similar dimensions. This is done here by expressing the k, e relationship in the form of a length, and for a series of rods we have thus a method of proportioning the dimensions so as to get results of the same order of exactitude in all the cases.

Since the Fourier solution begins to be inexact when we get down the list say as far as bismuth (on account of the impossibility of thinning down the bars to the proper size) a second approximation becomes desirable. It may be arrived at as follows: taking one additional term in the values of $J_0(\lambda r)$ and $\frac{\partial J(\lambda r)}{\partial r}$, we have

$$J_0(\lambda r) = 1 - \frac{\lambda^2 r^2}{4}, \qquad (18)$$

$$\frac{\partial J_0(\lambda r)}{\partial r} = -\frac{\lambda^2 r}{2} + \frac{\lambda^4 r^3}{16}, \qquad (19)$$

The surface equation (8) therefore becomes

$$ka^3\lambda^4 - 4a(2k + ea)\lambda^2 + 16e = 0,$$

or

$$\lambda^2 = \frac{2(2k + ea) \pm 2\sqrt{4k^2 + e^2a^2}}{ka^2},$$

$$= \frac{4k + 2ea \pm \left(4k + \frac{e^2a^2}{2k}\right)}{ka^2}.$$

Replacing $\frac{k}{e}$ by L we have, after some reductions, the two values for λ^2.

$$\frac{16L^2 + 4aL + a^2}{2a^2L^2}, \quad \frac{4aL - a^2}{2a^2L^2}. \qquad (20)$$

Denoting these by λ_1^2, λ_2^2, we have as solution

$$v = A \exp(-\lambda_1 x)\left(1 - \frac{\lambda_1^2 r^2}{4}\right) + B \exp(-\lambda_2 x)\left(1 - \frac{\lambda_2^2 r^2}{4}\right) \qquad (21)$$

To determine the constants A and B we have

$$V = A\left(1 - \frac{\lambda_1^2 r^2}{4}\right) + B\left(1 - \frac{\lambda_2^2 r^2}{4}\right),$$

and, therefore (since this must hold for all values of r when x is zero)

$$A + B = V, \qquad A\lambda_1^2 + B\lambda_2^2 = 0.$$

These give

$$A=-\frac{\lambda_2^2 V}{\lambda_1^2-\lambda_2^2},\qquad B=\frac{\lambda_1^2 V}{\lambda_1^2-\lambda_2^2}, \quad . \quad . \quad (22)$$

and the complete solution on this second approximation is therefore

$$v=\frac{V}{\lambda_1^2-\lambda_2^2}\left[\lambda_1^2 \exp\,(-\lambda_2 x)\left(1-\frac{\lambda_2^2 r^2}{4}\right)\right.$$
$$\left.-\lambda_2^2 \exp(-\lambda_1 x)\left(1-\frac{\lambda_1^2 r^2}{4}\right)\right]. \quad . \quad (23)$$

For an axial point at distance x

$$v=\frac{V}{\lambda_1^2-\lambda_2^2}\left[\lambda_1^2 \exp(-\lambda_2 x)-\lambda_2^2 \exp(-\lambda_1 x)\right]. \quad . \quad (24)$$

Numerical calculation will show that in most cases $\lambda_2^2 \exp\,(-\lambda_1 x)$ is negligible in comparison with $\lambda_1^2 \exp\,(-\lambda_2 x)$ unless x be small. The following table of values is cited in illustration for the case of bismuth bars of two different radii. L is taken as 60 cms. For substances for which L is greater or a is smaller, the relative magnitude of the two expressions is still smaller.

	x.	$\lambda_1^2 \exp\,(-\lambda_2 x)$.	$\lambda_2^2 \exp\,(-\lambda_1 x)$.
L=60......... $a=4$ .... $\lambda_1^2=0{\cdot}5085$. $\lambda_2^2=0{\cdot}0082$. $\lambda_1=0{\cdot}7131$... $\lambda_2=0{\cdot}09055$.	1	0·4645	0·0040
	5	0·3233	0·00023
	10	0·2056	0·000007
	20	0·0832	0·000000005
L=60......... $a=1$ .... $\lambda_1^2=8{\cdot}0335$. $\lambda_2^2=0{\cdot}0332$. $\lambda_1=2{\cdot}8344$... $\lambda_2=0{\cdot}1822$...	1	6·695	0·0019
	5	3·231	0·00000002
	10	1·299	$0{\cdot}0_{13}2$
	20	0·210	$0{\cdot}0_{26}8$

All lengths are expressed in centimetres.

The result (23) may therefore be taken

$$v=\frac{V}{\lambda_1^2-\lambda_2^2}\left[\lambda_1^2 \exp\,(-\lambda_2 x)\left(1-\frac{\lambda_2^2 r^2}{4}\right)\right]. \quad . \quad (25)$$

The family of isothermal surfaces will therefore be given by

$$-\lambda_2 x+\log\left(1-\frac{\lambda_2^2 r^2}{4}\right)=\text{a parameter},$$

or

$$r^2=-\frac{4}{\lambda_2}x+c, \qquad (26)$$

where c is a parameter depending upon the temperature of the isothermal considered. We have, therefore, a family of similar coaxial paraboloids of revolution. Their concavities are towards the hot end, their common axis is the axis of the cylindrical rod, and the distance from focus to vertex (AS) is for each $\frac{1}{\lambda_2}$.

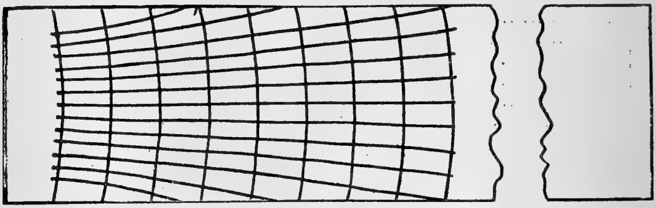
This constant of the family, AS or $\frac{1}{\lambda_2}$, has by (20) the value

$$\frac{a\mathrm{L}\sqrt{2}}{\sqrt{4a\mathrm{L}-a^2}},$$

or

$$\sqrt{\frac{a\mathrm{L}}{2}}\left\{1+\frac{a}{8\mathrm{L}}\right\}. \qquad (27)$$

In the diagram these paraboloidal surfaces are shown to scale for the case of a bismuth rod of 4 cms. radius. Close to the origin this form is deviated from because there $\lambda_2^2\epsilon^{-\lambda_1 x}$ becomes comparable with $\lambda_1^2\epsilon^{-\lambda_2 x}$, and at the origin we have the isothermal surface becoming, of course, a plane. The greater L is for a series of bars of substances under similar thermal conditions the greater is the value of the constant AS, and therefore the paraboloids approach more nearly to the planes of the first approximation.



$\frac{a}{2}=2$, L=60, AS $\left\{\sqrt{\frac{\mathrm{L}a}{2}}\left(1+\frac{a}{8\mathrm{L}}\right)\right\}=11$. $l=50$.

Isothermals $y^2=-44x+\mathrm{C}$.

Lines of Flow $y=\mathrm{A}\epsilon^{x/22}$.

In this second approximation the four characteristic lengths are the semi-radius ($a/2$), the thermal length modulus (L), the distance from focus to vertex of the paraboloidal surface

$\left(\text{AS or } \frac{1}{\lambda_2}\right)$, and the length of the bar l. Similar statements as to their ratios must hold as in the first approximation.

The lines of flow (shown in the diagram) are given by the conjugate family of logarithmic curves

$$y = \text{A} \exp(\lambda_2 x/2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where A is a parameter.

The following table gives numerical values for the temperatures at the axis and at the surface for bismuth rods of radii 4 cms. and 1 cm. respectively. For calculation the formula

$$v = \frac{\text{V}}{\lambda_1^2 - \lambda_2^2}\left[\lambda_1^2 \exp(-\lambda_2 x)\left(1 - \frac{\lambda_2^2 r^2}{4}\right)\right]$$

is employed, and the results of the preceding table may be used. It will be seen that even for the rod of smaller radius the difference between the surface and axial values is quite appreciable, although the curvature of the isothermals would not show in a diagram of the same scale as that given for the larger radius. The rod is supposed to have its hot end kept at 100°.

	x.	Axial value.	Fourier value.	Surface value.
L=60…… a=4 …… V=100 …	1	92·8	91·3	89·8
	5	64·6	63·4	62·5
	10	41·1	40·1	39·8
	20	16·6	16·1	16·1
L=60…… a=1 …… V=100 …	1	83·7	83·3	83·0
	5	40·4	40·1	40·0
	10	16·2	16·1	16·1
	20	2·6	2·6	2·6

The only other conductivity measurement of interest in this connexion (beyond these of Despretz and Wiedemann and Franz) is that of Ångström; for in the Forbes and Tait method, though bars are used, yet the calculation goes direct to the fundamental definitions, and does not employ the Fourier formula, while in the Berget method and several others radiation is avoided altogether. In the periodic method of Ångström the effect of radiation is minimized by (1) using bright bars, (2) by making the period of the end variation small, (3) by measuring axial temperatures of a fairly thick rod. The radiation can be made negligible while the essence of the method is not affected. In the class of problems here considered, on the other hand, if we diminish the radiation beyond a certain point we nullify the thermal equation altogether, and get a problem requiring a different treatment. The essential point is that the radiation should be small, but not so small as to be ineffective.

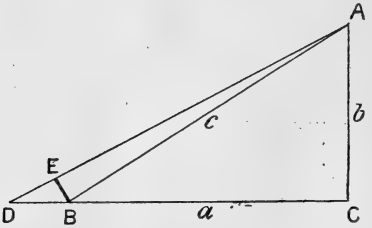
I have to acknowledge with pleasure kind suggestions and criticisms from Professor Gray in the preparation of this paper.

Glasgow University, May 8th, 1902.

XXVI. *On a Method of mechanically obtaining θ from the Hyperbolic Trigonometrical Functions of θ.* *By* T. H. Blakesley, *M.A.*, *M.Inst. C.E.*[*]

LET A B C be a triangle having a right angle at C; and let *a*, *b*, *c* be the sides opposite the angles A, B, C. Let *b* be constant.

Fig. 1.



The point B is supposed to travel from the point C, and therefore *a* is the independent variable. D is a point in this line of motion infinitesimally near to B, and B E is a perpendicular from B upon the line A D.

Then it is clear that if θ is such a quantity that

$a = b \text{ shin } \theta$, it will also be true that

$c = b \cosh \theta$, because

$c^2 - a^2 = b^2$.

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[*] Communicated by the Author.

Also $\mathrm{DB}=\delta a=b\,.\,\delta\,\mathrm{shin}\,\theta=b\,.\,\frac{d\,\mathrm{shin}\,\theta}{d\theta}\,.\,\delta\theta\,.\,=b\cosh\theta\,.\,\delta\theta$;

and $\quad\mathrm{ED}=\delta c=b\,.\,\delta\cosh\theta=b\,.\,\frac{d\cosh\theta}{d\theta}\,.\,\delta\theta=b\,\mathrm{shin}\,\theta\,.\,\delta\theta.$

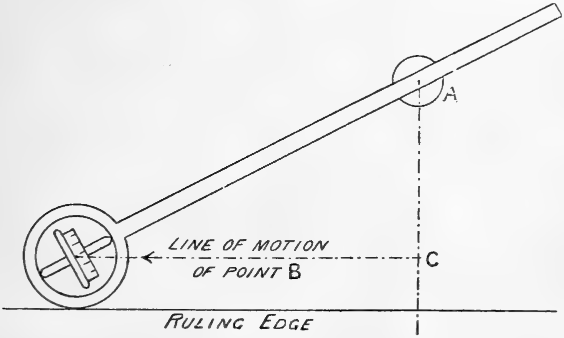
And the triangle B E D being similar to the triangle A C B,

$$\frac{\mathrm{BE}}{b}=\frac{\mathrm{DB}}{c}=\frac{b\,.\cosh\theta}{c}\delta\theta=\delta\theta.$$

$$\therefore\quad \frac{\Sigma(\mathrm{BE})}{b}=\theta.$$

Therefore θ can be obtained by summing such small elements as BE, and dividing the result by b. BE, in fact, is that component of the motion of B which is at right angles to AB.

Fig. 2.



Suppose that at the point A there is a circular pin in a drawing-board, but capable of moving round a vertical axis exactly coinciding with the geometrical point A.

In the head of this pin is a horizontal slot in which a bar slides.

This bar is enlarged at one end, as shown in the sketch, so as to carry a small wheel moved, by friction against the board, about an axis exactly coinciding with the centre line of the bar.

It will be clear that the movement in arc of a point in the circumference of this wheel will give the quantity $\Sigma(\mathrm{BE})$ or $\theta\,.\,b$ if the point of contact of the wheel with the board is carried along C B. If the circumference of the wheel is equal to b, the turns of the wheel will give θ, and these may be given by arrangements (not shown in the sketch) similar to those in Amsler's planimeter.

The enlargement necessary to carry the wheel may be conveniently made circular (at least in the portion remote from A) round the point B as centre. In this case it will be easily moved along a ruling-edge set parallel to the motion of B.

The bar may be graduated in units of b from the point B as zero, and the slotted pin-head may have a vernier for reading $\cosh\theta$. Of course CB on the same scale will be $\text{shin}\,\theta$.

XXVII. *On the Heat Evolved or Absorbed when a Liquid is brought in contact with a Finely Divided Solid.* By G. J. Parks [*].

I. INTRODUCTION.

POUILLET [†] discovered the fact that when a powder is put into a liquid which does not exert any solvent or chemical action upon it, there is a rise of temperature. In some of the experiments made by Pouillet with mineral substances, the rise of temperature varied from ·3° to 1° C. This discovery was confirmed by several other investigators, but nearly all the earlier observations were merely thermometric, and are therefore of little value for purposes of comparison, since the rise of temperature must obviously depend on the thermal capacity of the whole mass throughout which the heat is distributed. In fact, by suitably varying the conditions of the experiment it has been found possible to obtain any rise of temperature up to 30° C. or more.

Junck [‡] found that when sand is placed in water the temperature of which is above 4° C. there is a rise of temperature, and when the temperature of the water is below 4° C. there is a fall of temperature. This is quite in accordance with what would be expected on the supposition that the *Pouillet effect* is due to a pressure at the surface of the powder, and the variation of pressure for a given variation of temperature can be calculated from the equation $dp=\frac{J.c.\rho}{\tau\,.\,a}.d\tau$, where a is the coefficient of expansion of the liquid at constant pressure, ρ the density, c the specific heat, τ the absolute temperature, and J the mechanical equivalent of heat.

Meissner [§] showed that when certain powders are placed

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[*] Communicated by the Physical Society: read June 20, 1902.

[†] Pouillet, *Ann. de Chim. et de Physique*, xx. p. 141 (1822).

[‡] Junck, Pogg. *Ann.* cxxv. p. 292 (1865).

[§] Meissner, Wied. *Ann.* xxix. p. 114 (1886).

in water at a temperature below 4° C., a *rise* of temperature is observed, and he accordingly rejected the physical hypothesis of surface pressure, and adopted a chemical or physicochemical hypothesis which had been advanced by Cantoni [*], and which has been more fully developed by Martini [†]. It has, however, been pointed out that the experiments of Meissner do not disprove the validity of the hypothesis of surface pressure, for as the pressure increases the point of maximum density of water is lowered, and at a pressure of about 200 atmospheres the point of maximum density of water is at or near 0° C., as shown by Tait, Amagat, Lussana, and others [‡].

Lagergren [§] has shown that the pressure at the surface of silica and water would, from the above equation, amount to some thousands of atmospheres.

Martini, on the other hand, is unwilling to admit such an enormous pressure at the surface, and he supposes that, just as some solids are dissolved by liquids and thereby become liquid, so liquids are absorbed by powders and thereby become solid, the heat evolved being equivalent to the latent heat which the liquid gives up in solidifying.

Other investigators who have made experiments on the Pouillet effect and allied phenomena are Tate [||], Melsens [¶], Chappuis [**], Wiedemann and Lüdeking [††], Gore [‡‡], Ercolini [§§], Bellati [||||], and Linebarger [¶¶].

In Gore's experiments, a powder such as silica or alumina was dropped from the air into water which contained some soluble salt; the liquid was not stirred, and the temperature observed was that of the powder which sank to the bottom of the liquid. The object of these experiments was to discover

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[*] Cantoni, *Rend. del R. Istituto Lombardo*, viii. p. 135 (1866).

[†] Martini, *Atti del R. Istituto Veneto*, viii. (1896); ix. (1897); xii. (1900).

[‡] Tait, Proc. R. Soc. of Edinburgh, 1881–82, 1882–83; Marshall, Smith and Omond, Proc. Roy. Soc. Edinburgh, 1881–82; Amagat, *Comptes Rendus*, cxvi. p. 946 (1893); Lussana, *Nuovo Cimento* (4) ii. p. 233 (1895).

[§] Lagergren, *Kongl. Vetenskaps Akademiens*, B. 24, Afd. ii., Stockholm, 1899.

[||] Tate, Phil. Mag. [4] xx. p. 508 (1860).

[¶] Melsens, *Mémoires de l'Academie de Belgique*, xxiii. (1873); *Ann. de Chim. et de Phys.* [5] iii. p. 522 (1874).

[**] Chappuis, Wied. *Ann.* xix. p. 21 (1883).

[††] Wiedemann and Lüdeking, Wied. *Ann.* xxv. p. 145 (1885).

[‡‡] Gore, Phil. Mag. xxxvii. p. 306 (1894); Birm. Phil. Soc. Proc. vol. ix. pt. 1 (1893).

[§§] Ercolini, *Nuovo Cimenti*, Serie 4, vol. ix., Feb. 1899.

[||||] Bellati, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, 1900.

[¶¶] Linebarger, Physical Review, vol. xiii. No. 1, July 1901.

the influence of the substance in solution; and in fact the whole research was the outcome of another investigation in which Dr. Gore showed that a powder has the property of abstracting from a liquid part of the substance in solution. One remark of Dr. Gore bears on the present investigation: having made observations on precipitated silica and sand, he states that the action is purely a surface one, and he suggests that if the relation between the rise of temperature and the area of the surface were known, the method could be employed to obtain the area of the surface of a powder.

Prof. FitzGerald* regarded the Pouillet effect as due to a pressure at the surface of the powder and the liquid; he suggested the application of the laws of thermodynamics, and he pointed out the need of further investigation and quantitative treatment.

Notwithstanding the large number of observations which have been made in connexion with this phenomenon, there are no data by means of which we are enabled to express the quantity of heat evolved as a function of the area of the surface. The experiments of Martini, Ercolini, and others show that for the *same* powder and liquid the quantity of heat evolved is proportional to the mass of the powder used in the experiment, but no attempts have been made to calculate the area of the surface exposed to the liquid. The equation used by Ercolini is $M + pc - \frac{p}{\theta} \cdot k = 0$, where M is the mass of the water, including the water equivalent of the calorimeter, p is the mass of the powder, and c the specific heat of the powder, θ is the observed rise of temperature, k is a constant and represents the amount of heat evolved on putting one gram of the powder into water.

The value of k is, however, not really constant, but diminishes very slightly as p increases. Martini explains this on the supposition that some of the water is solidified on the powder and its specific heat is thereby reduced to ·5. Bellati has, however, shown by direct experiment that this supposition is wrong. Some silica was well dried, and then exposed to aqueous vapour so that it absorbed moisture, the mass of which was determined by weighing the silica before and after its exposure; the specific heat of the water was then found by means of a Bunsen's ice-calorimeter, an assumed value being taken for the specific heat of silica. The specific heat of the water was found to be much greater than ·5, and it did not differ very much from 1.

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* FitzGerald, 'Nature,' vol. xlix. pp. 293, 316 (1894).

It seems highly probable that the specific heat of the water close to the surface of the silica differs from the specific heat of the water which is farther away from the surface, but any attempt to distinguish clearly between the two must necessarily lead to some doubtful assumptions. A consideration of the Pouillet effect is, however, incomplete if the possibility of such a variation in the specific heat of the liquid is not taken into account. There is also another possible source of variation in the quantity of heat evolved, which none of the investigators have considered, namely, the variation of the heat evolved with the temperature. In many of the records of experiments the initial temperature of the calorimeter is not even stated, and in other cases, where the temperatures are recorded, it is impossible to decide whether the variations in the quantity of heat evolved depend upon differences in the initial temperature of the liquid and powder, or upon change of specific heat of the liquid, or upon some cause of error in the experiment.

The objects of the present investigation were to obtain a relation between the quantity of heat evolved and the area of the surface exposed, to find the rate of variation of heat evolved with variation of temperature, and to apply to the results the laws of thermodynamics.

The nearest approach to a relation connecting the quantity of heat evolved with area of surface is the statement of Mr. Linebarger, that the finer the powder the greater the heat effect, and in the case of water and silica the heat effect is about proportional to the fineness of the powder. This conclusion is based upon a very few experiments with two samples of silica of different degrees of fineness, and it is directly opposed to the views of Martini, who states that the fineness of the powder does not influence the result to any important extent[*].

II.

On the Relation between the Area of Surface of Silica and the Heat evolved on bringing the Surface in contact with Water.

In making any experiment on the Pouillet effect, it is essential that the powder should be perfectly dry and that it should be at exactly the same temperature as the liquid. Very few of the investigators have succeeded in securing these

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[*] Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda (1900), p. 622 (Non è dunque la sottigliezza dei granuli della polvere che influisca in modo sostanziale sul fenomeno come ce lo provano le tre qualità di carbonato di calce).

conditions, but Mr. Linebarger's methods seem to leave nothing to be desired, and the experiments now to be described were made in a similar way.

The precipitated silica, sand, or other substance to be experimented upon, was heated in an evaporating dish to dull red-heat. A test-tube was drawn out to a narrow neck at about seven or eight centimetres from the closed end, and the tube was then weighed. Some of the powder was now placed in the tube while it was still hot, and the tube was connected to an air-pump, and the air was exhausted as completely as possible, the powder being at the same time heated until the tube showed signs of softening and closing in under the atmospheric pressure. The bulb was now sealed at the narrow neck, and when cold the whole of the tube and the powder were weighed together; the difference between this weighing and the first weighing gave the mass of the powder, and a third weighing gave the mass of bulb and powder.

The calorimeter used in these experiments was a copper vessel, 9 cm. in height and 7·5 cm. in diameter; it weighed 104·605 grammes, and its water equivalent was 9·95 grammes. This was suspended by silken threads inside another copper vessel, this again was placed in a glass beaker containing water, and the glass beaker was placed inside another glass beaker, the space between the two beakers being filled with "glass wool" or "cotton silicate," which is a very bad conductor of heat. The whole apparatus was kept in a cupboard with glass doors. The temperature of the calorimeter could therefore be kept constant for a considerable time.

The thermometers were divided to ·02° C., and the readings were taken to the tenth of a division, so that there was a possible error in each reading of not more than ·002° C.

An instrument was used to serve the purpose of crushing the bulb, thus liberating the powder under the surface of the water, and it also served as a stirrer to keep the temperature of the water uniform. A piece of brass tubing about an inch in diameter was filed away in the middle, thus leaving two rings at the ends about an inch apart and connected by that part of the tube between them which had not been filed away. A nut was soldered on to the tube between the rings and a screw worked in the nut, the axis of the screw being at right angles to the axis of the tube, so that when the glass bulb was placed in the tube it was held firmly by the screw pressing against it, and a few more turns of the screw were sufficient to break the bulb. The top of the screw was flattened to a sharp edge, which engaged in a split at the end of a stout brass wire; this wire could thus be used to turn the screw, and then could be immediately removed. A piece of glass tubing was attached to the brass tube so that the screw worked along the axis of the glass tube, which served as a handle of non-conducting material. The water equivalent of this instrument was 2·35 grammes, and that of each thermometer was 1·50 grammes.

In making an experiment, the bulb containing the powder was placed under the surface of the water in the calorimeter, and allowed to remain there for some hours, generally about twenty-four hours. The temperature was then observed every five minutes, and if several consecutive readings were the same, the bulb was broken, and the temperature again observed until it was constant. The rise of temperature was generally complete in three minutes or less, the liquid being gently stirred together with the powder.

The mass of water, M, was always large compared with the mass of the powder, p, and hence the error, if any, involved in taking the specific heat of the water as 1, must have been exceedingly small. The temperatures at which the experiments were made did not differ very much, and the variation due to these small differences of temperature was neglected; from theoretical considerations it follows that the variation in the heat evolved is not more than ·3 per cent. per degree centigrade, and later experiments tend to confirm this.

The specific heat of the glass bulb and its contents was taken as ·19; any error in this assumption could not have affected the results, since the mass of the bulb and its contents was always small compared with the mass of water.

The average diameter of the grains of powder was obtained by measuring many hundreds of grains by means of a microscope supplied with stage micrometer and eyepiece micrometer. The microscope was so adjusted that thirty divisions of the eyepiece micrometer exactly corresponded to one tenth of a millimetre on the stage micrometer, so that one division of the eyepiece micrometer represented $\frac{1}{3000}$ cm. It was found that in the dry state the smaller grains of powder were often joined together, forming larger grains, and it was not easy to distinguish a lump consisting of several small grains from a complete grain; hence any measurements of powder in the dry state are likely to make the powder appear much coarser than it really is. When the powder was put in a drop of water on a glass slide under the microscope and stirred with a small brush, the larger pieces of silica were seen to break up into smaller grains of fairly uniform size. The average diameter of the grains was found to be $\frac{3}{4}$ of a division of the eyepiece micrometer, that is ·00025 cm. Suppose now there are n such average grains to a gramme of powder, then, since the specific gravity of the powder is 2·2, we have

$$n \times \frac{\pi}{6}(\cdot 00025)^3 \times 2\cdot 2 = 1$$

on the assumption that the grains are spherical, and the area of surface is equal to

$$n \, . \, \pi(\cdot 00025)^2 = 6 \times \frac{1}{2\cdot 2} \times \frac{1}{\cdot 00025} = 10900 \text{ sq. cm.}$$

That is, one gramme of the precipitated silica exposed a surface of about 10900 sq. cm. Another variety of silica used in these experiments was examined under the microscope, and the average diameter of the grains was found to be 1·2 divisions or ·00040 cm., so that the area of surface per gramme was

$$6 \times \frac{1}{\cdot 0004} \times \frac{1}{2\cdot 2} = 6820 \text{ sq. cm.}$$

Experiments were also made with some fine grey sand of specific gravity 2·6; the average diameter of the grains was ·010 cm., and the area of the surface exposed by one gramme of the sand was therefore

$$6 \times \frac{1}{2\cdot 6} \times \frac{1}{\cdot 01} = 231 \text{ sq. cm.,}$$

on the assumption that the grains were spherical.

The probable error in estimating the surface of a powder by this method is considerable, because the particles are irregular in shape and size, especially those of the sand. Experiments were therefore made with "cotton silicate" or "glass wool," a kind of glass of specific gravity 2·7, in the form of fine filaments which, when examined under the microscope, are seen to be almost perfect cylinders, of fairly uniform size. The length of each cylindrical filament was very great compared with its diameter, so that in calculating the area of its surface only the curved surface was considered. The average diameter was found to be ·00175 cm.; hence the area of surface exposed by one gramme of the silicate was

$$\frac{4}{2\cdot 7 \times \cdot 00175} = 847 \text{ sq. cm.}$$

The accompanying table (I.) shows the results of some of the experiments. Other experiments were made, but the results are not shown because they are considered to be unreliable. In several experiments, there was a slight crack in the bulb before it was placed in the calorimeter, and in these instances the result obtained was far too low, though the crack was not large enough to admit any visible quantity of water; this shows the great importance of keeping the powder dry until the moment of the experiment. Other experiments were rejected because there was a rapid variation in the temperature of the room at the time, so that the final temperature of the calorimeter did not reach a constant value until long after the time usually occupied in making an experiment. The rise of temperature observed in the experiments with sand and cotton silicate was only about $\frac{1}{50}$° C., and hence the results are only given to the second significant figure.

TABLE I.

Number of Experiment.	Nature of Substance.	Diameter (cm.).	Estimated area of surface per gramme.	Mass of substance in grammes.	Mass of bulb.	Mass of water including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temperature (Centigrade).	Rise of Temperature.	Calories per gramme of the substance.	Calories per sq. cm. of the surface.
1.	Silica (precipitated)	·00025	10900	3·749	3·34	205·51	6°·334	°·208	11·4	·00105
2.	,, ,,	,,	,,	3·563	3·55	210·31	6·552	·192	11·3	·00104
3.	,, ,,	,,	,,	4·169	3·61	210·05	7·012	·222	11·2	·00103
4.	,, ,,	,,	,,	4·037	3·53	239·74	7·586	·194	11·5	·00105
5.*	,, ,,	·00040	6820	3·940	4·03	207·26	7·320	·136	7·15	·00105
6.	Sand	·010	231	20·050	3·70	220·03	5·400	·022	·24	·0010
7.	,,	,,	,,	20·589	4·57	240·10	5·482	·020	·23	·0010
8.	,,	,,	,,	22·033	3·81	252·28	8·320	·020	·23	·0010
9.	,,	,,	,,	20·188	4·14	255·15	9·228	·018	·23	·0010
10.	Silicate (cylindrical filaments)	·00175	847	2·240	3·81	200·10	5·742	·010	·89	·0011
11.	,, ,,	,,	,,	4·006	3·50	210·93	5·722	·018	·95	·0011
12.	,, ,,	,,	,,	4·138	3·47	211·75	6·052	·018	·92	·0011

* See Table II. for results of other experiments with silica.

It is considered that these results justify the enunciation of the following law:—

"*When silica, sand, or glass, is brought in contact with water, at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimetre is approximately* ·00105 *calorie when the temperature is near* 7° *C.*

III.

Application of the Laws of Thermodynamics.

Assuming that the phenomenon of Pouillet is reversible, we may apply the laws of thermodynamics. Let h be the amount of heat developed per square centimetre at the surface of the solid and liquid at constant temperature, let c be the specific heat of the liquid when the surface remains constant, let s be the area of surface of the powder exposed to one gramme of the liquid, the volume of which is supposed to remain constant, let P be the surface-pressure for the given solid and liquid. Then, with the usual notation of thermodynamics,

$$dQ = c \,.\, dt - h \,.\, ds, \quad \ldots\ldots \quad \text{(i.)}$$

and $dQ = \tau \,.\, d\phi$, hence

$$\tau \,.\, d\phi = c \,.\, dt - h \,.\, ds. \quad \ldots\ldots \quad \text{(ii.)}$$

The variation of the internal energy is

$$dU = J \,.\, dQ - P \,.\, ds = J \,.\, c \,.\, dt - (J \,.\, h + P)ds, \quad \text{(iii.)}$$

where J represents the mechanical equivalent of heat. Imposing the condition that the variation of the internal energy is a perfect differential, we obtain

$$J\left(\frac{dc}{ds} + \frac{dh}{dt}\right) = -\frac{dP}{dt}. \quad \ldots\ldots \quad \text{(iv.)}$$

Imposing the condition that the variation of entropy, $d\phi$, is a perfect differential, we obtain

$$\frac{dc}{ds} + \frac{dh}{dt} = \frac{h}{\tau}. \quad \ldots\ldots \quad \text{(v.)}$$

From equations (iv.) and (v.) we have

$$h = -\frac{\tau}{J} \cdot \frac{dP}{dt} \quad \ldots\ldots \quad \text{(vi.)}$$

and

$$\frac{dc}{ds} = \frac{\tau}{J} \cdot \frac{d^2P}{dt^2}. \quad \ldots\ldots \quad \text{(vii.)}$$

Applying these equations to the results obtained for water and silica, we find that the surface-pressure diminishes with rise of temperature, for since heat is evolved when the surface of water and silica is extended, h is positive, and hence from equation (vi.) $\frac{dP}{dt}$ is negative. Taking h as ·00105 when r is 280°

and $J = 4{\cdot}2 \times 10^7$, we have $\frac{dP}{dt} = -157$; that is, at 7° C. the surface-pressure of water and silica diminishes at the rate of 157 dynes per cm. for an increase of temperature of 1° C.

From equation (v.) we have $\frac{dc}{ds} + \frac{dh}{dt} = \frac{{\cdot}00105}{280} = {\cdot}0000037$ at a temperature of 7° C.

From equation (v.) it is clear that if either $\frac{dc}{ds}$ or $\frac{dh}{dt}$ is known, the other can be found, and if *both* of these could be determined with precision, a value for absolute zero could be obtained, which would be independent of the air-thermometer.

IV.

On the Rate of Variation of the Heat evolved with Change of Temperature.

The accompanying Table II. shows the results of experiments made to determine, at least approximately, the value of

TABLE II.

Experiments with precipitated Silica. Average diameter of grains ·00040 cm. Estimated area of surface per gramme 6820 sq. cm.

Number of Experiment.	Mass of powder in grammes.	Mass of of bulb.	Mass of water, including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temp. (Cent.).	Rise of Temperature.	Calories per gramme of powder.	Calories per sq. cm. of surface.
1.	3·940	4·03	207·26	7°·320	°·136	7·15	·00105
2.	4·282	3·32	190·26	7·300	·164	7·29	·00107
3.	3·760	3·55	201·88	6·930	·134	7·19	·00105
4.	3·602	3·25	195·71	6·238	·132	7·17	·00105
5.	3·721	4·00	196·26	6·770	·136	7·17	·00105
6.	3·601	3·32	211·49	7·200	·122	7·17	·00105
7.	3·256	3·58	205·25	7·106	·114	7·19	·00105
8.	4·166	3·74	214·16	7·502	·138	7·09	·00104
9.	4·261	4·14	197·01	23·636	·164	7·58	·00111
10.	3·950	3·92	182·94	24·180	·162	7·50	·00110
11.	3·657	3·22	202·57	24·410	·138	7·64	·00112
12.	4·789	4·67	206·67	24·000	·178	7·68	·00113
13.	4·417	3·79	212·02	24·060	·160	7·68	·00113
14.	4·691	3·17	230·80	24·670	·154	7·58	·00111
15.	4·003	3·84	227·21	23·906	·130	7·38	·00108
16.	3·829	2·99	227·68	24·700	·124	7·37	·00108

the term $\frac{dh}{dt}$, which appears in the foregoing theoretical investigation. The *same* powder was used throughout, and the results are tabulated in calories per gramme as well as in calories per sq. cm., so that the data should be equally useful whatever be the hypothesis advanced.

The thermometers used in these experiments gave a range of temperature from 5° C. to 25° C.; hence the range over which experiments could be made was rather less than 20° C.

It was found necessary to modify the apparatus so that the calorimeter could be kept for some hours at constant temperature above that of the atmosphere. The cylindrical copper vessel in which the calorimeter was suspended was closed by a tightly fitting copper lid, under the rim of which was tightly packed an indiarubber ring which had previously been stretched around the top of the vessel. Into the copper lid, two copper tubes about two inches long were soldered; through one of these tubes the bulb of the thermometer could be put into the calorimeter, and through the other passed the handle of the crushing instrument. Thus the bulb could be crushed and the liquid stirred and the temperature observed without opening the vessel. The copper vessel was now immersed in several gallons of water, the top of the lid being about an inch below the surface. This water was kept at approximately constant temperature for several hours, during which time the bulb containing the powder was immersed in the water in the calorimeter, so that there could be no doubt about the powder and the water being at the same temperature.

This apparatus proved so satisfactory that it was finally adopted in the later experiments at the lower temperature, instead of the arrangement previously described.

In the first eight experiments the mean temperature was about 7°·1 C. and the mean heat evolved was 7·18 calories per gramme, or ·00105 calorie per sq. cm. In the last eight experiments, the mean temperature was about 24°·3 C. and the mean heat evolved was 7·55 calories per gramme or ·00111 calorie per sq. cm.

The mean value of $\frac{dh}{dt} = \frac{\cdot 00006}{17 \cdot 2} = \cdot 0000035$.

The mean value of $\frac{h}{\tau} = \frac{\cdot 00108}{288 \cdot 7} = \cdot 0000037$.

Hence, roughly speaking, $\frac{dh}{dt} = \frac{h}{\tau}$ and h varies as τ, that is the heat evolved is roughly proportional to the absolute temperature.

V.

On the Rate of Variation of the Specific Heat of Water with Extension of the Water-Silica Surface.

It has been shown that $\frac{dc}{ds}=\frac{h}{\tau}-\frac{dh}{dt}$, and hence from the results stated above it follows that $\frac{dc}{ds}$ must be very small. If the values of $\frac{dh}{dt}$ and $\frac{h}{\tau}$ are correct to the second significant figure the value of $\frac{dc}{ds}$ is 2×10^{-7}, and this may be taken as indicating the *order* of magnitude of the term $\frac{dc}{ds}$.

For an accurate determination of $\frac{dc}{ds}$, experiments would have to be made over a much wider range of temperature, and it would be advisable also to obtain, if possible, a silica of much finer and more uniform quality than that used in these experiments.

It is known that the surface-tension of a liquid in contact with air can be represented approximately as a linear function of the temperature, and hence, from equation (vii.), $\frac{dc}{ds}$ is approximately zero. But it cannot be assumed that the surface-pressure of water and silica follows the same law as the surface-tension of a liquid in contact with air.

In making any experiment to determine directly the specific heat of water in contact with silica, we are met at once with the difficulty that the specific heat of silica is not accurately known.

According to Joly [*] the specific heat of amorphous silica is ·2375, but it has been suggested [†] that this value is too high, and that the error arose through neglect of the Pouillet effect; a similar question in regard to the specific heat of carbon has been investigated by Kopp, Wüllner & Bettendorf, and Weber [‡].

Bellati [§], in his attempt to determine the specific heat of moisture absorbed by silica, took for the specific heat of the silica the value ·1993 as the mean of the various values obtained for different forms of silica.

The value of $\frac{dc}{ds}$ cannot, however, be obtained by direct

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[*] Joly, Proc. R. Soc. xli. p. 250 (1886).

[†] Martini, *Atti del R. Istituto Veneto,* Tomo lix., Parte seconda, p. 637.

[‡] Weber, *Pogg. Ann.* t. 154, pp. 367–423 (1875).

[§] Bellati, *Atti del R. Istituto Veneto,* Tomo lix., Parte seconda, p. 945.

experiments such as those made by Bellati. Suppose, for example, p grammes of silica having a specific heat k, and w grammes of water, are mixed and raised to a temperature t, and the mixture is then put into a Bunsen's ice calorimeter and cooled to 0° C., the heat given up is

$$\left(pk+w+p\,.\,s\,.\,\frac{dc}{ds}-p\,.\,s\,.\,\frac{dh}{dt}\right)t=\left(pk+w-p\,.\,s\,.\,\frac{h}{\tau}\right).\,t,$$

approximately, from equation v.

It is necessary, therefore, to distinguish between the *true* or *absolute* variation and the *apparent* variation in the specific heat of water in contact with a solid. The *true* variation in the specific heat is proportional to $\frac{dc}{ds}$, and is probably very small; but since in any experiment it is impossible to prevent the evolution or absorption of heat at the surface depending on the term $\frac{dh}{dt}$, the *apparent* variation in the specific heat, that is, the variation actually observed in any experiment, is proportional to the difference of the terms $\frac{dc}{ds}$ and $\frac{dh}{dt}$, that is, approximately proportional to $\frac{h}{\tau}$.

Hence the *apparent* specific heat of water in contact with a solid is approximately $\left(1-\frac{A}{w}\cdot\frac{h}{\tau}\right)$, where A is the area of the surface of the water in contact with the solid, and w the mass of the water. For example, in the earlier experiments of the present investigation, the mass of water was about 200 grammes and the area of surface exposed by 4 grammes of powder was $4\times 10900=43600$ sq. cm., and the value of $\frac{h}{\tau}$ was 37×10^{-7}: hence the *apparent* specific heat of the water was equal to $(1-\frac{43600}{200}\times 37\times 10^{-7})=\cdot 99919$. It is evident that if the mass of water is small compared with the mass of powder, the variation in the apparent specific heat may be very great, so that it is not necessary to assume, as Martini did, that some of the water is solidified on the surface of the powder, in order to account for the apparent variation in the specific heat.

VI. *Experiments with Mercury.*

Experiments were made to show a *fall* of temperature on putting a finely divided solid into mercury. After several fruitless attempts with silica, the following method was adopted.

About 3000 grammes of mercury were placed in a glass beaker, and some cotton silicate was placed in the same beaker above the mercury; above the cotton silicate was a cardboard disk which covered the silicate entirely, except that a space was left for the insertion of the thermometer, and a little space was allowed for the edge of the disk to clear the sides of the beaker. On pressing down the disk the cotton silicate was suddenly immersed in the mercury, and in some experiments there was a fall of temperature amounting to ·016° C. But the results were not consistent, for in other experiments there was a slight rise of temperature, caused probably by the cotton silicate being at a higher temperature than the mercury. After leaving the cotton silicate immersed in the mercury for some time, so as to take the same temperature, it was suddenly released, and a rise of temperature was the invariable result. With 11 grammes of cotton silicate the rise of temperature was about ·02° C., and with 30 grammes of silicate the rise of temperature was about ·05° C., but the results varied considerably.

These experiments do not lend themselves to quantitative measurement, for the surface of the mercury cannot be determined. When the filaments of cotton silicate are put into mercury they tend to cling together in bundles or tufts, and the mercury breaks up into a great number of little globules between the tufts of silicate. The surface exposed by the mercury is thus large and indeterminate. The results show, however, that the sudden contraction of a mercury surface causes an evolution of heat and corresponding rise of temperature, and the effect can be regarded as a modification of the Pouillet effect for a liquid which does not *wet*, or enter into intimate contact with the solid.

H.M. Dockyard School, Portsmouth,
March 1902.

XXVIII. *On some of the Consequences of the Emission of Negatively Electrified Corpuscles by Hot Bodies.* By J. J. THOMSON, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge*[*].

IT was shown by Elster and Geitel[†] that an incandescent metal wire in a good vacuum emits negative electricity; in 1899 I showed that the carriers of this negative electricity were "corpuscles," *i. e.* were identical with the carriers of

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[*] Communicated by the Author.

[†] Elster and Geitel, Wied. *Ann.* xxxvii. p. 315.

negative electricity in the cathode-rays[*]. Quite recently Mr. O. W. Richardson[†] has made a series of measurements at the Cavendish Laboratory of the rate at which the electricity escapes at different temperatures. The results of these measurements are very interesting; they show that surprisingly large currents can pass in the best vacua between a negatively electrified incandescent wire and a conductor placed in its neighbourhood; thus Richardson has shown that the negative electricity streams so fast from carbon at a white heat as to be equivalent to a current of about 1 ampere for each square centimetre of carbon surface. If we suppose that the corpuscles which carry the negative charge have the same kinetic energy as the same number of molecules of a perfect gas at the same temperature, this stream of corpuscles would carry with them from the metal energy at the rate of about $\frac{1}{10}$ of a calorie per square centimetre of surface per second: the number of corpuscles coming in each second from this area is about 5×10^{18}. The question naturally suggests itself whether this great crowd of corpuscles does not produce other effects besides the electrical ones already mentioned: it is the object of this paper to indicate some of these effects.

In the first place, since the corpuscles carry a charge of negative electricity, they will move when acted on by an electric force; so that, assuming the Electromagnetic Theory of Light, they will be set in motion by a wave of light; they will thus absorb energy from the wave and give out this energy as scattered light. We can easily calculate the energy in the light scattered in this way.

The rate at which a small charged particle, charge e and acceleration f, radiates energy is equal to

$$\frac{1}{3}\frac{e^2 f^2}{\mathrm{V}}$$

where V is the velocity of light. If the charged particle is acted on by an electric force X, then

$$f = \frac{\mathrm{X}e}{m},$$

where m is the mass of the particle; hence the rate at which the charged particle is emitting energy is equal to

$$\frac{1}{3}\frac{e^4}{m^2}\frac{1}{\mathrm{V}}\mathrm{X}^2.$$

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[*] J. J. Thomson, Phil. Mag. xlviii. p. 547.

[†] O. W. Richardson, Proc. Camb. Phil. Soc. xi. p. 286.

Now if the electric force is that in a light-wave the mean energy E per unit volume in the wave is equal to the mean value of $X^2/4\pi V^2$; hence we see that the mean rate at which the particle is emitting energy (this is the rate of emission of the energy of the scattered light) is

$$\frac{4\pi}{3}\frac{e^4}{m^2}\text{VE}.$$

If there are N corpuscles per unit volume the energy in the scattered light coming from each unit of volume per second is equal to

$$\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}\text{VE}.$$

The scattered light will be polarized in the same way as light reflected from small particles. This scattering of the light will cause the medium to absorb light. We can find the coefficient of absorption as follows:—Suppose the axis of z is the direction of propagation of the light. Let AB and CD be two planes at right angles to z separated by a distance δz, CD being in front. Then if A is the area of either of these planes, the rate at which energy is being scattered by the particles between the planes is equal to

$$\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}\text{VE}\,.\,\text{A}\delta z.$$

Now when things are in a steady state this energy must be supplied by the excess of the energy flowing into the region between AB and CD through AB, over that flowing out through CD: the average rate at which energy flows across AB is AEV; the rate at which it flows out across CD is $\text{A}(\text{E}+\delta\text{E})\text{V}$: hence we have

$$-\text{A}\delta\text{EV}=\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}\text{VEA}\delta z;$$

or

$$\frac{d\text{E}}{dz}=-\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}\text{E};$$

thus

$$\text{E}=\text{C}\epsilon^{-\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}z};$$

and thus the coefficient of absorption is $\frac{4\pi}{3}\frac{\text{N}e^4}{m^2}$.

Thus the region round incandescent metals or carbon will, in virtue of the corpuscles coming from these substances, scatter light; and the scattered light will be polarized in the same way as if the light had been reflected from small particles. Since the corpuscles are in rapid motion if the incident light is homogeneous, the spectrum of the scattered light will by Döpler's principle broaden out into a band. Similarly, if the corpuscles were illuminated by light showing Frauenhofer's dark lines, these will be obliterated in the scattered light.

The most conspicuous example of a hot body is the sun, the photosphere of which is supposed to contain large quantities of carbon or silicon at a temperature far higher than any we can produce by artificial means. Thus the photosphere must be emitting corpuscles in large quantities, these coming from such hot bodies will be moving with great velocities, and may leave the sun and travel out through the solar system. These corpuscles will scatter the light from the sun; and since the corpuscles are densest close to the sun, we should get a distribution of luminosity due to the scattered light which would be most intense close to the sun, and would fade away at greater distances from it. The rate of decay would be fairly rapid; for not only would the intensity of the incident light diminish inversely as the square of the distance, the number of corpuscles per unit volume would also diminish according to the same law; so that the intensity of the light scattered from the corpuscles would vary inversely as the fourth power of the distance. It seems to me probable that many of the phenomena of the corona may be due to light scattered by corpuscles ejected from the sun. Since cathode-rays produce luminosity when they pass through rarefied gas, the corpuscles ejected from the photosphere would in their passage through the chromosphere cause the gases in the latter to become luminous. The presence of some of the corpuscles throughout the solar system would cause each part of this system to scatter a certain amount of light, so that no part of it would be absolutely dark, nor would it be perfectly transparent. I am not aware of the existence of any observations bearing on the absorption of light by interplanetary space.

The corpuscles when under the action of a wave or pulse of electric and magnetic force will be pushed forward in the direction in which the wave is travelling; and thus if these waves proceed from the sun, the latter will appear to repel the corpuscles.

To show this, let the direction of propagation of the wave be along the axis of z, let X the electric force in the wave-front be parallel to the axis of x, H the magnetic force parallel to y. Let x, y, z be the coordinates of the corpuscle.

Then we have, since $X=VH$, where V is the velocity of light,

$$m\frac{d^2x}{dt^2}=Xe-He\frac{dz}{dt}=He\left(V-\frac{dz}{dt}\right)=-He\frac{d\zeta}{dt}, \quad (1)$$

$$m\frac{d^2y}{dt^2}=0, \quad \ldots \quad (2)$$

$$m\frac{d^2z}{dt^2}=He\frac{dx}{dt}, \qquad m\frac{d^2\zeta}{dt^2}=He\frac{dx}{dt}, \quad \ldots \quad (3)$$

where $\zeta=z-Vt$.

Let us first take the case where a pulse of constant electric force is passing over the corpuscle. Then if x, z vanish when $t=0$ and u and w are the initial values of $\frac{dx}{dt}$ and $\frac{dz}{dt}$, we get from (1) and (3)

$$z=Vt+\frac{m}{e}\frac{u}{H}(1-\cos\omega t)+\frac{\omega-V}{\omega}\sin\omega t,$$

and

$$\frac{dz}{dt}=V+u\sin\omega t+(\omega-V)\cos\omega t,$$

where $\omega=He/m$.

Thus if the pulse lasts for a time T, long enough to make ωT large, the corpuscle will be set in motion in the direction in which the wave is travelling, and the average velocity of the corpuscle will be that of the wave. Now

$$\omega T=THe/m=10^7 . T . H;$$

thus if T the time the pulse takes to pass over the corpuscle is large compared with $1/10^7H$ seconds, the corpuscle will be shot forward with great velocity in the direction in which the pulse is travelling. If ωT were small, the velocity acquired by a particle starting from rest would be $\frac{1}{2}V\omega^2T^2$.

Let us now take the case of a periodic disturbance; let H be given by the equation

$$H=A\cos\frac{2\pi}{\lambda}(Vt-z)=A\cos\frac{2\pi}{\lambda}\zeta.$$

Equations (1) and (3) become

$$m\frac{d^2x}{dt^2}=-Ae\cos\frac{2\pi}{\lambda}\zeta.\frac{d\zeta}{dt}, \quad \ldots \quad (4)$$

$$m\frac{d^2\zeta}{dt^2}=\ Ae\cos\frac{2\pi}{\lambda}\zeta.\frac{dx}{dt}; \quad \ldots \quad (5)$$

from (4) we get

$$m\frac{dx}{dt}=-\mathrm{A}e\frac{\lambda}{2\pi}\sin\frac{2\pi}{\lambda}\zeta.$$

If dx/dt and ζ vanish simultaneously, substituting in (5), we have

$$m\frac{d^2\zeta}{dt^2}+\frac{\mathrm{A}^2e^2}{4\pi m}\lambda\sin\frac{4\pi}{\lambda}\zeta=0;$$

or writing θ for $\frac{4\pi}{\lambda}\zeta$, we have

$$\frac{d^2\theta}{dt^2}+\frac{\mathrm{A}^2e^2}{m^2}\sin\theta=0.$$

The equation of motion of a simple pendulum. Integrating this equation, we find

$$\frac{1}{2}\left(\frac{4\pi}{\lambda}\right)^2\left(\frac{d\zeta}{dt}\right)^2=\mathrm{C}+\frac{\mathrm{A}^2e^2}{m^2}\cos\frac{4\pi}{\lambda}\zeta,$$

where C is the constant of integration. Substituting for ζ its value $z-\mathrm{V}t$, we have

$$\frac{1}{2}\left(\frac{4\pi}{\lambda}\right)^2\left(\mathrm{V}-\frac{dz}{dt}\right)^2=\mathrm{C}+\frac{\mathrm{A}^2e^2}{m^2}\cos\frac{4\pi}{\lambda}(\mathrm{V}t-z).$$

If dz/dt vanish when $\zeta=0$, we have

$$\frac{1}{2}\left(\frac{4\pi}{\lambda}\right)^2\left[\left\{\mathrm{V}-\frac{dz}{dt}\right\}^2-\mathrm{V}^2\right]=\frac{\mathrm{A}^2e^2}{m^2}\left\{\cos\frac{4\pi}{\lambda}(\mathrm{V}t-z)-1\right\}.$$

If w is the maximum value of dz/dt, we have

$$\mathrm{V}^2-(\mathrm{V}-w)^2=\frac{\lambda^2}{4\pi^2}\frac{\mathrm{A}^2e^2}{m^2};$$

hence if

$$\frac{\lambda^2\mathrm{A}^2e^2}{4\pi^2m^2}=\mathrm{V}^2,$$

the maximum value of the velocity of the corpuscle will be equal to the velocity of light. If $\lambda^2\mathrm{A}^2z^2/\mathrm{V}^2\pi^2m^2$ is a small quantity, then the maximum value of w is given by the equation

$$w=\frac{1}{2}\frac{\lambda^2\mathrm{A}^2e^2}{4\pi^2m^2}\frac{1}{\mathrm{V}}.$$

Now $e/m=10^7$, $\mathrm{V}=3\times10^{10}$; hence $\frac{\lambda^2\mathrm{A}^2e^2}{4\pi^2m^2\mathrm{V}^2}=2{\cdot}5\mathrm{A}^2\lambda^2 10^{-9}$,

Here A is the maximum value of the magnetic force and λ the wave-length. We see that for waves of sunlight

$A^2\lambda^2 \times 10^{-8}$ would be very small; so that the maximum velocity acquired by the corpuscles would be very small compared with the velocity of light. If, however, the sun gave out Hertzian waves of considerable wave-length, these would communicate to the corpuscles velocities comparable with the velocity of light, so that the sun would appear to repel the corpuscles with great vigour. Thus, for example, if a comet by near approach to the sun got raised to such a high temperature that the corpuscles began to come off, these would be repelled if any Hertzian waves came from the sun, and appear behind the comet as a luminous tail.

I now pass on to consider another result of the emission of these negatively electrified corpuscles: we may regard these corpuscles coming out of the metal as evidence for the existence in the metal itself of streams of corpuscles which move freely between the molecules of the metal. Some of these moving at more than a certain speed are able to escape from the attraction of the metal, and produce the stream of negative electricity coming from the metal. These corpuscles moving through the metal constitute streams of cathode-rays, and when they come into collision with the molecules will give rise to pulses of electric and magnetic force analogous to those produced by the stoppage of cathode-rays in a vacuum-tube; inasmuch, however, as the velocity of the corpuscles in a hot body is small compared with that of cathode-rays in a vacuum-tube, the pulses produced by the corpuscles will be very "soft" compared with the Röntgen rays produced in a vacuum-tube, *i. e.* the pulses produced in the hot body are very much thicker than those produced in a vacuum-tube. A succession of sufficiently broad pulses would, however, on the electromagnetic theory of light, produce a continuous spectrum of the kind given out by a hot body. Part of the radiation from a hot metal might arise in this way; and this part would have the characteristic property of radiation from a solid of increasing very rapidly with the temperature. For we may regard the corpuscles in the metal as analogous to the molecules of a liquid, and the escape of the corpuscles from the metal as analogous to the evaporation of the liquid. The corpuscles are supposed to be attracted by the metal; so that it is only those escape from the surface which start from near the surface and move so rapidly that their velocity is sufficient to carry them beyond the region of the attraction of the metal. Thus suppose that c is the distance at which the attraction of the metal on the corpuscles is appreciable—c is analogous to the range of molecular attraction in Laplace's Theory of Capillarity—and consider a layer of the metal of thickness c next the surface: as soon as a corpuscle enters this layer it will be acted upon by a force directed away from the surface; if the corpuscle has only a small amount of kinetic energy it will soon be stopped, and will turn back without ever reaching the surface, one with greater velocity will get nearer to the surface, and those moving above a certain speed will be able to reach the surface and escape from the metal. If the distance c is comparable with the thickness of metal required to absorb the radiation of the type produced by the impact of the molecules against the corpuscles, then the rate of emission of radiation from the metal will depend chiefly upon the more rapidly moving corpuscles. For not only do these possess greater energy, and therefore when in collision produce the more intense pulses, but they travel nearer to the surface so that the radiation which they emit has not to travel through so great a thickness of metal, and is consequently not so much absorbed.

To calculate the rate at which energy is radiated from the metal by the electromagnetic waves produced by the collisions between the corpuscles and the molecules, we require to know the attraction exerted by the molecules on the corpuscles; for without this knowledge we cannot tell how near to the surface a molecule moving with a given velocity will penetrate; we also require to know how much of the radiant energy produced by the collision is absorbed in passing from the place of collision to the outside of the metal. In default of information on these points let us calculate the rate of emission of radiant energy on the assumption that only those corpuscles whose velocity is greater than v_1 get near enough to the surface for any of their radiation to escape, and that all the radiation from those moving with a velocity greater than v_1 escapes without absorption. Assuming Maxwell's law of distribution, and that the energy in the electromagnetic pulse produced by the collision is proportional to the square of the velocity, we find that the rate at which energy is emitted from the metal is proportional to

$$\theta^{-\frac{3}{2}}\int^{\infty} v^5 \epsilon^{-\frac{mv^2}{\theta}}\, dv,$$

where θ is the absolute temperature. If mv_1^2 is large compared with θ, this expression increases very rapidly with θ.

The collision of free corpuscles with the molecules will not be the only source of radiation—indeed if it were only conductors of electricity would radiate—similar radiation will be produced by the motion of corpuscles inside molecules from which they never become detached. The electromagnetic effect will evidently be of much the same character, whether the velocity of a corpuscle is reversed by a collision or by swinging round a closed orbit under the action of a central force. If the orbits of the corpuscles in the molecules are circular, the calculation of the amount of energy radiated from them is very simple. A corpuscle moving with an acceleration f emits radiant energy at the rate $\frac{1}{3}\frac{e^2f^2}{\mathrm{V}}$, where V is the velocity of light. If the corpuscle moving with a velocity v describes a circle of radius r,

$$f=\frac{v^2}{r}=\frac{\mu}{r^n} \text{ if } \mu/r^n \text{ is the force on the corpuscle divided by its mass.}$$

Thus $f^2=\frac{v^{\frac{4n}{n-1}}}{\mu^{n-1}}$,

and this is proportional to the rate at which the corpuscle is emitting energy. Thus this rate is proportional to the kinetic energy of the particle raised to the power $2n/n-1$: and if we assume that the kinetic energy of the corpuscles is proportional to the absolute temperature θ, the rate of radiation from the corpuscles varies as $\theta^{\frac{2n}{n-1}}$. If the force on the corpuscle varies inversely as the square of the distance $n=2$, the rate of radiation will be proportional to the fourth power of the absolute temperature. To calculate the rate at which energy comes out of the body we require to know the law of absorption; if the corpuscles are moving with different velocities, the character of the radiation emitted by a corpuscle will depend upon its velocity; if the absorption does not depend upon the character of the radiation, the rate at which energy is emitted from the body is proportional to the fourth power of the absolute temperature (assuming $n=2$); but this is not the case if the absorption depends upon the character of the radiation. If, for example, as in the case of Röntgen rays, the greater the velocity of the corpuscles the more penetrating the radiation they originate, a larger proportion of the radiation from the quicker corpuscles would emerge from the body than of that from the slower corpuscles, and the rate of escape of the radiation would increase more rapidly than the fourth power of the temperature; while if the law of absorption went the other way it would vary less rapidly. Although the calculation of the amount of radiation depends upon a knowledge of the law of absorption which we do not at present possess, it is interesting to find that a collection of corpuscles describing circles under forces varying inversely as the square of the distance in the molecules of a substance which shows no selective absorption would, like the ideal "black" body, radiate at a rate proportional to the fourth power of the absolute temperature.

XXIX. *On Spontaneous Nucleation and on Nuclei produced by Shaking Solutions.* *By* C. BARUS *.

SPONTANEOUS NUCLEATION.

IN 'Science' (xv. Jan. 1902, p. 178) I communicated some results which seemed to give evidence of the spontaneous production of nuclei from certain organic liquids. Though my own work is rather more concerned with the diffusion of the nuclei with an ulterior view to their velocity, no matter how the nuclei may be localized, it nevertheless seemed interesting to elucidate the subject incidentally. I therefore made a series of experiments in which condensation was produced by the expansion method in case of gasoline, benzine, petroleum, benzol, carbon bisulphide, and water.

Hydrocarbons.—The first three hydrocarbon liquids may be dismissed summarily. The air above them, if carefully freed from nuclei by precipitation, remained free from nuclei indefinitely. The test was made by leaving the receiver without interference for fifteen or more hours, all the cocks being shut off, except the one communicating with the atmosphere through a filter of compressed cotton, half a metre long. A perfect filter is essential throughout. In case of petroleum it is exceedingly difficult to remove the nuclei by precipitation alone; but they vanish in the lapse of time (days), and thereafter the air remains permanently without nucleation.

In case of benzol I was for a long time erroneously of the opinion that nuclei arise spontaneously out of this liquid, and consistent results leading to this inference were obtained in great number. Doubt was cast on this supposition by the behaviour of the hydrocarbons just mentioned. The true explanation was subsequently found: on removing nuclei by precipitation with the object of obtaining dust-free air, a couche of nuclei is apt to remain brooding immediately over the surface of the benzol, where it escapes detection. It is

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* Communicated by the Author.

in this couche that the nuclei which subsequently diffuse[*] into and fill the whole vessel originate. They do not come out of the benzol.

To account for these couches, which occur more or less frequently with all hydrocarbons and other volatile liquids, it is necessary to consider the manner in which the nuclei are introduced into the receiver. This is done expeditiously by partially exhausting the receiver and allowing the inflowing air to pass over phosphorus, or glowing charcoal, or near a sulphur flame. In the case of water vapour the nuclei after entrance remain permanently apart. The nucleated air is always homogeneous and the coronas regular. Semi-coronas never occur. This indefinite suspension of nuclei means that they remain small, diffuse relatively fast, and gravitate very slowly. The phenomenon is very similar to the suspension of particles of clay in water. The speed of subsidence is a minimum.

In case of the hydrocarbons &c. the occurrences are very different. What goes on while the nuclei are being introduced is not of course visible; but the first exhaustion after nucleation shows a horizontally graded distribution, in which the nuclei are wholly confined to a narrow stratum, usually immediately above the liquid, as already stated. The fog stratum may, however, show itself at the top of the vessel, or even between two hemispheres of clear non-nucleated air. Indeed the air is rarely, if ever, nucleated uniformly.

The distribution, therefore, is one of density; and from the relatively insignificant number of nuclei, it may be further supposed that to influence the density of the strata, the nuclei have been loaded on influx, almost without supersaturation, even though the fog particles are small enough to remain invisible. In such a case it is hardly probable that the nuclei have remained individualized as in the case of water vapour; it is more probable that they grow by coalescence or cohesion, until they are large enough to condense hydrocarbon vapour with the minimum of supersaturation or none at all. This again is remarkably like the subsidence of clay in hydrocarbon liquids, in which, from the cohesion of particles, the precipitation is, relatively speaking, instantaneous.

It is not necessary, however, to assume loading. If the nucleus diffuses slowly enough in organic vapours to virtually

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[*] The rate of diffusion (roughly, ·015 centim./sec., upward in benzol vapour, for instance) is the feature of these experiments on which I am now at work. Incidentally one may note that the "granular" particles in water vapour should diffuse much more rapidly than the "flocculent" particles in benzol vapour, the nuclei being otherwise the same.

stick to the layers in question, and if there is any slight difference in temperature between the air inside of the receiver and the inflowing air, couches will result from convection. Conversely, the entire non-occurrence of semi-coronas &c. in case of water vapour is an indication of relatively rapid diffusion, and therefore of nuclei of minimum size. *The nucleus depends for its size,* cæt. par., *on the medium in which it is suspended.* Nuclei from the same source will diffuse under otherwise like conditions 100 or 200 times more rapidly in water vapour than in benzol vapour.

Under these conditions there would be fewer particles as compared with water vapour for like nucleation, &c., and normal coronas may appear at once in volatile hydrocarbons, whereas they are only reached after many exhaustions in water vapour. Experiment * bears this out. Moreover, the particles in the former case being larger require less supersaturation, and are more quickly removed, which is also true of the volatile liquids.

Carbon Bisulphide.—The case of carbon bisulphide is peculiar, inasmuch as in addition to the occurrence of couches of the kind just described, this liquid emits nuclei spontaneously. I would not wish to assert this for the fresh and perfectly pure liquid; but from carbon bisulphide which has been subjected to evaporation and contains sulphur, nuclei are continually evolved at a definite rate. Curiously enough, the addition of nuclei from without, whether coming from sulphur, punk, or atmospheric air (without shaking of the liquid) is almost insignificant. A couche a few centims. high is usually seen on first exhaustion, the remainder of the receiver being clear.

After shaking the first corona is annular, coarse, and normal, the aperture of its white disk $s=3°\cdot 7$. The next exhaustion brings out semicircles concave upward or semi-annuli, the succeeding exhaustion quarter-annuli, &c., the colour eventually vanishing in a filmy veil. Left to themselves, these partial nucleations gradually diffuse upward, and full coronas may be again obtained in the lapse of time. The same result occurs if the air above the liquid has been *quite* freed of nuclei by repeated precipitation, as the nuclei are now supplied by the liquid itself. These coronas are first partial, then filmy and small but complete. Gradually they become larger and stronger until a limiting aperture and great intensity is reached. In other words, nuclei are emitted by the liquid in the dark, terminating in a state of saturation

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* *Cf.* American Journ. Sci., (4) xiii. pp. 81–94 (1902).

of the air above. The following are typical data; s is the aperture *:—

Time of Diffusion, upward.	15 min.	30 min.	60 min.	2h. 40 min.	3 h.	6 h.	15 h.
Corona	Film, 5 cm. high.	Partial, faint.	Full, faint, diffuse.	Strong, $s=1^\circ\cdot8$.	Strong, $s=2^\circ\cdot25$.	Strong $s=3^\circ\cdot4$.	Intense. $s=3^\circ\cdot1$.

If the evaporation is accelerated, after shaking, as in a warm bright room, the saturated condition may be reached in two hours or less. Usually the coronas of the first hour, though full, are too faint for measurement. On successive exhaustions, the intense coronas vanish by passing through three-quarter, half, quarter coronas, &c., in turn.

PERSISTENT LIQUID NUCLEI.

Hydrocarbons, &c.—Nuclei obtained by vigorously shaking all the volatile liquids examined above, showed no tendency to vanish until removed by gravity. I will cite special instances at random bearing on this remarkable behaviour. Coronas produced by precipitating gasoline vapour on the nuclei produced by shaking the liquid, were observed with undiminished strength 7 minutes and 30 minutes after shaking, and might have been seen after an indefinitely longer time. The average apertures were $s=1^\circ\cdot4$, corresponding to the diameter of particle $d=\cdot0029$ centim. In petroleum the coronas were observed strongly an hour after shaking; in benzol similarly intense 5 min., 30 min., 44 min., and 60 min. after shaking; they were distinct 3 hours after but absent next day, about 15 hours after. In carbon bisulphide the coronas due to shaken nuclei coalesce with the coronas due to spontaneous nuclei, so that they persist indefinitely.

From the excessively volatile character of these liquids persistence, even beyond a few minutes, would be impossible if the liquids were quite pure. For the small drops would evaporate and the large drops subside. Consequently the droplets must be solutions obtained by concentrating the impurities throughout the continued evaporation of the liquid by the addition of nuclei, &c. It is difficult to keep these liquids quite pure in an apparatus of which rubber tubing † is an essential part. Apparatus made entirely of glass parts

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* Source of light and goniometer are on opposite sides of the receiver, each 2·5 metres distant. The aperture s subtends the central white disk of the normal corona. If d is the diameter of particle, $d=\cdot00144/s$ centim. nearly.

† Rubber tubing through which carbon bisulphide has been passed will furnish nuclei to precipitate water vapour for days after. Fresh tubing must therefore be provided for each new experiment.

fused together would be undesirable for practical reasons. To avoid these dilemmas experiments may be made with water, in which the difficulties mentioned do not occur, and a definite decision may be reached.

Water.—If all precautions be taken to insure clean and new apparatus and appurtenances and perfect filtration, the air above the water, if free from nuclei, remains so indefinitely. Spontaneous nucleation does not occur.

If a clean vessel free from nuclei is vigorously shaken so as to comminute the water, nuclei are produced in considerable quantity, as is evidenced by the strong coronas seen on exhaustion. But these coronas are short-lived, as shown by the following table:—

Time elapsed after shaking.	Corona.
7 min.	All but absent.
6 "	"
5 "	"
3 "	"
2 "	"
1 "	Faint corona, not measurable. Rain.
½ "	Corona, aperture, $s=1^\circ{\cdot}45$.
None	Strong corona lasting 15 seconds.

These nuclei are obviously water globules, which speedily evaporate or subside, vanishing in a few minutes.

Let a small quantity of sodic carbonate be added to the water; the result is a phenomenal increase in the persistence of the nuclei produced by shaking, as for instance:

Time elapsed after shaking.	Corona.
1 hour.	Strong. $s=1^\circ{\cdot}4$
2 "	" $s=1^\circ{\cdot}6$
3 "	" $s=0^\circ{\cdot}9$
15 "	Just visible.
15 "	Absent.
15 " (violent shaking.)	Distinct, clear, small.

The size and persistence depends on the violence of shaking, the apertures varying from $s=1^\circ{\cdot}4$ to $s=2^\circ{\cdot}0$ correspondingly. In the lapse of time the corona contracts, but may, in favorable cases, be seen much after 15 hours.

The body in solution in this case is solid, and one is liable to conclude that the nucleus in question is the solid residue left after evaporation. This, as will presently be shown, is not necessarily true; the nucleus is liquid, being a more or less concentrated solution both here and in the above experiments with hydrocarbons, &c.

To decide the question as to the cause of the indefinite persistence of the nuclei produced by shaking solutions (apart from gravitation), it is necessary to test a chemically dissolved gas like hydrochloric acid or ammonia. Pure water was first taken and the evanescence of the nuclei (say within 4 minutes) confirmed. Pure hydrochloric acid was then added, and the persistence of the nuclei established, as shown by the following example :—

Time elapsed after shaking dilute HCl.	Corona.
½ min.	Strong. $s = 1°\cdot65$
10 "	Strong.
30 "	"
15 hours.	Distinct. Weak.

Tested with pure water again, the fleeting coronas persisted somewhat longer (vanished in 10 minutes) than before, showing that traces of HCl still lingered in the clean apparatus. On again adding HCl the above results were confirmed.

Dilute ammonia was next tested in the same way. Great care had to be taken after the vessel was thoroughly cleaned to remove lingering traces of HCl. When this was done air free from nuclei remained so above dilute ammonia indefinitely. No nuclei arise spontaneously from the liquid.

On shaking the ammonia nucleus behaved like the nucleus of dilute hydrochloric acid, or of sodic carbonate solution, showing indefinite persistence apart from removal by gravity.

With these experiments the indefinite persistence of nuclei produced by shaking solutions, whatever be the original state of aggregation of the solute, may be considered established. It is finally necessary to inquire into the reasons.

Cause of Persistence.—Inasmuch as the nuclei are equally persistent, no matter whether the solute is gaseous or whether it is liquid or solid, it is not permissible to accentuate the possible occurrence of solid residues as the cause of persistence. At first sight one would be liable to conclude that the persistent nuclei are loose molecular aggregates ; but their size, which probably embraces many thousands of molecules, is unfavourable to such an assumption. They cannot owe their condensational activity to ionization, for the effect is equally marked with the most pronounced hydrocarbon and other insulators. Frictional electricity seems equally negligible ; it would not account for the difference of behaviour of pure water and solutions ; for the electric field within the receiver is a closed field.

The endeavour must therefore be made to explain the phenomenon in terms of surface-tension. If p_r and p_∞ be the vapour-pressures corresponding to radii r and ∞, T the surface-tension, ρ and σ the densities of liquid (solution) and vapour, Kelvin's equation asserts

$$p_r - p_\infty = 2\mathrm{T}\sigma/\rho r, \text{ nearly, if } \rho \text{ replaces } (\rho-\sigma).$$

The present liquid, however, is a solution and its vapour-pressure, p_∞, lies below the normal value for the pure liquid.

Furthermore, as the large drops grow at the expense of the smaller, the vapour-pressure for capillary reasons alone would decrease in the former case and increase in the latter case. At the same time, however, the larger drops becoming more dilute, increase their vapour-pressure, while the smaller drops becoming more concentrated decrease it correspondingly. The second group of influences therefore tend to counteract the effect of capillarity. It is quite conceivable that a state of equilibrium may eventually be reached in which the drops, large and small, will all have the same vapour-pressure (namely, that of the free surface of the liquid), that further evaporation will thereafter cease and the droplets persist, however small.

In fact, after the lapse of time the preceding equation will be replaced for a given drop by

$$p'_{r'} - p'_\infty = 2\mathrm{T}'\sigma/\rho' r',$$

since the pressure, tension, size, and density of the droplet of solution have all changed by evaporation.

If the more concentrated droplet of radius r' now persists, $p'_{r'} = p_\infty$, the vapour-pressure at the flat surface of the original solution. Hence

$$p_\infty - p'_\infty = 2\sigma\mathrm{T}'/\rho' r'.$$

For the case in which a solid is dissolved its mass remains fixed within each suspended drop while the water alone evaporates. When a gas like HCl or H_3N is dissolved the same will also probably be true, for the receiver is filled to the full partial pressure with the gas in question. Hence ρ' may be expressed in terms of ρ, or if $c = r^3/r'^3$,

$$\rho' = 1 + (\rho - 1)\,.\,c,$$

whence finally, if $\delta p = p_\infty - p'_\infty$,

$$r' = 2\sigma\mathrm{T}'/\overline{(1+(\rho-1)\,.\,c)\,.\,\delta p}.$$

For dilute solutions, $\rho = 1$, and the last equation is simply $r' = 2\sigma\mathrm{T}'/\delta p$.

Hence the nuclei produced by shaking dilute aqueous solutions may be considered as subject to this condition, in which all sizes of particles are represented. If $r'=\infty$, $p'_\infty = p_\infty$, the vapour-pressure at the flat surface.

Neglecting the factor for electrolytes, if δp is expressed in terms of Raoult's law, n/N and n/N' being the original and final ratios respectively, of the numbers of molecules in solute and solvent, and p the vapour-pressure at the flat surface of the reservoir of solution,

$$\delta p = p(n/\mathrm{N}' - n/\mathrm{N})/(1+n/\mathrm{N}').$$

Furthermore, if the law discovered empirically by Quincke* ($\mathrm{T}=83+187\ n/\mathrm{N}$ dynes) be adduced,

$$\mathrm{T}' = \mathrm{T} + 187(n/\mathrm{N}' - n/\mathrm{N})$$

where T is the initial and T′ the final surface-tension in dynes per centim.

Thus, finally, if $(n/\mathrm{N}' - n/\mathrm{N}) = k$, for brevity,

$$n' = 2\sigma(\mathrm{T}+187k)(1+n/\mathrm{N}')/\overline{p\,.\,(1+(\rho-1)c)k}.$$

Supposing the electrolytic factor supplied, this equation expresses the relation of the radius of the droplets in terms of the original and final ratios of the numbers of molecules of solute and solvent in solution. It implies that if the nuclei produced by shaking are originally of different sizes this difference will be accentuated. There is thus a curious discrepancy between equation and observation; coronas produced from nuclei due to shaking are always annular on first exhaustion, whatever be the vapour or however long the lapse of time. They eventually vanish annularly, in case of the most volatile hydrocarbon liquid. This can only occur if the shaken nuclei are of about the same size originally, which, in fact, is approximately seen on trial. A reason for it, however, seems difficult to discern. The fact that mere agitation † of the liquid should leave nuclei in its wake so nearly of a size as to produce coronas at all is the essential question.

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* Winkelmann's *Handbuch*, vol. i. p. 466 (Breslau, 1891). An excellent account of the capillary coefficients of solutions will here be found, due to Prof. F. Braun.

† Lenard's experiments (Wied. *Ann.* xlvi. p. 584, 1892) on the electricity of waterfalls might be recalled.

XXX. *On the Velocity of Reaction before Complete Equilibrium and the Point of Transition are reached, &c.*—Part II.* *By* MEYER WILDERMAN, *Ph.D.*, *B.Sc.* (*Oxon.*)†.

CONTENTS.

I. Velocity of reaction before complete equilibrium, &c., and the theory of real and apparent freezing-points, boiling-points, vapour-pressures, solubility, &c.
II. Velocity of reaction before complete equilibrium, &c., and physical geography and meteorology.

I. *Velocity of Reaction before Complete Equilibrium and the Point of Transition are reached, and the Theory of Real and Apparent Freezing-Points, Boiling-Points, Vapour-Pressures, Solubility, &c.*

THE equation for the velocity of ice-melting and ice-separation established in Part I., shows that the equations used in my paper "On the Real and Apparent Freezing-points and the Freezing-point Methods" (Phil. Mag. Dec. 1897) have only to be corrected by the addition of the instability constant in order that the theory of real and apparent freezing-points should be placed on a perfectly correct basis. As is to be seen from Tables I. and II., the values of C which are obtained from the middle part of the curve, when the equation

$$\frac{dt}{dz}=\mathrm{C}(t_o-t)(t-t_{ov}) \text{ instead of } \frac{dt}{dz}=\mathrm{C}(t_o-t)(t-t_{ov}+\mathrm{K})$$

is used, differ only a little from the correct value of C, obtained when K is taken into consideration. For this reason the numerical data used for C in the above paper (see the corrections in Phil. Mag., January 1898), which were obtained with the sensitive 1/100° mercury-thermometer, do not differ much from those which were obtained later on under much more favourable experimental conditions, and by means of the platinum thermometer. We can therefore safely assume, that the theoretical conclusions and numerical values given in the above paper, for my own method as well as for those used by others, are essentially correct. Among other things we may regard it as finally established, that the difference between the real and apparent freezing-points, as well as the difference between the real and apparent freezing-point depressions, are, in the method used by me, only 0°·00002 to 0°·00004, when the convergence temperature is below the freezing temperature. In the same way all the rules given

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* For Part I. see Phil. Mag. July 1901, p. 50.

† Communicated by the Author.

in detail in my publications of 1896 (see Proc. of the Royal Society, 1896; *Zeitschrift für physikalische Chemie*, January 1896) are essentially necessary for securing reliable results of great accuracy. In the theoretical treatment of the subject of freezing-points, there were some essential differences between Nernst and myself, and as it is now intended to extend the problem to a very much larger field (of vapour-pressures, boiling-points, sublimation-pressures, solubility, &c.) it becomes necessary to deal here in a few words with those differences.

In his theoretical consideration of the subject of freezing-points Nernst started (see *Zeitschr. für physik. Chemie,* 1896; see also full translation in my paper, Phil. Mag. December 1897) from the experiments of Boguski on the velocity of solution of metals and marble in acids. He there makes the assumption that the velocity of ice-melting represents the same kind of phenomena as those observed by Boguski, and that it consequently has to be expressed by the equation given by Boguski for the above reactions. He further correspondingly assumes that the apparent freezing-point always depends on the velocity of ice-melting, the term $\frac{C(t_g-t)}{C''}$ having a positive or negative value according as t_g (the convergence temperature) is greater or smaller than t' or t_0, *i. e.*, is above or below the freezing temperature. On the contrary, I thought that *between the reactions of Boguski and that of ice-melting there is no analogy whatever, both representing reactions* sui generis. *My considerations of the theory of the subject were based on the notion of perfect equilibrium,* and the conclusion was arrived at that when the convergence temperature is above the freezing-point the reaction of *ice-melting*, and when below that of *ice separation*, is to be taken into account. The two reactions are of opposite kind, must or may have different velocity constants, and have first to be studied and investigated independently. As will be seen later on, this conception proved to be the correct one. Not only does the reaction of Boguski and that of ice-melting prove each to be *sui generis,* but Boguski's equation for the velocity of solution of metals and of marble in acids is, in all probability, an incorrect one, contradicting as it does the well-established laws of mass action; the phenomenon itself represented by Boguski's reaction has not been (as will be seen later on) even correctly conceived in its true nature, though the misconception was a natural one.

Having now arrived at the result that the velocity of all *reactions before complete equilibrium follows the same general law*

$$\frac{dt}{dz}=C(t_o-t)(t-t_{ov}+K),$$

we are now entitled to regard all those reactions as being of one and the same nature. If it be further considered that *in the establishing of all the different kinds of equilibrium there is always a cooling or warming of the system by the surrounding medium,* it becomes evident that *not only have we to deal with real and apparent freezing-points, but also with real and apparent vapour-pressures, sublimation-pressures, boiling-points, solubilities, &c.* In all these cases one of the two opposite reactions (evaporation, sublimation, solution, or condensation to liquid or solid, separation of the solid from supersaturated solutions, &c.) comes into consideration according as the convergence temperature is above or below the point of equilibrium. This equation must necessarily be connected with that of cooling or warming of the system by the surrounding medium. *The general equation is in all cases*

$$\frac{dt}{dz}=C'(t_o-t)(t-t_{ov}+K)+C(t_g-t),$$

when during the reaction the surface of contact of the solid with the liquid or the gas varies (in the case of freezing-points, solubility, &c.); or

$$\frac{dt}{dz}=C''(t_o-t)+C(t_g-t),$$

when the surface of contact remains constant (vapour-pressures, boiling-points, &c.). When $\frac{dt}{dz}$ becomes $=0$, we get *not the real, but an apparent point of equilibrium.* The apparent point of equilibrium is always obtained between the real point of equilibrium and the convergence temperature. It is above or below the real point of equilibrium, according as the convergence temperature is, at the given arrangements of the experiment, above or below the real point of equilibrium. *The difference between the real and apparent equilibrium, or the error of the observed results,* depends upon how far we succeed by the given arrangements of the experiment in keeping the latter fraction as small and as constant as possible in the equation T′ (observed apparent point of equilibrium) $=T_o$ (the real point of equilibrium)

$$+\frac{C(t_g-t)}{C'(t_o-t_{ov}+K)} \text{ or } +\frac{C(t_g-t)}{C''}$$

(which gives the value of the experimental error). *The difference between the real and apparent lowering of the vapour-pressure or of the rise of boiling-points, &c.,* is

$$(t'-t'')-(t_o-t_o')=\frac{C(t_g-t')}{C'(t_o-t_{ov}+K)}-\frac{C_1(t_g'-t'')}{C_1'(t_o'-t_{ov}'+K')},$$

and the value of the right side of the equation must be kept by the arrangements of the experiment as small as possible, so that their value may be neglected on the side of t_o-t_o'.

The present considerations are only of a preliminary nature, and it is hoped in the future to give a full statement of the subject.

The boiling-point method gives moderately satisfactory results if very great accuracy is not required. The velocity constant of evaporation C″ is moderately great at the boiling-point, the equilibrium being always reached in a comparatively short time. So also 100 c. cm. of liquid and an air-bath are the quantities commonly used (Beckmann). Thus C″ is great enough and C is not very small. Further improvements on the method will be made by the use of a greater quantity of liquid, and by the arrangement of the convergence temperature as near as possible to the boiling-point of the given liquid.

With *the methods for vapour-pressures* we have also been unable up to now to get satisfactory results, even in the case of moderately dilute solutions, where the boiling-point method is already capable of giving satisfactory results. The reason of this is to be found in the fact that the velocity constant C″ of evaporation is very small. As is the case with all reactions, the velocity of evaporation becomes smaller with the fall of temperature; and it is a well-known fact that the time necessary for obtaining the maximum vapour-pressure is, at ordinary temperature, already very considerable. Since the total value of the observed vapour-pressure is at the ordinary temperature very small, the values of $\frac{C(t_g-t')}{C''}$ and of $\frac{C(t_g-t')}{C''}-\frac{C(t_g'-t'')}{C_1''}$ form a considerable part of the value of $T'-T''$ or of T_o-T_o'. It was shown (Phil. Mag. Dec. 1897) that even in the freezing-point method, when 100 c. cm. of liquid, a liquid-bath of −0°·3, and a quantity of ice at equilibrium =0°·3 are used, the experimental error in the obtained freezing-points and freezing-point depressions becomes already about 200 times greater than in my method, and amounts to several thousandths of a degree. It is clear that the results obtained with the different methods of measuring vapour-pressures must be considerably worse than those of the freezing-points. In the first instance the equilibrium in the case of freezing-points is completely reached after about 15 seconds, while in the case of vapour-pressures it takes hours: therefore the value of C'' is in the case of vapour-pressures several hundred times smaller. In the second instance the quantity of the liquid used to the present in these methods is, in comparison with that now used for freezing-points, very small, a liquid jacket is always employed, and the surface of evaporation T_o-T_{ov} cannot be increased *ad libitum*, as in the case of freezing-points. No care we find is also taken for getting the convergence-temperature near the point of equilibrium. To this we must add other very serious sources of error, such as the variation of concentration and temperature at the evaporating surface, which cannot be easily avoided, &c. From the above remarks it is clear in what direction, on which lines, and how far the methods for measuring vapour-pressures can be effectually advanced. We cannot change the value of C'', but we can use greater quantities of liquid, try to keep the evaporating surface larger, keeping the liquid rather wide than deep; we can provide the whole apparatus with an air-bath placed in a liquid- or vapour-bath of a constant temperature, &c., and get the convergence-temperature as near as possible to the point of equilibrium (there is almost an unlimited number of liquids or solutions to choose from, boiling at any desired temperature), so also we have to provide some arrangements for shaking the liquid. It is obvious that the values of C'' and of T_o-T_{ov} make it in this case very imperative that great effort should be made to get the value of T_g-T_o very small. The experiments will, because of this, necessarily be very tedious, but it is unavoidable. No doubt the results will always remain less accurate than may be desirable, limited as we are by the nature of the phenomenon itself in our capacity of making progress. It is further to be considered that an error of 0·001 mm. mercury causes for one molecule normal solution of a nonelectrolyte already an error of 1·2 per cent. in the total value of the observed depression of the vapour-pressure, and 12 per cent. for 0·1 mol. normal solution, while in the freezing-point methods even an error of 0°·0015 does not form 0·1 per cent. error in the total observed value of the freezing-point depression of one molecule normal solution (the aggregate error of my method, however, does not reach the value of 0°·0001–0°·0003). For this reason also much more accurate readings than to 0·001 mm. mercury become necessary, *if even moderately dilute solutions should be investigated.* The present systems of reading the pressure up to 0·001 mm. seem to me also not to be reliable and accurate to the same extent.

Passing *to the methods of solubility*, we have to note in the first instance that the value of C'' in the equation

$$\frac{dt}{dz} = C''(t_o - t)(t - t_{ov} + K)$$

is considerably smaller in case of separation of the salt from a supersaturated solution, than in the case of separation of ice from an aqueous solution. The first reactions last a few minutes, while the second ones only last from 15^s to 30^s. The value of C'' is accordingly (see tables in Part I.) about ten times smaller for the first than for the last. In the different methods in use about 100 c. cm. liquid and a liquid-bath are usually employed, no account being taken of the proper arrangement of the convergence-temperature. On the contrary, the value of T_o T_{ov} or the surface of the solid salt in contact with the liquid is usually great, and can be taken even considerably greater than in the case of the freezing-point method. The principles to be followed here for the development of the method are the same as in all other cases: a greater quantity of the liquid in an air-bath, which is placed in a liquid- or vapour-bath of a suitable constant temperature, should be used, and the convergence-temperature should be kept very near the point of equilibrium. A great value of $T_o - T_{ov}$ should be provided for so as to compensate for the small value of C''. For this the solid should be present in great quantity and finely divided in the liquid, &c. The method can also be arranged in a way quite analogous to that of freezing-point, and the experiments given above show that the results in this case are very successful. Since C'' is not very great here, and all the conditions necessary for securing a successful experiment have to the present not been taken sufficiently into account, there is no wonder that the results obtained by different investigators almost always differ considerably from one another, and that almost all of the results in this region of investigation cannot claim to be of great accuracy. Especially at higher temperatures, where the values of $C(t_g - t)$, or velocity of cooling by the surrounding medium, become very great, we find that the results prove to be very much affected by experimental errors, as could be easily illustrated on the run of a great number of curves.

II. *Velocity of Reaction, Complete Equilibrium, and Physical Geography and Meteorology.*

The formation and melting of ice, snow, hail, glaciers, snowfields, &c., the evaporation of water (of the atmosphere, of the sea, rivers, &c.), the condensation of saturated vapours (to water, clouds, rain, dew, &c.), the solution and carrying away as well as separation of the solid components of the earth, in short, all the most important phenomena which form the main subject of physical geography and of meteorology, follow in their velocity the law given above

$$\frac{dt}{dz}=C(t_o-t)(t-t_{ov}+K).$$

From the form of the equation it follows that all those reactions, even in their pure form, can never reach the point of perfect equilibrium. But, besides, here especially do the phenomena become always more complicated, owing to the interference of other factors, such as the cooling or warming of the surrounding temperature. For this reason always only apparent and never real points of equilibrium are reached in nature, therefore all the phenomena in nature never come to a state of perfect rest, but everything in nature is in a state of eternal reaction. All the above phenomena must therefore henceforth be considered not only in the light of the theoretical points of equilibrium, as it has been up to the present, but also in the light of their actual state, in the light of velocity of reaction. This I shall endeavour to do in due course in a future publication. Since the convergence-temperature, owing to the continual variations in the surrounding temperature, is continually changing, the apparent point of equilibrium of a given system also undergoes continuous variations and shiftings. In considering the above phenomena the importance of the *instability constant K* must not be overlooked, because *it alone explains how a heterogeneous system can be formed from a homogeneous one* without having it necessary as a condition for such a transforming that the newly-formed part should first be present in the system (*e.g.* it explains why overcooled water separates ice, not only when an ice-crystal is first introduced, and an unstable heterogeneous system is thus first formed, but also why this separation takes place without such a crystal having been introduced, see Part I.). The instability constant, it must be remarked, depends upon a series of factors, internal and external. For instance a supercooled liquid or a supersaturated solution begins to crystallize too early if the liquid is shaken, or if a speck of dust has fallen into it; the same liquid can be much more supercooled in narrow tubes than in wider vessels; the same liquid can be more supercooled if the cooling proceeds slowly, and if the temperature is equalized through the whole mass of the liquid, than when this is done rapidly. On the whole, the limit to which a liquid can be supercooled, a solution supersaturated, &c., depends upon the nature of the solvent, of the dissolved substance, and upon the nature of the reaction itself.

XXXI. *Notices respecting New Books.*

Mathematical and Physical Papers. By Sir GEORGE GABRIEL STOKES, *Bart., M.A., D.C.L., LL.D., F.R.S., Fellow of Pembroke College and Lucasian Professor of Mathematics in the University of Cambridge.* Vol. III. Cambridge: At the University Press, 1901. Pp. viii+415.

AFTER the long interval which has elapsed since Sir G. Gabriel Stokes published Vol. II. of his collected papers, the present volume will be eagerly welcomed by all students of mathematical physics. The immense convenience of having the papers of our great leaders in science collected in book form can hardly be overestimated, especially in view of the ever-swelling stream of modern scientific literature, which makes such demands on the time of those eager to keep in touch with recent progress—time that can be ill-spared for the purpose of wading through a mass of bulky volumes in search of some classical paper of much earlier date. We sincerely hope that the author will find time and strength to complete the collection of his papers at an early date.

About one-fourth of the present volume is occupied by the important memoir "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums." Then follows a paper on "the possible effect of the Radiation of Heat on the Propagation of Sound," and the remainder of the book is taken up with various papers, chiefly on Light—"On the Colours of Thick Plates"; "On a New Elliptic Analyser"; "On the Conduction of Heat in Crystals"; "On the Total Intensity of Interfering Light"; On the Composition and Resolution of Streams of Polarised Light from different Sources," and "On the Change of Refrangibility of Light."

In the prefatory note to this volume, the author explains the reason of the long delay in its publication. It had been his intention to enter on "some rather elaborate and in part laborious calculations bearing on two of the papers which appear in the present volume." This intention had, unfortunately, to be abandoned, and the papers referred to appear in their original form.

Ueber die Anwendung der Lehre von den Gasionen auf die Erscheinungen der atmosphärischen Elektricität. *Von* Prof. Dr. Hans Geitel. Braunschweig: F. Vieweg und Sohn. 1901. Pp. 28.

In this interesting pamphlet, the distinguished author seeks to explain the phenomenon of atmospheric electricity by the aid of recent researches regarding the discharging effect of air on charged conductors. The theory advanced possesses the merit of great simplicity, and, should subsequent quantitative researches furnish additional evidence in support of it, will mark a distinct step towards the solution of an extremely difficult problem.

Meteorologische Optik. *Von* J. M. Pernter. I. Abschnitt. Wien und Leipzig: Wilhelm Braumüller. 1902. Pp. viii+54.

This is the first part of a treatise on meteorological optics, and it deals with such problems as the apparent shape of the heavenly vault, the apparent altitude of the heavenly bodies, the apparent increase in the size of the sun and moon when near the horizon, &c., a thorough discussion of each problem from a physico-physiological standpoint being given. The treatise is to be completed in four parts.

La Géométrie Non Euclidienne. *Par* P. Barbarin. Paris: C. Naud, 1902. Pp. 78. ("Scientia" Series, No. 15.)

Euclid's celebrated axiom regarding the intersection at some finite distance of two straight lines which meet a third line so as to make the sum of the two interior angles on the same side of it less than two right angles, has been the subject of much discussion among geometers, and in modern times has given rise to two systems of non-Euclidian geometry, associated with the names of Lobatchewsky and Riemann. The author of the little book before us gives a very thorough and critical exposition of the new geometries, and the work may be recommended to the notice of those interested in the philosophical basis of geometrical reasoning.

Primary Batteries. Their Theory, Construction and Use. By W. R. Cooper, *M.A.*, *B.Sc.* London: The Electrician Printing and Publishing Company, Limited. Pp. vi+324.

Notwithstanding the numerous forms of primary batteries which have been invented at different times, the theory of the action of such a battery has been one of the most difficult problems confronting the scientific investigator, and one which, after a century of research, is still shrouded in mystery. The chemical changes which go on in a voltaic cell have, of course, been known for a very long time; but the precise way in which the chemical and electrical effects are related to one another, and the mechanism by which they are linked together, are problems of much greater difficulty and complexity. When Nernst boldly advanced his elegant theory of electrolytic solution pressure and applied it to explain the action of a primary cell, it was thought that at last a satisfactory solution of the problem had been arrived at. Unfortunately, some recent work has placed serious obstacles in the way of Nernst's theory, and the theory of ionization has by no means received unqualified support from physicists.

It is probably owing to the somewhat chaotic state of the theory that no writer was found bold enough to write a comprehensive treatise on the primary cell, dealing with it in all its aspects. This task has now been accomplished—and accomplished most successfully—by Mr. W. R. Cooper in the book before us.

In the first few chapters we have a brief historical introduction and an account of the actions going on in a simple voltaic cell, including local action and polarization. Exception might be taken to the manner in which some of the terms are defined in these early chapters. Thus, electromotive force is explained to mean "that force which causes the current to flow in any circuit." This semi-popular method of definition seems somewhat out of place in a book which is not intended for beginners. In chapters IV. and V. we have a very clear and interesting account of the theory of the voltaic cell; a careful perusal of these chapters will probably convince the reader that the theory of the voltaic cell has by no means reached finality. Chapter VI. deals with non-chemical cells and thermopiles. Some useful hints are contained in the next chapter, on the testing of cells. Then follows a detailed account of various forms of cells, the subdivision into one-fluid, two-fluid, and dry cells being adopted. Standard cells receive special consideration in Chapter XI.

Since the introduction of the dynamo as a generator of electrical energy, the field of usefulness of the primary cell has been considerably restricted. In all cases, however, in which comparatively small currents are required at intervals, the primary cell has been able to hold its own. As standards of E.M.F., certain forms of cells will always be used. Within recent years, however, numerous attempts have been made by various inventors to produce a primary cell which should rival the steam-engine and dynamo as a current-generator. For this purpose the cell must be arranged to consume a cheap fuel—carbon. To all those who hope for great things from a carbon-consuming cell we earnestly commend the closing chapter of Mr. Cooper's book, in which the subject of carbon-consuming cells is dealt with in a masterly fashion. The enthusiasts who look for a complete revolution in the cost of producing electrical energy when the long-wished-for carbon-consuming cell makes its appearance, will be somewhat sobered by the clear and critical account of the subject which is to be found in Mr. Cooper's book. Such enthusiasts entirely overlook the fact that the cost of the fuel forms only one item in the total cost of production. Even a carbon-consuming cell would not enable us to obtain electrical energy at an entirely trifling cost. But such a cell is very long in making its appearance—so long, in fact, that we may be pardoned for regarding it as we should do the philosopher's stone or the elixir of life—things highly desirable, perhaps, but impossible of attainment.

Mr. Cooper's book is certain to appeal to a wide circle of readers, and we have no doubt whatever that it will at once take its place as the standard treatise on the subject.

Géométrographie ou Art des Constructions Géométriques. *Par* ÉMILE LEMOINE. C. Naud, 1902. Pp. 87. ("Scientia" Series, No. 18.)

MOST problems in geometrical construction admit of more than one solution, but among them there is generally one which involves the least number of operations, and is therefore the simplest. This simplest solution constitutes the *geometrographic* construction. The instruments employed consist of a straight-edge, dividers, and set-square. The various operations involved—adjusting the straight-edge so that it passes through one or two given points, drawing a straight line, setting the dividers to a given length, drawing a circle, &c.—are denoted by symbols. The complexity of the solution may then be ascertained from the symbolical expression for the operations involved, and the number of these latter is termed the *coefficient of simplicity* (as the author properly points out, the coefficient of complexity would be a more appropriate term). By a careful study of the problem, the author has in many cases succeeded in reducing considerably the coefficient of simplicity. One case is mentioned in which, by the joint efforts of a number of geometers, this coefficient was reduced from 78 (involving the tracing of 17 straight lines and 20 circles) to 35 (7 straight lines and 5 circles). The author gives the solutions of 69 problems, in some cases giving several solutions one of which (the simplest) is the geometrographic one. The construction is first explained, and is then followed by a symbolical formula, the coefficient of simplicity, and the number of straight lines and circles drawn in the course of the construction.

Théorie de la Lune. *Par* H. ANDOYER. Paris: C. Naud, 1902. Pp. 86. ("Scientia" Series, No. 17.)

IN this little book, the author develops, in the simplest possible form, the principal portions of the lunar theory, without, however, considering the numerical values of the various constants which appear in the equations. On account of the highly abstruse nature of the subject, the book is necessarily intended for specialists, and to them should prove very useful.

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[SIXTH SERIES.]

SEPTEMBER 1902.

XXXII. *On the Weights of Atoms.*

By Lord KELVIN, *G.C.V.O.*

[Concluded from page 198.]

§ 52. A NEW method of finding an inferior limit to the number of molecules in a cubic centimetre of a gas, very different from anything previously thought of, and especially interesting to us in connexion with the wave-theory of light, was given by Lord Rayleigh[*], in 1899, as a deduction from the dynamical theory of the blue sky which he had given 18 years earlier. Many previous writers, Newton included, had attributed the light from the sky, whether clear blue, or hazy, or cloudy, or rainy, to fine suspended particles which divert portions of the sunlight from its regular course; but no one before Rayleigh, so far as I know, had published any idea of how to explain the blueness of the cloudless sky. Stokes, in his celebrated paper on Fluorescence[†], had given the true theory of what was known regarding the polarization of the blue sky in the following "significant remark" as Rayleigh calls it: "Now this result "appears to me to have no remote bearing on the question of "the directions of the vibrations in polarized light. So long "as the suspended particles are large compared with the waves "of light, reflexion takes place as it would from a portion of "the surface of a large solid immersed in the fluid, and no "conclusion can be drawn either way. But if the diameter

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[*] Rayleigh, Collected Papers, vol. i. art. viii. p. 87.

[†] "On the Change of Refrangibility of Light," Phil. Trans. 1852, and Collected Papers, vol. iii.

"of the particles be small compared with the length of a wave "of light, it seems plain that the vibrations in a reflected ray "cannot be perpendicular to the vibrations in the incident "ray"; which implies that the light scattered in directions perpendicular to the exciting incident ray has everywhere its vibrations perpendicular to the plane of the incident ray and the scattered ray; provided the diameter of the molecule which causes the scattering is very small in comparison with the wave-length of the light. In conversation Stokes told me of this conclusion, and explained to me with perfect clearness and completeness its dynamical foundation; and applied it to explain the polarization of the light of a cloudless sky, viewed in a direction at right angles to the direction of the sun. But he did not tell me (though I have no doubt he knew it himself) why the light of the cloudless sky seen in any direction is blue, or I should certainly have remembered it.

§ 53. Rayleigh explained this thoroughly in his first paper (1871), and gave what is now known as Rayleigh's law of the blue sky; which is, that, provided the diameters of the suspended particles are small in comparison with the wave-lengths, the proportions of scattered light to incident light for different wave-lengths are inversely as the fourth powers of the wave-lengths. Thus, while the scattered light has the same colour as the incident light when homogeneous, the proportion of scattered light to incident light is seven times as great for the violet as for the red of the visible spectrum; which explains the intensely blue or violet colour of the clearest blue sky.

§ 54. The dynamical theory shows that the part of the light of the blue sky, looked at in a direction perpendicular to the direction of the sun, which is due to sunlight incident on a single particle of diameter very small in comparison with the wave-lengths of the illuminating light, consists of vibrations perpendicular to the plane of these two directions: that is to say, is completely polarized in the plane through the sun. In his 1871 paper *, Rayleigh pointed out that each particle is illuminated, not only by the direct light of the sun, but also by light scattered from other particles, and by earth-shine, and partly also by suspended particles of dimensions not small in comparison with the wave-lengths of the actual light; and he thus explained the observed fact that the polarization of even the clearest blue sky at 90° from the sun is not absolutely complete, though it is very nearly so.

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* Collected Papers, vol. i. p. 94.

There is very little of polarization in the light from white clouds seen in any direction, or even from a cloudless sky close above the horizon seen at 90° from the sun. This is partly because the particles which give it are not small in comparison with the wave-lengths, and partly because they contribute much to illuminate one another in addition to the sunlight directly incident on them.

§ 55. For his dynamical foundation, Rayleigh definitely assumed the suspended particles to act as if the ether in their places were denser than undisturbed ether, but otherwise uninfluenced by the matter of the particles themselves. He tacitly assumed throughout that the distance from particle to particle is very great in comparison with the greatest diameter of each particle. He assumed these denser portions of ether to be of the same rigidity as undisturbed ether; but it is obvious that this last assumption could not largely influence the result, provided the greatest diameter of each particle is very small in comparison with its distance from next neighbour, and with the wave-lengths of the light: and, in fact, I have found from the investigation of §§ 41, 42 of Lecture XIV. for *rigid* spherical molecules embedded in ether, exactly the same result as Rayleigh's; which is as follows

$$k=\frac{8\pi^3 n}{3}\left(\frac{D'-D}{D}\frac{T}{\lambda^2}\right)^2=82{\cdot}67\,n\left(\frac{D'-D}{D}\frac{T}{\lambda^2}\right)^2 \quad . \quad . \quad (1);$$

where λ denotes the wave-length of the incident light supposed homogeneous; T the volume of each suspended particle; D the undisturbed density of the ether; D' the mean density of the ether within the particle; n the number of particles per cubic centimetre; and k the proportionate loss of homogeneous incident light, due to the scattering in all directions by the suspended particles per centimetre of air traversed. Thus

$$1-\epsilon^{-kx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the loss of light in travelling a distance x (reckoned in centimetres) through ether as disturbed by the suspended particles.

It is remarkable that D' need not be uniform throughout the particle. It is also remarkable that the shape of the volume T may be anything, provided only its greatest diameter is very small in comparison with λ. The formula supposes $T\,(D'-D)$ the same for all the particles. We shall have to consider cases in which differences of T and D' for different particles are essential to the result ; and to include these we shall have to use the formula

$$k=\frac{82\cdot67}{\lambda^4}\Sigma\left[\frac{(D'-D)T}{D}\right]^2 \quad . \quad . \quad . \quad . \quad (3),$$

where $\Sigma\left[\frac{(D'-D)T}{D}\right]^2$ denotes the sum of $\left[\frac{(D'-D)T}{D}\right]^2$ for all the particles in a cubic centimetre.

§ 56. Supposing now the number of suspended particles per cubic wave-length to be very great, and the greatest diameter of each to be small in comparison with its distance from next neighbour, we see that the virtual density of the ether vibrating among the particles is

$$D+\Sigma T(D'-D) \quad . \quad . \quad . \quad . \quad . \quad (4);$$

and therefore, if u and u' be the velocities of light in pure ether, and in ether as disturbed by the suspended particles, we have (Lecture VIII. p. 80)

$$u'^2=u^2\left[1+\Sigma\frac{T(D'-D)}{D}\right] \quad . \quad . \quad . \quad . \quad (5).$$

Hence, if μ denote the refractive index of the disturbed ether, that of pure ether being 1, we have

$$\mu=\left[1+\Sigma\frac{T(D'-D)}{D}\right]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (6);$$

and therefore, approximately,

$$\mu^2-1=\Sigma\frac{T(D'-D)}{D} \quad . \quad . \quad . \quad . \quad . \quad (7).$$

§ 57. In taking an example to illustrate the actual transparency of our atmosphere, Rayleigh says * ; " Perhaps the " best data for a comparison are those afforded by the varying " brightness of stars at various altitudes. Bouguer and others " estimate about ·8 for the transmission of light through the " entire atmosphere from a star in the zenith. This corre- " sponds to 8·3 kilometres (the " height of the homogeneous " atmosphere" at 10° Cent.) of air at standard pressure." Hence for a medium of the transparency thus indicated we

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* Phil. Mag. April 1899, p. 382.

have $\epsilon^{-830000k} = \cdot 8$; which gives $1/k = 3720000$ centimetres = 37·2 kilometres.

§ 58. Suppose for a moment the want of perfect transparency thus defined to be *wholly* due to the fact that the *ultimate molecules* of air are not infinitely small and infinitely numerous, so that the "suspended particles" hitherto spoken of would be merely the molecules N_2, O_2; and suppose further $(D'-D)T$ to be the same for nitrogen and oxygen. The known refractivity of air ($\mu - 1 = \cdot 0003$), nearly enough the same for all visible light, gives by equation (7) above, with n instead of Σ,

$$\frac{n(D'-D)T}{D} = \cdot 0006.$$

Using this in (1) we find

$$k = \frac{29\cdot 76}{n\lambda^4 . 10^6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

for what the rate of loss on direct sunlight would be, per centimetre of air traversed, if the light were all of one wave-length, λ. But we have no such simplicity in Bouguer's datum regarding transparency for the actual mixture which constitutes sunlight: because the formula makes k^{-1} proportional to the fourth power of the wave-length; and every cloudless sunset and moonset and sunrise and moonrise over the sea, and every cloudless view of sun or moon below the horizon of the eye on a high mountain, proves the transparency to be in reality much greater for red light than for the average undimmed light of either luminary, though probably not so much greater as to be proportional to the fourth power of the wavelength. We may, however, feel fairly sure that Bouguer's estimate of the loss of light in passing vertically through the whole atmosphere is approximately true for the most luminous part of the spectrum corresponding to about the D line, wavelength $5\cdot 89 . 10^{-5}$ cm., or (a convenient round number) $6 . 10^{-5}$ as Rayleigh has taken it. With this value for λ, and $3\cdot 72 . 10^6$ centimetres for k^{-1}, (8) gives $n = 8\cdot 54 . 10^{18}$ for atmospheric air at 10° and at standard pressure. Now it is quite certain that a very large part of the loss of light estimated by Bouguer is due to suspended particles; and therefore it is certain that the number of molecules in a cubic centimetre of gas at standard temperature and pressure is considerably greater than $8\cdot 54 . 10^{18}$.

§ 59. This conclusion drawn by Rayleigh from his dynamical theory of the absorption of light from direct rays through air, giving very decidedly an inferior limit to the number of molecules in a cubic centimetre of gas, is perhaps the most thoroughly well founded of all definite estimates hitherto made regarding sizes or numbers of atoms. We shall see (§§ 73 ... 79 below) that a much larger inferior limit is found on the same principles by careful consideration of the loss of light due to the ultimate molecules of pure air *and to suspended matter* undoubtedly existing in all parts of our atmosphere, even where absolutely cloudless, that is to say, warmer than the dew-point, and therefore having none of the liquid spherules of water which constitute cloud or mist.

§ 60. Go now to the opposite extreme from the tentative hypothesis of § 58 and, while assuming, as we know to be true, that the observed refractivity is wholly or almost wholly due to the ultimate molecules of air, suppose the opacity estimated by Bouguer to be wholly due to suspended particles which, for brevity, we shall call dust (whether dry or moist). These particles may be supposed to be generally of very unequal magnitudes: but, for simplicity, let us take a case in which they are all equal, and their number only 1/10000th of the $8{\cdot}54 . 10^{18}$, which in § 59 we found to give the true refractivity of air, with Bouguer's degree of opacity for $\lambda = 6 . 10^{-5}$. With the same opacity we now find the contribution to refractivity of the particles causing it, to be only 1/100th of the known refractivity of air. The number of particles of dust which we now have is $8{\cdot}54 . 10^{14}$ per cubic centimetre, or 1107 per cubic wave-length, which we may suppose to be almost large enough or quite large enough to allow the dynamics of § 56 for refractivity to be approximately true. But it seems to me almost certain that $8{\cdot}54 . 10^{14}$ is vastly greater than the greatest number of dust particles per cubic centimetre to which the well-known haziness of the clearest of cloudless air in the lower regions of our atmosphere is due; and that the true numbers, at different times and places, may probably be such as those counted by Aitken * at from 42500 (Hyères, 4 p.m. April 5, 1892) to 43 (Kingairloch, Argyllshire, 1 p.m. to 1.30 p.m. July 26, 1891).

§ 61. Let us, however, find how small the number of particles per cubic centimetre must be to produce Bouguer's degree of opacity, without the particles themselves being so

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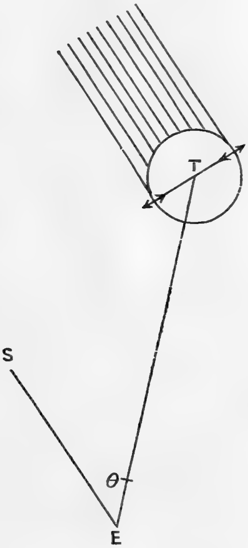
* Trans. R. S. E. 1894, vol. xxxvii. part iii. pp. 675, 672

large in comparison with the wave-length as to exclude the application of Rayleigh's theory. Try for example $T=10^{-3}.\lambda^3$ (that is to say, the volume of the molecule 1/1000th of the cubic wave-length, or roughly diameter of molecule 1/10th of the wave-length) which seems small enough for fairly approximate application of Rayleigh's theory ; and suppose, merely to make an example, D' to be the optical density of water, D being that of ether; that is to say, $D'/D=(1\cdot3337)^2=1\cdot78$. Thus we have $(D'-D)\ T/D=\cdot0007\lambda^3$: and with $\lambda=6\,.\,10^{-5}$, and with $k^{-1}=3\cdot72\,.\,10^6$, (1) gives $n=1\cdot48\,.\,10^6$, or about one and a half million particles per cubic centimetre. Though this is larger than the largest number for natural air counted by Aitken, it is interesting as showing that Bouguer's degree of opacity can be accounted for by suspended particles, few enough to give no appreciable contribution to refractivity, and yet not too large for Rayleigh's theory. But when we look through very clear air by day, and see how far from azure or deep blue is the colour of a few hundred metres, or a few kilometres of air with the mouth of a cave or the darkest shade of mountain or forest for background ; and when in fine sunny weather we study the appearance of the *grayish* haze always, even on the clearest days, notably visible over the scenery among mountains or hills ; and when by night at sea we see a lighthouse light at a distance of 45 or 50 kilometres, and perceive how little of redness it shows; and when we see the setting sun shorn of his brilliance sufficiently to allow us to look direct at his face, and yet only ruddy, rarely what could be called ruby red ; it seems to me that we have strong evidence for believing that the want of perfect clearness of the lower regions of our atmosphere is in the main due to suspended particles, too large to allow approximate fulfilment of Rayleigh's law of fourth power of wave-length.

§ 62. But even if they were small enough for Rayleigh's theory the question would remain, Are they small enough and numerous enough to account for the refractivity of the atmosphere? To this we shall presently see we must answer undoubtedly "No"; and much less than Bouguer's degree of opacity, probably not as much as a quarter or a fifth of it, is due to the ultimate molecules of air. In a paper by Mr. Quirino Majorana in the Transactions of the R. Accademia dei Lincei (of which a translation is published in the Philosophical Magazine for May 1901), observations by himself in Sicily, at Catania and on Mount Etna, and by Mr. Gaudenzio Sella, on Monte Rosa in Switzerland, determining the ratio of the brightness of the sun's surface to the brightness of the sky seen in any direction, are described. This ratio they denote by *r*. One specially notable result of Mr. Majorana's is that "the value of *r* at the crater of Etna is about five times greater than at Catania." The barometric pressures were approximately 53·6 and 76 cms. of mercury. Thus the atmosphere above Catania was only 1·42 times the atmosphere above Etna, and yet it gave five times as much scattering of light by its particles, and by the particles suspended in it. This at once proves that a great part of the scattering must be due to suspended particles; and more of them than in proportion to the density in the air below the level of Etna than in the air above it. In Majorana's observations, it was found that "except for regions close to the horizon, the luminosity of the "sky had a sensibly constant value in all directions when "viewed from the summit of Etna." This uniformity was observed even for points in the neighbourhood of the sun, as near to it as he could make the observation without direct light from the sun getting into his instrument. I cannot but think that this apparent uniformity was only partial. It is quite certain that with sunlight shining down from above, and with equal light everywhere shining up from earth or sea or haze, illuminating the higher air, the intensities of the blue light seen in different directions above the crater would be largely different. This is proved by the following investigation; which is merely an application of Rayleigh's theory to the question before us. But from Majorana's narrative we may at all events assume that, as when observing from Catania, he also on Etna chose the least luminous part of the sky (Phil. Mag., May 1901, p. 561), for the recorded results (p. 562) of his observations.

§ 63. The diagram, fig. 1 below, is an ideal representation of a single molecule or particle, *T*, with sunlight falling on it indicated by parallel lines, and so giving rise to scattered light seen by an eye at *E*. We suppose the molecule or particle to be so massive relatively to its bulk of ether that it is practically unmoved by the ethereal vibration; and for simplicity at present we suppose the ether to move freely through the volume *T*, becoming denser without changing its velocity when it enters this fixed volume, and less dense when it leaves. In §§ 41, 42, of Lecture XV. above, and in Appendix A, a definite supposition, attributing to ether no other property than elasticity as of an utterly homogeneous perfectly elastic solid, and the exercise of mutual force between itself and ponderable matter occupying the same space, is explained: according to which the ether within the atom will react upon moving ether outside just as it would if our present convenient temporary supposition of magically augmented density within the volume of an absolutely fixed molecule were realized in nature. For our present purpose, we may if we please, following Rayleigh, do away altogether with the ponderable molecule, and merely suppose *T* to be a denser portion of the ether. And if its greatest diameter is small enough relatively to a wave-length, it will make no unnegligible difference whether we suppose the ether in *T* to have the same rigidity as the surrounding free ether, or suppose it perfectly rigid as in §§ 1—46 of Lecture XIV. dealing with a rigid globe embedded in ether.

Fig. 1.



§ 64. Resolving the incident light into two components having semi-ranges of vibration ϖ, ρ, in the plane of the paper and perpendicular to it ; consider first the component in the plane having vibrations symbolically indicated by the arrowheads, and expressed by the following formula

$$\omega \sin \frac{2\pi u t}{\lambda},$$

where u is the velocity of light, and λ the wave-length. The greater density of the ether within *T* gives a reactive force on the surrounding ether outside, in the line of the primary vibration, and against the direction of its acceleration, of which the magnitude is

$$\frac{T(D'-D)\varpi}{D}\,\frac{2\pi u}{\lambda}\cos\frac{2\pi ut}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

This alternating force produces a train of spherical waves spreading out from T in all directions, of which the displacement is, at greatest, very small in comparison with ϖ; and which at any point E at distance r from the centre of T, large in comparison with the greatest diameter of T, is given by the following expression *

$$\xi\cos\frac{2\pi}{\lambda}(ut-r),$$

with

$$\xi=\varpi\frac{\pi T(D'-D)}{r\lambda^2 D}\cos\theta \quad . \quad . \quad . \quad . \quad (10),$$

where θ is the angle between the direction of the sun and the line TE. This formula, properly modified to apply it to the other component of the primary vibration, that is, the component perpendicular to the plane of the paper, gives for the displacement at E due to this component

$$\eta\cos\frac{2\pi}{\lambda}(ut-r),$$

with

$$\eta=\rho\frac{\pi T(D'-D)}{r\lambda^2 D} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11).$$

Hence for the quantity of light falling from T per unit of time, on unit area of a plane at E, perpendicular to ET, reckoned in convenient temporary units, we have

$$\xi^2+\eta^2=\left[\frac{\pi T(D'-D)}{r\lambda^2 D}\right]^2(\varpi^2\cos^2\theta+\rho^2) \quad . \quad (12).$$

§ 65. Consider now the scattered light emanating from a large horizontal plane stratum of air 1 cm. thick. Let T of fig. 1 be one of a vast number of particles in a portion of this

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* This formula is readily found from §§ 41, 42 of Lecture XIV. The complexity of the formulas in §§ 8–40 is due to the inclusion in the investigation of forces and displacements at small distances from T, and to the condition imposed that T is a rigid spherical figure. The dynamics of §§ 33–36 with $c=0$, and the details of §§ 37–39 further simplified by taking $v=\infty$, lead readily to the formulas (10) and (11) in our present text.

stratum subtending a small solid angle Ω viewed at an angular distance β from the zenith by an eye at distance r. The volume of this portion of the stratum is $\Omega \sec \beta\, r^2$ cubic centimetres; and therefore, if Σ denotes summation for all the particles in a cubic centimetre, small enough for application of Rayleigh's theory, and q the quantity of light shed by them from the portion $\Omega \sec \beta\, r^2$ of the stratum, and incident on a square centimetre at E, perpendicular to ET, we have

$$q = \frac{\pi^2}{\lambda^4}\Sigma\left[\frac{T(D'-D)}{D}\right]^2 \Omega \sec\beta(\varpi^2\cos^2\theta+\rho^2) \quad . \quad . \quad (13).$$

Summing this expression for the contributions by all the luminous elements of the sun and taking

$$\int q = Q$$

to denote this summation, we have instead of the factor

$$\varpi^2\cos^2\theta+\rho^2,$$

$$\cos^2\theta\int\varpi^2+\int\rho^2:$$

and we have

$$\int\omega^2=\int\rho^2=\tfrac{1}{2}S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14),$$

where S denotes the total quantity of light from the sun falling perpendicularly on unit of area in the particular place of the atmosphere considered. Hence the summation of (13) for all the sunlight incident on the portion $\Omega \sec \beta\, r^2$ of the stratum, gives

$$Q=\frac{\pi^2}{\lambda^4}\Sigma\left[\frac{T(D'-D)}{D}\right]^2\Omega\sec\beta(\tfrac{1}{2}\cos^2\theta+\tfrac{1}{2})S \quad . \quad (15).$$

§ 66. To define the point of the sky of which the illumination is thus expressed, let ζ be the zenith distance of the sun, and ψ the azimuth, reckoned from the sun, of the place of the sky seen along the line ET. This place and the sun and the zenith are at the angles of a spherical triangle SZT, of which ST is equal to θ. Hence we have

$$\cos\theta=\cos\zeta\cos\beta+\sin\zeta\sin\beta\cos\psi \quad . \quad . \quad . \quad (16).$$

Let now, as an example, the sun be vertical: we have $\zeta=0$, $\theta=\beta$, and (15) becomes

$$Q=\frac{\pi^2}{\lambda^4}\Sigma\left[\frac{T(D'-D)}{D}\right]^2\Omega.\tfrac{1}{2}(\cos\beta+\sec\beta)S \quad . \quad . \quad (17).$$

This shows least luminosity of the sky around the sun at the zenith, increasing to ∞ at the horizon (easily interpreted). The law of increase is illustrated in the following table of values of $\frac{1}{2}(\cos\beta+\sec\beta)$ for every 10° of β from 0° to 90°.

β.	$\frac{1}{2}(\cos\beta+\sec\beta)$.	β.	$\frac{1}{2}(\cos\beta+\sec\beta)$.
0°	1·000	50°	1·099
10°	1·000	60°	1·250
20°	1·002	70°	1·633
30°	1·010	80°	2·966
40°	1·036	90°	∞

§ 67. Instead now of considering illumination on a plane perpendicular to the line of vision, consider the illumination by light from our one-centimetre-thick great* horizontal plane stratum of air, incident on a square centimetre of horizontal plane. The quantity of this light per unit of time coming from a portion of sky subtending a small solid angle Ω at zenith distance β is $Q\cos\beta$. Taking $\Omega=\sin\beta d\beta d\psi$ and integrating, we find for the light shed by the one-centimetre-thick horizontal stratum on a horizontal square centimetre of the ground,

$$\int_0^{2\pi} d\psi \int_0^{\frac{1}{2}\pi} d\beta \sin\beta . Q\frac{\cos\beta}{\Omega} = \frac{4\pi^3}{3\lambda^4}\Sigma\left[\frac{T(D'-D)}{D}\right]^2 S \quad . (18).$$

Now each molecule and particle of dust sheds as much light upwards as downwards. Hence (18) doubled expresses the quantity of light lost by direct rays from a vertical sun in crossing the one-centimetre-thick horizontal stratum. It agrees with the expression for k in (1) of § 55, as it ought to do.

§ 68. The expression (15) is independent of the distance of the stratum above the level of the observer's eye. Hence if H denote the height above this level, of the upper boundary of an ideal homogeneous atmosphere consisting of all the ultimate molecules and all the dust of the real atmosphere scattered uniformly through it, and if s denote the whole light on unit area of a plane at E perpendicular to ET, from all the molecules and dust in the solid angle Ω of the real atmo-

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* We are neglecting the curvature of the earth, and supposing the density and composition of the air to be the same throughout the plane horizontal stratum to distances from the zenith very great in comparison with its height above the ground.

sphere, due to the sun's direct light incident on them, we have

$$\frac{s}{S}=H\sec\beta\frac{\pi^2}{\lambda^4}\Sigma\left[\frac{T(D'-D)}{D}\right]^2\Omega.\tfrac{1}{2}(\cos^2\theta+1)\;.\quad.\quad.\quad(19)\;;$$

provided we may, in the cases of application whatever they may be, neglect the diminution of the direct sunlight in its actual course through air, whether to the observer or to the portion of the air of which he observes the luminosity, and neglect the diminution of the scattered light from the air in its course through air to the observer. This proviso we shall see is practically fulfilled in Mr. Majorana's observations on the crater of Etna for zenith distances of the sun not exceeding 60°, and in Mr. Sella's observation on Monte Rosa in which the sun's zenith distance was 50°. But for Majorana's recorded observation on Etna at 5.50 a.m. when the sun's zenith distance was 81°·71, of which the secant is 6·927, there may have been an important diminution of the sun's light reaching the air vertically above the observer, and a considerably more important diminution of his light as seen direct by the observer. This would tend to make the sunlight reaching the observer less strong relatively to the skylight than according to (19); and might conceivably account for the first number in col. 3 being smaller than the first number in col. 4 of the Table of § 69 below; but it seems to me more probable that the smallness of the first two numbers in col. 3, showing considerably greater luminosity of sky than according to (19), may be partly or chiefly due to dust in the air overhead, optically swelled by moisture in the early morning. The largeness of the luminosity of the sky indicated by the smallness of the last number in col. 3 (376), in comparison with the last number of col. 4 (460), may conceivably be explained by earthshine from air and volcanic ash and rock and forest and vineyard and sea below the level of the crater adding considerably to the illumination which the sky experiences from above by direct sunlight. This addition would be much greater at 11 a.m., when the sun's zenith distance was 29°·9, than at 9 a.m., when it was 44°·6.

§ 69. The results of Majorana's observations from the crater of Etna are shown in the following Table, of which the first and third columns are quoted from the Philosophical Magazine for May 1901, and the second column has been kindly given to me in a letter by Mr. Majorana. The values of *S*/*s* shown in column 4 are calculated from § 68 (19), with the factor of

$\sec\beta(\cos^2\theta+1)$ taken to make it equal to Majorana's r for sun's zenith distance 44°·6, on the supposition that the region of sky observed was in each case (see § 62 above) in the position of minimum luminosity as given by (19). It is obvious that this position is in a vertical great circle through the sun, and on the opposite side of the zenith from the sun; and thus we have $\theta=\zeta+\beta$. Hence (19) becomes

Col. 1.	Col. 2.	Col. 3.	Col. 4.	Col. 5.
Time.	Zenith distance of sun. ζ.	Ratio of luminosity of sun's disc to luminosity of sky. r.	$\frac{S}{s}$.	Zenith distance of least luminous part of sky. β.
5.50 A.M.	81°·7	2570000	3280000	5°·5
7	68·0	3125000	3350000	14·4
8	56·1	3650000	3600000	21·7
9	44·6	3930000	3930000	27·8
11	29·9	3760000	4600000	33·6

$$\frac{s}{S}=H\frac{\pi^2}{\lambda^4}\;\Sigma\left[\frac{T\,(D'-D)}{D}\right]^2\Omega.\tfrac{1}{2}\sec\beta\left[\cos^2(\zeta+\beta)+1\right]\quad.\quad(20).$$

To make (20) a minimum we have

$$\tan\beta=\frac{2\sin 2\,(\beta+\zeta)}{3+\cos 2\,(\beta+\zeta)}\quad.\;.\;.\;.\;.\;.\quad(21).$$

The value of β satisfying this equation for any given value of ζ is easily found by trial and error, guided by a short preliminary table of values of β for assumed values of $\beta+\zeta$. Col. 5 shows values of β thus found approximately enough to give the values of S/s shown in col. 4 for the several values of ζ.

§ 70. Confining our attention now to Majorana's observations at 9 A.M. when the sun's altitude was about 44°·6; let e be the proportion of the light illuminating the air over the crater of Etna which at that hour was due to air, earth, and water below; and therefore $1-e$ the proportion of the observed luminosity of the sky which was due to the direct rays of the sun, and expressed by § 68 (19). Thus, for $\beta=27°·8$, $\zeta=44°·6$, and $\theta=72°·4$, we have $S/s=3930000/(1-e)$, instead of the *S/s* of col. 4, § 69. With this, equation (20) gives

$$\Sigma\left[\frac{T(D'-D)}{D}\right]^2=\frac{\lambda^4(1-e)}{H\Omega}\,.\,4{\cdot}18\,.\,10^{-8}\quad . \quad (22).$$

Here, in order that the comparison may be between the whole light of the sun and the light from an equal apparent area of the sky, we must take

$$\Omega=\pi/219{\cdot}4^2{*}=1/15320,$$

being the apparent area of the sun's disc as seen from the earth. As to H, it is what is commonly called the "height of the homogeneous atmosphere" and, whether at the top of Etna or at sea-level, is

$$7{\cdot}988\,.\,10^5\left(1+\frac{t}{273}\right)\text{ centimetres};$$

where t denotes the temperature at the place above which H is reckoned. Taking this temperature as 15° C., we find

$$H=8{\cdot}44\,.\,10^5\text{ centimetres.}$$

Thus (22) becomes

$$\Sigma\left[\frac{T(D'-D)}{D}\right]^2=\lambda^4(1-e)\,.\,{\cdot}759\,.\,10^{-9}\quad . \quad . \quad (23).$$

§ 71. Let us now denote by f and $1-f$ the proportions of (23) due respectively to the ultimate molecules of air and to dust. We have

$$n\left[\frac{T(D'-D)}{D}\right]^2=\lambda^4 f(1-e)\,.\,{\cdot}759\,.\,10^{-9}\quad . \quad (24);$$

where n denotes the number of the ultimate molecules in a cubic centimetre of the air at the top of Etna; and $T(D'-D)/D$ relates to any one of these molecules; any difference which there may be between oxygen and nitrogen being neglected. Now assuming that the refractivity of the atmosphere is practically due to the ultimate molecules, and that no appreciable part of it is due to the dust in the air, we have by § 56 (7),

$${\cdot}0002=n\frac{T(D'-D)}{2D}\quad . \quad . \quad . \quad . \quad . \quad . \quad (25),$$

the first number being approximately enough the refractivity

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* The sun's distance from the earth is 219·4 times his radius.

of air at the crater of Etna (barometric pressure, 53·6 centimetres of mercury). Hence

$$\left[\frac{T(D'-D)}{D}\right]^2=\frac{1}{n^2}1{\cdot}6\,.\,10^{-7} \quad . \quad . \quad . \quad (26),$$

and using this in (24) we find

$$n=\frac{211}{\lambda^4 f(1-e)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27).$$

Here, as in § 57 in connexion with Bouguer's estimate for loss of light in transmission through air, we have an essential uncertainty in respect to the effective wave-length ; and, for the same reasons as in § 57, we shall take $\lambda=6\,.\,10^{-5}$ cm. as the proper mean for the circumstances under consideration. With this value of λ, (27) becomes

$$n=\frac{1}{f(1-e)}1{\cdot}63\,.\,10^{19} \quad . \quad . \quad . \quad . \quad . \quad (28).$$

§ 72. In Mr. Sella's observations on Monte Rosa the zenith distance of the sun was 50°, and the place of the sky observed was in the zenith. He found the brightness of the sun's disc to be about 5000000 times the brightness of the sky in the zenith. Dealing with this result as in §§ 70, 71, with $\beta=0$ in (20), and supposing the temperature of the air at the place of observation to have been 0° C., we find

$$n'=\frac{1}{f'(1-e')}2{\cdot}25\,.\,10^{19} \quad . \quad . \quad . \quad . \quad . \quad (29),$$

where e', f', and n' are the values of e, f, and n, at the place of observation on Monte Rosa. Denoting now by N the number of molecules in a cubic centimetre of air at 0° C. and pressure 75 centimetres of mercury, we have, by the laws of Boyle and Charles, on the supposition that the temperature of the air was 15° on the summit of Etna, and 0° on Monte Rosa

$$N=n\frac{75}{53{\cdot}6}\left(1+\frac{15}{273}\right)=n'\frac{75}{49},$$

or

$$N=1{\cdot}48n=1{\cdot}53n' \quad . \quad . \quad . \quad . \quad . \quad (30).$$

From these, with (28) and (29), we find

$$N=\frac{2{\cdot}41}{f(1-e)}\,.\,10^{19}=\frac{3{\cdot}44}{f'(1-e')}\,.\,10^{19} \quad . \quad . \quad (31).$$

§ 73. To estimate the values of e and e' as defined in §§ 70, 72, consider the albedos* of the earth as might be seen from a balloon in the blue sky observed by Majorana and G. Sella over Etna and over Monte Rosa respectively. These might be about ·2 and ·4, the latter much the greater because of the great amount of snow contributing to illuminate the sky over Monte Rosa. With so much of guess-work in our data we need not enter on the full theory of the contribution to sky-light by earthshine from below according to the principle of §§ 67, 68, interesting as it is; and we may take as very rough estimates ·2 and ·4 as the values of e and e'. Thus (31) becomes

$$N=\frac{3{\cdot}01}{f}\,.\,10^{19}=\frac{5{\cdot}73}{f'}\,.\,10^{19} \quad . \quad . \quad . \quad (32).$$

§ 74. Now it would only be if the whole light of the sky were due to the ultimate molecules on which the refractivity depends that f or f' could have so great a value as unity. If this were the case for the blue sky seen over Monte Rosa by G. Sella in 1900, we should have $f'=1$, and therefore $N=5{\cdot}73\,.\,10^{19}$. But it is most probable that even in the very clearest weather on the highest mountain, a considerable portion of the light of the sky is due to suspended particles much larger than the ultimate molecules N_2, O_2, of the atmosphere; and therefore the observations of the luminosity of the sky over Monte Rosa in the summer of 1900 render it probable that N is greater than $5{\cdot}73\,.\,10^{19}$. If now we take our estimate of § 50, for the number of molecules in a cubic cm. of air at 0°, and normal pressure, $N=10^{20}$, we have $1-f={\cdot}699$ and $1-f'={\cdot}427$; that is to say, according to the several assumptions we have made, ·699 of the whole light of the portion of sky observed over Etna by Majorana was due to dust, and only ·427 of that observed by Sella on

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* Albedo is a word introduced by Lambert 150 years ago to signify the ratio of the total light emitted by a thoroughly unpolished solid or a mass of cloud to the total amount of the incident light. The albedo of an ideal perfectly white body is 1. My friend Professor Becker has kindly given me the following table of albedos from Müller's book *Die Photometrie der Gestirne* (Leipsic, 1897) as determined by observers and experimenters.

Mercury	0·14	Uranus	0·60
Venus	0·76	Neptune	0·52
Moon	0·34	Snow	0·78
Mars	0·22	White Paper	0·70
Jupiter	0·62	White Sandstone	0·24
Saturn	0·72	Damp Soil	0·08

Monte Rosa was due to dust. It is quite possible that this conclusion might be exactly true, and it is fairly probable that it is an approximation to the truth. But on the whole these observations indicate, so far so they can be trusted, the probability of at least as large a value as 10^{20} for N.

§ 75. All the observations referred to in §§ 57–74 are vitiated by essentially involving the physiological judgment of perception of difference of strengths of two lights of different colours. In looking at two very differently tinted shadows of a pencil side by side, one of them blue or violet cast by a comparatively near candle, the other reddish-yellow cast by a distant brilliantly white incandescent lamp or by a more distant electric arc-lamp, or by the moon, when practising Rumford's method of photometry, it is quite wonderful to find how unanimous half-a-dozen laboratory students, or even less skilled observers, are in declaring This is the stronger! or, That is the stronger! or, Neither is stronger than the other! When the two shadows are declared equally strong, the declaration is that the differently tinted lights from the two shadowed places side by side on the white paper are, according to the physiological perception by the eye, equally strong. But this has no meaning in respect to any definite component parts of the two lights; and the unanimity, or the greatness of the majority, of the observers declaring it only proves a physiological agreement in the perceptivity of healthy average eyes (from which colour-blind eyes would no doubt differ wildly). Two circular areas of white paper in Sella's observations on Monte Rosa, a circle and a surrounding area of ground glass in Majorana's observations with his own beautiful sky-photometer on Etna, are seen illuminated respectively by diminished sunlight of unchanged tint and by light from the blue sky. The sun-lit areas seem reddish-yellow by contrast with the sky-lit areas which are azure blue. What is meant when the two areas differing so splendidly are declared to be equally luminous? The nearest approach to an answer to this question is given at the end of § 71 above, and is eminently unsatisfactory. The same may be truly said of the dealing with Bouguer's datum in § 57, though the observers on whom Bouguer founded do not seem to have been disturbed by knowledge that there was anything indefinite in what they were trying to define or to find by observation.

§ 76. To obtain results not vitiated by the imperfection of the physiological judgment described in § 75, Newton's prismatic analysis of the light observed, or something equivalent to it, is necessary. This was done by Rayleigh himself for the blue light of the sky actually before he had worked out his dynamical theory. He compared the prismatic spectrum of light from the zenith with that of sunlight diffused through white paper; and by aid of a curve drawn from about thirty comparisons ranging over the spectrum from C to beyond F, found the following results for four different wave-lengths.

	C.	D.	b^3.	F.
Wave-length .	656·2	589·2	517·3	486·2
Calculated . .	1	1·54	2·52	3·34
Observed . .	1	1·64	2·84	3·60

On these he makes the following remarks:—"It should "be noticed that the sky compared with diffused light was "even bluer than theory makes it, on the supposition that the "diffused light through the paper may be taken as similar to "that whose scattering illuminates the sky. It is possible "that the paper was slightly yellow; or the cause may lie in "the yellowness of sunlight as it reaches us compared with "the colour it possesses in the upper regions of the atmosphere. "It would be a mistake to lay any great stress on the obser-"vations in their present incomplete form; but at any rate "they show that a colour more or less like that of the sky "would result from taking the elements of white light in "quantities proportional to λ^{-4}. I do not know how it may "strike others; but individually I was not prepared for so "great a difference as the observations show, the ratio for "F being more than three times as great as for C." For myself I thoroughly agree with this last sentence of Rayleigh's. There can be no doubt of the trustworthiness of his observational results; but it seems to me most probable, or almost certain, that the yellowness or orange-colour of the sunlight seen through the paper, caused by larger absorption of green, blue, and violet rays, may explain the extreme relative richness in green, blue, and violet rays which the results show for the zenith blue sky observed.

§ 77. An elaborate series of researches on the blue of the sky on twenty-two days from July 1900 to February 1901 is described in a very interesting paper, "Ricerche sul Bleu del Cielo," a dissertation presented to the Royal University of Rome by Dr. Giuseppe Zettwuch, as a thesis for his degree of Doctor in Physics. In these researches prismatically analysed light from the sky was compared with prismatically analysed direct sunlight reduced by passage through a narrow slit; and the results were therefore not vitiated by unequal absorptions of direct sunlight in the apparatus. A translation of the author's own account of his conclusions is published in the Philosophical Magazine for August 1902; by which it will be seen that the blueness of the sky, even when of most serene azure, was always much less deep than the true Rayleigh blue defined by the λ^{-4} law. Hence, according to Rayleigh's theory (see § 53 above) much of the light must always have come from particles not exceedingly small in proportion to the wave-length. Thus in Zettwuch's researches we have a large confirmation of the views expressed in §§ 54, 58, 61, 74 above, and §§ 78, 79 below.

§ 78. Through the kindness of Professor Becker, I am now able to supplement Bouguer's 170-year old information with the results of an admirable extension of his investigation by Professor Müller of the Potsdam Observatory, in which the proportion (denoted by p in the formula below) transmitted down to sea-level of homogeneous light entering our atmosphere vertically is found for all wave-lengths from $4{\cdot}4 \, . \, 10^{-5}$ to $6{\cdot}8 \, . \, 10^{-5}$, by comparison of the solar spectrum with the spectrum of a petroleum flame for different zenith distances of the sun. It is to be presumed, although I do not find it so stated, that only the clearest atmosphere available at Potsdam was used in these observations. For the sake of comparison with Rayleigh's theory, Professor Becker has arithmetically resolved Müller's results into two parts; one constant, and the other varying inversely as the fourth power of the wave-length, expressed in the following formula* modified to facilitate comparison with §§ 57–59 above:

$$p = \epsilon^{-({\cdot}0887 + {\cdot}0772 z^{-4})} = {\cdot}9152 \epsilon^{-{\cdot}0772 z^{-4}} \quad . \quad . \quad . \quad (33),$$

where $z = \lambda \div {\cdot}6 \, . \, 10^{-5}$. In respect to the two factors here shown, we may say roughly that the first factor is due to suspended particles too large, and the second to particles not too large, for the application of Rayleigh's law. For the case of $\lambda = 6 \, . \, 10^{-5}$ ($z = 1$) this gives

$$p = \epsilon^{-({\cdot}0887 + {\cdot}0772)} = {\cdot}9152 \, . \, {\cdot}9258 = {\cdot}847 \quad . \quad . \quad (34).$$

§ 79. Taking now the last term in the index and the last factor shown in (34) and dealing with it according to §§ 57–59 above, and still, as in § 55, using k to denote the

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* Müller, *Die Photometrie der Gestirne*, p. 140.

proportionate loss of light per centimetre due to particles small enough for Rayleigh's theory, whether "suspended particles" or ultimate molecules of air or both, we have $\epsilon^{-830000k} = {\cdot}9258$ which gives $k^{-1} = 10{\cdot}75 \,.\, 10^6$ cms. Hence if, as in § 58, we suppose for a moment the want of perfect transparency thus defined to be wholly due to the ultimate molecules of air, we should have by the dynamics of refractivity $n\frac{T(D'-D)}{D} = {\cdot}0006$; and thence by (1) of § 55 with $\lambda = 6 \,.\, 10^{-5}$ we should find for the number of molecules per cubic centimetre $n = 2{\cdot}469 \,.\, 19^{19}$. But it is quite certain that a part, and most probably a large part, of the want of transparency produced by particles small enough for Rayleigh's theory is due to "suspended particles" larger than the ultimate molecules: and we infer that the number of ultimate molecules per cubic centimetre is greater than, and probably very much greater than, $2{\cdot}469 \,.\, 10^{19}$. Thus from the surer and more complete data of Müller regarding extinction of light of different wave-lengths traversing the air, we find an inferior limit for the number of molecules per cubic centimetre nearly three times as great as that which Rayleigh showed to be proved from Bouguer's datum.

§ 80. Taking, somewhat arbitrarily, as the result of §§ 23–77 that the number of molecules in a cubic centimetre of a perfect gas at standard temperature and pressure is 10^{20}, we have the following interesting table of conclusions regarding the weights of atoms and the molecular dimensions of liquefied gases, of water, of ice, and of solid metals.

Substance.	Mass of atom or of H_2O in grammes.	Density.	Number of atoms in cub. cm.	Distance from centre to centre if ranged in cubic order with actual density.
H	$0{\cdot}45 \,.\, 10^{-24}$	Liquid at 17° absolute... ·090	$200 \,.\, 10^{21}$	$1{\cdot}71 \,.\, 10^{-8}$
O	7·15 „	„ „ freezing-point 1·27	178 „	1·78 „
H_2O	8·05 „	Water .... 1·00	124 „	2·00 „
H_2O	8·05 „	Ice .... ·917	114 „	2·06 „
H_2O	8·05 „	Vapour at 0° C...... $\cdot 487 \,.\, 10^{-5}$	$605 \,.\, 10^{15}$	118·2 „
N	6·29 „	Liquid .... 1·047	$166 \,.\, 10^{21}$	1·82 „
Argon	17·81 „	„ .... 1·212	68·1 „	2·45 „
Gold	88·52 „	Solid........................19·32	218 „	1·66 „
Silver	48·47 „	„ ....10·53	217 „	1·66 „
Copper	28·43 „	„ .... 8·95	311 „	1·475 „
Iron	25·15 „	„ .... 7·86	313 „	1·47 „
Zinc	29·30 „	„ .... 7·15	244 „	1·60 „

XXXIII. *On the Forms of the Lines of Electric Force and of Energy Flux in the neighbourhood of Wires leading Electric Waves. By* W. B. Morton, *M.A., Professor of Natural Philosophy, Queen's College, Belfast*[*].

§ 1. *Contents of the Paper.*

IN the case of electromagnetic waves which are guided through a dielectric by imperfectly conducting leads, it is generally stated[†] that the flow of energy, as defined by the Poynting vector, is nearly parallel to the conductor, but converges slowly upon it, the lines of flow striking the surface of the wire at a small angle, and part of the energy being turned into heat in the wire. Since the magnetic force is in planes perpendicular to the wire the above statement implies that the lines of electric force leave the wire with a slight forward tilt; there is a large radial and a small longitudinal component.

Now an examination of the periodic vectors as worked out in detail by J. J. Thomson[‡], Sommerfeld[§], and Mie[||] brings to light the fact that there is a certain difference of phase between the radial and longitudinal components of the electric force. Therefore these components do not change sign together, and for a part of each wave-length the lines of force will be tilted *backwards.* In this region the flow of energy instead of being, as elsewhere, onward and inward, must be either onward and outward or backward and inward. The direction of the magnetic force decides between these alternatives. A flux of energy outwards across an element of surface of the wire indicates that, at this section, the energy of the magnetic field in the wire is being drawn upon, not only for the energy dissipated, but also to increase the magnetic energy in the adjoining dielectric.

It seemed of interest to examine the state of affairs in this eddy of the energy-flow. In what follows I have worked out in some detail the case of two parallel similar wires, which in some respects is simpler than that of a single wire. I have used the first approximation to Mie's complete solution for this case, which, as I have shown in former papers[¶], can be very simply deduced from the single-wire solution, and can be readily applied to more complicated cases. The main

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[*] Communicated by the Author.

[†] *Cf.* Heaviside, 'Electromagnetic Theory,' vol. i. p. 79.

[‡] J. J. Thomson, Recent Researches, p. 262.

[§] Sommerfeld, Wied. *Ann.* lxvii. p. 233 (1899).

[||] Mie, *Ann. d. Phys.* ii. p. 202 (1900).

[¶] Phil. Mag. [5] vol. l. p. 605 (1900), and [6] vol. i. p. 563 (1901).

results arrived at are as follows:—The state of affairs in the wire is governed, as is well known, by the magnitude of the quantity $a\sqrt{\frac{\mu p}{\rho}}$, where a is the radius of the wire, μ, ρ its permeability and resistivity, and $\frac{p}{2\pi}$ the frequency. When this is large we have the "skin-effect" well developed. Let us suppose for simplicity that ρ alone is altered. Then starting with the limiting case of very great conductivity and very thin skin, we find the region of eddy amounts to a quarter of each half wave-length, or say 45° in the argument of the periodic vectors. Further, as we should expect from the smallness of the dissipation of energy, the flow is outward in the eddy and onward everywhere. As the resistance of the wire is increased the extent of the eddy-region at first diminishes, reaches a minimum, and then increases again. In a case which I have worked out numerically the minimum is 18°. The anomalous flow is now partly outward and partly backward. As the resistance of the wire becomes very great the length of the eddy again approaches the limiting value of 45°, but the flow is now everywhere inward; it is backward in the eddy, forward elsewhere.

In the course of the investigation I have obtained the equations to the lines of force and of Poynting flux in the plane of the wires, inside and out. In order to show the properties of the curves I have plotted them in an exaggerated form, *i. e.* using constants of a different order of magnitude from those actually occurring in the physical cases.

§ 2. *Values of Electric and Magnetic Vectors.*

Take first the case of a *single wire* in a dielectric of permittivity K and permeability unity. Let Z, R be the longitudinal and radial components of electric force, H the magnetic force in circles round the wire. Then, measuring z along the direction of propagation and r outwards from the axis of the wire, the differential equations to be satisfied are

$$\left.\begin{aligned} -\frac{\partial \mathrm{H}}{\partial z} &= \frac{4\pi \mathrm{R}}{\rho}, \text{ or } \mathrm{K}\frac{\partial \mathrm{R}}{\partial t} \\ \frac{1}{r}\frac{\partial}{\partial r}(\mathrm{H}r) &= \frac{4\pi \mathrm{Z}}{\rho}, \text{ or } \mathrm{K}\frac{\partial \mathrm{Z}}{\partial t} \\ \frac{\partial \mathrm{R}}{\partial z} - \frac{\partial \mathrm{Z}}{\partial r} &= -\mu\frac{\partial \mathrm{H}}{\partial t}, \text{ or } -\frac{\partial \mathrm{H}}{\partial t} \end{aligned}\right\}, \quad . \quad . \quad . \quad (1)$$

according as we are dealing with wire or dielectric.

Write the common periodic factor in the form $e^{i(mz-pt)}$, then $m=\frac{2\pi}{\lambda}+i\kappa$, where λ is the wave-length and κ the attenuation-constant.

Let
$$k_1=\frac{p}{V}=\frac{2\pi}{\lambda_0}, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where λ_0 is the wave-length for the same frequency in free space, V the velocity of radiation,
$$k_2=(1+i)\sqrt{\frac{2\pi\mu p}{\rho}}, \quad . \; . \; . \; . \; . \; . \quad (3)$$
$$c^2=k_1{}^2-m^2=\left(\frac{2\pi}{\lambda_0}\right)^2-\left(\frac{2\pi}{\lambda}+i\kappa\right)^2 . \; . \; . \; . \quad (4)$$

Then the equations are satisfied by the following scheme, omitting the periodic factor.

$$\begin{array}{lll} & \textit{Inside.} & \textit{Outside.} \\ Z \ldots\ldots\ldots & dJ_0(k_2r), & DK_0(cr) \\ R \ldots\ldots\ldots & -d\,.\,\frac{im}{k_2}J_1(k_2r), & -D\frac{im}{c}K_1(cr) \\ H \ldots\ldots\ldots & -d\,.\,\frac{ik_2}{\mu p}J_1(k_2r), & -D\frac{ik_1{}^2}{pc}K_1(cr) \end{array}\Bigg\} . \; . \quad (5)$$

The J's and K's are the cylinder functions, vanishing for zero and infinite arguments respectively, d and D are constants. The argument of the J's should strictly be $\sqrt{k_2{}^2-m^2}\,.\,r$, but, as Thomson and Sommerfeld have shown, m is in actual cases negligible in comparison with k_2. Further, c is a very small quantity, so we can put for the K's the approximate values
$$K_0(cr)=\log\frac{2i}{\gamma cr},$$
$$K_1(cr)=\frac{1}{cr},$$

where γ is Euler's constant 1·781.

In the case of *two wires* at distance b apart, if $\frac{a^2}{b^2}$ can be neglected in comparison with unity, then, as I have shown in a former paper *, the state of affairs inside each wire is unaltered, and, outside, we get the approximate values by superposing two single wire solutions.

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* Phil. Mag. l. p. 605. Wrong signs appear in the values given for m, k_2, R, and H in this paper, but the results arrived at are not affected.

Confining our attention to points in the plane of the wires we thus obtain for points between the wires the values

$$\left.\begin{aligned} Z&=D\log\frac{b-r}{r},\\ R&=-D\frac{im}{c^2}\left(\frac{1}{r}+\frac{1}{b-r}\right)\\ H&=-D\frac{ik_1^2}{pc^2}\left(\frac{1}{r}+\frac{1}{b-r}\right) \end{aligned}\right\}, \quad \ldots \ldots \quad (6)$$

and for points not between the wires

$$\left.\begin{aligned} Z&=D\log\frac{b+r}{r},\\ R&=-D\frac{im}{c^2}\left(\frac{1}{r}-\frac{1}{b+r}\right),\\ H&=-D\frac{ik_1^2}{pc^2}\left(\frac{1}{r}-\frac{1}{b+r}\right) \end{aligned}\right\}, \quad \ldots \ldots \quad (7)$$

The further discussion of phase-differences and lines of force is a good deal simplified by the fact that the constant $\frac{2i}{\gamma}$, which appears in "Z" for a single wire, goes out in the present case.

An application of the surface conditions leads to the equation for c^2

$$c^2\log\frac{b}{a}=\frac{k_1^2J_0(k_2a)}{k_2aJ_1(k_2a)}. \quad \ldots \ldots \quad (8)$$

§ 3. *The Relative Phases of the Components.*

We shall now investigate the phase-differences existing between the periodic magnitudes Z R H in the dielectric at the surface of a wire. As the expression for Z is real, the arguments of the complex quantities occurring in R and H will give their phase-differences in advance of Z. Let α and β represent these quantities for R H respectively, so that if at a given point of the wire we have

$$Z=Z_0\sin pt,$$

we shall have

$$R=R_0\sin(pt+\alpha),$$

$$H=H_0\sin(pt+\beta).$$

Then

$$\left.\begin{aligned}\alpha&=-\frac{\pi}{2}+\text{arg. } m-\text{arg. }(c^2)\\ \beta&=-\frac{\pi}{2}-\text{arg. }(c^2)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

Using equation (8) and remembering that arg. $(k_2a)=\frac{\pi}{4}$, we have

$$\text{arg. }(c^2)=-\frac{\pi}{4}-\text{arg. }\frac{J_1(k_2a)}{J_0(k_2a)}. \quad . \quad . \quad . \quad . \quad (10)$$

$$\begin{aligned}\therefore \quad \alpha&=\text{arg. }\frac{J_1(k_2a)}{J_0(k_2a)}-\frac{\pi}{4}+\text{arg. } m\\ \text{and} \quad \beta&=\text{arg. }\frac{J_1(k_2a)}{J_0(k_2a)}-\frac{\pi}{4}\end{aligned}\quad . \quad . \quad . \quad (11)$$

It is now necessary to examine the values of arg. $\frac{J_1(k_2a)}{J_0(k_2a)}$ for different values of the variable, and also arg. m.

Taking first $\frac{J_1}{J_0}$ we have for *small* values of k_2a

$$\frac{J_1}{J_0}=\tfrac{1}{2}k_2a,$$

the argument is $\frac{\pi}{4}$, and $\beta=0$.

For very *large* values $\frac{J_1}{J_0}=i$, giving $\beta=\frac{\pi}{4}$. To trace the course of the magnitude β between these limits we can use the tables of $J_0(x\sqrt{i})$ and $J_1(x\sqrt{i})$, which have been computed by Aldis*. His argument x corresponds to $2a\sqrt{\frac{\mu p\pi}{\rho}}$, and runs between values 0·1 and 6·0; the corresponding values of arg. $\frac{J_1}{J_0}$ come out 44° 23′ and 86° 10′. The curve marked β in fig. 1 is plotted by calculation from Aldis's tables.

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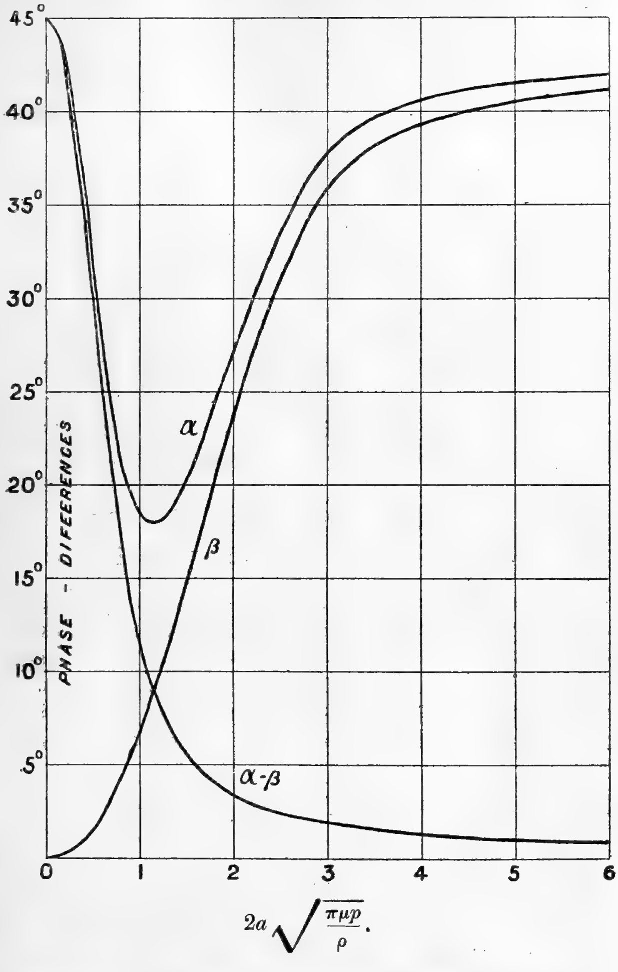
* Aldis, Proceedings of Roy. Soc. vol. lxvi. pp. 42, 43 (1899).

Fig. 1.



Turning now to arg. m, equation (8) with (4) gives

$$m^2 = k_1^2 - c^2 = k_1^2 \left\{ 1 - \frac{J_0(k_2a)}{\log\frac{b}{a} \,.\, k_2a \,.\, J_1(k_2a)} \right\},$$

$$\therefore \text{ arg. } m = \tfrac{1}{2} \text{ arg.} \left\{ 1 - \frac{J_0(k_2a)}{\log\frac{b}{a} \,.\, k_2a \,.\, J_1(k_2a)} \right\}. \quad . \quad (12)$$

To obtain numerical values it is necessary to assume a particular value of $\frac{b}{a}$. I have taken this as 100, and have calculated arg. m by aid of Aldis's tables. The result is shown in the curve marked $(\alpha-\beta)$ on fig. 1. The addition of the two curves obtained gives the α-curve, showing the phase-difference between R and Z.

To form an idea of the position on this diagram of actual experimental cases, we may take those given in Sommerfeld's paper as extreme cases in opposite directions. His first case, typical of skin-conduction and very small attenuation, is that of copper wire of 4 mm. diameter with frequency of 10^9 alternations per sec. This gives 1358 as the value of $2a\sqrt{\frac{\mu\pi p}{\rho}}$, and so lies far out to the right, where α and β are both practically 45°.

His other extreme case is that of platinum wire of 0·004 mm. diameter and a frequency of 3×10^8. This gives 0·256 for the determining constant; α comes on the inner side of the minimum position for α.

The quantity $(\alpha-\beta)=\text{arg. } m=\tan^{-1}\frac{k\lambda}{2\pi}$ is, for small values at least, proportional to the attenuation with given wave-length. It runs down to zero with increasing development of surface-conduction, towards the right in the diagram.

Looking now at the state of things just *inside* the wire we have of course the same phase-difference as before between H and Z. For R the advance of phase on Z is from equations (5)

$$=-\frac{\pi}{2}+\text{arg. } m-\text{arg. } k_2+\text{arg. } \frac{J_1}{J_0},$$

$$=-\frac{3\pi}{4}+\text{arg. } m-\text{arg. } \frac{J_1}{J_0},$$

$$=\alpha-\frac{\pi}{2}.$$

or the radial electric force inside is 90° behind that outside.

§4. *Directions of the Lines of Force and of Energy-flow at the Surface of the Wires.*

It is easy to see that when Z and R have opposite signs the lines of force are tilted backwards; when H Z are opposite the energy-flow is outward; and when H R are opposite the flow is backward. Taking, then, a half wave-length (from 0 to π) between points at which the lengthwise electric force Z vanishes, we find the flow of energy

Outside.

$$\left.\begin{array}{ll} \text{from } 0 \text{ to } (\pi-\alpha) & \text{forward, in} \\ \text{from } (\pi-\alpha) \text{ to } (\pi-\beta) & \text{backward, in} \\ \text{from } (\pi-\beta) \text{ to } \pi & \text{forward, out} \end{array}\right\} \quad . \quad . \qquad (13)$$

Inside.

$$\left.\begin{array}{ll} \text{from } 0 \text{ to } \left(\frac{\pi}{2}-\alpha\right) & \text{backward, in} \\ \text{from } \left(\frac{\pi}{2}-\alpha\right) \text{ to } (\pi-\beta) & \text{forward, in} \\ \text{from } (\pi-\beta) \text{ to } \pi & \text{backward, out} \end{array}\right\} \quad . \qquad (14)$$

The extent of the eddy in the external energy-flow is given by α. Its course as shown by the curve is in accordance with the statement in § 1. For the limiting case of mere surface-conduction (k_2a large) $\alpha=\beta=45°$, the section $(\pi-\alpha)$ to $(\pi-\beta)$ shrinks to nothing, *i. e.* the energy-flow is everywhere in the direction of propagation of the waves. At the other extreme (k_2a small) when α again approaches 45°, β becomes zero, and the region of outward flow disappears.

§ 5. *Forms of External Lines of Force and Flow.*

We may write for points between the wires

$$\left.\begin{array}{l} Z=\log\dfrac{b-r}{r}e^{-kz}\sin\dfrac{2\pi z}{\lambda} \\ R=\dfrac{A}{r(b-r)}e^{-kz}\sin\left(\dfrac{2\pi z}{\lambda}+\alpha\right) \end{array}\right\} \quad . \quad . \quad . \qquad (15)$$

where

$$A=\left|\frac{mb}{c^2}\right|.$$

The differential equation to the lines of electric force is therefore

$$\frac{dr}{dz}=\frac{A}{r(b-r)\log\dfrac{b-r}{r}}\cdot\frac{\sin\left(\dfrac{2\pi}{\lambda}z+\alpha\right)}{\sin\dfrac{2\pi z}{\lambda}}, \quad . \quad . \quad . \qquad (16)$$

and the integral of this

$$\frac{A\lambda}{2\pi}\left\{\cos\alpha\,.\,\frac{2\pi z}{\lambda}+\sin\alpha\log\sin\frac{2\pi z}{\lambda}\right\}$$

$$=C-\tfrac{1}{6}\{(b+2r)(b-r)^2\log(b-r)+(3b-2r)r^2\log r+br(b-r)\}. \quad (17)$$

The differential equation to the lines of the Poynting flux

$$-\frac{dz}{dr}=\frac{\mathrm{R}}{\mathrm{Z}}$$

gives as integral

$$\frac{b\lambda}{2\pi \mathrm{A}}\left\{\cos\alpha\frac{2\pi z}{\lambda}-\sin\alpha\log\sin\left(\frac{2\pi z}{\lambda}+\alpha\right)\right\}$$
$$=\mathrm{C}'+\log.\log.\frac{b-r}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

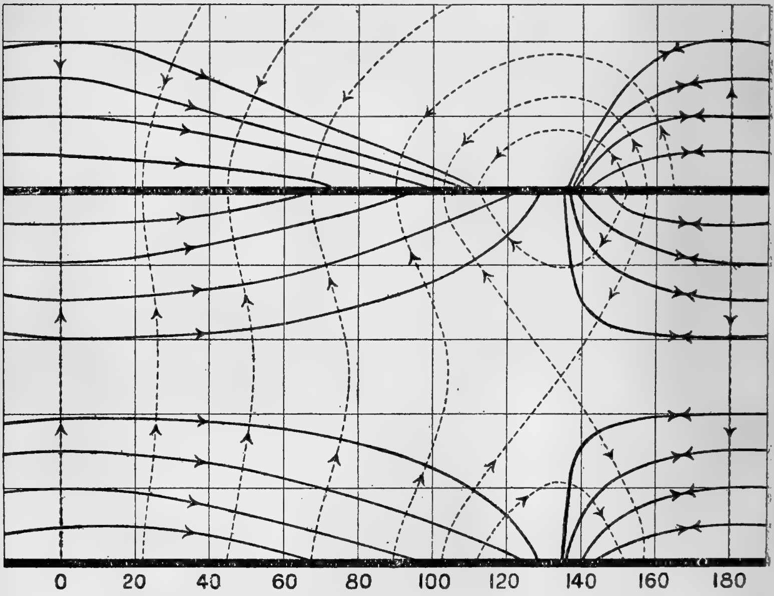
C and C′ are arbitrary constants.

For points not between the wires the corresponding equations differ from these in having $(b-2r)$, $(3b+2r)$, and $(b+r)$ instead of the terms $(b+2r)$, $(3b-2r)$, and $(b-r)$.

In the actual case the constant A has a very large value, say order 10^4, in accordance with the fact that the lines of electric force are very nearly perpendicular to the wires *. In order to make visible the general form of the curves I have plotted fig. 2 with the following values:—

$$\alpha=45^\circ, \qquad a=1, \qquad b=100, \qquad \lambda=360,$$
$$\frac{b\lambda}{2\pi \mathrm{A}}\cdot\frac{1}{\sqrt{2}}=\frac{1}{2}.$$

Fig. 2.



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* Sommerfeld, *loc. cit.* p. 282.

The diagram thus gives a distorted picture of the arrangement of the lines in the two opposite extreme cases referred to above. The broken lines represent the lines of force and the full lines those of Poynting flux. In the eddy region from 135° to 180° the arrows on the energy lines are taken in or out according as we are dealing with a case of "k_2a" small or large, as already explained.

To pass to the actual arrangement in experimental conditions one has to imagine the sag of the lines of force reduced and the region of re-entrant lines to shrink to a very small length at 135°. So that except in the immediate neighbourhood of this point, where the radial force vanishes, the lines go practically straight across.

§ 6. *Forms of Internal Lines of Force and Flow.*

To the degree of approximation adopted in this paper, these are the same as for the case of a single wire, the return current being carried by the dielectric (Sommerfeld's case). When there is axial symmetry in the field we can, as Hertz showed *, express the quantities Z and R in the forms

$$Z=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \pi}{\partial r}\right),$$

$$R=-\frac{1}{r}\frac{\partial}{\partial z}\left(r\frac{\partial \pi}{\partial r}\right),$$

so that the lines of force are given by

$$r\frac{\partial \pi}{\partial r}=\text{const.}$$

Using this method Sommerfeld (*loc. cit.* p. 285) has given a diagram showing the course of the internal and external lines of force, with distortion, for the case of surface conduction (k_2a large). He does not draw attention to the backward tilted lines and, to judge from his figure, seems not to have plotted lines in this region.

As I wish to get the lines of energy-flow also, I shall proceed directly from the differential equation, taking separately the cases of (*a*) k_2a large, (*b*) k_2a small.

(*a*) In this case the conduction is confined to a small thickness at the surface of the wire, so that we may use for $J_0(k_2r)$ and $J_1(k_2r)$ occurring in Z, R, the forms appropriate to large values of the argument.

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* Hertz, 'Electric Waves' (English translation), p. 140.

Write

$$k_2=(1+i)h, \qquad \text{so that} \quad h=\sqrt{\frac{2\pi\mu p}{\rho}}, \quad . \quad . \quad . \quad (19)$$

and let y denote the distance of a point below the surface of the wire or $(a-r)$. After a little reduction we find for the components of electric force

$$\left.\begin{aligned} Z&=\frac{e^{-hy}}{\sqrt{a-y}}\sin\left(\frac{2\pi z}{\lambda}+hy\right), \\ R&=\frac{\pi\sqrt{2}}{h\lambda}\cdot\frac{e_{-hy}}{\sqrt{a-y}}\sin\left(\frac{2\pi z}{\lambda}+hy-\frac{\pi}{4}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (20)$$

The attenuation constant κ is here neglected in comparison with $\frac{2\pi}{\lambda}$.

Therefore for lines of force

$$\frac{dy}{dz}=-\frac{\pi\sqrt{2}}{h\lambda}\,\frac{\sin\left(\frac{2\pi z}{\lambda}+hy-\frac{\pi}{4}\right)}{\sin\left(\frac{2\pi z}{\lambda}+hy\right)}, \quad . \quad . \quad . \quad . \quad (21)$$

leading to

$$hy=\log\sin\left(\frac{2\pi z}{\lambda}+hy+\frac{\pi}{4}\right)+\text{const.} \quad . \quad . \quad (22)$$

and for lines of flow we get

$$\begin{aligned} my(h^2+m^2)-hz(2h^2+m^2)=hm\log\{&(2h^2+m^2)\sin(mz+hy) \\ &-m^2\cos(mz+hy)\}+\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23) \end{aligned}$$

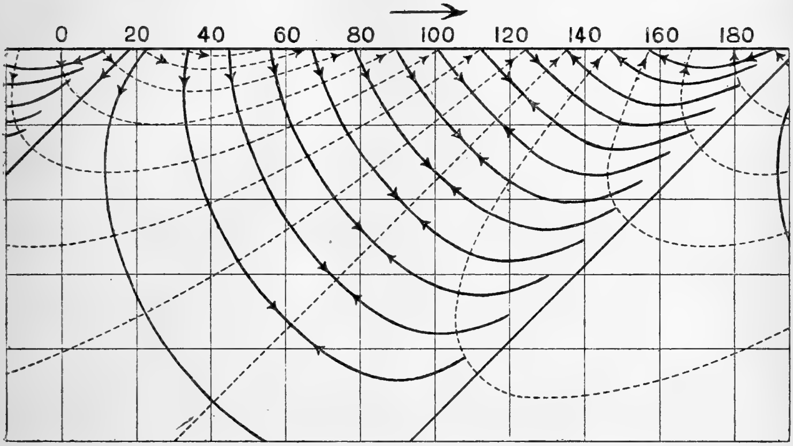
In the last equation m is written for $\frac{2\pi}{\lambda}$.

In fig. 3 these two families of curves are plotted for the simple case $m=h=1$. It will be seen that all the curves of either family can be got by moving one of them in a direction making an angle of 45° with the negative direction of z.

The angles marked on the diagram give the phase-angles of the lengthwise electric force. The magnetic force being 45° in advance of the lengthwise electric vanishes at all points of the straight line of electric force which meets the surface at 135°. The flow of energy is therefore oppositely directed on the two sides of this line, as shown by the arrows on the lines of flow. An inspection of the figure shows that the flow of energy at the surface is backward and inward from 0° to 45°, forward and inward from 45° to 135°, and backward and outward from 135° to 180°, agreeing with

(14) when $\alpha=\beta=45°$. In the actual case the lines of force are almost parallel to the surface. This is seen from (21)

Fig. 3.



when we remember that h is by hypothesis very large. Accordingly we have to imagine the straight lines of force in the diagram twisted round so as to meet the boundary at a very small angle instead of at 45°.

(*b*) *Case of k_2a very small*, the current diffused through the whole wire. Here we may put unity for $J_0(k_2r)$ and $\frac{1}{2}k_2r$ for $J_1(k_2r)$.

Further, as we have seen in § 3, the argument of m approaches 45°, so we may write

$$m=\frac{2\pi}{\lambda}(1+i).$$

So we have

$$\left.\begin{aligned} Z&=e^{\frac{-2\pi z}{\lambda}}.\sin\frac{2\pi z}{\lambda} \\ R&=e^{\frac{-2\pi z}{\lambda}}.\frac{\pi\sqrt{2}}{\lambda}.r.\sin\left(\frac{2\pi z}{\lambda}-\frac{\pi}{4}\right) \end{aligned}\right\} \quad . \quad . \quad (24)$$

It is remarkable that h disappears from the expressions, or in other words, as we approach this limit the properties of the wire cease to have an effect on the distribution of the field inside.

The equation to the lines of force is

$$\frac{dr}{dz} = r \cdot \frac{\pi\sqrt{z}}{\lambda} \cdot \frac{\sin\left(\frac{2\pi z}{\lambda} - \frac{\pi}{4}\right)}{\sin\frac{2\pi z}{\lambda}}, \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

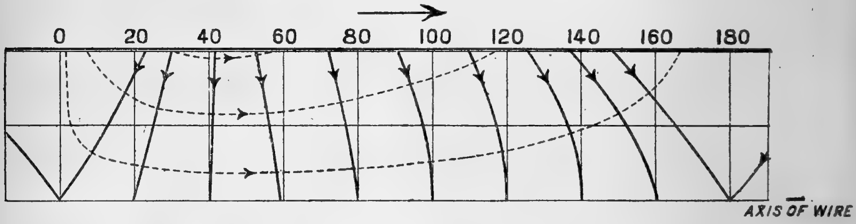
$$2 \log r = \frac{2\pi z}{\lambda} - \log \sin\frac{2\pi z}{\lambda} + \text{const.} \quad . \quad . \qquad (26)$$

The equation to the lines of flow comes out

$$-\frac{2\pi^2}{\lambda^2} r^2 = \frac{2\pi z}{\lambda} + \log \sin\left(\frac{2\pi z}{\lambda} - \frac{\pi}{4}\right). \quad . \quad . \qquad (27)$$

These curves are shown on fig. 4, beginning, in this case, from the *axis* of the wire. It may be noted that if we plot one line of force the others are got simply by extending proportionally the ordinates measured from the axis.

Fig. 4.



In this case the magnetic force vanishes along with the longitudinal electric. The energy-flow is backward and inward from 0° to 45°, and forward and inward for the remainder of the half wave-length. The exaggeration of the diagram in this case consists in making the radius of the wire much too great in comparison with the wave-length, in order to get room to show the trend of the curves.

Queen's College, Belfast,
20th June, 1902.

XXXIV. *Deviable Rays of Radioactive Substances.*

By E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, and* A. G. Grier, *M.Sc., Demonstrator in Physics, McGill University, Montreal* *.

§ 1. THE experiments † of Giesel, Becquerel, Curie, Meyer, and Schweidler have shown that radium gives out some rays deflectable by a magnet.

Becquerel, in addition, has shown that uranium, and the excited radioactivity due to radium, also emit rays deviable by a magnetic field. Becquerel has employed the photographic method for detecting deviable rays, while the Curies, Meyer, and Schweidler have used the electrical method for analysis of the deviable rays from radium.

Further experiments have shown that these deviable rays are similar in all respects to cathode-rays. Dorn ‡ showed that they were deflected in an electrostatic field, while the Curies § showed that they carried with them a negative charge. Becquerel determined the velocity of these "electrons" by observing the magnetic and electrostatic deviation of the rays. He found that the rays from radium were complex, and had widely different velocities. Some travelled at more than half the speed of light. The ratio of the charge to the mass $\frac{e}{m}$ was found to be about the same as for cathode-rays. These results have recently been confirmed by Kaufmann ||, who has shown that some of these electrons travel with a speed nearly equal to that of light, while the ratio of $\frac{e}{m}$ is somewhat less than for the comparatively low velocity cathode-rays, and appears to decrease with the velocity of the electron. This points to the conclusion that for these high-speed electrons a portion of the effective mass is electrical in origin ¶.

The authors have found that, in addition to uranium and radium, thorium compounds, and also excited radioactivity due to thorium, give out some rays deviable by a magnetic field.

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* Communicated by the Authors. Communicated to the American Physical Society, April 21, 1902.

† See reports on radioactivity by Becquerel and Curie to Congrès International de Physique, 1900, tome iii.

‡ *C. R.* cxxx. p. 1126.

§ *Ibid.* cxxx. p. 647.

|| See Heaviside, 'Electrician,' April 4, 1902.

¶ *Gött. Nach.* ii. 1901.

The main object of the investigations described in this paper was to obtain some experimental evidence of the connexion, if any, between the deviable and non-deviable rays emitted by the radioactive substances uranium, thorium, and radium. It is known that cathode-rays striking on a solid body give rise to Röntgen rays, and also that Röntgen rays impinging on bodies in their turn give rise to a secondary radiation, part of which is composed of rays similar to cathode-rays.

It thus appears possible, as Becquerel has suggested, that the non-deviable rays may be due directly to the action of the deviable rays. A similar suggestion was put forward by one of the authors * to account for the presence of the two types of rays given out by uranium, one of which was far more penetrating than the other. The relation is, however, much more complicated than such simple analogies would suggest. A discussion of the question, with especial reference to the important results on the partial separation of the active products of uranium and thorium, is reserved till the conclusion of this paper.

§ 2. In these experiments the electric method has been employed throughout. It has many advantages over the photographic method, especially where quantitative comparisons and rapidity of measurement are required.

Fig. 1 shows the general experimental arrangement. The radioactive substance to be investigated was spread uniformly on the bottom of a shallow paper vessel, which fitted inside a lead box 3 cms. square and 2 cms. deep. The paper vessel rested on a wire gauze 1 cm. from bottom of vessel, and, by means of a water-pump, a steady stream of air was drawn downwards through the apparatus. This carried off the radioactive *emanation* emitted by thorium and radium, the presence of which in the testing-apparatus would seriously interfere with the measurements. The lead box was placed between pole-pieces, 3·2 cms. square, of a large electromagnet, which were generally placed 3·2 cms. apart.

The testing-vessel V was a rectangular zinc vessel, 10·5 cms. square and 30 cms. high. The outside was connected to one pole of a battery of 100 volts. A brass rod formed the inside electrode, which was connected to the electrometer. A guard-ring, connected to earth, ensured that there was no natural leak from the charged cylinder to the inside electrode.

The testing-vessel was placed on an insulated metal plate, with a hole in the centre 3·2 cms. square, over the air-gap of

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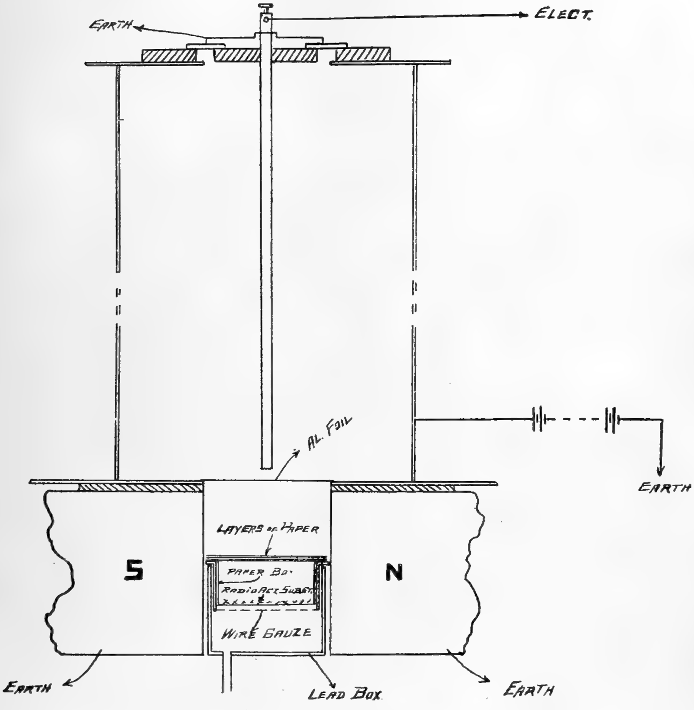
* E. Rutherford, Phil. Mag. Jan. 1899.

the electromagnet. This was covered over with a layer of aluminium-foil ·00034 cm. thick.

Fig. 1.



Special precautions were taken to completely secure the electrometer and connexions from electrostatic disturbances of all kinds.

It is easy to investigate the magnetic deviation of radium-rays in such an apparatus with an ordinary electrometer, as the ionization action of the radium-rays is very large.

For uranium and thorium, however, the ionization due to the deviable rays is very small, and a specially sensitive electrometer is required to measure the effects with accuracy. The Dolezalek electrometer, described in a previous paper by one of us *, was found sufficiently sensitive for this purpose.

All the radioactive substances emit non-deviable as well as deviable rays, and generally the ionizing action of the non-deviable rays is much greater than that caused by the

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* *Phys. Zeit.* no. 11, p. 225 (1902).

deviable rays. With the bare radioactive substances the ionization in the testing-vessel is chiefly due to the non-deviable rays. In consequence of this a strong magnetic field does not much alter the ionization-current observed in the electrometer. The non-deviable rays can, however, be completely absorbed by two or more layers of paper, while the deviable rays pass through with very little absorption.

The deviable rays consist of rapidly moving electrons, and ionize the air in their passage through it by collision with the molecules. The average deviable rays are so penetrating that they will probably pass through more than a metre of air before the ionizing action is cut down to one half.

When a strong magnetic field is applied, the paths of the rays are curved, so that only a small fraction of the rays enter the testing-vessel.

In the experiment a magnetic field of 2200 C.G.S. units was generally employed. This usually reduced the ionization current in the testing-vessel to about 20 per cent. of its previous value. By increasing the strength of field the current steadily diminished, showing that the effect in testing was principally due to deviable rays. A small percentage of the amount of ionization in the testing-vessel was due, in the case of radium, to some extremely penetrating non-deviable rays. These rays have been examined by the photographic method by Villard and Becquerel. The difference between the current in testing-vessel with magnet on and off was taken as a measure of the amount of deviable rays.

§ 3. *Variation of Amount of Deviable Rays with Thickness of Radioactive Layer.*

Different weights of the radioactive substance to be tested were spread over an area of about 9 sq. cms. Four layers of paper over this completely absorbed the α-radiation.

The following numbers show the result from uranium and radium. The amount of deviable rays is expressed in divisions per sec. of the electrometer-scale, and represents the difference between ionization-current in the testing-vessel with the magnet off and on.

Uranium Oxide.		Radium Chloride.	
Wt.	Divns. per sec.	Wt.	Divns. per. sec.
·25 gr.	·47	·25	1·5
·50 ,,	·90	·5	2·9
1 ,,	1·26	1	5·5
2 ,,	1·70	1·55	6·7
5 ,,	1·96		

In the case of radium a capacity of ·005 microfarad was in parallel with the electrometer.

The results for uranium are in agreement with the view that each portion of the mass is sending out electrons uniformly. The number of electrons which escape is at first proportional to the thickness, but tends towards a maximum as the electrons from the lower layers are absorbed before reaching the surface.

The table for radium shows, as far as it goes, a similar action, only in that case we did not have a sufficient amount of substance to investigate the effect of thicker layers. In this sample of radium (from P. de Haen, Hannover) the deviable rays were 250 times as intense as from an equal weight of uranium oxide.

§ 4. *Deviable Rays from Thorium Compounds.*

Thorium oxide is much weaker in deviable rays than an equal weight of uranium oxide, although the non-deviable rays are of about the same intensity. For this reason the presence of the deviable rays in thorium is more difficult to detect and measure than for uranium. In measurements on thorium compounds precautions must be taken that the presence of the radioactive emanation and the excited radioactivity produced by it are not responsible for the deviable rays observed.

About 5 gr. of the thorium compound was spread uniformly in a rectangular lead vessel 3 cms. long, 2 cms. wide, and 1 cm. deep., and a very thin plate of mica waxed down over the top. This allowed most of the deviable rays to pass through, but absorbed most of the non-deviable rays, and was impervious to the emanation. Observations were taken as soon as possible after the thorium was placed in the vessel, and the difference of current observed with the magnetic field off and on. By means of side-tubes in the lead vessel a slow current of air was then passed over the thorium, carrying away the emanation. The amount of deviable rays was found to be unchanged, showing that the deviable rays (if any) from the emanation did not appreciably affect the result. If the side-tubes of the lead vessel were closed, and the thorium left undisturbed for 24 hours, the amount of deviable rays was considerably increased. This increase was found to be due to the deviable rays given out by the excited radioactivity produced by the emanation on the whole interior of the containing vessel. This was directly tested by removing the mica plate from the thorium vessel and placing it between the poles of the electromagnet. It was found to give out both deviable and non-deviable rays, due to the excited radioactivity produced on it.

The amount of deviable rays for equal weights of different thorium compounds was found to vary considerably, as the following table shows :—

Compound.	Amount of Deviable Rays.
Oxide	1
Deemanated oxide	1·35
Nitrate	·94
Sulphate	·83
Oxalate	·76
Uranium oxide	6·7

In the above table the amount of deviable rays from ordinary thorium oxide is taken as unity, and the others expressed in terms of it. For the purpose of comparison the amount of deviable rays from an equal weight of black uranium oxide is added.

The comparisons in the above table were not made directly by noting the effect of a magnetic field, but by an indirect method, explained in § 9, which is based on the observed fact that the penetrating rays from thorium as well as uranium are chiefly deviable rays.

Four grammes of the compound in the form of powder were uniformly spread in a lead vessel of area 22 sq. cms. A layer of aluminium, thickness ·006 cm., was waxed down over the top. This absorbed all the non-deviable rays, but allowed most of the deviable rays to pass through. The ionization-current due to these penetrating rays was determined in the usual way, and was taken as a measure of their intensity.

The deemanated oxide, *i e.* the oxide which had been largely deprived of its power of giving off a radioactive emanation by raising it to a white heat, gives more deviable rays than the ordinary oxide ; while the nitrate is nearly as active as the ordinary oxide, although containing only about half the amount of thorium.

It was also found that the increase of deviable rays with time, when the thorium was kept in a closed vessel for 24 hours, varied very considerably for different compounds. The increase was much greater for the ordinary oxide than for the deemanated sample, while thorium carbonate, which gives out five times as much emanation as the oxide, showed still greater differences.

This increase of deviable rays with time in a closed vessel is directly proportional to the emanating power of the compound, and is due to the deviable rays produced by excited radioactivity on the walls of the vessel.

These results point to the conclusion that a portion, at least, of the deviable rays from thorium is due to the presence of excited radioactivity throughout the mass of the compound itself. If the emanation, which is apparently produced by all thorium compounds, is unable to escape rapidly into the air it produces excited radioactivity throughout the compound. In the deemanated oxide consequently more excited radioactivity is produced than in the ordinary oxide, from which more emanation escapes into the air. Since excited radioactivity gives rise to deviable rays the effect will be greater for the deemanated than the ordinary oxide.

§ 5. *Deviable Rays from Excited Radiations due to Thorium and Radium.*

A small proportion of the rays emitted by thorium- and radium-excited radiation is deviable by a magnetic field. As these excited radiations decay with the time it was of importance to see if the deviable rays decayed at the same rate.

A lead wire was made the cathode in a cylindrical closed vessel containing the emanation from radium, which had been obtained by bubbling air through a solution of radium chloride. The wire was left exposed for one day in order that the excited radiation should have reached a steady value. The lead wire was then bent into a small spiral and placed between the poles of the electromagnet of fig. 1.

Observations were taken at regular intervals, both of the current due to the deviable and non-deviable rays. Fig. 2 (p. 322) shows the results graphically; Curve I. shows the decay with time of the non-deviable rays, Curve II. the decay with time of the deviable rays. For the purpose of comparison the maximum value of each is taken as 100.

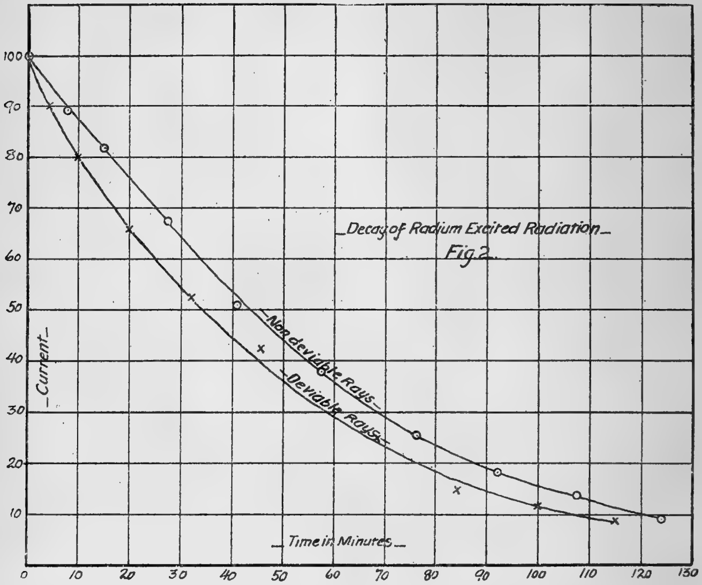
Similar observations were made on the excited radioactivity from thoria.

An aluminium plate, 3 × 2 cms., was made the cathode in a closed vessel containing about 200 grs. of thoria and left two days. The following table shows the decay of the two types of rays. The initial value of each is taken as unity for comparison:—

Time.	Non-deviable rays.	Deviable rays.
0	1	1
3 hrs.	·77	·83
19 ,,	·38	·33
42 ,,	·08	·07

The results for both thorium- and radium-excited radiation show that the deviable rays decay at nearly the same rate as the non-deviable. This result shows that there is a very close connexion between the production of these two types of radiation.

Fig. 2.



§ 6. *Active Products Separated from Thorium and Uranium.*

In a previous paper (Rutherford and Soddy, Proc. Chem. Soc., Jan., and Trans. Chem. Soc., April 1902) it has been shown that a very active product can be separated from thorium as a result of the precipitation of thorium nitrate by ammonium hydroxide. If the filtrate, free from thorium, is evaporated down to dryness and the ammonium salts driven off by ignition, a very small residue is obtained intensely active, possessing in some cases 1000 times the activity of thoria. This radioactive fraction has been termed Thorium X. At the same time the radioactivity of the precipitated thoria is diminished in most cases to about ·36 of its original value.

The investigation on the radioactivity of thoria has been continued by E. Rutherford and F. Soddy, and at the same time parallel experiments have been made on the partial separation of the active products from uranium by the methods of Crookes and Becquerel. The results of these investigations will appear shortly, but the authors of this communication are indebted to Mr. Soddy, of the Chemical Department, for his kindness in making the chemical preparations of thorium and uranium which are tested in this paper.

On examination it was found that the Th. X. emitted both deviable and non-deviable rays, and also a radioactive emanation. The deviable radiation is complex, as in the case of the ordinary thoria, and contains a large fraction of easily absorbed deviable rays. If a large number of successive precipitations are performed the thoria can be almost completely freed from deviable rays, although about 30 per cent. of the non-deviable rays still remain.

We thus see that non-deviable rays persist in thoria when the product responsible for deviable rays is completely removed.

Very similar actions have been observed for the active products separable from uranium by the methods of Crookes and Becquerel. Crookes* obtained very active residues from uranium by two methods. In one case it was found that if ether was added to uranium nitrate part of the nitrate was soluble in the ether. The part that was insoluble in the ether was far more radioactive than the part which was not. In the other case the nitrate was dissolved in water and an excess of ammonium carbonate added. A small precipitate remaining behind was found intensely active compared with an equal weight of uranium. This active fraction was called by Crookes Ur. X.

Becquerel† found that as a result of continued precipitation of barium sulphate in a mixture of uranium and barium chloride, he could entirely free the uranium from the photographic action, while the barium sulphate carried with it a very active fraction. In course of time the uranium recovered the original radioactivity, while the barium sulphate became inactive.

On examination of the Ur. X. of Crookes and the active barium sulphate of Becquerel, it was found that the radiation was composed almost entirely of deviable rays. The conductivity due to the deviable rays was more than $\frac{2}{3}$ of the total, while the conductivity due to the deviable rays of a thin layer of uranium is not more than one per cent. of the total (see § 7).

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* Proc. Roy. Soc., May 1900.

† *C. R.* Dec. 9, 1901.

The uranium from which the active fraction had been removed by the three methods was found almost completely free from deviable rays, while the non-deviable rays were not much reduced. Not a trace of deviable rays was obtained from uranium after 12 precipitations with barium sulphate, although $\frac{1}{2}$ per cent. of the original amount could have been readily detected. We thus see that by different chemical methods the part responsible for the deviable radiation in both uranium and thorium can be separated from the main body, while part at least of the non-deviable radiation is unaffected.

§ 7. *Other Results.*

No trace of deviable rays could be detected by the electric method from polonium. This is in agreement with the results of Becquerel by the photographic method. We have so far been unable to obtain any conclusive evidence of the existence of deviable rays in the emanation of thorium, although the emanation gives off strong non-deviable rays.

§ 8. *Penetrating Power of the Deviable Rays.*

By noting the diminution of magnetic effect in the testing cylinder when successive layers of thin aluminium or tinfoil were placed over the radioactive substance, the penetrating power of the deviable rays can be compared.

When the magnetic effect falls off in geometric progression with the thickness the rays may be supposed to be fairly homogeneous in character. If the absorption is greater for the first few layers than for succeeding layers, the rays are complex, *i. e.* the rays are made up of streams of electrons differing in velocity, and consequently in penetrative power.

Tested in this way it was found:

(1) That uranium, and the excited radioactivity due to thorium, gave out deviable rays approximately homogeneous in character and of about the same penetrating power.

(2) Thorium and radium both gave out very complex rays. This has been shown by Becquerel for radium, using the photographic method. He found that the magnetic deviation of the rays varied within wide limits. Thorium X gives out a large proportion of easily absorbed deviable rays.

(3) Radium and thorium and the excited radioactivity due to them all emit some deviable rays of about the same penetrating power as those from uranium. The rays from uranium pass through about ·5 mm. of aluminium before the intensity is reduced to one half.

§ 9. *Comparison of the Amount of Ionization Produced by Deviable and Non-deviable Rays.*

In 1899 one of us* showed that uranium oxide emits two types of radiation which were for convenience termed the α and β radiations. The β radiation was far more penetrating in character than the α-rays. By the electrical method we have found that *the β radiation is made up almost entirely of deviable rays* of a penetrating character.

For brevity and convenience we will call the non-deviable rays of *all* radioactive substances *α-rays* and the deviable rays *β-rays.*

The magnetic-deviation apparatus of fig. 1 is not suitable for a direct comparison of the ionizing action of two types of rays. Since, however, the α-rays are in all cases easily absorbed, and we have experimentally found that the greater proportion of the penetrating rays of uranium, thorium, and radium are magnetically deviable, a simple indirect method can be employed.

The ionization current between two large parallel metal plates was observed with a large P.D. between the plates,

(1) with the radioactive substances bare,
(2) with a layer of metal over the substances sufficiently thick to absorb all the non-deviable rays.

In (1) we have the effect of the α- and β-rays, and in (2) that of the β-rays alone.

Since the amount of the α-rays emitted reaches a practical maximum for a very thin layer of radioactive substance a comparison of the ionizing effects of the two kinds is best made with a very thin layer.

In the apparatus employed about $\frac{1}{10}$ gr. of the finely powdered radioactive substance was uniformly spread over an area of about 80 sq. cms. The distance between the testing-plates was 5·7 cms. and the P.D. between the plates 300 volts.

The results of previous experiments have shown that the α-radiations of uranium, thorium, and radium are almost completely absorbed in passing through a distance of 5 cms. of air, so that the current with the bare substance was a measure of the *total* number of ions produced by α-rays, together with a small fraction only of the ions produced by β-rays.

A layer of aluminium ·009 cm. thick was found sufficient to completely absorb the α-radiation. The following table

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* E. Rutherford, Phil. Mag. Jan. 1899.

illustrates the quantitative connexions between the ionizing action of α- and β-rays for the conditions of the experiment:—

	Total ionization. α-rays.	Ionization. β-rays.	Ratio ionization. $\frac{\beta}{\alpha}$.
Uranium ...	1	1	·0074
Thorium ...	1	·27	·0020
Radium ...	2000	1350	·0033

In the above table the total number of ions produced by α- and β-rays of uranium is, in each case, taken as unity for purposes of comparison. The third column gives the actual ratio of β to α observed for equal weights of substance.

The results are only approximate, for the ionizing action of the rays from a given weight of substance depends on its fineness of division.

It will be observed that the ratio ionization of β to α is greatest for uranium and least for thorium. The intensity of α- and β-rays of radium of course depends on the purity of radium. In this experiment radium obtained from Paris was used. The radium from P. de Haen, Hannover, gave similar results.

For increasing thicknesses of the radioactive substance the ratio of ionization $\frac{\alpha}{\beta}$ steadily decreases to a constant value, since the α-rays are more readily absorbed than the β in the radioactive substance itself.

§ 10. *Comparison of energy radiated by α- and β-rays.*

On the assumptions that

(1) The same energy is required to produce an ion for both α- and β-rays;

(2) That all the energy emitted into the air from a radioactive substance is used up in producing ions;

we can form an approximate estimate of the ratio of the energy radiated by the α- and β-rays.

If λ is the coefficient of absorption of the deviable rays in air, the rate of production of ions per unit volume at a distance x from the source is $qe^{-\lambda x}$, where q is the rate of ionization at the source.

The total number of ions produced by complete absorption of the rays is

$$\int_0^{\infty} qe^{-\lambda x}dx = \frac{q}{\lambda}.$$

Now λ is difficult to measure experimentally for air, but we can get an approximate estimate of its value from Lenard's results that the absorption of cathode-rays is proportional to the density of any given substance and independent of its chemical nature.

Now λ for aluminium for β-rays from uranium is about 14, and λ divided by the density is 5·4. Now taking density of air as ·0012, we find that

$$\lambda \text{ for air} = {\cdot}0065.$$

The total number of ions produced in air is thus 154 q when rays are completely absorbed.

Now, from the above table, we see that the ionization of deviable rays is ·0074 of the ions produced by α-rays when β-rays passed over a distance of 5·7 cms. of air.

We thus have approximately

$$\frac{\text{Total number of ions produced by } \beta\text{-rays}}{\text{Total number of ions produced by } \alpha\text{-rays}} = \frac{{\cdot}0074}{5{\cdot}7} \times 154 = {\cdot}2.$$

Thus about $\frac{1}{6}$ of energy radiated into air by a thin layer of uranium is carried by the electrons. The ratio for thoria is about $\frac{1}{22}$, and for radium about $\frac{1}{14}$, assuming the rays to have about the same average value of λ.

This calculation only takes into account the energy which is radiated out into the surrounding gas: but on account of the ease with which the α-rays are absorbed, even with a thin layer, the greater proportion of the radiation is absorbed by the radioactive substance itself. This is seen to be the case when we recall that the α-radiation of thorium or radium is reduced to half value after passing through a thickness of about ·0005 cm. of aluminium. Taking into consideration the great density of the radioactive substances, it is probable that most of the radiation which escapes into the air is due to a thin skin of the powder not much more than ·0001 cm. in thickness.

We can, however, form an estimate of the relative rate of emission of energy by the α- and β-rays in the following way:—

The total energy W_1 radiated to the surface per sec. by a thickness d, is given by

$$\begin{aligned} W_1 &= \frac{1}{2}\int_0^d E_1 \sigma e^{-\lambda_1 x}\,dx \\ &= \frac{E_1\sigma}{2\lambda}(1-e^{-\lambda_1 d}) \\ &= \frac{E_1\sigma}{2\lambda_1} \text{ if } \lambda_1 d \text{ is large.} \end{aligned}$$

For simplicity let us suppose a thick layer of radioactive substance spread uniformly over a large plane area. There seems to be no doubt that the radiations are emitted uniformly from each portion of the mass; consequently, radiation which produces the ionizing actions in the gas above the radioactive layer is the sum total of all the radiation which reaches the surface of the layer. Let λ_1 be the average coefficient of absorption of the rays in the radioactive substance, and σ the specific gravity of the substance. Let E_1 be the total energy radiated per sec. per unit mass of the substance where the absorption of the rays in the substance itself is disregarded. The energy per sec. radiated to the surface by a thickness dx of a layer of unit area distant x from the surface is given by

$$\tfrac{1}{2}E_1\sigma e^{-\lambda x}dx.$$

In a similar way it may be shown that the energy W_2 radiated per sec. by the β-rays for a very thick layer is given by

$$W_2=\frac{E_2\sigma}{2\lambda_2}$$

where E_2 is the total rate of emission of energy of unit mass disregarding absorption, and λ_2 the coefficient of absorption of rays in the substance. Therefore

$$\frac{W_1}{W_2}=\frac{E_1}{E_2}\frac{\lambda_2}{\lambda_1},$$

or

$$\frac{E_1}{E_2}=\frac{\lambda_1}{\lambda_2}\frac{W_1}{W_2}.$$

It is difficult to determine λ_1 and λ_2 directly for the radioactive substance itself; but it is probable that the ratio is not widely different from the ratio of the absorption-coefficients for another substance like aluminium, which has been directly determined. This follows from the general result that the absorptions of α- and β-radiations in any substance are approximately proportional to the density of the substance.

$\frac{W_1}{W_2}$ is the ratio of the number of ions produced by the α- to those produced by the β-rays, and can be determined in the way already explained for a thin layer.

The ratio $\frac{E_1}{E_2}$ has been determined for uranium from the following experimental data. A thick layer of uranium oxide was spread over an area 22 sq. cms., and the ratio of the current produced by the α- and β-rays determined between two parallel plates distant 6·1 cms. apart.

It was found that

$$\frac{\text{current due to } \alpha\text{-rays}}{\text{current due to } \beta\text{-rays}} = 12{\cdot}7.$$

Thus

$$\frac{W_1}{W_2} = \frac{\text{total number of ions due to } \alpha\text{-rays}}{\text{total number of ions due to } \beta\text{-rays}}$$

$$= \frac{12{\cdot}7 \times 6{\cdot}1}{154}$$

$$= {\cdot}5 \text{ approx.},$$

since we have previously calculated number of ions produced by the β-rays is 154 times the number produced for 1 cm. distance between the plates *.

Now

$$\frac{E_1}{E_2} = \frac{\lambda_1 W_1}{\lambda_2 W_2} = \frac{5\lambda_1}{\lambda_2} = \frac{5 \times 2740}{14} = 1000 \text{ approx.},$$

since the value of λ_1 for aluminium = 2740 for the α-rays and λ_2 for the β-rays = 14.

We therefore see that for uranium about 1/1000 of the total energy radiated is carried off in the form of electrons. The ratio is still smaller for thorium and radium. It thus appears that in the permanent radioactive substances the electrons driven off represent only a small fraction of the energy dissipated.

§ 11. *Discussion of Results.*

We have seen that the three well-recognized radioactive substances, uranium, thorium, and radium, all emit both deviable and non-deviable rays. In this respect they differ from polonium, which gives out no deviable rays. As Becquerel has pointed out, there is little doubt that polonium (radioactive bismuth) cannot be considered as a permanent radioactive substance, for its radiation steadily diminishes with the time.

We have shown that uranium gives out more deviable rays than radium or thorium, compared with the amount of non-deviable, but the ratio of the amounts of the two types of rays is of the same order.

In considering the question of the relation between the α- and β-rays, the results of the chemical separation are of

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* Phil. Mag. June 1902.

great importance. It seems certain that we cannot regard the α-rays as having the same relation to β-rays as cathode-rays have to Röntgen rays which they produce; for we have shown that the separated active products from uranium and thorium contain all the substance responsible for the β-rays. The radioactive material, which has thus been temporarily freed from β-rays, still, however, retains its power of giving out, in the case of uranium a large proportion, and in the case of thorium about 30 per cent. of the original α-rays.

This α-radiation persists, in the case of uranium, several days, and, in the case of thorium several hours, without any appreciable change in intensity. If the α-rays are due directly to the β-rays, it is necessary to assume that the radiation persists for long intervals after its exciting cause is removed. This view also fails to explain, without additional assumptions, why the radiation from Ur.X. does not excite similar α-radiations in itself.

Without, at this stage, going into views on the mechanism of radioactivity, it seems probable that most of the deviable rays from uranium and thorium are given out by a secondary product produced by a disintegration of the uranium or thorium atom or molecule. These secondary products differ in chemical properties from the uranium and thorium, and can be separated from them by chemical means, and thus give rise to Ur.X. and Th.X. The non-deviable radiation may be either due to the other secondary product of the reaction, or may be due to an action of the product responsible for the deviable rays in the mass of the radioactive material.

McGill University, Montreal.
May 7, 1902.

XXXV. *On the Ebullition of Rotating Water.—A Lecture Experiment.* By T. C. Porter, *Eton, Bucks.*[*]

If the water in a beaker, having approximately vertical sides, be caused to rotate about an axis concentric with the vertical geometrical axis of the beaker, it is obvious that in any horizontal section of the water the pressure is least in the centre, and increases from the centre outwards. It is also a well-known fact that the temperature at which water boils depends upon the pressure to which it is subjected, being lower the lower this pressure is. Thus if a beaker of water were at a temperature just below the boiling-point, and it could be *suddenly* made to rotate throughout its mass without cooling it, the water would turn into vapour in and about the axis of least pressure, from the surface downwards, forming, at all events for the

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[*] Communicated by the Physical Society: read May 23, 1902.

moment, a thin core of steam in the middle of the water. In practice, however, water cannot be made to rotate throughout its mass suddenly; and if the rotation is generated gradually, the water-vapour is also, as a rule, gradually formed, and is given off from the surface without ebullition, in the quantity sufficient to relieve the tension of those particles of water for which the pressure is diminished. The very form taken by the water as it rotates, increases its surface area, and thus tends to promote evaporation, and so to check ebullition. For these reasons the writer has failed to exhibit the experiment to be described in this its simplest form. If, however, the water is supplied with heat whilst it is rotating, the steam is formed only in the region of least pressure, forming a gaseous core in the rotating water, as in fig. 1. The experiment is an exceedingly simple one both to make and to photograph; it may be well to give a few details as to its performance, though the four figures given are only careful drawings from four of the original photographs.

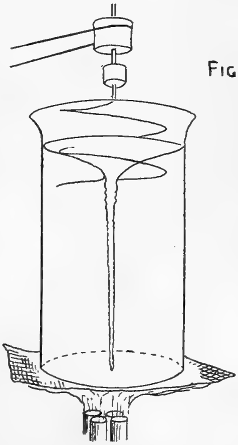


FIG. 1.

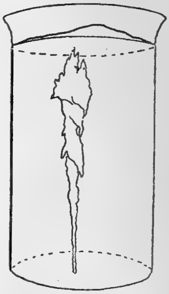
In fig. 1 the spiral wire stirrer used is seen near the surface of the water; whilst beneath the wire gauze, on which the large beaker rests, and which serves to distribute the heat more evenly, are visible the flames and upper parts of the four Bunsen burners employed to heat the water. The spiral stirrer was driven by a small motor; but experience soon proved that results as good, if not better, could be obtained by stirring the water *by hand*, using a long glass rod completely covered by a piece of indiarubber tubing in order to avoid the risk of breaking the glass vessel. After giving to the water throughout its depth the necessary and rapid rotation, and before taking the photographs, this rod was rapidly withdrawn from the beaker, its stirring motion being carefully maintained during the act of withdrawal. Some of the photographs were taken by diffused daylight combined with that of the electric arc, the latter being concentrated by a lens, so as to illuminate the whole of the beaker and its contents as brightly as possible. The plates were Edwardes's Isochromatic Instantaneous, and the exposures were about the $\frac{1}{40}$ of a second. A dilute developer should be used, and as much as 30 min. or more allowed for development.

Thus far the experiment illustrates in an apparently simple and beautiful way the lowering of the boiling-point of water under reduced pressure; but there are some very curious phenomena to be presently described, which are shown by the column of steam, if the water is first stirred and then left to come to rest, whilst the heating is continued. Just after the stirrer has been removed, the appearance presented is that recorded in fig. 1.

The lengths of the multitude of curved lines, shown in the original photographs near the bottom of the beaker, and formed by the rotation of small stray bubbles, are an index to the speed with which the water is rotating when the duration of the exposure for the photograph is remembered; and in fig. 1 the rate of rotation is much higher than in the subsequent figures, which are taken at later stages. In fig. 1 there is a markedly concave surface to the water in the beaker, and the column of steam is practically continuous from base to summit where it joins the air. This phase lasts about a minute, when the water has been stirred as rapidly as is possible by hand, and then it will be noticed that *pulsations* set in: at first these are feeble, and succeed each other with great rapidity; but their period rather rapidly lengthens till it may last four seconds or more, and at the same time they become more and more violent.

The course of events during a single pulsation is as follows:—1st phase, the surface-curve of the water flattens, and in the later stages of the experiment the curvature disappears; whilst, so far as can be judged by eye and from the photographs, at the instant when the surface of the water is most nearly level, or just before it, a column of steam springs up with great rapidity from the base of the beaker to the surface of the water, heaving this up in its central portion, and in the later stages of the experiment often causing the ejection of water from the beaker. This phase is shown in fig. 2, where the reversal of the surface curvature is very evident. Immediately after the eruption of the steam, and whilst the steam-column still stretches from the base of the beaker to the surface of the water, follows the 2nd phase. The steam-column seems to condense and breaks up, leaving only a few small bubbles, which either hang stationary or move *downwards* in the liquid; whilst if the water has dust in it the motion of the dust particles shows that a curious kind of annular wave, concentric with the steam-

Fig. 2.



column and at any moment occupying a horizontal plane, traverses the water *from top to bottom*, and spreads out in so doing, apparently causing in its course the partial or almost complete condensation of the steam and the curious brief *downward* movement of the bubbles left: at the same time the surface of the water in the beaker becomes deeply indented, perhaps sinking in to take the place of the steam which has condensed, (though the writer does not feel at all certain that this is the cause of the depression formed). This second part of the pulsation is illustrated by fig. 3. After this the apex of the surface vortex rises, and the first phase of the phenomenon recurs. This state of pulsations continues for perhaps three or four minutes: the eruptions of steam are very violent towards the close of the period, especially if the water has been boiled for long, or is made slightly alkaline (the conditions for boiling with bumping), and fig. 4 shows the effect of such a condition of things. The original photograph was taken midway through the pulsation period and in the 2nd phase. In this photograph it will be noticed that the point where the steam was first formed is not on the surface of the beaker as it generally is, but in the water itself. Some other photographs were taken at the close of the pulsation period, when the axis of rotation of the water begins to "wobble," and consequently the point where the steam is formed is not, as a rule, in the geometrical vertical axis of the beaker. Soon after this "wobbling" sets in the steam begins to be formed anywhere, at, or near, the bottom of the beaker—and all evidence of the effects of rotation vanishes.

Fig. 3.

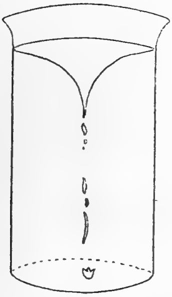
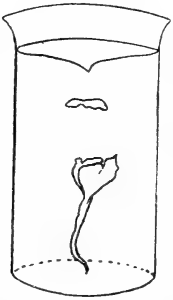


Fig. 4.



The curve of the surface of the water throughout is never a *parabola*, as it would be if the angular velocity of the water were everywhere equal: thus the divergence from the parabolic form indicates how very much more rapidly the water rotates as it nears the axis of rotation. This fact is also evident from the inspection of the lines formed by the small bubbles rotating near the base of the steam-column as already mentioned. One might naturally expect that the outbursts of steam, (those which occur during the pulsation period), would occur when the surface vortex was deepest,—instead of which the exact opposite is the case. At times, too, large bubbles of steam form suddenly in the water and condense, without the surface-level of the water in the jar being *simultaneously* visibly disturbed: at any rate, if it be so—and it would seem that it must be, considering the high elasticity and incompressibility of water,—the disturbance is anything but easy to observe.

With respect to the cause of the pulsations already alluded to, it may be well to state that by stirring *cold* water in a beaker-shaped jar, having a small hole in its bottom through which a stream of air-bubbles can be blown (to imitate the generation of the steam, but not its condensation), there is abundant evidence from the motion of small bubbles that pulsations set in in this case also, and indeed there is some evidence of a similar phenomenon when an ordinary glass of water is stirred: hence it does not seem likely that in the case of the hot water the pulsations are directly caused by either the formation or condensation of the steam, although this may reinforce them when once they have been set up.

Lastly, the form of the steam-columns often presents an unmistakable likeness to those of solar prominences, which can scarcely be altogether fanciful; for there is every reason to believe that the latter are explosive emissions of gaseous matter projected through and above the solar atmosphere. May not their immediate cause be the diminution of pressure on the sun's surface at and near the centre or centres of "depressions" caused by violent cyclonic disturbances in the solar atmosphere? The enormous velocity with which such ejected matter is seen to rise, and also the rapidity with which it is dispersed, have their counterparts in the experiments which have been described: no one who sees these last for himself can fail to be impressed by the great velocity with which the steam-column rises in the water, and by the suddenness with which it condenses, and that, too, in water at, or at any rate very near to, its boiling-point,—whilst the hanging filaments such as appear in fig. 3 recall most vividly some well-known drawings of solar prominences as they die out: the fact that in both cases the filaments hang with their length vertical, and do not lie horizontally, seems to the writer very significant.

This short paper is little more than a description of a phenomenon of which the writer has never seen any account given elsewhere; it makes hardly any attempt to explain much of it; still it is offered in the hope that some one more conversant with hydrodynamics than the author may give the true solutions to the questions it suggests.

Eton, Bucks, May 1902.

XXXVI. *On the Comparison of Vapour-Temperatures at Equal Pressures.* *By* Professor J. D. EVERETT, *F.R.S.*[*]

RAMSAY and YOUNG seem to have been the first to call attention (Phil. Mag. Jan. 1886) to the fact that the ratio t/t' of the absolute temperatures at which two vapours (at saturation) have the same pressure p remains nearly constant for changes of p of very considerable magnitude. In the case of vapours of kindred constitution, their results show that a twentyfold increase of p only changes t/t' by about $\frac{1}{2}$ per cent.

They further lay down, for the comparison of vapours generally, the law—now known as "Ramsay and Young's law"—that if t_1, t_2 denote the absolute temperatures of one vapour at the pressures p_1 p_2, and t_1' t_2' those of another vapour at the same pressures, we shall have

$$\frac{t_2}{t_2'}-\frac{t_1}{t_1'}=c(t_2-t_1), \quad \ldots \ldots \quad (1)$$

c being a small positive or negative constant multiplier, depending on the substances compared.

To the eye of the mathematician there is an awkward one-sidedness about this formula; it is not symmetrical as between t and t'. It can, however, be rendered symmetrical by first writing it in the form

$$\frac{t}{t'}-ct=k,$$

(k being a constant), and then dividing by ct. We thus obtain an equation of the form

$$\frac{x}{t}+\frac{y}{t'}=1, \quad \ldots \ldots \ldots \quad (2)$$

x and y standing for $-k/c$ and $1/c$, which are constants. A

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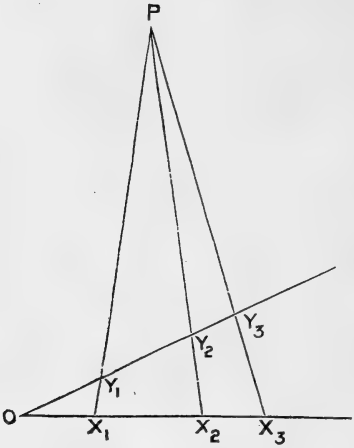
[*] Communicated by the Physical Society.

straight line making intercepts t, t' on the axes is represented by equation (2) and will pass through the fixed point $x=-k/c$, $y=1/c$. In practice k is positive; hence one of the two coordinates of the fixed point is positive and the other negative. As c is small, the point is at a considerable distance.

Ramsay and Young's law is thus equivalent to the following statement (see fig. 1):—*If the absolute temperatures at which two vapours have equal pressures are represented by lengths* O X, O Y *laid off along two lines inclined at any angle, the line* X Y *joining their extremities will, when produced, pass through a fixed point* P *lying at a considerable distance.* Two pairs of corresponding temperatures (preferably far apart) are theoretically sufficient to determine the position of P; and then the temperature of one substance corresponding to a given temperature of the other is found by merely drawing a line through two given points.

Fig. 1.



It is not necessary to use the same scale for t' as for t; for equation (2) may be written

$$\frac{x}{t}+\frac{2y}{2t'}=1,$$

showing that the effect of doubling the scale for t' is simply to double the ordinate y of the fixed point. A table given by Ramsay and Young shows that the absolute temperature of mercury vapour is rather more than double that of ether vapour at the same pressure. The scale for mercury might therefore be conveniently taken double of that for ether.

The best general formula that has been propounded for the relation between t and p is Rankine's, which is discussed in the first of his 'Collected Papers,' and shown to give good results for very various substances. His tables of steam-pressure were calculated by it. It is

$$\log p = \alpha - \frac{\beta}{t} - \frac{\gamma}{t^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the second and third terms being in practice always negative.

If we omit the third term, as Rankine does in cases where the data are not very accurate, we have, for two vapours

$$\log p = \alpha - \frac{\beta}{t} = \alpha' - \frac{\beta'}{t'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence

$$\frac{\beta}{t} - \frac{\beta'}{t'} = \alpha - \alpha',$$

indicating that the line X Y passes through the fixed point

$$x = \frac{\beta}{\alpha - \alpha'}, \quad y = -\frac{\beta'}{\alpha - \alpha'}.$$

Ramsay and Young's law is thus deducible from Rankine's shortened formula.

Treating Rankine's full formula in the same way, we get

$$\frac{\beta + \gamma/t}{t} - \frac{\beta' + \gamma'/t'}{t'} = \alpha - \alpha',$$

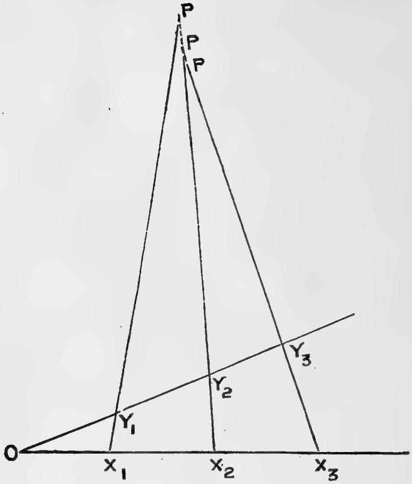
showing that the ultimate intersection of two consecutive positions of X Y is

$$x = \frac{\beta + \gamma/t}{\alpha - \alpha'}, \quad y = -\frac{\beta' + \gamma'/t'}{\alpha - \alpha'}. \quad . \quad . \quad . \quad . \quad (5)$$

As t and t' increase, the absolute magnitudes of x and y diminish. Instead of strictly meeting in a point P, as in fig. 1, the lines X Y will accordingly touch a curve with its concavity turned away from the origin, like the dotted curve P P P in fig. 2 (p. 338).

The fact that Ramsay and Young's formula is deducible from Rankine's shortened formula is indicated by Ayrton and Perry in a paper to the Physical Society*, in which the accuracy of Rankine's complete formula is strongly insisted on.

Fig. 2.



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XXXVII. *Change of Length of Ferromagnetic Wires under Constant Tension by Magnetization. By* K. HONDA, *Rigakushi, and* S. SHIMIZU, *Rigakushi* †.

1. IN his earliest systematic experiments on the change of length by magnetization of iron and steel rods, Joule ‡ noticed that the effect of tension is to diminish the elongation, and that if the tension exceeds a certain limit the magnetization causes contraction instead of elongation. Repeating the same experiment, S. Bidwell § made special investigation on this point, and confirmed Joule's results. Besides iron he examined nickel wire; the magnetic contraction of the wire is decreased by tension in weak fields, but it is increased in strong. These changes also increase with

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* Phil. Mag. [5] xxi. p. 255; Proc. Phys. Soc. vii. p. 372 (1886).

† Communicated by Prof. Nagaoka.

‡ Joule, Phil. Mag. xxx. pp. 76, 225 (1847).

§ Bidwell, Proc. Roy. Soc. xl. p. 109 (1885); tom. cit. p. 257 (1886); ibid. xlvii. p. 469 (1890); Ewing's Magnetic Induction, p. 240.

tension. B. Brackett[*], G. Klingenberg[†], K. Tangl[‡], have also investigated the same subject, and obtained results similar to those of Bidwell.

In Bidwell's experiment, which is generally regarded as the most reliable, the wire to be tested carried the magnetizing coil with it, so that even the smallest tension was greater than 3 kilog. per square millimetre. Hence the effect of small loading, which is remarkable in nickel, was not well studied. The sensibility of his apparatus cannot, moreover, be considered as sufficiently delicate at the present day. It was, therefore, thought desirable to repeat his experiment with an arrangement giving higher accuracy. Besides iron and nickel we also examined nickel-steels kindly placed at our disposal by Dr. Ch. Ed. Guillaume, which showed a remarkable anomaly with regard to the change of length and of volume.

2. The apparatus used in the present experiment is in principle the same as that of Prof. Nagaoka. The chief difference consists in using a rotating cylinder[§] to cause a reflecting mirror to turn through a minute angle, instead of three-pivots system.

Fig. 1.

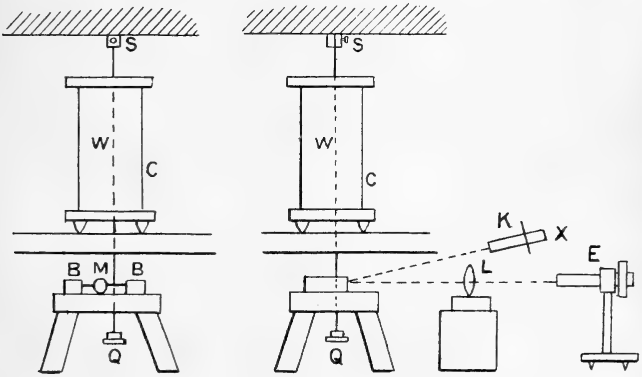

Fig. 1 shows the front and side views of the apparatus. C is the magnetizing coil and W the wire to be tested, whose upper end is clamped to the support S, while its lower end carries a weight Q. M is a reflecting mirror fixed to the

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[*] Brackett, Phys. Rev. v. (5) p. 275 (1897).

[†] Klingenberg, Inaug. Diss., Berlin, 1897; Beibl. xxi. p. 897 (1897); Inaug. Diss., Rostock, 1899; Beibl. xxiii. p. 270 (1899).

[§] K. Tangl, *Ann. der Phys.* vi. p. 34 (1901).

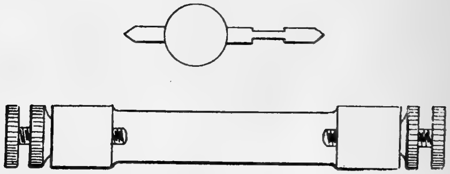
[||] Hertz, *Instrumentenkunde*, iii. p. 17 (1883); *Gesammelte Werke*, Bd. i. p. 227.

rotating cylinder, the ends of which terminate in cones and fit in the agate cups fixed on the heads of screws in the brass socket BB. K is a collimator, L a lens, and E a micrometer with ocular scale. The slit of the collimator is illuminated by a gas-flame; the light leaves the collimator adjusted for a parallel beam, and is reflected by the mirror M, and converges in the micrometer field through the lens L. In the middle of the slit a very fine glass fibre is stretched parallel to the edge, the image of which is clearly seen in the micrometer. The vertical wire touches the rotating cylinder under a suitable pressure; if the wire elongates or contracts the mirror rotates through a small angle, and the corresponding displacement of the image of the fibre is observed in the micrometer field.

The magnetizing coil is 30 cm. long and gives a field of 37·97 C.G.S. units at the centre by passing a current of one ampere. The wire to be tested is soldered into well annealed soft copper wires of about the same diameter, as shown in fig. 2. It is hung vertically in the axial line of the magnetizing coil so as to lie in a nearly uniform field. The pan attached to the lower end of the wire carries in its under face a few pieces of cotton which softly touch a wooden stand for the purpose of damping, without producing sensible pressure. The forms of the rotating cylinder and the brass socket are drawn in fig. 3.

Fig. 2.

Fig. 3.



The stand on which the brass socket is fixed can be made to move up and down as well as forward and backward by means of screws. By this arrangement the cylinder can be made to touch the vertically suspended wire with suitable pressure, and a small rotation of the mirror given at our disposal. This arrangement is omitted in the above figures. The rotating cylinder is made of steel and is 1·51 mm. thick, and the sensibility of our apparatus is such that one division of the micrometer ocular corresponds to a change of length of $2\cdot72 \times 10^{-7}$ per cm. of the ferromagnetic wire.

3. The method of observation was as follows:—The wire to be tested was hung vertically and stretched by a weight of 5 kilograms for three or four hours to make it straight. To begin with, all the weights were removed, and then the wire was again loaded with ½ or 1 kilogram. The wire was then completely demagnetized, and magnetized by passing gradually increasing currents, and the corresponding deflexions were taken, the demagnetization being effected before each magnetization. A set of observations being thus taken, successively increasing loadings were applied and the corresponding sets of observations noted.

Since the resistance of the magnetizing coil was only 0·6 Ω the thermal expansion of the ferromagnetic wire due to the magnetizing current was negligibly small for the currents used in the present experiments. The electromagnetic action between the steel cylinder and the coil was also found to be negligibly small. When the pressure in the contact surface between the cylinder and the wire was moderate repeated applications and removals of the magnetizing field showed no trace of slipping on the cylinder.

The wires tested had the following dimensions:—

Metals......	Soft iron.	Wolfram steel.	Nickel.	Nickel-steel (45 p. c. Ni).	Nickel-steel. (35 p. c. Ni).
Length ...	20·74 cm.	20·97 cm.	20·70 cm.	20·75 cm.	20·73 cm.
Diameter...	0·139	0·060	0·136	0·150	0·144

4. *Soft Iron.*—Fig. 4 (p. 342) represents the curves of the change of length plotted against the magnetizing field; T is the tension per square millimetre. The specimen was very well annealed, and so the initial elongation was greatly reduced. From the figure we see that the effect of tension is to reduce the initial elongation. This reduction becomes greater as the tension increases, till the initial elongation vanishes at a tension of about 4 kilograms per square millimetre. When the tension exceeds this value the curvature of the curve is reversed. In fields greater than 40 C.G.S. units all the curves are nearly parallel to each other. The effect of tension on the change of length is comparatively larger when the load is small than when it is heavy.

By making use of fig. 4 the curves showing the relation between the change of length and the tension under constant field are obtained; some of them are given in fig. 5. We learn from these curves that the effect of loading on the magnetic change of length is not proportional to the load.

Fig. 4.

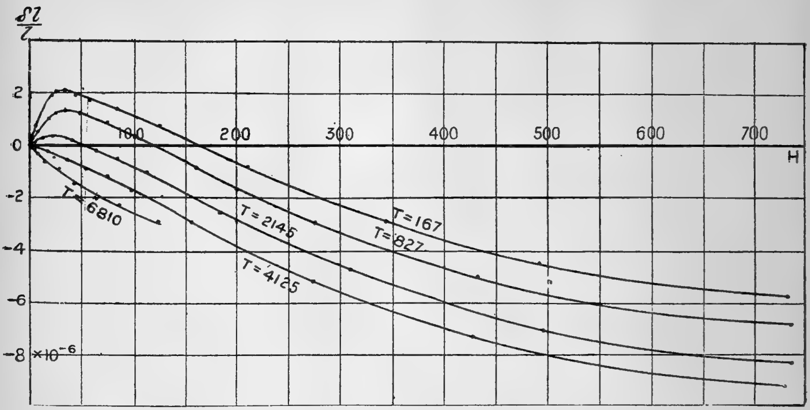
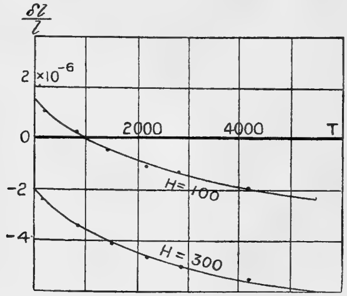


Fig. 5.

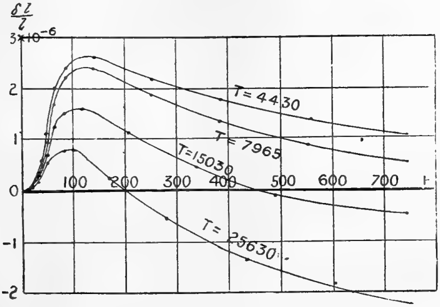


Generally speaking these results coincide with those of Bidwell. In our case the reduction of the initial elongation by tension is far greater than that with Bidwell's wire. The smallest tension at which the elongation vanishes is about four times greater in the latter case than in the former. The discrepancy perhaps arises from the fact that our specimen is comparatively soft as regards magnetization.

5. *Wolfram Steel.*—Fig. 6 represents the result for Wolfram steel hardened by stretching; the anomaly in the change of length for the steel was already pointed out by Prof. Nagaoka and one of us. This anomaly gradually disappears when the tension is increased, and at a tension of

25·63 kilograms per square millimetre the steel behaves like well annealed soft iron. The amount of the change due to tension is decidedly small compared with other ferromagnetic metals.

Fig. 6.



From fig. 7 we see that in Wolfram steel the effect of tension on the magnetic elongation is nearly proportional to the tension.

Fig. 7.

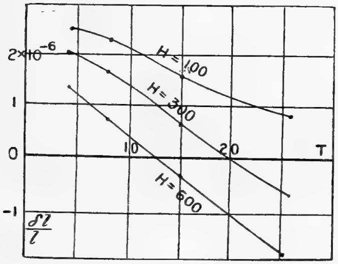
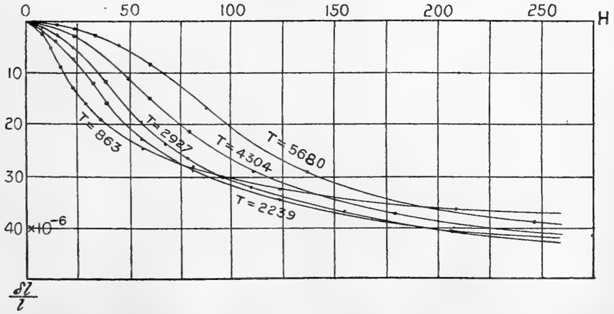


Fig. 8.

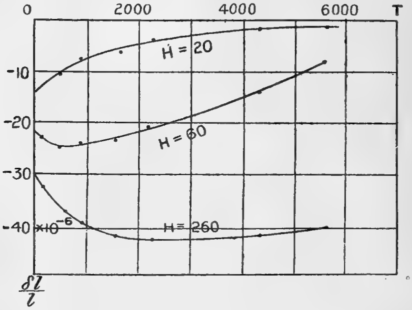


6. *Nickel.*—The results in nickel wire are graphically shown in fig. 8. In weak fields the effect of tension is to

decrease the contraction of length, and the amount of diminution increases with tension. In strong fields the contrary is the case. The tension increases the magnetic change of length by an amount which increases with tension.

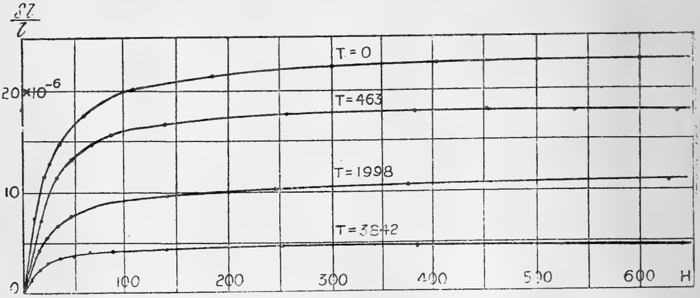
Each curve in fig. 9, showing the relation between the change of length and the tension under constant field, has a minimum point except in weak fields. This minimum occurs at a greater load as the field is increased. These results generally agree with those of Bidwell.

Fig. 9.



7. *Nickel-Steels.*—The change of length under constant tension of the annealed nickel-steel (45 per cent. Ni) is shown in fig. 10. The change of length under ordinary conditions was already observed by Prof. Nagaoka and one of us. The maximum elongation, which is characteristic for iron, is not observed, but the wire simply elongates to an asymptotic value as the field is increased. Compared with other ferromagnetics the effect of tension is comparatively large. It diminishes elongation; by a tension of 1·4 kilograms per

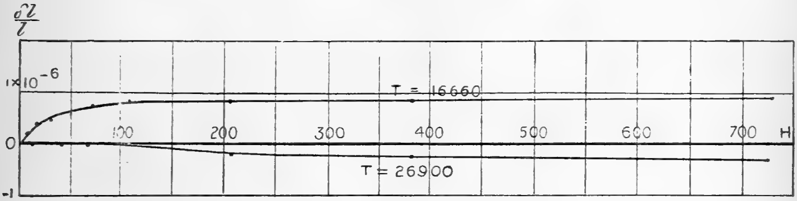
Fig. 10.



square millimetre the elongation is already diminished by one half of its value corresponding to no tension.

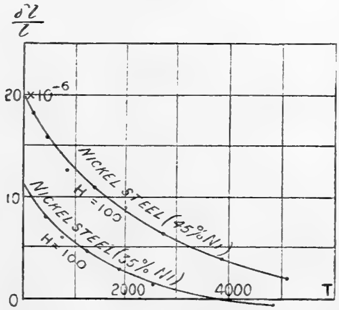
To study the effect of heavy loading a wire of 0·50 mm. thick was made of the same alloy. After a moderate annealing it was subjected to an experiment to see whether it becomes shorter than the initial length when magnetized under a heavy loading. This actually occurred as given in fig. 11. With a tension of 26·9 kilograms per square millimetre the length of the wire decidedly shortens when magnetized. Since the degree of annealing is different in the thick from the thin wire, the changes of length in these two wires for the same field and tension do not exactly coincide with each other.

Fig. 11.



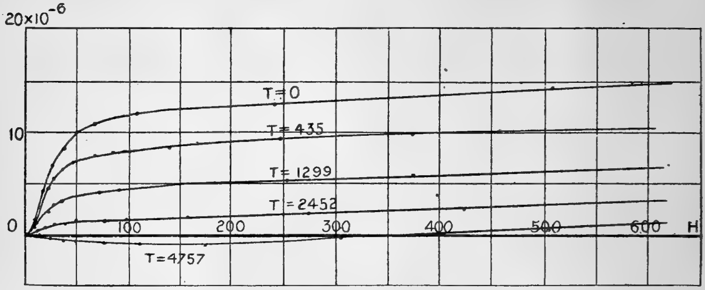
The curve showing the relation between the change of length and the tension under constant field is shown in fig. 12; here we notice that the rate of the diminution of the change of length becomes less as the tension is increased.

Fig. 12.



With another specimen of nickel-steel (35 per cent. Ni) the nature of the change of length and the effect of tension on it are generally the same as those of the former metal, as shown in figs. 12 and 13. The course of the curves for large tension is, however, quite different from that for small tension.

Fig. 13.



For a tension of 4·76 kilograms per square millimetre the wire first contracts and then elongates when the field is increased. The curve of the change of length is therefore similar to that for cobalt. From fig. 12 we see that the rate of diminution decreases as the tension is increased.

In these two sorts of nickel-steels the curves for T=0 are the results of measurement obtained by Prof. Nagaoka and one of us, and reproduced here for the sake of comparison. It was at first our intention to perform the same experiment on a cobalt wire; but having at present no such material at our disposal, we leave the subject for future consideration.

In conclusion, we wish to express our best thanks to Prof. H. Nagaoka and also to Prof. A. Tanakadate for useful advice and kind guidance.

XXXVIII. *The Diffraction of Light from a Dense to a Rarer Medium, when the Angle of Incidence exceeds its Critical Value.* *By* EDWIN EDSER, *A.R.C.S., Lecturer on Physics, Woolwich Polytechnic*; *and* EDGAR SENIOR, *Lecturer on Photography, Woolwich Polytechnic*[*].

THE well-known law of refraction

$$\sin i = \mu' \sin r,$$

indicates that, for a refracted ray to be formed, the angle of incidence, i, must be less than a certain critical value given by the equation

$$\sin i = \mu'.$$

[*] Communicated by the Authors.

For this equation to admit of a real solution, μ' must be equal to, or less than, unity. When $\mu'=1$ no refraction takes place; when μ' is less than unity, the medium traversed by the incident ray is optically denser than that on the further side of the refracting surface. If μ is the index of refraction from the second to the first medium, then the critical value of i is given by the equation

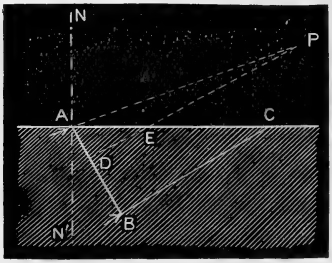
$$\sin i=\mu'=\frac{1}{\mu}.$$

A very simple explanation of this result is afforded by the Wave Theory of Light. The more salient features of the problem have received ample attention; but it happens that, in a certain direction, the theory has not been followed to its logical conclusion, with the result that a phenomenon, somewhat paradoxical from the ordinary point of view, has escaped observation. This circumstance will, we hope, afford an excuse for a brief preliminary consideration of the Wave Theory, as far as applies to the refraction of light from a dense to a rarer medium.

According to the Huyghens-Fresnel theory of wave-propagation, each point of a wave-surface must be considered as a separate source of disturbance, whence originates a secondary wavelet, which is spherical if the medium is isotropic, and which enlarges at a rate dependent only on the nature of the medium. After any lapse of time the new wave-front is formed by the mutual reinforcement of the various secondary wavelets; at points where reinforcement does not occur, destructive interference takes place. Further, when a wave is incident on the interface between two different media, each point of the interface becomes a source of disturbance as the incident waves sweep past. At each of these points two secondary wavelets originate: one spreads outwards into the medium beyond the interface, while the other spreads out into the medium containing the incident wave. The reinforcement of the wavelets propagated in the medium containing the incident wave gives rise to the reflected wave-front. The wavelets propagated in the medium beyond the interface may or may not be able to reinforce each other, with the result that a refracted wave may or may not be formed, according to circumstances. If no refracted wave is formed, the secondary wavelets in the medium beyond the interface destructively interfere with each other throughout that medium; but in all cases secondary wavelets are formed in each of the media separated by the interface.

Let AC (fig. 1) be a plane surface of separation between two media, of which the lower is the denser; and let AB be the trace of one of a series of plane waves, incident in the direction BC on the surface. In order that there should be a resultant disturbance at P, a point in the upper medium, wavelets originating in the immediate neighbourhood of some point A must reach P in the same phase. Let NAN′ be the normal to the surface at A. Then if i is the angle of incidence, this will be equal to the angle BAC which the incident wave makes with the surface AC. Let the angle PAN be equal to θ, and let the upper medium be the free æther, while the refractive index of the lower medium is equal to μ. Then in order that wavelets from A and E, two neighbouring points on the surface AC, should reach P in the same phase, we must have

Fig. 1.



$$AP = \mu \,.\, DE + EP, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where DE is the perpendicular distance of the point E from the plane wave AB.

Let $AP = d$, while $AE = \delta$. Then

$$(EP)^2 = d^2 + \delta^2 - 2d\delta \sin\theta$$

$$DE = \delta \sin i,$$

and from (1),

$$d = (d^2 + \delta^2 - 2d\delta\sin\theta)^{\frac{1}{2}} + \mu\delta\sin i,$$

$$\therefore\ \sin\theta = \mu\sin i - \frac{\delta}{2d}(\mu^2\sin^2 i - 1). \quad . \quad . \quad (2)$$

If δ is of very small magnitude, and the point P is at an appreciable distance from A, d will be very great in comparison with δ, and the second term to the right of (2) will be negligibly small. In these circumstances

$$\sin\theta = \mu\sin i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which determines the direction AP in which the disturbance travels in the upper medium.

When $\mu \sin i = 1$, $\theta = \frac{\pi}{2}$, and the disturbance travels along the surface AC. When $\mu \sin i > 1$, no value of θ can be found which will satisfy (3), and therefore no refracted ray can be formed.

Equation (2), however, shows that when $\mu \sin i > 1$, a disturbance travels from the surface AC to a small distance within the upper medium. For when d is very small, the numerical value of the second term to the right of (2) may attain an appreciable value, and as this value is subtracted from that of $\mu \sin i$ in the first term, the value of $\sin \theta$ may be reduced to less than unity. Thus when the angle of incidence exceeds its critical value, the secondary wavelets in the rarer medium reinforce each other only in the space lying very close to the surface of separation, and in this space alone is a resultant disturbance produced.

The existence of a superficial disturbance within the rarer medium when the angle of incidence exceeds its critical value is confirmed by a well-known experiment. The hypotenuse face of a right-angled prism is laid upon the convex surface of a lens, and the point of contact is viewed through one of the remaining faces of the prism by means of light incident through the other remaining face. The point of contact is seen to be surrounded by a black spot, generally encircled with coloured rings. When the eye is so placed that the light reaching it is reflected at an angle exceeding the critical angle, the coloured rings disappear, but the black spot remains. The existence of this black spot proves that light reaches the eye not only from the face of the prism, but also from the surface of the lens; and as, at the edge of the black spot, the thickness of the air-film between the prism and the lens amounts to about a quarter wave-length of light, it follows that light must penetrate from the surface of the prism into the air, at least to a distance equal to a quarter wave-length of light.

Thus far the theory here developed presents no new feature. But the existence of the secondary wavelets in the rarer medium, even when they do not reinforce each other to produce a refracted wave, entails interesting consequences which have, we believe, heretofore escaped recognition. When the angle of incidence exceeds its critical value, the wavelets originating in the immediate neighbourhood of A (fig. 1) are incapable of arriving in the same phase at any point in the upper medium. Nevertheless it is possible to find a position of the point E such that

$$AP+\lambda=\mu\,.\,DE+EP,$$

where λ is the wave-length of the incident light. In this case the wavelets from A and E reinforce each other at P, their phases differing by 2π. If, then, we stop out the rest of the surface, so as to intercept the wavelets which would ordinarily interfere with those from A and E, light will arrive at P. We may go further and stop out portions of the surface AC, leaving a number of clear spaces from which the wavelets arrive at P in phases differing by multiples of 2π. In this case we have virtually described a zone plate on the refracting surface, and light is diffracted into the rarer medium. Since there is only a superficial disturbance in the rarer medium when the surface is free, it follows that the zone plate must be in optical contact with the surface.

The particular case which is most readily verified experimentally corresponds to the location of the point P at an infinite distance from A. In this instance the zone plate takes the form of an ordinary diffraction-grating, the lines being placed perpendicular to the plane of incidence. If δ represents the sum of the widths of a space and a ruling, then for the diffracted rays to reinforce each other at infinity, in a direction making an angle θ with the normal to the surface, we must have

$$\delta(\mu\sin i-\sin\theta)=n\lambda,$$

where n is an integer. Using white light as an illuminant, we shall obtain diffraction spectra similar to those ordinarily observed by the aid of a grating; but when $\mu\sin i>1$, the central undiffracted image (corresponding to $n=0$) will be absent. Further, for large angles of incidence, the number of lines per centimetre must exceed a certain value, otherwise the smallest possible value for n will correspond to a diffracted spectrum of such high order that the latter will be too faint to be seen; for here, as in the ordinary case, the intensity of a diffraction spectrum varies inversely as the square of the order, to a first approximation. Let the light be incident at an angle of 45° on the grating, and let $\mu=1{\cdot}5$. Then if the 8th diffraction spectrum for $\lambda=\cdot00006$ cm. is to be seen along the surface ($\theta=90°$), we must have

$$\delta=\frac{8\times\cdot00006}{1\cdot05-1}=\cdot0096\text{ cm.}$$

Thus the grating must possess more than 100 lines per centimetre, or more than 250 lines to the inch. For the first diffraction spectrum to be seen in a direction corresponding to $\theta=90°$, a grating of more than 2000 lines to the inch is required.

We have been able to realize experimentally the results deduced from theory above. We used a reproduction of a Nobert's grating, of 3000 lines to the inch, photographed on a very thin collodion film, and afterwards intensified with mercury. The clear side of the glass carrying the grating was cemented with Canada balsam to the hypotenuse face of a right-angled prism, of which the remaining angles were each equal to 45°. The lines of the grating were adjusted to be perpendicular to the triangular ends of the prism. The whole was then mounted on the central table of a spectrometer, one of the mutually rectangular faces of the prism being normal to the parallel beam from the collimator, while the lines of the grating were vertical. Brilliant diffraction spectra were seen on looking at the grating surface, either with the unaided eye or through a telescope focussed on infinity. The brightest spectrum was that seen on looking along the surface (θ nearly equal to 90°). In directions corresponding to smaller values of θ spectra of higher orders were seen; the brightness of these spectra decreased as the order increased, but they only became invisible at an angle of diffraction equal to 10° or 15°. On rotating the prism and grating through a small angle the central undiffracted image was brought into view; this, of course, took the form of a prismatic spectrum, the light having been refracted at the prismatic faces inclined at an angle of 45°. The central image was easily recognized owing to the circumstance that the blue ends of the diffraction spectra on either side of it were turned towards each other. On rotating the prism so as to increase the angle of internal incidence on the grating surface the central image disappeared, *but no change occurred in the general appearance of the diffraction spectra.* On continuing to rotate the prism in the same direction one after another of the diffraction spectra disappeared, but light still emerged when the prism had been rotated through 25° or 30°. A careful examination left no doubt in our minds that the spectra were formed in accordance with the theory sketched out above.

Of course in the present case the light escaped into the air from the surface of the collodion film. But it is easily proved that when the light is incident on the glass-collodion interface at an angle exceeding the critical angle for glass-air, the light refracted into the collodion must fall on the collodion-air surface at an angle exceeding the critical value for collodion-air. The refractive index of Canada balsam is so nearly equal to that of glass that no appreciable effect is produced by the film of that substance between the face of the prism and the unruled surface of the grating.

On looking through the face of the prism which was perpendicular to that through which the incident light entered, a white image of the slit was seen, together with diffraction spectra on either side of it.

Another experiment was performed, using a grating ruled on glass with 300 lines to the inch. The width of a ruling was very small in comparison with that of a space. The grating was of a cheap kind, and the spacing was probably not very regular; nevertheless phenomena similar to those described above were observed. When the light was incident at an angle of 45° on the grating only a few spectra, of high orders, were seen.

When a strip of a screen such as is used for half-tone process work was used as a grating the number of lines to the inch being equal to 135, no diffraction spectra were seen when the angle of incidence was equal to 45°.

The probable existence of the diffraction phenomena described above was, in the first place, deduced by one of us from theoretical considerations; subsequently the experiments described were devised and executed. The singularity of the results obtained entirely vanishes when the point of view chosen is that of the wave theory of light. On the other hand, the failure of light to penetrate a free surface, combined with the readiness with which it traverses the same surface when parts are rendered opaque, afford sufficient interest, we hope, to merit this short notice. At an earlier date, when the wave theory was in more need of confirmation than at present, the experiments described might possibly have appeared as of a fairly crucial nature. At present they may at least serve to illustrate, in a striking manner, certain important points in the wave theory of light.

XXXIX. *Experiments on Induced-Radioactivity in Air, and on the Electrical Conductivity produced in Gases when they pass through Water. By* J. J. Thomson, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge*[*].

It has been shown by Elster and Geitel[†] that a wire, if strongly negatively electrified for several hours either in the open air or, as in one of their experiments, in a large

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[*] Communicated by the Author.

[†] *Physikalische Zeitschr.* ii. p. 563.

cellar becomes radio-active, *i. e.*, it increases the electrical conductivity of the air in its neighbourhood. The most natural explanation of this phenomenon is that, as Elster and Geitel suppose, the atmosphere contains some radio-active constituent which is attracted to the negatively electrified surface ; this constituent of the atmosphere behaving like the "emanation" from thorium which has been shown by Rutherford* to induce radio-activity in bodies with which it comes in contact and to be attracted to negatively electrified surfaces. I have, however, as the result of the experiments described below come to the conclusion that though the existence of this radio-active substance in the air is possible it is not necessary for the explanation of the effect observed by Elster and Geitel, and that negatively electrified surfaces may become radio-active without the deposition upon them of substances having specific radio-active properties.

As long as we have to experiment either in the open air or in large rooms, it is exceedingly difficult to alter the conditions sufficiently to afford an adequate test of any proposed explanation ; I have therefore been experimenting with air contained in a closed vessel of moderate size, and although under normal conditions I have not been able to get any appreciable amount of induced radio-activity, I have found that a negatively electrified wire placed in the vessel acquired, when the gas in the vessel was exposed to Röntgen rays or had been bubbled through water, properties analogous to those found by Elster and Geitel in wires placed in the open air. The effects with the gas which had bubbled through water were very large.

The method was as follows :—a large cylindrical zinc gas-holder 102 cm. long and 75 cm. in diameter, was supported on insulating feet, and closed by a lid made of millboard ; the outer portions of the top and bottom of the lid were put in metallic connexion with the gas-holder by rings of tinfoil which overlapped the lid and were fastened to the cylinder ; circular guard-rings of tinfoil connected with the earth were pasted on the upper and under surfaces of the lid, these prevented any leakage of electricity across the lid from the cylinder to a metal rod placed along its axis; this rod, which was connected with the electrometer, passed through a short metal tube in an ebonite disk which occupied the central portion of the lid, a flange on the rod resting on the top of the tube. The current between the rod and the cylinder was measured by an electrometer which was connected with the

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* Phil. Mag. [6] i. pp. 1 & 161.

rod. This rod before the measurement of the current was connected with the earth, and the cylinder with one terminal of a battery of small storage-cells, the other terminal of which was connected with the earth. The battery contained 500 cells; these were found sufficient in all cases to produce the saturation-current, when the air was in the normal state a very much smaller number of cells was sufficient to do this. As the rod had to be strongly electrified in order to investigate the induced radio-activity, there was some danger that the ebonite disk with which it was connected might get charged with electricity, and this electrification by leaking back to the rod produce effects which were not due to the conductivity of the air. To avoid this two ebonite disks were used, the one used to support the rod whilst it was electrified was removed before the current through the vessel was measured and replaced by the second, which was carefully kept free from electrification.

In the earlier experiments four different rods were used as electrodes, these were pieces of brass tubing of the same length and diameter. The procedure was as follows: in the morning the current through the vessel was measured, using each of the rods as electrode in turn: the deflexion of the electrometer in one minute, which is proportional to the current through the vessel, rarely differed by more than about one part in 75 for the four rods. During the day these rods were subjected to different treatment; one was put aside to serve as a standard, a second was connected with the negative terminal of a Wimshurst machine, and exposed to the air of the room, the Wimshurst machine was giving sparks about 3 cm. long; the third rod was often connected with the positive terminal of the machine and exposed to the air, while the fourth rod was kept in the tank and connected in some experiments with the negative terminal of the machine, in others with the positive. The electrical machine was kept going all day long, and tested from time to time to see that its electrification did not reverse, and at the end of the day the current through the tank was measured, using each of the rods as electrode. If a rod had become radio-active, the current through the tank with this rod as electrode would be greater than it was when the rod was in its normal state, owing to the additional ionization due to the rod. With the air in the tank in its normal state I was never able to detect any change in the rod due to its long negative electrification. The volume of air in the tank, about 440 litres, was too small to produce the radio-active effects observed by Elster and Geitel. As the current coming up to the rod in the tank was much smaller than if the rod had been electrified in the open air, I tried the effect of increasing the current by ionizing the gas in the tank by means of Röntgen rays: the tube giving out the rays was placed outside the tank, the rays passing into the tank through the millboard cover; this had, of course, the effect of greatly increasing the saturation-current through the tank, and it was found that now prolonged negative electrification of the rod produced an appreciable effect; the saturation-current, when the rod which had been negatively electrified in the tank was used as electrode, was considerably larger than when the electrode was a rod which had not been so treated. The magnitude of the effect is indicated by the numbers given below, which represent the deflexions of the electrometer in one minute; these numbers are proportional to the saturation-current:—

Current at 11 A.M. with rod (1) as electrode . . .	74
Current at 5 P.M. after rod (1), which remained in the tank, had been attached to the negative terminal of a Wimshurst machine while the gas in the tank was ionized by Röntgen rays.	86
Current at 11 A.M. with rod (2) as electrode . . .	74
Current at 5 P.M. with rod (2) as electrode, this rod having been exposed to the air of the room and connected with the negative terminal of a Wimshurst machine.	76
Current at 11 A.M. with rod (3) as electrode . . .	72
Current at 5 P.M. with rod (3) as electrode, this rod having been exposed to the air of the room and connected with the positive terminal of a Wimshurst machine.	71

The above experiments were made on the same day. We see that with the negatively electrified rod in the tank there was an appreciable increase; in the case of the other rods the changes were too small to allow any conclusions to be drawn. A considerable number of experiments of this type were made: it will be sufficient to give one more example:—

Current at 11 A.M. with rod (1) as electrode . . .	77
Current at 5 P.M. with rod (1) as electrode, the rod having been in the tank in the interval, connected with the negative terminal of a Wimshurst machine and the air ionized by Röntgen rays.	88
Current at 11 A.M. with rod (2) as electrode	76
Current at 5 P.M. with rod (2) as electrode, the rod having been kept in the tank but not electrified in the interval.	74

The rods which had been made active by long negative electrification gradually lost this activity, and after the lapse of about one hour the current with these rods as electrodes sank to about its normal value. When the rod in the gas exposed to the Röntgen rays was either positively electrified or not electrified at all, no change took place in the saturation-current sent through the gas before and after the electrification from this wire as electrode, thus in these experiments, as in those of Elster and Geitel, *negative* electrification is required to make the rod active.

When a rod is in the active state, the current in the direction corresponding to a flow of positive electricity from the rod is slightly greater than the current in the opposite direction. When the rod is in the normal state the two currents are equal. The effects produced on the rods in the preceding experiments are not very great ; but the method described below gives very large effects, exceeding even those produced by electrification in the open air.

Properties of Air Bubbled through Water.

I made further experiments to see whether the induced radio-activity on negatively electrified bodies could be detected in the space of an ordinary-sized room without artificial ionization of the air. I endeavoured to produce throughout the air in the room an electric field of greater average intensity than that produced by a negatively-electrified wire. With this object very finely-divided water-spray strongly negatively electrified was projected into the room ; the spray was produced by forcing a jet of water under high pressure through a small hole in a negatively-electrified plate ; the spray as it fell was collected on filter-paper which, when drenched by the spray, was placed in the tank through which the saturation-current was measured. Very large effects were obtained in this way, so large, indeed, that it seemed unlikely that they were due to induced radio-activity on the negatively-electrified spray. A series of experiments were accordingly made to see whether wet paper produced any effect when the water had not previously been electrified. Strips of wet filter-paper were wrapped round the rods used as electrodes in the preceding experiments, and much larger saturation-currents were obtained with these electrodes than with bare rods. The current was found to vary much with the nature of the paper—filter, blotting, tissue, cartridge, and foolscap papers were tried—and also with the nature of the solution; the results obtained were complex and irregular, and this method of investigating the action of water was for the time abandoned in favour of the following, which gave quite regular effects.

The air in the large tank, previously described, was made to circulate through water. To effect this two tubes were fastened into the tank, through one of these the air was sucked by a water-pump into a closed vessel, from which it found its way back into the tank through the other tube; the air got thoroughly mixed up with water during the process of pumping. A plug of glass wool was placed in the return-tube to stop water-spray.

The air which had thus been forced through water was found to be a very much better conductor of electricity than air in the normal state, the increase in the conductivity is surprisingly large; thus, after the circulation of the air through water had continued for about two hours, the saturation-current was more than twenty times the value before the circulation commenced. The air, when once it has been modified in this way, retains its new properties for a very long time: thus, if the tank is kept closed so that the air cannot diffuse out, it takes several days after the stoppage of the circulation for the conductivity of the air to fall to its normal value. The following numbers give an idea of the rate at which the modified gas returns to its normal condition. At 5.20 P.M. on Saturday afternoon the current through the tank with the central wire positively charged was 600, with the central wire negatively charged it was 330; at 10 A.M. on Monday, *i.e.*, after more than 40 hours, the current with the central wire + was 143, with the central wire − 115. The saturation-current through air in the normal state was 30 whichever way the wire was electrified.

The properties of the modified air cannot be explained by the negative electrification which Lord Kelvin has shown to be present in air which has bubbled through distilled water, nor could they be explained by supposing that the bubbling of the air through the water filled it once for all with a supply of positive as well as of negative ions. In the air modified by passing through water there must be a continuous production of ions. A gas which contains a mixture of positive and negative ions, but in which no fresh ions are being produced, though it will conduct electricity, will exhibit peculiarities which will distinguish it from a gas in which spontaneous ionization is taking place; the current through a gas in which no fresh ionization is taking place will increase with the electromotive force acting on the gas; each increase in the electromotive force producing an increase in the current. There will be no approach to the state of saturation, indeed in many such cases the tendency is for the current to increase more rapidly than the electromotive force. In the gas in which continuous ionization is taking place the current gets saturated, the maximum current being the one which takes out of the gas in one second all the ions which are produced in the gas in that time; the current will not increase beyond this, however much the electromotive force is increased, provided that the electric field does not become so strong that it gives rise to spark or brush discharge.

Air which has been modified by passing through water shows all the peculiarities of a gas in which continuous ionization is taking place; the current gets saturated; although, as is natural, from the much greater conductivity of the gas the electromotive force required to saturate it is much greater than when the gas is in the normal state.

Many experiments on the relation between the current through the modified gas and the electromotive force acting upon it were made. The following tables embody the results of two such experiments.

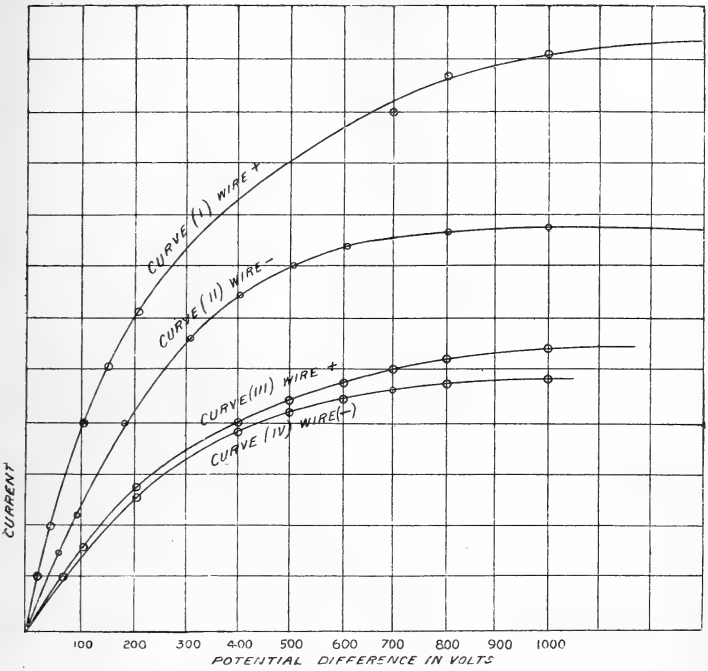
Potential-difference in volts between the central wire and the cylinder.	Current.	
	wire +.	wire −.
40	40	30
80	66	45
120	80	70
160	107	80
200	122	97
400	150	126
600	200	139
800	220	138
1000	230	150

These results are represented graphically in the curves in fig. 1. These curves clearly show the approach to saturation. The following observations were taken with air of considerably smaller conductivity than that used in the preceding experiments:—

Potential-difference in volts between the central wire and the cylinder.	Current.	
	wire +.	wire −.
40	18	17
80	29	28
120	36	36
200	58	55
400	80	78
600	92	85
800	105	95
1000	110	95

Curves representing the results of these experiments are shown in fig. 1.

Fig. 1.



In these experiments the central electrode was not supported by the ebonite plate at the centre of the lid of the vessel containing the modified gas, but was supported above the vessel and passed into the vessel through a hole in the lid which it did not touch.

The air when in the modified state produced by bubbling through water can be transferred from one vessel to another and still retain some, at least, of its conductivity. To show this a second vessel was prepared. This was a large galvanized iron cistern supported on insulating feet, a central wire placed along its axis was kept connected with the electrometer, and the current between this wire and the case of the cistern measured. This vessel, which we shall call B, was connected by a metal pipe about 150 cm. long and 1 cm. in diameter with the vessel A, in which the modified gas was stored. When air was blown from A to B the saturation-current through A diminished, while that through B increased.

The gas, while passing through the tube between A and B, could easily be subjected to various physical processes, and by observing the rate at which the conductivity in B increased—the rate of flow of air through the tube being kept constant—the effect of these processes on the conductivity of the modified gas could be determined. Thus a plug of glass-wool was placed in the tube, and it was found that the modified gas could pass through this without losing its conductivity.

If the conductivity of the modified gas did not arise from some process of continuous ionization, but was due to the presence of ions placed once for all in a gas in which there was no further creation of ions, it should be destroyed like that of gases sucked from flames by passing the gas through a strong electric field. To test this point a long metal tube, about 1 metre long and 1 cm. in diameter, with an insulated wire along its axis, was inserted between the vessels A and B. The modified gas could pass through this tube when there was a potential-difference of 1000 volts between the wire and the tube without losing its conductivity. Thus, in this respect, the modified gas resembles a gas mixed with the "emanation" from thorium. Rutherford has shown that in this case the conductivity is not destroyed by a strong electric field.

The modified gas passed through a tube filled with wire gauze heated to a dull red heat without losing its conductivity: when, however, the gauze was at a bright red heat the conductivity was destroyed.

The conductivity was also destroyed when the gas passed slowly through a spiral tube immersed in a freezing-mixture of ether and solid carbonic acid.

The conductivity can be taken out of the gas by passing it slowly through a tube filled with glass beads moistened with sulphuric acid; if the gas is merely allowed to bubble through sulphuric acid it escapes with a considerable amount of conductivity.

Experiments with a Gouy Sprayer.

The water-pump arrangement, although very convenient for testing the effects of water and air, was not suitable for use with other liquids and gases. To test the effect of different liquids air was forced through a Gouy spray. The air, after passing through the sprayer, was found to have a high conductivity, and when it passed into either of the testing vessels A or B, the saturation-current through this vessel was increased. By measuring the increase produced after the current of air from the sprayer had passed into the testing vessel for a given time an estimate could be formed of the conductivity given to the gas by passing through the liquid in the sprayer; by changing this liquid the effect of the nature of the liquid on the conductivity communicated to a gas passing through it could easily be determined.

The following is an example of some experiments of this kind:—

Vessel B, normal saturation-current before spraying	wire + 16, wire − 16
Pure distilled water in the sprayer, the air after passing through the sprayer went into B, duration of experiment 15 minutes, saturation-current . .	wire + 33, wire − 30
Air blown out of B, saturation-current .	wire + 15, wire − 15
Strong solution of NaCl in the sprayer, air passed through sprayer as before for 15 minutes, saturation-current .	wire + 30, wire − 28

Thus there is no clearly-marked difference between the effects of pure water and brine. Solutions of rosaniline, phenol, hydrogen peroxide, and sulphuric acid were tried, and all gave much the same effects as pure water: the amount of electrification given to the air by bubbling through these solutions is very different, so that these experiments afford another proof of the difference between the conductivity communicated to a gas and the amount of electric charge. Another illustration of this is that though when air is first bubbled through distilled water it is strongly negatively electrified, it loses its charge much more rapidly than its conductivity, and after the lapse of an hour or so the charge will be unappreciable while the conductivity will be almost as large as it was at first.

Ether, alcohol, and turpentine were placed in the sprayer and air forced through them, but with these liquids no appreciable conductivity was produced.

When coal-gas was forced through distilled water in the sprayer the conductivity was much less than when the same volume of air was passed through.

Induced Radio-Activity produced on a Negatively-Electrified Surface immersed in Modified Gas.

The experiments already described have shown that when air is in its normal state the volume of air in the closed vessel A is too small to give the induced radio-activity observed in a negatively electrified wire placed in the open air. We have seen too that when the current of electricity through the vessel is increased by exposing the gas in it to Röntgen rays, a negatively electrified wire acquires the property of ionizing the air around it; this effect is, however, shown to a very much greater extent by the gas when it is in the modified state produced by bubbling it through water.

To show this the tank A was filled with the modified conducting gas, while the air in B was kept in its normal condition, a clean wire electrode was taken and the saturation-current through B with this wire as electrode measured; the wire was then placed in A and kept negatively electrified by a Wimshurst machine for periods ranging from 30 minutes to 7 hours; the wire was then taken out of A and replaced in B, and the current through B again measured with this wire as electrode: the current was found to be considerably greater than before the electrification of the wire. The following numbers show the magnitude of this effect:—

Current through B with a potential-difference of 1000 volts before wire was electrified	wire + 24, wire − 17
Current after wire had been negatively electrified in the vessel A for 7 hours	wire + 54, wire − 54

The conductivity of the air in the tank A was about 10 times normal.

In another experiment when the conductivity in A was about 12 times normal, the results were:—

Current through B before wire was electrified	wire + 22, wire − 17
After 7 hours' negative electrification of the wire in A the current through B was	wire + 74, wire − 67

Larger effects were obtained with electrodes having larger surfaces than that of the straight wire. Thus, when a cylinder of copper wire-gauze was used as the electrode, the current through B before the gauze was electrified was: gauze + 22, − 21. After 7 hours' electrification in A the current through B was: gauze + 400, − 200.

The amount of ionization produced by a wire after negative electrification does not seem to depend to any great extent on the material of which the wire is made. Wires of the same diameter and length made of zinc, lead, iron, copper, amalgamated copper, copper covered with a layer of water and glycerine, copper wet with alcohol, which all gave when used as electrodes equal currents through B before electrification, gave approximately equal currents (much larger than the previous ones) after negative electrification in A. To ensure that the wires were exposed to similar influences in the vessel A they were usually tested in pairs, which were connected together and placed in symmetrical positions with respect to the axis of A.

The amount of induced radio-activity on negatively electrified surfaces exposed to the emanation from thorium, or placed in the open air, seems also to be independent of the nature of the surface.

The ionizing power of the wire is only produced by negative electrification. If the wire when placed in the modified conducting gas in A is positively electrified, or if it is not electrified at all, then no change in the current through B with this wire as electrode is produced by the immersion of the wire in the vessel A.

To show the ionization produced by a wire after negative electrification in A, it is not necessary to use the wire itself as the electrode in measuring the current through B, an independent wire may be used as electrode, and the ionization due to the wire can be detected by the increase in the saturation-current which takes place when the wire is put into B after its negative electrification in A: the effect, although very distinct, is not so large as when the electrified body is itself used as the electrode; it is desirable to use a piece of metal of considerable area for the body which is negatively electrified.

The ionizing power possessed by the active metal is very easily cut off by thin layers of solids. I have, however, been able to detect that an appreciable effect is produced by the negatively electrified metal even when surrounded by thin aluminium foil or paper. In this connexion it may be mentioned that if the conductivity of air when in the modified state is due to rays given out from centres of ionization, these rays must have very little penetrating power, as I have drawn modified air possessing high conductivity over a photographic plate in the dark for more than four hours without producing an impression on the plate.

The active state in which a metal rod is put after being negatively electrified in the modified air is not a permanent one. As soon as the negative electrification stops, the activity of the metal begins to diminish, and after a few hours it entirely disappears: measurements of the rate at which this activity disappeared showed that it fell off rapidly at first and then much more slowly: the time taken for the activity to fall to half its initial value was about 45 minutes. It varied a little in the different experiments.

When once a wire has been put into the active state it can stand very rough treatment without losing its ionizing power.

Thus, for example, washing the wire with water and drying it by heating with a bunsen does not destroy its activity, nor does heating it in a bunsen to a red heat seem to have much effect upon it; an amalgamated copper wire was made active and then heated until the mercury was given off, even after this treatment it retained some activity.

Theory of the preceding Phenomena.

These experiments show, I think, that induced radioactivity caused by negative electrification is not necessarily due to the deposition of a radio-active substance. This hypothesis does not seem admissible in the case of the preceding experiments; for when the air is put in the modified state by means of the water-pump, only a limited supply of air is used, the volume of which, as we have seen, is too small to give rise to radio-activity when the air is in its normal condition, hence if in these experiments the effects produced by negative electrification are due to the deposition of a radioactive substance, such a substance must have come from the water. In the experiments with the Gouy sprayer, however, the amount of water used was very small: to see whether there was any radio-active substance in it which could produce the observed effects, the water in the sprayer was evaporated to dryness on a metal plate; the plate, however, after this treatment did not show any ionizing power. Again, the amount of air passed through the sprayer was not large enough to produce a supply of radio-active substance large enough to produce the observed effects, for a larger volume of air than that passed through the sprayer was drawn past a negatively-electrified wire without imparting to it any ionizing power. The experiments have led me to the conclusion that the ionizing power imparted to the wire in the preceding experiments arises in the following way:—In consequence of the negative electrification of the wire positive ions move up to it when it is placed in the modified gas; some of these ions do not discharge to the wire, but stick close to it, forming a coating of positive electricity around it. Between this coating and the wire there will be a strong electric field tending to draw negative electricity from the wire. Now there are many phenomena which lead us to the conclusion that a wire, even at ordinary temperatures, contains rapidly-moving negatively-electrified corpuscles which, under ordinary circumstances, remain in the wire because their kinetic energy is not sufficient to carry them beyond the attraction of the metal. When, however, there is a layer of positive electricity just outside the metal, the attraction of this on the negative corpuscles drags the latter from the wire; as the corpuscles move across the space between the coating and the wire they acquire additional kinetic energy, and if the difference of potential between the coating and the wire exceeds a certain value they will emerge from the positive coating with sufficient kinetic energy to enable them to ionize the molecules of the gas with which they come into collision; for this to be the case the potential-difference between the positive coating and the wire must exceed 2 volts, as Mr. H. A. Wilson has shown that the energy required to ionize a molecule of a gas is of the order of that given to a charge equal to that on a corpuscle when it moves through a potential-difference of about two volts.

Thus, on this view, the ionizing power of the wire is due to a kind of polarization, which produces an electric field which makes the wire into a cathode emitting cathode-rays of feeble penetrating power which ionize the gas in the neighbourhood of the wire.

If the wire, when in the conducting gas, had been positively electrified the electric field due to the polarization would have tended to force back the corpuscles into the wire rather than pull them out; there would therefore in this case be no emission of cathode-rays and no ionization of the gas.

The amount of polarization seems to depend upon the way the gas in which the negatively-electrified wire is placed is ionized. Thus we have seen that when the gas is made a conductor by bubbling through water the effect on the negatively electrified wire is much greater than when the gas is made a conductor by Röntgen rays, although the conductivity of the gas is greater in the latter case than in the former. Again, I made the gas in the vessel a very good conductor by keeping a Bunsen burner burning in the vessel, but in this case I could not detect any ionizing power in a negatively-electrified wire which had been kept in the vessel. Air which has been passed over phosphorus is a conductor of electricity, but I could not detect any ionizing power in a negatively-electrified wire immersed in it.

The principle by which we have explained the ionizing power of the negatively electrified wire—the emission of cathode-rays from the wire under the influence of a coating of positive electricity close to the surface of the wire—will also, I think, explain the conductivity produced in air when it bubbles through water. We may suppose that by this process very minute drops of water get mixed with the air, these drops must be exceedingly small, otherwise they would not be able to pass through a plug of glass-wool; the very slow rate at which the conductivity dies away also shows that the drops must settle down exceedingly slowly, so slowly that they take some days to fall through 1 metre ; from this we may conclude that the diameter of the drop cannot greatly exceed 10^{-5} cm. If each little drop gets surrounded by a layer of positive electricity then, just as in the case of the wire, the drop might emit cathode-rays which would ionize the air in its immediate neighbourhood ; thus each little drop would act as a centre of ionization, and thus make the air a conductor. The formation of a layer of positive electricity outside the drop is what we should expect if any chemical combination went on between the water of the drop and the oxygen of the air leading to the formation of such a compound as H_2O_2, for, in forming this compound, the water would combine with a negative oxygen ion and not with a positive one ; thus from the layer of oxygen outside the drop the water would pick out the negative and leave the positive ions, this would lead to the production of the coating of positive electricity round the drop required to make it act as an ionizing agent.

The drops of water as well as acting as producers of ions would also act as traps to catch ions moving through the air in which they are suspended ; they thus tend to reduce the conductivity, because when an ion gets attached to one of these drops, it is as it were anchored to it, and only moves with great difficulty ; in some cases the presence of drops of water diminishes the conductivity of the gas instead of increasing it : thus I found that squirting a steam-jet into either of the tanks A or B materially diminished the saturation-current through the tank.

The ordinary polarization of the electrodes in the electrolysis of liquids is usually explained by the existence of a layer of electrification close to the surface of the electrode, thus the polarized electrode resembles in this respect the electrified wire and the small drop of water on the preceding theory. I therefore thought it of interest to see whether a polarized electrode, when taken out of the electrolytic cell, would ionize the gas. Two platinum plates or wires were immersed in a solution of sulphuric acid of about the maximum conductivity, and a current of from 1 to 5 amperes sent from one electrode to the other for about an hour ; the electrodes were then taken out, washed with distilled water, and dried with filter-paper ; they were then placed in tank B and the saturation-current through the tank when these were used as electrodes measured. It was found that the one which had been used as the negative electrode (*i. e.* the one against which the hydrogen was liberated) now gave considerably higher currents than before the electrolysis, in some cases twice the current, while the positive electrode gave the same current as before. On first charging up the negative electrode positively, there was frequently a very large current for a short time, which was not repeated on the second charging, as if there were some positive ions loosely attached to the electrode which got driven away; the smaller increase to which I have alluded lasted for about half-an-hour. The amount of the increase varied a good deal; in one or two experiments there was no change in the current. The experiments with liquid electrolytes are more ambiguous than those with gases, as there is the possibility of some acid adhering to the plate and not getting entirely removed by the washing and drying, and then setting up some chemical action. Against this explanation we have the fact that the increase only occurs with one electrode—the negative, not with the positive—so that if it is due to the chemical action it must be caused by something produced at the negative terminal and not at the positive. Hydrogen peroxide seemed to me the most likely substance, so I immersed a platinum plate in a strong solution of H_2O_2, and washed and dried it in the same way as the electrodes. I found, however, in this case no change in the current through the tank B.

I have much pleasure in thanking my assistant, Mr. E. Everett, for the help he has given me in these experiments.

June 1902.

XL. *On the Influence of Convection on Optical Rotatory Polarization.* By J. Larmor *.

THE postscript (this volume, p. 220) to Lord Rayleigh's account of his decisive determination that the orbital motion of the Earth is without influence on the rotatory polarization produced by quartz, has brought to my notice the recent paper by Prof. H. A. Lorentz there quoted.

The fundamental character of Lord Rayleigh's negative result may be illustrated by reference to Prof. Lorentz's *Versuch einer Theorie* . . ., p. 119 (1895), where the opposite conclusion is considered as not unlikely in view of the formal possibilities that are open. But the main object of this note is to entirely admit the demur made by Prof. Lorentz, that my criticism ('Æther and Matter,' p. 214) of his calculation of rotational effect, there given, is not well founded. The conclusion which I had reached was in fact that for light *of given absolute wave-length* the optical rotation would be

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* Communicated by the Author.

independent of the Earth's motion, if the form of the constitutive relation which connects electric polarization with electric force, for the material medium, is not altered by its convection; but, not reflecting that reversal of the direction of light in a moving medium alters its wave-length, a hasty inference was made that this negative deduction represented the negative experimental result long ago announced as probable by M. Mascart.

I understand that Prof. Lorentz assents to, or at any rate admits as probable, the application of the principle (which rests indeed on a development in the molecular direction of his own previous analysis), that uniform convection does not affect the constitution of a permanent material system formed of groups of electrons or material ions that interact by electrodynamic agency alone; except in so far that, instead of the ordinary time, we must refer the convected system to a new time-variable, the "local time" of Prof. Lorentz. The constitutive relations of a rotational medium, as well as all properties depending on extinction of light, form a case in point. Considering radiation propagated in the direction of the axis of the rotational quality of the medium, say the direction of x, the relation between the material polarization $(0, g', h')$ and the electric force $(0, \mathrm{Q}, \mathrm{R})$ in its undulations is expressed ('Æther and Matter,' p. 211) in the form

$$g' = \frac{\mathrm{K}-1}{4\pi\mathrm{C}^2}\mathrm{Q} + \frac{1}{4\pi\mathrm{C}^2}\left(\epsilon_1\frac{\delta}{dt} + \epsilon_2\frac{d}{dx}\right)\mathrm{R},$$

$$h' = \frac{\mathrm{K}-1}{4\pi\mathrm{C}^2}\mathrm{R} - \frac{1}{4\pi\mathrm{C}^2}\left(\epsilon_1\frac{\delta}{dt} + \epsilon_2\frac{d}{dx}\right)\mathrm{Q},$$

in which the coefficient ϵ_2 represents the structural and ϵ_1 the magnetic type of rotation. When the material medium, instead of being at rest, is being convected in the direction of x with velocity v, this structural relation should thus remain true when for t is substituted the local time t' (*loc. cit.* p. 168) equal to $t - \frac{v}{\mathrm{C}^2}x$, so that every function $\phi(x, t)$ becomes $\phi\left(x, t - \frac{v}{\mathrm{C}^2}x\right)$; this keeps $\frac{d\phi}{dt}$ unaltered, but changes $\frac{d\phi}{dx}$ into $\left(\frac{d}{dx} - \frac{v}{\mathrm{C}^2}\frac{d}{dt}\right)\phi$. Thus the effect of the convection will be to maintain the coefficient of magnetic rotation $\epsilon_1\frac{\delta}{dt}$ unaltered, but to change the structural coefficient $\epsilon_1\frac{d}{dx}$ into the mixed type $\epsilon_2\frac{d}{dx} - \epsilon_2\frac{v}{\mathrm{C}^2}\frac{d}{dt}$; and the equation of electric constitution of the medium being thus modified, the rotation produced by it remains unaltered by convection. This is, in fact, merely a paraphrase of Prof. Lorentz's argument (*Proc. Amst. Acad.* April 19, 1902).

The conclusion to be drawn from Lord Rayleigh's result may thus be held to stand as before, that in the more complex circumstances of rotational media as well as in ordinary optical propagation in matter, the ions or electrons that form the connexion between the matter and the æther interact in all their relations according to laws of purely electrodynamic type.

The single principle that electrification is of atomic character, with or without a distinct material basis, so that when the medium is convected the ions belonging to it exert the ordinary electrodynamic influence of moving charges, suffices to abolish all first-order effects of uniform convection on the electric and optical properties of material media ; rotational optical phenomena being therein included. It is only when the absence also of second-order effect of uniform convection has to be accounted for that more questionable hypothesis must enter. It appears to be established that, if it could be granted that the molecules of matter are constituted entirely on an electric basis, no second-order effects either electric or optical would arise. Such an electric basis of matter implies that, an ordinary molecule being made up somehow of a group of ultimate atoms describing steady orbits round each other after the manner of a stellar system, the mutual actions of these ultimate atoms, as also their inertia, are wholly electrodynamic, and are thus really resident in the interconnecting æther in which the atoms constitute mere singular points or centres of strain. If this hypothesis could be admitted,—and no independent reason can be assigned for its validity, except that fundamental presumption of simplicity which we are not unaccustomed to find justified in physical analysis,—the negative second-order optical observation of Michelson and Morley would be explained. Electric effects of the second order would also be absent ; and there appears to be one such (an outcome of a suggestion of FitzGerald's) which would otherwise exist, that in Prof. Trouton's hands will probably furnish an independent experimental test[*].

Although the constitution of a molecule has not been systematically elucidated on this purely æthereal hypothesis any more than it has on any other, an increasing tendency to consider it as a working scheme may be remarked[†]. And in this connexion it may be noticed that there is no necessity for restricting the singularity in the constitution of the æther to

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[*] See Trouton Trans. Roy. Dub. Soc. vii. (1902); also FitzGerald's 'Scientific Papers,' pp. 557, 566, lxi.

[†] *E. g.* Planck, *Berlin. Sitzungsberichte*, xxiv. p. 486 (1902).

be a mere point; the region of misfit (to borrow an expressive term from Prof. Osborne Reynolds) might, if necessary, have definite extension and structure. Hypotheses of this type are most naturally (indeed, as it seems to me, unavoidably) expressed in terms of an æther which is only locally disturbed by each moving ion; so that a congeries of connected atoms like the Earth does not push it along bodily and establish any finite flow. But there may be philosophers who prefer not to employ the term æther at all, who are satisfied with a colourless phenomenology, and who manage to escape the consideration of the possibility of an æther whose parts maintain their positions notwithstanding the motion of matter through it, by saying merely that if a certain scheme of formal relations between variables which are symbols of things unknown is altered in a certain formal way, probably originally suggested by the use of dynamical analogies such as have been referred to, the scheme will continue to group the facts under the wider conditions, and they would thus feel freed from any necessity of considering images or models, probably imperfect, of things which being outside ourselves we cannot intrinsically know.

Cambridge, August 7, 1902.

XLI. *The Cause and Nature of Radioactivity.*—Part I.

By E. Rutherford, *M.A., D.Sc., Macdonald Professor o Physics, and* F. Soddy, *B.A.* (*Oxon.*), *Demonstrator in Chemistry, McGill University, Montreal*[*].

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I. *Introduction.*

The following papers give the results of a detailed investigation of the radioactivity of thorium compounds which has thrown light on the questions connected

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[*] Communicated by the Authors. Accounts of these researches, during the progress of the investigation, have already been given to the London Chemical Society.

with the source and maintenance of the energy dissipated by radioactive substances. Radioactivity is shown to be accompanied by chemical changes in which new types of matter are being continuously produced. These reaction products are at first radioactive, the activity diminishing regularly from the moment of formation. Their continuous production maintains the radioactivity of the matter producing them at a definite equilibrium-value. The conclusion is drawn that these chemical changes must be sub-atomic in character.

The present researches had as their starting-point the facts that had come to light with regard to thorium radioactivity (Rutherford, Phil. Mag. 1900, vol. xlix. pp. 1 & 161). Besides being radioactive in the same sense as the uranium compounds, the compounds of thorium continuously emit into the surrounding atmosphere a gas which possesses the property of temporary radioactivity. This "emanation," as it has been named, is the source of rays, which ionize gases and darken the photographic film *.

The most striking property of the thorium emanation is its power of exciting radioactivity on all surfaces with which it comes into contact. A substance after being exposed for some time in the presence of the emanation behaves as if it were covered with an invisible layer of an intensely active material. If the thoria is exposed in a strong electric field, the excited radioactivity is entirely confined to the negatively charged surface. In this way it is possible to concentrate the excited radioactivity on a very small area. The excited radioactivity can be removed by rubbing or by the action of acids, as, for example, sulphuric, hydrochloric, and hydrofluoric acids. If the acids be then evaporated, the radioactivity remains on the dish.

The emanating power of thorium compounds is independent of the surrounding atmosphere, and the excited activity it produces is independent of the nature of the substance on which it is manifested. These properties made it appear that both phenomena were caused by minute quantities of special kinds of matter in the radioactive state, produced by the thorium compound.

The next consideration in regard to these examples of radioactivity, is that the activity in each case diminishes regularly with the lapse of time, the intensity of radiation at each instant being proportional to the amount of energy remaining to be radiated. For the emanation a period of

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* If thorium oxide be exposed to a white heat its power of giving an emanation is to a large extent destroyed. Thoria that has been so treated is referred to throughout as "de-emanated."

one minute, and for the excited activity a period of eleven hours, causes the activity to fall to half its value.

These actions—(1) the production of radioactive material, and (2) the dissipation of its available energy by radiation—which are exhibited by thorium compounds in the secondary effects of emanating power and excited radioactivity, are in reality taking place in all manifestations of radioactivity. The constant radioactivity of the radioactive elements is the result of an equilibrium between these two opposing processes.

II. *The Experimental Methods of investigating Radioactivity.*

Two methods are used for the measurement of radioactivity, the electrical and the photographic. The photographic method is of a qualitative rather than a quantitative character; its effects are cumulative with time, and as a rule long exposures are necessary when the radioactivity of a feeble agent like thoria is to be demonstrated. In addition, Russell has shown that the darkening of a photographic plate is brought about also by agents of a totally different character from those under consideration, and, moreover, under very general conditions. Sir William Crookes (Proc. Roy. Soc. (1900) lxvi. p. 409) has sounded a timely note of warning against putting too much confidence in the indications of the photographic method of measuring radioactivity. The uncertainty of an effect produced by cumulative action over long periods of time quite precludes its use for work of anything but a qualitative character.

But the most important objection to the photographic method is that certain types of rays from radioactive substances, which ionize gases strongly, produce little if any effect on the sensitive film. In the case of uranium, these protographically inactive rays form by far the greatest part of the total radiation, and much of the previous work on uranium by the photographic method must be interpreted differently (Soddy, Proc. Chem. Soc. 1902, p. 121).

On the other hand, it is possible to compare intensities of radiation by the electrical method with greater rapidity and with an error not exceeding 1 or 2 per cent. These methods are based on the property generally possessed by all radiations of the kind in question, of rendering a gas capable of discharging both positive and negative electricity. These, as will be shown, are capable of great refinement and certainty. An ordinary quadrant electrometer is capable of detecting and measuring a difference of potential of at least 10^{-2} volts. With special instruments, this sensitiveness may be increased a hundredfold. An average value for the capacity of the electrometer and connexions is 3×10^{-5} microfarads; and when this is charged up to 10^{-2} volts, a quantity of electricity corresponding to 3×10^{-13} coulombs is stored up. Now in the electrolysis of water one gram of hydrogen carries a charge of 10^5 coulombs. Assuming, for the sake of example, that the conduction of electricity in gases is analogous to that in liquids, this amount of electricity corresponds to the transport of a mass of 3×10^{-18} grams of hydrogen; that is, a quantity of the order of 10^{-12} times that detected by the balance. For a more delicate instrument, this amount would produce a large effect.

The examples of radium in pitchblende and of the thorium-excited radioactivity make it certain that comparatively large ionization effects are produced by quantities of matter beyond the range of the balance or spectroscope.

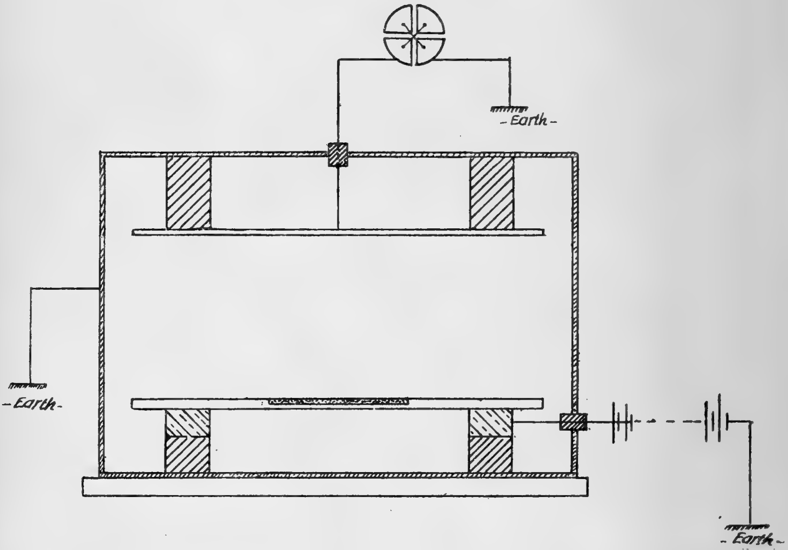
The electrometer also affords the means of recognizing and differentiating between the emanations and radiations of different chemical substances. By the rate of decay the emanation from thorium, for example, can be instantly distinguished from that produced by radium; and although a difference in the rate of decay does not of itself argue a fundamental difference of nature, the identity of the rate of decay furnishes at least strong presumption of identity of nature.

Radiations, on the other hand, can be compared by means of their penetration powers (Rutherford, Phil. Mag. 1899, vol. xlvii. p. 122). If the rays from various radioactive substances are made to pass through successive layers of aluminium-foil, each additional layer of foil cuts down the radiation to a fraction of its former value, and a curve can be plotted with the thickness of metal penetrated as abscissæ, and the intensity of the rays after penetration as ordinates, expressing at a glance the penetration power of the rays under examination. The curves so obtained are quite different for different radioactive substances. The radiations from uranium, radium, thorium, each give distinct and characteristic curves, whilst that of the last-named again is quite different from that given by the excited radioactivity produced by the thorium emanation. It has been recently found (Rutherford and Grier, *Phys. Zeit.* 1902, p. 385) that thorium compounds, in addition to a type of easily absorbed Röntgen-rays, non-deviable in the magnetic field, emit also rays of a very penetrating character deviable in the magnetic field. The latter are therefore similar to cathode-rays, which are known to consist of material particles travelling with a velocity approaching that of light. But thorium, in comparison with uranium and radium, emits a much smaller proportion of deviable radiation. The determination of the proportion between the deviable and non-deviable rays affords a new means of investigating thorium radioactivity.

The electrometer thus supplies the study of radioactivity with methods of quantitative and qualitative investigation, and there is therefore no reason why the cause and nature of the phenomenon should not be the subject of chemical investigation.

Fig. 1 shows the general arrangement. From 0·5 to 0·1 gram of the compound to be tested, reduced to fine powder, is uniformly sifted over a platinum plate 36 sq. cms. in area.

Fig. 1.



This plate was placed on a large metal plate connected to one pole of a battery of 300 volts, the other pole of which was earthed. An insulated parallel plate was placed about 6 cm. above it, and the whole apparatus inclosed in a metal box connected to earth, to prevent electrostatic disturbance. The shaded portions in the figure represented insulators. A door was made in the apparatus so that the plate could be rapidly placed in position or removed. Both pairs of quadrants are first connected to earth. On connecting the one pair with the apparatus, the deflexion of the needle from zero increases uniformly with time, and the time taken to pass over 100 divisions of the scale is taken by a stop-watch. The *rate* of movement is a measure of the ionization-current between the plates. The ratio of the currents for different substances is a comparative measure of their radioactivity.

With this apparatus ·5 gr. of thorium oxide produces a current of $1{\cdot}1 \times 10^{-11}$ amperes, which, with the electrometer used, working at average sensitiveness, corresponds to 100 divisions of the scale in 36 seconds. In certain cases a special modification of the Dolezalek electrometer was employed which is 100 times more sensitive. With this instrument the radioactivity of 1 milligram of thoria produces a measurable effect. If the substance gives off an emanation, the current between the plates increases with time. Under these conditions, when the thorium compound is exposed in thin layers with a maximum of radiating surface, all but one or two per cent. of the total effect is due to the straight-line radiation. Even when the effect due to the emanation has attained a maximum, this constitutes a very small fraction of the whole. This effect, however, may to a large extent be eliminated by taking the current between the electrodes immediately after the material is placed in the testing-apparatus. It may be completely eliminated by passing a current of air between the electrodes to remove the emanation as fast as it is formed.

The current between the plates observed with the electrometer at first increases with the voltage, but a stage is very soon reached when there is a very small increase for a large additional voltage. A P.D. of 300 volts was sufficient to obtain the maximum current, so that all the ions reached the electrodes before any appreciable recombination occurred.

It must, however, at once be pointed out that it is difficult to make any absolute measure of radioactivity. The radiation from thorium is half absorbed by a thickness of aluminium of ·0004 cm.; and since thorium oxide is far denser than aluminium, it is probable that the radiation in this case is confined to a surface-layer only ·0001 cm. deep. It is obvious that different preparations, each containing the same percentage of thorium but with different densities and different states of division, will not give the same intensity of radiation. In comparing two different specimens of the same compound, it is important that the final steps in their preparation should be the same in each case. As a rule absolute measurements of this kind have been avoided. It is possible, however, to trace with great accuracy the *change* of radioactivity of any preparation with time by leaving it undisturbed on its original plate, and comparing it with a similarly undisturbed constant comparison sample. Most of the investigations have been carried out by this method.

III. *The Separation of a Radioactive Constituent from Thorium Compounds.*

During an investigation of the emanating power of thorium compounds, to be described later, evidence was obtained of the separation of an intensely radioactive constituent by chemical methods. It had been noticed that in certain cases thorium hydroxide, precipitated from dilute solutions of thorium nitrate by ammonia, possessed an abnormally low emanating power. This led naturally to an examination being made of the filtrates and washings obtained during the process. It was found that the filtrates invariably possessed emanating power, although from the nature of their production they are chemically free from thorium. If the filtrate is evaporated to dryness, and the ammonium salts removed by ignition, the small residues obtained exhibit radioactivity also, to an extent very much greater than that possessed by the same weight of thorium. As a rule these residues were of the order of one-thousandth part by weight of the thorium salt originally taken, and were many hundred, in some cases over a thousand, times more active than an equal weight of thoria. The separation of an active constituent from thorium by this method is not all dependent on the purity of the salt used. By the kindness of Dr. Knöfler, of Berlin, who, in the friendliest manner, presented us with a large specimen of his purest thorium nitrate, we were enabled to test this point. This specimen, which had been purified by a great many processes, did not contain any of the impurities found in the commercial salt before used. But its radioactivity and emanating power were at least as great, and the residues from the filtrates after precipitation by ammonia were no less active than those before obtained. These residues are free from thorium, or at most contain only the merest traces, and when redissolved in nitric acid do not appear to give any characteristic reaction.

An examination of the penetrating power of the rays from the radioactive residue, showed that the radiations emitted were in every respect identical with the ordinary thorium radiation. In another experiment the nature of the emanation from a similar intensely active thorium-free residue was submitted to examination. The rate of decay was quite indistinguishable from that of the ordinary thorium emanation; that is, substances chemically free from thorium have been prepared possessing thorium radioactivity in an intense degree.

The thorium hydroxide which had been submitted to the above process was found to be less than half as radioactive as the same weight of thorium oxide. It thus appeared that a constituent responsible for the radioactivity of thorium had been obtained, which possessed distinct chemical properties and an activity of the order of at least a thousand times as great as the material from which it had been separated.

Sir William Crookes (Proc. Roy. Soc. 1900, lxvi. p. 409) succeeded in separating a radioactive constituent of great activity and distinct chemical nature from uranium, and gave the name UrX to this substance. For the present, until more is known of its real nature, it will be convenient to name the active constituent of thorium ThX, similarly. Like UrX, however, ThX does not answer to any definite analytical reactions, but makes its appearance with precipitates formed in its solution even when no question of insolubility is involved. This accords with the view that it is present in infinitesimal quantity, and possesses correspondingly great activity. Even in the case of the most active preparations, these probably are composed of some ThX associated with accidental admixtures large in proportion.

These results receive confirmation from observations made on a different method of separating ThX. The experiment was tried of washing thoria with water repeatedly, and seeing if the radioactivity was thereby affected. In this way it was found that the filtered washings, on concentration, deposited small amounts of material with an activity often of the order of a thousand times greater than that of the original sample. In one experiment, 290 grams of thoria were shaken for a long time with nine quantities, each of 2 litres of distilled water. The first washing, containing thorium sulphate present as an impurity, was rejected, the rest concentrated to different stages and filtered at each stage. One of the residues so obtained weighed 6·4 mg., and was equivalent in radioactivity to 11·3 grams of the original thoria, and was therefore no less than 1800 times more radioactive. It was examined chemically, and gave, after conversion into sulphate, the characteristic reaction of thorium sulphate, being precipitated from its solution in cold water by warming. *No other substance than thorium could be detected by chemical analysis,* although of course the quantity was too small for a minute examination. The penetrating power of the radiation from this substance again established its identity with the ordinary thorium radiation.

In another experiment, a small quantity of thoria was shaken many times with large quantities of water. In this case, the radioactivity of the residue was examined and found to be about 20 per cent. less radioactive than the original sample.

The influence of Time on the activity of Thorium and ThX.—The preparations employed in our previous experiments were allowed to stand over during the Christmas vacation. On examining them about three weeks later it was found that the thorium hydroxide, which had originally possessed only about 36 per cent. of its normal activity, had almost completely recovered the usual value. The active residues, on the other hand, prepared by both methods, had almost completely lost their original activity. The chemical separation effected was thus not permanent in character. At this time M. Becquerel's paper (*Comptes Rendus*, cxxxiii. p. 977, Dec. 9th, 1901) came to hand, in which he shows that the same phenomena of recovery and decay are presented by uranium after it has been partially separated from its active constituent by chemical treatment.

A long series of observations was at once started to determine—

(1) The rate of recovery of the activity of thorium rendered less active by removal of ThX;

(2) The rate of decay of the activity of the separated ThX;

in order to see how the two processes were connected. The results led to the view that may at once be stated. The radioactivity of thorium at any time is the resultant of two opposing processes—

(1) The production of fresh radioactive material at a constant rate by the thorium compound;

(2) The decay of the radiating power of the active material with time.

The normal or constant radioactivity possessed by thorium is an equilibrium value, where the rate of increase of radioactivity due to the production of fresh active material is balanced by the rate of decay of radioactivity of that already formed. It is the purpose of the present paper to substantiate and develope this hypothesis.

IV. *The Rates of Recovery and Decay of Thorium Radioactivity.*

A quantity of the pure thorium nitrate was separated from ThX in the manner described by several precipitations with ammonia. The radioactivity of the hydroxide so obtained was tested at regular intervals to determine the rate of recovery of its activity. For this purpose the original specimen of ·5 gram was left undisturbed throughout the whole series of measurements on the plate over which it had been sifted, and was compared always with ·5 gram of ordinary de-emanated thorium oxide spread similarly on a second plate and also left undisturbed. The emanation from the hydroxide was prevented from interfering with the results by a special arrangement for drawing a current of air over it during the measurements.

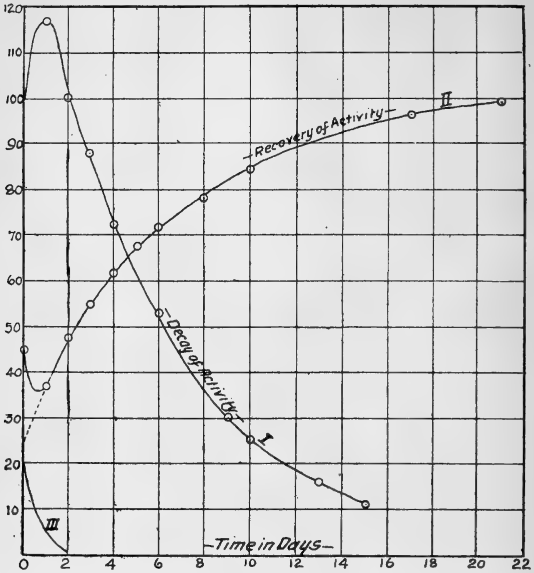
The active filtrate from the preparation was concentrated and made up to 100 c.c. volume. One quarter was evaporated to dryness and the ammonium nitrate expelled by ignition in a platinum dish, and the radioactivity of the residue tested at the same intervals as the hydroxide to determine the rate of decay of its activity. The comparison in this case was a standard sample of uranium oxide kept undisturbed on a metal plate, which repeated work has shown to be a perfectly constant source of radiation. The remainder of the filtrate was used for other experiments.

The following table gives an example of one of a numerous series of observations made with different preparations at different times. The maximum value obtained by the hydroxide and the original value of the ThX are taken as 100 :—

Time in days.	Activity of Hydroxide.	Activity of ThX.
0	44	100
1	37	117
2	48	100
3	54	88
4	62	72
5	68	
6	71	53
8	78	
9	...	29·5
10	83	25·2
13	...	15·2
15	...	11·1
17	96·5	
21	99	
28	100	

Fig. 2 shows the curves obtained by plotting the radioactivities as ordinates, and the time in days as abscissæ. Curve II. illustrates the rate of recovery of the activity of thorium, curve I. the rate of decay of activity of ThX. It will be seen that neither of the curves is regular for the first two days. The activity of the hydroxide at first actually diminished and was at the same value after two days as when first prepared. The activity of the ThX, on the other hand, at first increases and does not begin to fall below the original value till after the lapse of two days (compare section IX.). These results cannot be ascribed to errors of measurement, for they have been regularly observed whenever similar preparations have been tested. The activity of the residue obtained from thorium oxide by the second method of washing decayed very similarly to that of ThX, as shown by the above curve.

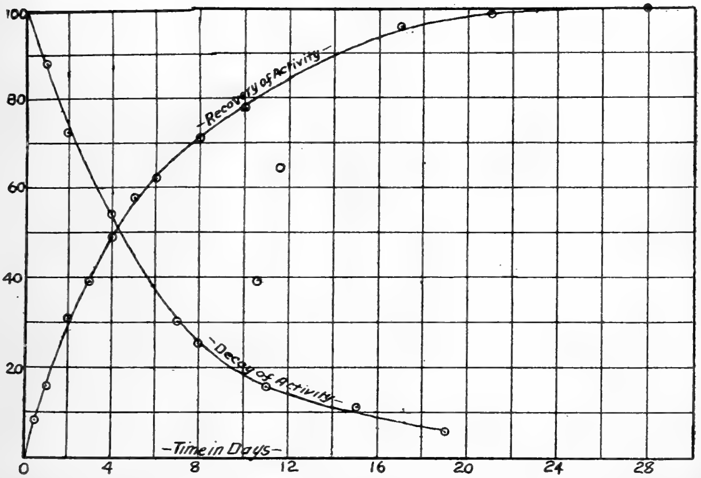
Fig. 2.



If for present purposes the initial periods of the curve are disregarded and the later portions only considered, it will be seen at once that the time taken for the hydroxide to recover one half of its lost activity is about equal to the time taken by the ThX to lose half its activity, viz., in each case about 4 days, and speaking generally the percentage proportion of the lost activity regained by the hydroxide over any given interval is approximately equal to the percentage proportion of the activity lost by the ThX during the same interval. If the recovery curve is produced backwards in the normal direction to cut the vertical axis, it will be seen to do so at a minimum of about 25 per cent., and the above result holds even more accurately if the recovery is assumed to start from this constant minimum, as, indeed, it has been shown to do under suitable conditions (section IX., fig. 4).

This is brought out by fig. 3, which represents the recovery

Fig. 3.



curve of thorium in which the percentage amounts of activity recovered, reckoned from this 25 per cent. minimum, are plotted as ordinates. In the same figure the decay curve after the second day is shown on the same scale.

The activity of ThX decreases very approximately in a geometrical progression with the time, *i. e.* if I_0 represent the initial activity and I_t the activity after time t,

$$\frac{I_t}{I_0} = e^{-\lambda t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ is a constant and e the base of natural logarithms.

The experimental curve obtained with the hydroxide for the rate of rise of its activity from a minimum to a maximum value will therefore be approximately expressed by the equation

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I_0 represents the amount of activity recovered when the maximum is reached, and I_t the activity recovered after time t, λ *being the same constant as before.*

Now this last equation has been theoretically developed in other places (compare Rutherford, Phil. Mag. 1900, pp. 10 and 181) to express the rise of activity to a constant maximum of a system consisting of radiating particles in which

(1) The rate of supply of fresh radiating particles is constant.

(2) The activity of each particle dies down geometrically with the time according to equation (1).

It therefore follows that if the initial irregularities of the curves are disregarded and the residual activity of thorium is assumed to possess a *constant* value, the experimental curve obtained for the recovery of activity will be explained if two processes are supposed to be taking place:

(1) That the active constituent ThX is being produced at a constant rate;

(2) That the activity of the ThX decays geometrically with time.

Without at first going into the difficult questions connected with the initial irregularities and the residual activity, the main result that follows from the curves given can be put to experimental test very simply. The primary conception is that the major part of the radioactivity of thorium is not due to the thorium at all, but to the presence of a non-thorium substance in minute amount which is being continuously produced.

V. *Chemical Properties of ThX.*

The fact that thorium on precipitation from its solutions by ammonia leaves the major part of its activity in the filtrate does not of itself prove that a material *constituent* responsible for this activity has been chemically separated. It is possible that the matter constituting the non-thorium part of the solution is rendered temporarily radioactive by its association with thorium, and this property is retained through the processes of precipitation, evaporation, and ignition, and manifests itself finally on the residue remaining.

This view, however, can be shown to be quite untenable, for upon it any precipitate capable of removing thorium completely from its solution should yield active residues similar to those obtained from ammonia. Quite the reverse, however, holds.

When thorium nitrate is precipitated by sodium or ammonium carbonate, the residue from the filtrate by evaporation and ignition is free from activity, and the thorium carbonate possesses the normal value for its activity.

The same holds true when oxalic acid is used as the precipitant. This reagent even in strongly acid solution precipitates almost all of the thorium. When the filtrate is rendered alkaline by ammonia, filtered, evaporated, and ignited, the residue obtained is inactive.

In the case where sodium phosphate is used as the precipitant in ordinary acid solution, the part that comes down is more or less free from ThX. On making the solution alkaline with ammonia, the remainder of the thorium is precipitated as phosphate, and carries with it the whole of the active constituent, so that the residue from the filtrate is again inactive.

In fact ammonia is the only reagent of those tried capable of separating ThX from thorium.

The result of Sir William Crookes with uranium, which we have confirmed working with the electrical method, may be here mentioned. UrX is completely precipitated by ammonia together with uranium, and the residue obtained by the evaporation of the filtrate is quite inactive.

There can thus be no question that both ThX and UrX are distinct types of matter with definite chemical properties. Any hypothesis that attempts to account for the recovery of activity of thorium and uranium with time must of necessity start from this primary conception.

VI. *The Continuous Production of ThX.*

If the recovery of the activity of thorium with time is due to the production of ThX, it should be possible to obtain experimental evidence of the process. The first point to be ascertained is how far the removal of ThX by the method given reduces the total radioactivity of thorium. A preliminary trial showed that the most favourable conditions for the separation are by precipitating in hot dilute solutions by dilute ammonia. A quantity of 5 grams of thorium nitrate, as obtained from the maker, was so precipitated by ammonia, the precipitate being redissolved in nitric acid and reprecipitated under the same conditions successively *without lapse of time.*

The removal of ThX was followed by measuring the activity of the residues obtained from the successive filtrates. The activity of the ThX from the first filtrate was equivalent to 4·25 grams of thoria, from the second to 0·33 gram, and from the third to 0·07 gram. It will be seen that by two precipitations practically the whole of the ThX is removed. The radioactivity of the separated hydroxide was 48 per cent. of that of the standard de-emanated sample of thoria.

Rate of production of ThX.—A quantity of thorium nitrate solution that had been freed from ThX about a month before, was again subjected to the same process. The activity of the residue from the filtrate in an experiment in which 10 grams of this nitrate had been employed was equivalent to 8·3 grams of thorium oxide. This experiment was performed on the same day as the one recorded above, in which 5 grams of new nitrate had been employed, and it will be seen that there is no difference in the activity of the filtrate in the two cases. In one month the activity of the ThX in a thorium compound again possesses its maximum value.

If a period of 24 hours is allowed to elapse between the successive precipitations, the activity of the ThX formed during that time corresponds to about one-sixth of the maximum activity of the total thorium employed. In three hours the activity of the amount produced is about one-thirtieth. The rate of production of ThX worked out from those figures well agrees with the form of the curve obtained for the recovery of activity of thorium, if the latter is taken to express the continuous production of ThX at a constant rate and the diminution of the activity of the product in geometrical progression with the time.

By using the sensitive electrometer, the course of production of ThX can be followed after extremely short intervals. Working with 10 grams of thorium nitrate, the amount produced in the minimum time taken to carry out the successive precipitations is as much as can be conveniently measured. If any interval is allowed to lapse the effect is beyond the range of the instrument, unless the sensitiveness is reduced to a fraction of its ordinary value by the introduction of capacities into the system. Capacities of ·01 and ·02 microfarad, which reduce the sensitiveness to less than one two-hundredth of the normal, were frequently employed in dealing with these active residues.

The process of the production of ThX is continuous, and no alteration was observed in the amount produced in a given time after repeated separations. In an experiment carried out for another purpose (section IX.) after 23 successive precipitations extending over 9 days, the amount formed during the last interval was as far as could be judged no less than what occurred at the beginning of the process.

The phenomenon of radioactivity, by means of the electrometer as its measuring instrument, thus enables us to detect and measure changes occurring in matter after a few minutes interval, which have never yet been detected by the balance or suspected of taking place.

VII. *Influence of Conditions on the Changes occurring in Thorium.*

It has been shown that in thorium compounds the decay of radioactivity with time is balanced by a continuous production of fresh active material. The change which produces this material must be chemical in nature, for the products of the action are different in chemical properties from the thorium from which they are produced. The first step in the study of the nature of this change is to examine the effects of conditions upon its rate.

Effect of conditions on the rate of decay.—Since the activity of the products affords the means of measuring the amount of change, the influence of conditions on the rate of decay must be first found. It was observed that, like all other types of temporary radioactivity, the rate of decay is unaltered by any known agency. It is unaffected by ignition and chemical treatment, and the material responsible for it can be dissolved in acids and re-obtained by the evaporation of the solution, without affecting the activity. The following experiment shows that the activity decays at the same rate in solutions as in the solid state. The remainder of the solution that had been used to determine the decay curve of ThX (fig. 2) was allowed to stand, and at the end of 12 days a second quarter was evaporated to dryness and ignited, and its activity compared with that of the first which had been left since evaporation upon its original platinum dish. The activities of the two specimens so compared with each other were the same, showing that in spite of the very different conditions the two fractions had decayed at equal rates. After 19 days a third quarter was evaporated, and the activity, now very small, was indistinguishable from that of the fraction first evaporated. Re-solution of the residues after the activity had decayed does not at all regenerate it. The activity of ThX thus decays at a rate independent of the chemical and physical condition of the molecule.

Thus the rate of recovery of activity under different conditions in thorium compounds affords a direct measure of the rate of production of ThX under these conditions. The following experiments were performed:—

One part of thorium hydroxide newly separated from ThX was sealed up in a vacuum obtained by a good Töpler pump, and the other part exposed to air. On comparing the samples 12 days later no difference could be detected between them either in their radioactivity or emanating power.

In the next experiment a quantity of hydroxide freed from

ThX was divided into two equal parts; one was exposed for 20 hours to the heat of a Bunsen burner in a platinum crucible, and then compared with the other. No difference in the activities was observed. In a second experiment, one half was ignited for 20 minutes on the blast, and then compared with the other with the same result. The difference of temperature and the conversion of thorium hydroxide into oxide thus exercised no influence on the activity.

Some experiments that were designed to test in as drastic a manner as possible the effect of the chemical condition of the molecule on the rate of production of ThX brought to light small differences, but these are almost certainly to be accounted for in another way. It will be shown later (section IX.) that about 21 per cent. of the normal radioactivity of thorium oxide under ordinary conditions consists of a secondary activity excited on the mass of the material. This portion is of course a variable, and since it is divided among the total amount of matter present, the conditions of aggregation, &c., will affect the value of this part. This effect of excited radioactivity in thorium makes a certain answer to the question difficult, and on this account the conclusion that the rate of production of ThX is independent of the molecular conditions is not final. The following experiment, however, makes it extremely probable.

A quantity of thorium nitrate as obtained from the maker was converted into oxide in a platinum crucible by treatment with sulphuric acid and ignition to a white heat. The de-emanated oxide so obtained was spread on a plate, and any change in radioactivity with time, which under these circumstances could certainly be detected, was looked for during the first week from preparation. None whatever was observed, whereas if the rate of production of ThX in thorium nitrate is different from that in the oxide, the equilibrium point, at which the decay and increase of activity balance each other, will be altered in consequence. There should have therefore occurred a logarithmic rise or fall from the old to the new value. As, however, the radioactivity remained constant, it appears very probable that the changes involved are independent of the molecular condition.

It will be seen that the assumption is here made that the proportion of excited radioactivity in the two compounds is the same, and for this reason compounds were chosen which possess but low emanating power. (Compare section IX. last paragraph.)

Uranium is a far simpler example of a radioactive element than thorium, as the phenomena of excited radioactivity and emanating power are here absent. The separation of UrX and the recovery of the activity of the uranium with time appear, however, analogous to these processes in thorium, and the rate of recovery and decay of uranium activity are at present under investigation. It is proposed to test the influence of conditions on the rate of change more thoroughly in the case of uranium, as here secondary changes do not interfere.

VIII. *The Cause and Nature of Radioactivity.*

The foregoing conclusions enable a great generalization to be made in the subject of radioactivity. Energy considerations require that the intensity of radiation from any source should die down with time unless there is a constant supply of energy to replace that dissipated. This has been found to hold true in the case of all known types of radioactivity with the exception of the "naturally" radioactive elements—to take the best established cases, thorium, uranium, and radium. It will be shown later that the radioactivity of the emanation produced by thorium compounds decays geometrically with the time under all conditions, and is not affected by the most drastic chemical and physical treatment. The same has been shown by one of us (Phil. Mag. 1900, p. 161) to hold for the excited radioactivity produced by the thorium emanation. This decays at the same rate whether on the wire on which it is originally deposited, or in solution of hydrochloric or nitric acid. The excited radioactivity produced by the radium emanation appears analogous. All these examples satisfy energy considerations. In the case of the three naturally occurring radioactive elements, however, it is obvious that there must be a continuous replacement of the dissipated energy, and no satisfactory explanation has yet been put forward.

The nature of the process becomes clear in the light of the foregoing results. The material constituent responsible for the radioactivity, when it is separated from the thorium which produces it, then behaves in the same way as the other types of radioactivity cited. Its activity decays geometrically with the time, and the rate of decay is independent of the molecular conditions. The normal radioactivity is, however, maintained at a constant value by a chemical change which produces fresh radioactive material at a rate also independent of the conditions. The energy required to maintain the radiations will be accounted for if we suppose that the energy of the system after the change has occurred is less than it was before.

The work of Crookes and Becquerel on the separation of UrX and the recovery of the activity of the uranium with time, makes it appear extremely probable that the same explanation holds true for this element. The work of M. and Mme. Curie, the discoverers of radium, goes to show that this body easily suffers a temporary decrease of its activity by chemical treatment, the normal value being regained after the lapse of time, and this can be well interpreted on the new view. All known types of radioactivity can thus be brought under the same category.

IX. *The Initial Portions of the Curves of Decay and Recovery.*

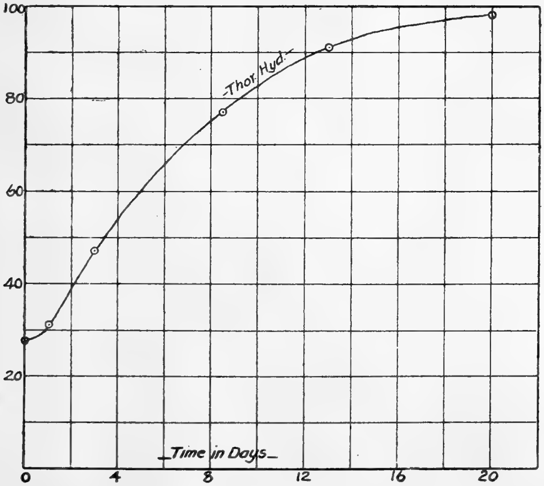
The curves of the recovery and decay of the activities of thorium and ThX with time suggested the explanation that the radioactivity of thorium was being maintained by the production of ThX at a constant rate. Before this can be considered rigidly established, two outstanding points remain to be cleared up. 1. What is the meaning of the early portion of the curves? The recovery curve drops before it rises, and the decay curve rises before it drops. 2. Why does not the removal of ThX render thorium completely inactive? A large proportion of the original radioactivity is not affected by the removal of ThX.

A study of the curves (fig. 2) shows that in each case a double action is probably at work. It may be supposed that the normal decay and recovery are taking place, but are being masked by a simultaneous rise and decay from other causes. From what is known of thorium radioactivity, it was surmised that an action might be taking place similar to that effected by the emanation of exciting radioactivity on surrounding inactive matter. It will be shown later that the ThX, and not thorium, is the cause of the emanating power of thorium compounds. On this view, the residual activity of thorium might consist in whole or in part of a secondary or excited radioactivity produced on the whole mass of the thorium compound by its association with the ThX. The drop in the recovery-curve on this view would be due to the decay of this excited radioactivity proceeding simultaneously with, and at first reversing the effect of the regeneration of ThX. The rise of the decay-curve would be the increase due to the ThX exciting activity on the matter with which it is associated, the increase from this cause being greater than the decrease due to the decay of the activity of the ThX. It is easy to put this hypothesis to experimental test. If the ThX is removed from the thorium as soon as it is formed over a sufficient period, the former will be prevented from exciting activity on the latter, and that already excited will decay spontaneously. The experiment was therefore performed. A quantity of nitrate was precipitated as hydroxide in the usual way to remove ThX, the precipitate redissolved in nitric acid, and again precipitated after a certain interval. From time to time a portion of the hydroxide was removed and its radioactivity tested. In this way the thorium was precipitated in all 23 times in a period of 9 days, and the radioactivity reduced to a constant minimum. The following table shows the results:—

	Activity of Hydroxide. per cent.
After first precipitation	46
After precipitations at three intervals of 24 hours	39
At three more intervals each of 24 hours, and three more each of 8 hours	22
At three more each of 8 hours	24
At six more each of 4 hours	25

The constant minimum thus attained—about 25 per cent. of the original activity—is thus about 21 per cent. below that obtained by two successive precipitations without interval, which has been shown to remove all the ThX separable by the process. The rate of recovery of this 23 times precipitated hydroxide was then measured (fig. 4). It will be seen that it is now quite normal, and the initial drop characteristic of the ordinary curve is quite absent. It is in

Fig. 4.



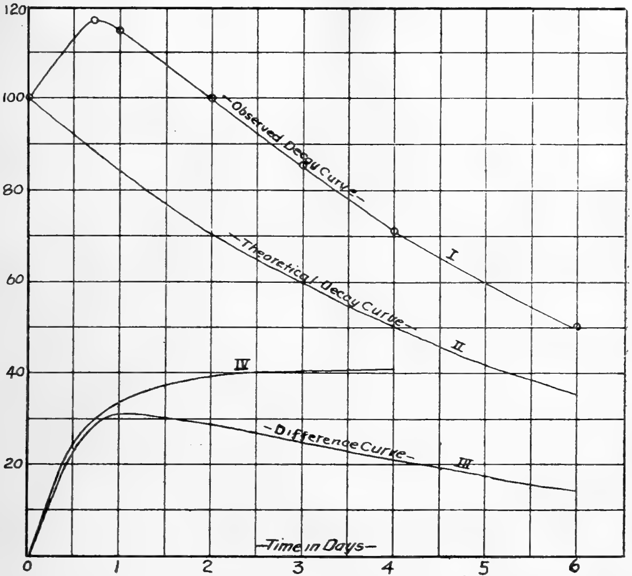
fact almost identical with the ordinary curve (fig. 2) that has been produced back to cut the vertical axis, and there is thus no doubt that there is a residual activity of thorium unconnected apparently with ThX, and constituting about one fourth of the whole.

The decay-curves of several of the fractions of ThX separated in this experiment after varying intervals of time were taken for the first few days. All of them showed the initial rise of about 15 per cent. at the end of 18 hours, and then a normal decay to zero. The position is thus proved that the initial irregularities are caused by the secondary radiation excited by ThX upon the surrounding matter. By suitably choosing the conditions the recovery-curve can be made to rise normally from a constant minimum, and the decay-curve be shown to consist of two curves, the first the rate of production of excited radioactivity, and the second the rate of decay of the activity as a whole.

So far nothing has been stated as to whether the excited radioactivity which contributes about 21 per cent. of the total activity of thorium is the same or different from the known type produced by the thorium emanation. All that has been assumed is that it should follow the same general law; *i. e.* the effect will increase with the time of action of the exciting cause, and decrease with time after the cause is removed. If the rate of rise of the excited activity be worked out from the curves given (fig. 5) it will be found to agree with that of the ordinary excited activity, *i. e.* it rises to half value in about 12 hours. Curve 1 is the observed decay-curve for ThX; curve 2 is the theoretical curve, assuming that it decreases geometrically with time and falls to half value in four days. Curve 3 is obtained by plotting the difference between these two, and therefore constitutes the curve of excited activity. Curve 4 is the experimental curve obtained for the rise of the excited radioactivity from the thorium emanation when the exciting cause is constant. But the exciting cause (ThX) in the present case is not constant, but is itself falling to half value in 4 days, and hence the difference curve, at first almost on the other, drops away from it as time goes on, and finally decays to zero. There is thus no reason to doubt that the effect is the same as that produced by the thorium emanation, which is itself a secondary effect of ThX. Curve 3 (fig. 2) represents a similar difference curve for *the decay* of excited activity, plotted from *the recovery curve* of thorium.

Since this effect of excited activity is caused by the emanation, it seemed reasonable to suppose that it will be greater, the less the emanation succeeds in escaping in the radioactive state, and therefore that de-emanated compounds should

Fig. 5.



possess a greater proportion of excited radioactivity than those with high emanating power. This conclusion was tested by converting a specimen of thorium carbonate with an emanating power five times that of ordinary thoria, into oxide and de-emanating by intense ignition. The energy that before escaped in the form of emanation is now, all but a few per cent., prevented from escaping. The radioactivity of the oxide so prepared rose in the first three days about thirty per cent. of its original amount, and there thus seem to be grounds for the view that the excited radioactivity will contribute a much greater effect in a non-emanating thorium compound than in one possessing great emanating power.

Additional confirmation of this view is to be found in the nature of the radiations emitted by the two classes of compounds (Section XI.).

X. *The Non-separable Radioactivity of Thorium.*

It has not yet been found possible by any means to free thorium from its residual activity, and the place of this part in the scheme of radioactivity of thorium remains to be considered. Disregarding the view that it is a separate phenomenon, and not connected with the major part of the activity, two hypotheses can be brought forward capable of experimental test, and in accordance with the views advanced on the nature of radioactivity, to account for the existence of this part. First, if there was a second type of excited activity produced by ThX similar to that known, but with a very slow rate of decay, it would account for the existence of the non-separable activity. If this is true it will not be found possible to free thorium from this activity by chemical means, but the continuous removal of ThX over a very long period would, as in the above case, cause its spontaneous decay.

Secondly, if the change which gives rise to ThX produces a second type of matter at the same time, *i. e.* if it is of the type of a decomposition rather than a depolymerization, the second type would also in all probability be radioactive, and would cause the residual activity. On this view the second type of matter should also be amenable to separation by chemical means, although it is certain from the failure of the methods already tried that it resembles thorium much more closely than ThX. But until it is separated from the thorium producing it, its activity will not decay spontaneously. Thus what has already been shown to hold for ThX will be true for the second constituent if methods are found to remove it from the thorium.

It has been shown (Soddy, *loc. cit.*) that uranium also possesses a non-separable radioactivity extremely analogous to that possessed by thorium, and whatever view is taken of the one will in all probability hold also for the other. This consideration makes the second hypothesis, that the residual activity is caused by a second non-thorium type of matter produced in the original change, the more probable of the two.

XI. *The Nature of the Radiations from Thorium and ThX.*

From the view of radioactivity put forward it necessarily follows that the total radioactivity of thorium is altered neither in character nor amount by chemical treatment. With regard to the first, the amount of activity, it has been pointed out that the intensity of radiations *emitted* do not furnish alone a measure of the activity. The absorption in the mass of material must be considered also. The radiations of thorium oxide are derived from a very dense powder; those from ThX, on the other hand, have only to penetrate a very thin film of material. The difficulty can be overcome to some extent by taking for the comparison the radioactivity of a thin film of a soluble thorium salt produced by evaporating a solution to dryness over a large metal plate. Compared in this way, the radioactivity of ThX when first separated almost exactly equals the activity of the nitrate from which it is produced, while the hydroxide retains about two-fifths of this amount. The total activity of the products is therefore greater than that of the original salt; but this is to be expected, for it is certain that more absorption takes place in the nitrate than in the products into which it is separated.

Similar difficulties stand in the way of an answer to the second question, whether the nature of the radiations is affected by chemical treatment, for it has been experimentally observed that the penetrating power of these radiations decreases with the thickness of material traversed. The character of the radiations from ThX and thorium have, however, been compared by the method of penetration power. A large number of comparisons justifies the view that the character of thorium radioactivity is unaltered by chemical treatment and the separation of ThX, although the different types are unequally distributed among the separated products.

Determinations of the proportion of rays deviable by the magnetic field in thorium and ThX throws fresh light on the question. The general result is that ThX gives out both deviable and non-deviable rays, and the same applies to the excited activity produced by ThX. But in the experiment in which the excited radiation was allowed to spontaneously decay, by removing ThX as formed, the thorium compound obtained after 23 precipitations was found to be quite free from deviable radiation. This is one of the most striking resemblances between the non-separable radioactivities of uranium and thorium, and warrants the question whether the primary radiation of ThX is not, like that of UrX, composed entirely of cathode-rays. There is, however, no means of deciding this point owing to the excited radiation which always accompanies the primary radiation of ThX, and which itself comprises both types of rays.

Finally, it may be mentioned that the proportion of deviable and non-deviable radiation is different for different compounds of thorium. The nitrate and ignited oxide, compounds which hardly possess any emanating power, have a higher proportion of deviable radiation than compounds with great emanating power. This is indirect evidence of the correctness of the view already put forward (Section IX.), that when the emanation is prevented from escaping it augments the proportion of excited radioactivity of the compound.

XII. *Summary of Results.*

The foregoing experimental results may be briefly summarized. The major part of the radioactivity of thorium—ordinarily about 54 per cent.—is due to a non-thorium type of matter, ThX, possessing distinct chemical properties, which is temporarily radioactive, its activity falling to half value in about four days. The constant radioactivity of thorium is maintained by the production of this material at a constant rate. Both the rate of production of the new material and the rate of decay of its activity appear to be independent of the physical and chemical condition of the system.

The ThX further possesses the property of exciting radioactivity on surrounding inactive matter, and about 21 per cent. of the total activity under ordinary circumstances is derived from this source. Its rate of decay and other considerations make it appear probable that it is the same as the excited radioactivity produced by the thorium emanation, which is in turn produced by ThX. There is evidence that, if from any cause the emanation is prevented from escaping in the radioactive state, the energy of its radiation goes to augment the proportion of excited radioactivity in the compound.

Thorium can be freed by suitable means from both ThX and the excited radioactivity which the latter produces, and then possesses an activity about 25 per cent. of its original value, below which it has not been reduced. This residual radiation consists entirely of rays non-deviable by the magnetic field, whereas the other two components comprise both deviable and non-deviable radiation. Most probably this residual activity is caused by a second non-thorium type of matter produced in the same change as ThX, and it should therefore prove possible to separate it by chemical methods.

XIII. *General Theoretical Considerations.*

Turning from the experimental results to their theoretical interpretation, it is necessary to first consider the generally accepted view of the nature of radioactivity. It is well established that this property is the function of the atom and not of the molecule. Uranium and thorium, to take the most definite cases, possess the property in whatever molecular condition they occur, and the former also in the elementary state. So far as the radioactivity of different compounds of different density and states of division can be compared together, the intensity of the radiation appears to depend only on the quantity of active element present. It is not at all dependent on the source from which the element is derived, or the process of purification to which it has been subjected, provided sufficient time is allowed for the equilibrium point to be reached. It is not possible to explain the phenomena by the existence of impurities associated with the radioactive elements, even if any advantage could be derived from the assumption. For these impurities must necessarily be present always to the same extent in different specimens derived from the most widely different sources, and, moreover, they must persist *in unaltered amount* after the most refined processes of purification. This is contrary to the accepted meaning of the term impurity.

All the most prominent workers in this subject are agreed in considering radioactivity an atomic phenomenon. M. and Mme. Curie, the pioneers in the chemistry of the subject, have recently put forward their views (*Comptes Rendus*, cxxxiv. 1902, p. 85). They state that this idea underlies their whole work from the beginning and created their methods of research. M. Becquerel, the original discoverer of the property for uranium, in his announcement of the recovery of the activity of the same element after the active constituent had been removed by chemical treatment, points out the significance of the fact that uranium is giving out cathode-rays. These, according to the hypothesis of Sir William Crookes and Prof. J. J. Thomson, are *material* particles of mass one thousandth of the hydrogen atom.

Since, therefore, radioactivity is at once an atomic phenomenon and accompanied by chemical changes in which new types of matter are produced, these changes must be occurring within the atom, and the radioactive elements must be undergoing spontaneous transformation, The results that have so far been obtained, which indicate that the velocity of this reaction is unaffected by the conditions, makes it clear that the changes in question are different in character from any that have been before dealt with in chemistry. It is apparent that we are dealing with phenomena outside the sphere of known atomic forces. Radioactivity may therefore be considered as a manifestation of subatomic chemical change.

The changes brought to knowledge by radioactivity, although undeniably material and chemical in nature, are of a different order of magnitude from any that have before been dealt with in chemistry. The course of the production of new matter which can be recognized by the electrometer, by means of the property of radioactivity, after the lapse of a few hours or even minutes, might conceivably require geological epochs to attain to quantities recognized by the balance. However the well-defined chemical properties of both ThX and UrX are not in accordance with the view that the actual amounts involved are of this extreme order of minuteness. On the other hand, the existence of radioactive elements at all in the earth's crust is an *à priori* argument against the magnitude of the change being anything but small.

Radioactivity as a new property of matter capable of exact quantitative determination thus possesses an interest apart from the peculiar properties and powers which the radiations themselves exhibit. Mme. Curie, who isolated from pitchblende a new substance, radium, which possessed distinct chemical properties and spectroscopic lines, used the property as a means of chemical analysis. An exact parallel is to be found in Bunsen's discovery and separation of cæsium and rubidium by means of the spectroscope.

The present results show that radioactivity can also be used to follow *chemical changes occurring in matter.* The properties of matter that fulfil the necessary conditions for the study of chemical change without disturbance to the reacting system are few in number. It seems not unreasonable to hope, in the light of the foregoing results, that radioactivity, being such a property, affords the means of obtaining information of the processes occurring within the chemical atom, in the same way as the rotation of the plane of polarization and other physical properties have been used in chemistry for the investigation of the course of molecular change.

Macdonald Physics Building,
Macdonald Chemistry and Mining Building,
McGill University, Montreal.

XLII. *On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum.* By R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University*[*].

It is a well-known fact that in the spectra formed by a diffraction-grating the light is unevenly distributed, that is the total light in any one spectrum will not recombine to form white light.

I have been examining a most remarkable grating recently ruled on one of the Rowland dividing-engines in which this uneven distribution is carried to a degree almost incomprehensible. If the spectra of an incandescent lamp are viewed directly in the grating without any other optical appliance, at certain angles of incidence perfectly sharp monochromatic

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[*] Communicated by the Physical Society: read June 20, 1902.

images of the filament appear in different parts of the first order spectra. Sometimes these images are nearly black, and sometimes they are far brighter than the rest of the spectrum. On mounting the grating on the table of a spectrometer I was astounded to find that under certain conditions the drop from maximum illumination to minimum, a drop certainly of from 10 to 1, occurred within a range of wave-lengths not greater than the distance between the sodium lines. *In other words, this grating at a certain angle of incidence will show one of the* D *lines, and not the other.*

Setting the grating at nearly normal incidence, a bright narrow line appeared in the yellow, and a slightly broader dark line showed up in the green. On decreasing the angle of incidence these lines approached one another, one travelling up the spectrum, the other down. At an incidence angle of a few minutes they came in contact presenting an appearance very similar to one of the shaded lines in the spectrum of a Nova. On decreasing the angle of incidence to zero, the lines fused producing uniform illumination at the spot.

When the light is incident on the opposite side of the normal from the spectrum we find the red and orange extremely brilliant up to a certain wave-length, where the intensity suddenly drops almost to zero, the fall occurring, as I have said, within a range not greater than the distance between the D lines. A change of wave-length of 1/1000 is then sufficient to cause the illumination in the spectrum to change from a maximum to a minimum.

The theory of the diffraction-grating, as it stands at the present time, appeared to me to be wholly inadequate to explain this most extraordinary distribution of light, and I accordingly endeavoured to find out if possible the necessary modifications which must be introduced.

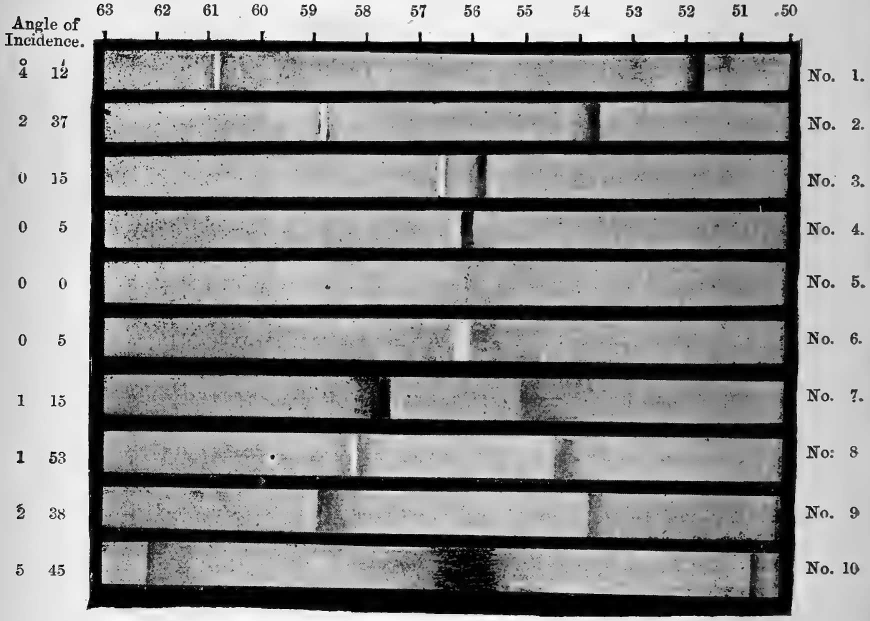
The ordinary theory shows that under certain conditions (square groove and normal incidence for example) the directly reflected light, or central image, may have certain wave-lengths wholly absent and appear strongly coloured in consequence. Coloured central images have been studied experimentally by Quincke, and Rayleigh has treated them theoretically for transmission-gratings, and Rowland for gratings acting by reflexion.

In studying the colours of these central images I have found that when the plane of polarization is parallel to the groove the colour is quite different from what it is when the plane is at right angles to the groove. The polarizing power of gratings has been experimentally investigated by Wien and Rubens, but to the best of my knowledge their experiments were confined to wire gratings, and dealt merely with the amount of light directly transmitted under the two conditions. So far as I know, polarization has never been introduced into the theory of gratings.

It occurred to me that polarization might prove to be the key to the explanation of the very singular behaviour of the grating of which I am writing. Experiment proved this to be the case, for it was found that *the singular anomalies were exhibited only when the direction of vibration (electric vector) was at right angles to the ruling.* On turning the nicol through a right angle all trace of the bright and dark bands disappeared. The bands are naturally much more conspicuous when polarized light is employed.

We will now examine in some detail the appearance of the spectrum at different angles of incidence. In fig. 1 we have the appearance of the spectrum for ten different angles of incidence. The position of the dark and light bands in the spectrum was determined by employing sunlight, and using the Fraunhofer lines as reference-marks. The wave-lengths are indicated at the top of the figure, and the angles of incidence at the left. Beginning with No. 1, we have the

Fig. 1.



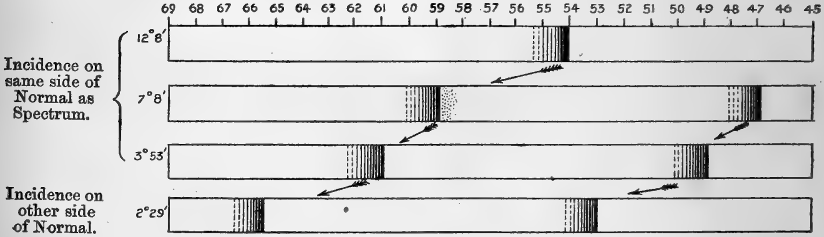
light incident at an angle of 4° 12′ on the same side of the normal as the spectrum. A bright line not much wider than the distance between the D lines appears at wave-length 609, and a dark band at 517 : the latter is sharp and black on one side and shades off gradually on the other. On decreasing the angle of incidence to 2° 37′ the bands approach, occupying the positions shown in No. 2.

Numbers 3 and 4 show two subsequent positions, and it will be noticed that the rate of progress along the normal spectrum is the same for each. In No. 4 we have the appearance which I have likened to the line in the spectrum of a Nova.

In No. 5 the incidence is normal and the lines have fused and disappeared. This is not merely an approximation, for I have found that if the grating be turned until the spectrum has this appearance, the light reflected back through the collimator passes through the slit. This furnishes us with a new method for adjusting *a* grating for normal incidence. On passing this position a narrow bright line appears which broadens into a very sharply defined rectangle, appearing, as is shown in No. 6, at an incidence angle of 5′ on the opposite side of the normal from the spectrum. This rectangle broadens as the angle of incidence increases, its edges becoming heavily shaded, as is shown in No. 7, where we have essentially two dark bands retreating from each other at equal rates as the angle of incidence increases. There is nothing especially peculiar about the one which is journeying towards the violet end of the spectrum, but the other behaves in a most singular manner, which could only be fully illustrated by a kinematograph-view of its changes. In No. 7 we find it very sharp and black on the right-hand edge, shading off towards the red end of the spectrum. As it moves along, a shadow appears on its right-hand side, the two shadows being separated, however, by a narrow bright region ; the right-hand shadow increases in depth, while the left-hand one clears up, until the band becomes symmetrical, a narrow bright line with a shadow on each side, as is shown in No. 8. On increasing the angle of incidence still further, the inverse of this operation takes place, until in No. 9 the shadow has transferred its position to the right, and appears with a sharp black edge as before only reversed in position. This process of turning inside out of the shadow marks the beginning of another curious event, for, as the reversed shadow travels along towards the red with increasing angle of incidence, an exceedingly black symmetrical band splits off from it and travels down the spectrum in the opposite direction, arriving at the position shown in No. 10, at an incidence angle of 5° 45′. This band is much wider than the others and seems to be absolutely black at the centre, even with a fairly wide slit.

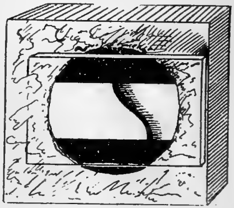
This represents the cycle when the grating is in air. If a piece of plane-parallel glass is cemented to the front of the grating with cedar oil the cycle is quite different. In this case we have a pair of unsymmetrical shaded bands which move in the same direction as the angle of incidence is changed. In fig. 2 I have given the appearance and position of these bands for three different angles of incidence. It will be observed that they remain distinct on passing through the position of perpendicular incidence.

Fig. 2.



It is impossible to identify these bands with those observed with the grating in air, since the jump in the refractive index of the medium in which the grating is immersed is too great. To determine the effect of increasing the refractive index of the medium on the position of a given band I fastened a plate of glass in front of the grating at a distance of about 0·3 mm. from the ruled surface. Water was introduced between the two, and glycerine applied to the lower edge. The denser fluid gradually diffused up into the water, and I observed the dark bands sharply curved, on looking at the spectrum directly in the grating without the aid of a telescope, the shift being towards the red, as the refractive index increased. The appearance of one of the bands is shown in fig. 3. It will be observed that the shift is in the same direction as when a resonator is immersed in a medium of high dielectric constant, and though there may be no connexion between the two phenomena, it seems perhaps worth while to mention it as there may be something akin to resonance in the action of this grating.

Fig. 3.



It is useless to attempt to fully explain the very complicated sequence of events which I have outlined, until some working hypothesis is established which will explain some one of them, and it appears to me that the first thing to do is to make some assumption which will explain the very remarkable fact that a change of wave-length of one part in a thousand is sufficient to change the illumination from a maximum to a minimum.

We know that this can take place if we are dealing with interference with a large difference of path. Hamy's "extincteur"* is a piece of apparatus which illustrates this better than anything with which I am familiar. It occurred to me that possibly the anomalies were to be referred in some way to the interference between disturbances coming from widely separated lines, though I had no very definite idea as to just how it could produce any of the anomalies, or how it was to be connected with the polarization effect. It seemed worth while, however, to investigate the matter, and I accordingly covered the grating with a thin sheet of black paper, leaving exposed only a strip about 0·3 mm. wide along one edge. By bringing the eye close up to this small strip the spectrum could be distinctly seen, but the sharpness of the dark bands seemed to be undiminished. As there were only about 200 lines acting there could not have been any very considerable difference of path between even the extreme rays. In consequence of this I am compelled to refer the matter to the form of the groove. The important fact which must be taken into account in any endeavour to explain the action of the grating is, that the anomalies only occur when the electric vector lies across the ridge. We can speculate about the action of the narrow ridges on the light waves, assuming, perhaps, something of the nature of resonance taking place across the ridge, or we can seek for the explanation in the behaviour of the transverse vibrations in between the ridges, but in any case we are confronted with the difficulty of explaining the tremendous change in the intensity of the illumination with the exceedingly small change of wave-length.

The study of this grating has been limited to the two or three days immediately preceding the closing of the laboratory for the summer, consequently I have been unable to give a very exhaustive account of its behaviour under other conditions, or secure any very satisfactory photographs of the peculiar spectra. The few photographs which I have taken and which are reproduced, were made on some old orthochromatic plates, without any especial appliances, the plates

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* M. Hamy, *Compt. Rend.* cxxv. p. 1092 (1897).

being applied to the end of the spectrometer tube, while the slit was illuminated with a Nernst lamp, which makes the best source of light possible when a continuous spectrum is required. The photographs are interesting as showing the sharpness of the bright and dark bands in the spectrum. I am of the opinion that a study of the colours of the central image with polarized light in the case of this grating may throw some further light on the problem, which is one of the most interesting that I have ever met with.

Baltimore, June 2nd, 1902.

XLIII. *On the Measurement of Young's Modulus. By* W. Cassie, *M.A., Professor of Physics in the Royal Holloway College* [*].

A reliable oscillation method of measuring the stretch modulus ought to have advantages in accuracy and convenience which would give it some practical value. A method depending upon the oscillations of a spiral spring has been given by Prof. L. R. Wilberforce [*], and a simplification of that method depending upon flexural vibrations of a straight piece of wire has been given by Mr. G. F. C. Searle [†]. The apparatus described in the present paper yields an oscillation method which is fairly simple, and it has the additional advantage that without any change of the apparatus a statical measurement of the stretch modulus can also be easily made.

If a horizontal bar AB, fig. 1 (hereafter called the needle), is symmetrically supported by two equal parallel wires *pq*, *rs* it may be made to execute a small oscillation in the plane of the paper about an axis passing through the middle point of *qs* perpendicular to the plane of the paper. This oscillation is accompanied by alternate extension and contraction of the supporting wires, so that the resistance to stretching of these wires controls the oscillation and determines its period. The period of the oscillation for a given pair of wires may be made of any convenient length by altering the moment of inertia of the needle. Some of the dimensions of the apparatus can be eliminated by observing other modes of oscillation of the system, so that in its simplest form the experiment gives an expression for the stretch modulus involving only four periods and the weight of the needle, quantities which can be measured with ease and accuracy.

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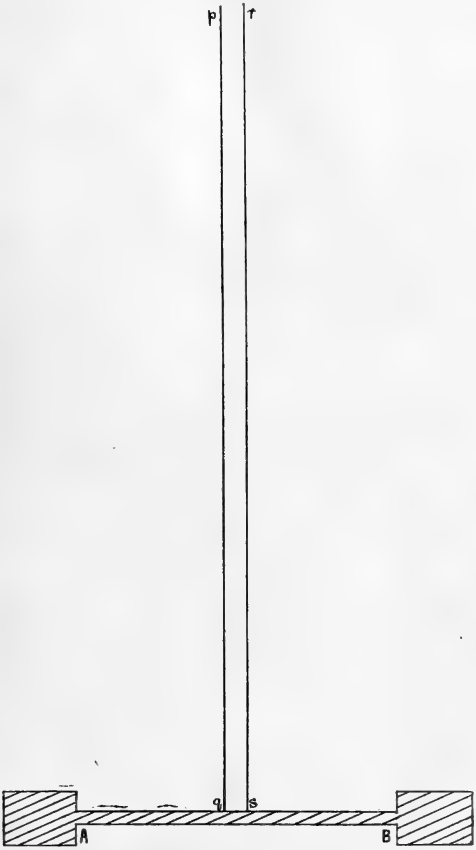
[*] Communicated by the Physical Society: read November 22, 1901.

[†] Phil. Mag. Oct. 1894.

[‡] Ibid. Feb. 1900.

In the statical method a small weight is hung on the needle at a measured distance from the centre. This produces

Fig. 1.



a known difference between the tensions in the wires, and the consequent difference in extension can be measured on a scale by a beam of light reflected from a small mirror attached to the needle. By hanging the small weight at various distances a series of measurements can be made.

I. First Oscillation Method.

The Needle.—The vibrating needle AB may be conveniently made of a straight bar or tube with a heavy cylinder fixed at each end of the bar by set screws. If these cylinders are hollow, and each made with four set screws placed as shown in figs. 2 and 3, their positions can easily be adjusted in

Fig. 2.

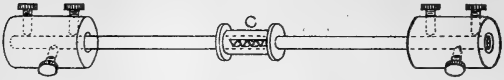
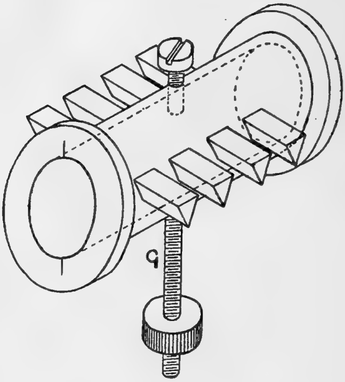


Fig. 3.

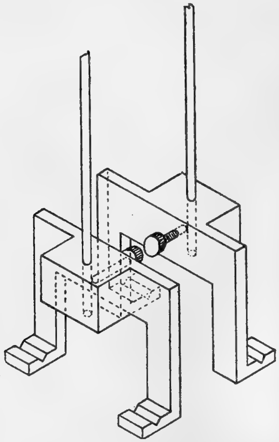
any way that may be required. The centre of the bar is fixed with a set screw into a short flanged tube, fig. 4, and

Fig. 4.



C fig. 2, with two pairs of parallel knife-edges projecting from the sides. These knife-edges rest on double hooks, fig. 5, which hang from the suspending wires. This flanged

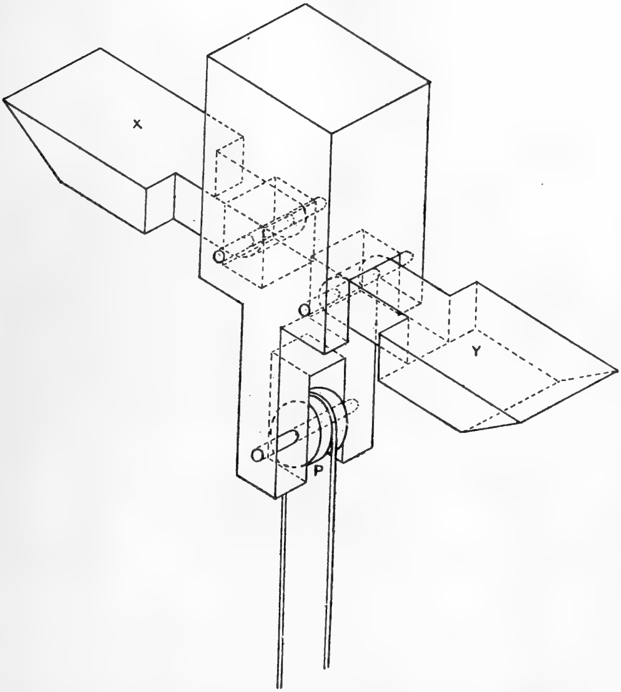
Fig. 5.



tube with the knife-edges carries also a vertical screw with a nut—a gravity bob—for adjusting the position of its centre of gravity.

The Suspension.—The parallel wires to be stretched consist of a single length of wire with its ends fixed below to the hooks supporting the needle, and passing above over a pulley, P (fig. 6), of diameter equal to the distance between the parallel knife-edges on the needle. A slight groove is made round the pulley to keep the wire in position. After the adjustments are complete the pulley is clamped between the blocks X, Y, fig. 6, which swing down to each side of it, so that the suspending wires are rigidly fixed at the top.

Fig. 6.



Adjustment.—To adjust the apparatus the needle is placed with its knife-edges on the hooks, and while the pulley is free to turn the needle is adjusted until it rests in a horizontal position. The centre of gravity of the needle is then in a vertical line midway between the suspending wires. The pulley is then clamped and the equality of tension of the wires tested by seeing that they give the same note when struck. If now the centre of gravity of the needle is at the same level as the knife-edges the pitching oscillation will be due entirely to the stretching and contraction of the wires. If in practice, however, the centre of gravity does not occupy exactly this position, the effect of a small error in this respect proves to be so small that it may usually be neglected. In any case it can be allowed for. The calculations are given below. The position of the centre of gravity of the central tube can be separately adjusted to the right level by means of the gravity bob, G, fig. 4, which is attached to the tube for that purpose. And as the weight of the central tube is a very small fraction of the whole weight of the needle, any outstanding error in the position of its centre of gravity would be quite inappreciable in its effect.

In the bifilar oscillation the period is affected by the resistance to torsion of the wires. This effect is eliminated by observing the periods with the needle suspended by first the inner, and second the outer pair of knife-edges, so that the suspending wires are at two different distances apart. The supporting pulleys on which the wires are clamped at the top are made of diameters equal to the distances between the knife-edges, so that the wires are parallel in each experiment. The free lengths of the wires are taken the same in each experiment; this can be secured automatically by an appropriate arrangement of the pulleys.

Calculation of the Periods.—Of the oscillations possible to this system we shall make use of three. They are rotations about three perpendicular axes through the centre of the needle, viz.:—

1. About a vertical axis—the bifilar oscillation.
2. About a horizontal axis perpendicular to the length of the needle—pitching.
3. About a horizontal axis along the length of the needle—rolling.

Let l be the length of each of the wires,
M the mass of the needle,
λ the modulus of stretching of each of the wires,
τ the modulus of torsion of each of the wires,
k_2 the radius of gyration of the needle about its axis of figure,
k_1 the radius of gyration of the needle about an axis perpendicular to its axis of figure through the centre of gravity. The needle is made a figure of revolution so that this radius of gyration may be taken the same in all such directions.

Firstly, assume that the mass of the hooks on which the knife-edges rest may be neglected in comparison with that of the needle, and that the centre of gravity of the needle is at the same level as the knife-edges. Then the equation of motion of the bifilar oscillation when the wires are distant $2c$ apart is

$$Mk_1^2\ddot{\theta} = -\left(Mg\frac{c^2}{l} + 2\tau\right)\theta,$$

and the frequency n_1 is given by

$$4\pi^2 k_1^2 n_1^2 = \frac{gc^2}{l} + \frac{2\tau}{M}.$$

Similarly the frequency n_1' when the wires are distant $2d$ apart is given by

$$4\pi^2 k_1^2 n_1'^2 = \frac{gd^2}{l} + \frac{2\tau}{M},$$

therefore

$$4\pi^2 k_1^2 (n_1^2 - n_1'^2) = \frac{g}{l}(c^2 - d^2). \quad . \quad . \quad . \quad (1)$$

Again the equation of motion for the pitching oscillation when the wires are distant $2c$ apart is

$$Mk_1^2\ddot{\theta} = -\frac{2\lambda c^2}{l}\theta,$$

and the frequency n_2 is given by

$$4\pi^2 k_1^2 n_2^2 = \frac{2\lambda c^2}{Ml}.$$

Likewise the frequency of pitching n_2' when the wires are distant $2d$ apart is given by

$$4\pi^2 k_1^2 n_2'^2 = \frac{2\lambda d^2}{Ml}.$$

Therefore

$$4\pi^2 k_1^2 (n_2^2 - n_2'^2) = \frac{2\lambda}{Ml}(c^2 - d^2). \quad . \quad . \quad . \quad (2)$$

Consequently

$$\lambda = \tfrac{1}{2}Mg\frac{n_2^2 - n_2'^2}{n_1^2 - n_1'^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a result requiring no measurement except the periods and the weight of the needle.

Secondly, if the centre of gravity of the needle is at a distance x below the level of the knife-edges the equation of motion for pitching with the wires $2c$ apart is

$$M(k_1^2 + x^2)\ddot{\theta} = -\left(\frac{2\lambda c^2}{l} + Mgx\right)\theta,$$

and the frequency is given by

$$4\pi^2 n_2^2 = \frac{2\lambda c^2}{(k_1^2+x^2)\mathrm{M}l} + \frac{gx}{k_1^2+x^2}.$$

Likewise the frequency with the wires $2d$ apart is given by

$$4\pi^2 n_2'^2 = \frac{2\lambda d^2}{(k_1^2+x^2)\mathrm{M}l} + \frac{gx}{k_1^2+x^2}.$$

Therefore

$$4\pi^2(n_2^2 - n_2'^2) = \frac{2\lambda(c^2-d^2)}{(k_1^2+x^2)\mathrm{M}l}. \quad . \quad . \quad . \quad (4)$$

The periods of the bifilar oscillation are the same as in the first case. So that equations (1) and (4) give

$$\lambda = \tfrac{1}{2}\mathrm{M}g\frac{n_2^2-n_2'^2}{n_1^2-n_1'^2}\left(1+\frac{x^2}{k_1^2}\right), \quad . \quad . \quad . \quad . \quad (5)$$

as x is always small compared to k_1. x^2/k_1^2 is usually negligible, and when this is so equation (5) reduces to (3).

Thirdly, to allow for the hooks supporting the knife-edges, let m be the sum of their masses, and k_3 their radius of gyration about a vertical axis through their common centre of gravity. Then if n_4 and n_4' are the frequencies of pitching, and n_3 and n_3' of bifilar oscillation with the wires distant $2c$ and $2d$ apart respectively, we have

$$4\pi^2 n_3^2 = \frac{gc^2}{l}\cdot\frac{\mathrm{M}+m}{\mathrm{M}k_1^2+mk_3^2} + \frac{2\tau}{\mathrm{M}k_1^2+mk_3^2},$$

$$4\pi^2 n_4^2 = \frac{2\lambda c^2}{l}\cdot\frac{1}{\mathrm{M}k_1^2+mc^2},$$

and corresponding equations with d substituted for c. Thus we get

$$\lambda = \tfrac{1}{2}(\mathrm{M}+m)g\frac{n_3^2-n_3'^2}{n_4^2-n_4'^2}\left(1+\frac{m}{\mathrm{M}}\cdot\frac{c^2+d^2-k_3^2}{k_1^2}\right), \quad . \quad (6)$$

since m is small compared with M, and c, d, and k_3 are small compared with k_1. When the fraction in the last bracket is negligible, or when the hooks are so shaped that $k_3 = \sqrt{c^2+d^2}$, equation (6) reduces to the original result of (3).

II. Second Oscillation Method.

In certain cases it is necessary to clamp the wires direct to the needle instead of attaching them to hooks which support the needle by knife-edges. In this case flexure of the wires has to be taken account of.

In the bifilar oscillation the effect of flexure is negligible.

In the rolling oscillation when the centre of gravity is at the same level as the points of attachment of the wires there is a quick oscillation due entirely to the resistance to flexure of the wires.

In the pitching oscillation both stretching and flexure of the wires are involved. The influence of flexure alone may be ascertained from the rolling oscillation, and by allowing for this in the pitching oscillation the stretch modulus may be deduced.

This method has the disadvantage of requiring the moments of inertia of the needle to be separately determined. This, however, can be avoided by the following modification of the experiment.

If the centre of gravity of the needle is raised above the level of the points of attachment of the wires the period of the rolling oscillation is lengthened; and by suitably adjusting the height of the centre of gravity this period may be made infinite. In that case the effect of gravity exactly counteracts the effect of flexure for a small rolling displacement. This being so, if we set the needle to pitch, the effects of gravity and of the flexure will still exactly counteract each other, and the resistance to stretching of the wires will alone control and determine the period of the pitching.

In adjusting the apparatus for this experiment it is necessary to take care that the moments of inertia involved in the bifilar and pitching oscillations are equal. This may be secured by fixing at each end of the bar of the needle a cross consisting of four equal screws at right angles to the length of the needle, two horizontal and two vertical. Nuts on these screws afford a convenient means of adjusting the position of the centre of gravity and the moments of inertia.

For the determination of the stretch modulus, however, this adjustment of the centre of gravity is not necessary. The double observation which eliminates the effect of torsion eliminates at the same time the effect of flexure of the wires.

The equation of motion of the pitching oscillation may be written

$$Mk_1^2\ddot{\theta} = -\left(\frac{2\lambda c^2}{l} + f\right)\theta,$$

where $f\theta$ expresses the couple due to flexure, this couple being independent of the distance between the wires. The frequencies of pitching with the wires $2c$ and $2d$ apart respectively are given by

$$4\pi k_1^2 n_2^2 = \frac{2\lambda c^2}{Ml} + \frac{f}{M},$$

and
$$4\pi k_1^2 n_2'^2 = \frac{2\lambda d^2}{Ml} + \frac{f}{M}.$$
so that
$$4\pi k_1^2(n_2^2 - n_2'^2) = \frac{2\lambda}{Ml}(c^2 - d^2). \quad . \quad . \quad . \quad . \quad (7)$$

The bifilar periods still satisfy equation (1), so that
$$\lambda = \tfrac{1}{2} Mg \frac{n_2^2 - n_2'^2}{n_1^2 - n_1'^2},$$
as before.

III. Statical Method.

The apparatus of the first method also lends itself readily to the statical measurement of the stretch modulus. Let the bar of the needle be divided in centimetres and let a small weight, say 100 grams, be hung on the needle at a succession of measured distances from the centre. Then in each position the small weight produces a known difference in the tensions of the suspending wires, and with a small mirror attached to the needle, the differences of extension of the wires may be read by a beam of light reflected on to a scale.

If the small mass hung on the needle is w, the distance between the vertical wires is $2a$, and the distance of the scale from the mirror on the needle is h, it is easily seen that if a displacement z of w along the needle produces a displacement y of the spot on the scale,
$$\lambda = \tfrac{1}{2} wg \cdot \frac{lh}{a^2} \cdot \frac{z}{y}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For if the displacement z of w turns the needle through an angle θ, one wire is stretched $2a\theta$ more than the other, and the tension on that wire is increased by an amount $\frac{wgz}{2a}$ more than the tension on the other. So that
$$\frac{wgz}{2a} = \lambda \cdot \frac{2a\theta}{l} = \lambda \cdot \frac{2a}{l} \cdot \frac{y}{2h}.$$

The chief precaution required in this experiment besides those usual in measuring a stretch modulus is to place the mirror so that the displacement of the spot on the scale due to the bifilar motion of the needle is at right angles to that due to the stretching of the wires.

XLIV. *On the Law of Atomic Weights.*

[Plate IV.]

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN 1888 I submitted to the Royal Society a paper on the Law of Atomic Weights, in which it was shown that the succession of atomic weights, when arranged as in Mendeléeff's table, follows two nearly coincident laws—one of which, if fully ascertained, would furnish the atomic weights of the artiads or elements of even atomicity; and the other, of the perissads or elements of odd atomicity.

The cause why atomic weights obey these laws is not known; but the fact that they do obey them can be established, and it is to be hoped that the much greater discovery of the cause of these laws will follow.

Exceptional difficulties, however, present themselves in the way of man's study of the cause, for reasons which are explained in the paper above referred to; and meantime we can only gain some knowledge of the laws empirically, *i. e.*, by finding whether definite equations, or definite curves, will furnish values for the atomic weights which lie within, or nearly within, the limits of the probable errors of the best determinations that have been made experimentally. By a *definite* curve is meant one which is not made up of portions of different curves put together, but is itself, and throughout its whole length, a single curve *capable of being represented analytically by a single equation.*

Each of the laws referred to in the first paragraph might be adequately represented in a diagram by the positions in which a slightly sinuous curve intersects equidistant vertical lines representing the successive steps of the Mendeléeff series, and it was shown that the two curves of this kind belonging respectively to the artiads and perissads, lie everywhere close to a simpler curve without sinuosities, which can be represented analytically by a very simple equation, and which we may call the central curve.

Accordingly another and convenient way of representing the facts diagrammatically is to take the positions in which this simpler curve intersects the equidistant vertical lines, and to apply to these positions one set of deviations for the artiads and another set of deviations for the perissads. It was found that this central curve may be either a logarithmic curve or an elliptic curve. These curves lie so close to one another throughout that part of their length of which it was necessary to make use, that either will answer, provided that we make the deviations slightly different according as we use the logarithmic or the elliptic curve for our central curve.

In the last two paragraphs a representation of the laws by a diagram referred to rectangular coordinates has been kept in view. It is the most convenient diagram for the study of deviations. But a spiral referred to polar cordinates, which is equally legitimate, makes the chemical grouping of the elements more conspicuous; and is that which was used in the original from which Plate IV. is copied. Equidistant radii are here what represent the steps of the Mendeléeff progression. The spiral as engraved is the central curve which is furnished by a logarithmic equation: if it had been plotted down from the corresponding elliptic equation, the part of the spiral represented in the diagram would have been nearly the same in all but its innermost coil, which would have been steeper.

Using either of these curves, the deviations from it follow one law for the artiads and another for the perissads, and these laws can be partly worked out. It will not be possible to work them out fully until atomic weights shall have been determined with greater accuracy and more certainty. However, some terms of the equations representing these laws were obtained; and the remarkable fact emerged that they both depend on a period of 18 places on the diagram of Pl. IV., whereas most chemical and physical properties of the elements are associated with the period of 16 places, which is represented on the diagram by each revolution of the spiral.

It is the existence in nature of these *deviations* that renders possible an apparent reversal of the Mendeléeff order of succession, such as almost certainly prevails between tellurium and iodine, where the element to which we must assign the greater atomic weight comes first in the ascending Mendeléeff series. That there are not several cases of this kind is only because the range of the deviations is everywhere small, in other words, the two sinuous curves nowhere recede far from their common central curve.

Another fact that came to light was that in order that it may be possible to represent the atomic weights of the elements by *definite* laws such as are above described, it is essential that we add to the Mendeléeff series, as it was known in 1888, the places indicated on sesqui-radius 16 of the accompanying diagram. The necessity for this addition made it certain that these places have a real existence in nature, although at the time no elements were known that occupied them. The anticipation that this was so has been in the most satisfactory way justified by the discovery in recent years of argon by Lord Rayleigh and Sir William

Ramsay, followed by the discovery of four other elementary gases—helium, neon, krypton, and xenon—by Sir William Ramsay. These new elements occupy the five places which had several years earlier been proved to be a necessary part of the Mendeléeff series. Moreover, there can be little doubt that the very unusual chemical behaviour of these new elements, is a consequence of their occupying a position which has sandwiched them between the elements on sesqui-radius 15 (fluorine, chlorine, bromine, and iodine) in which the electro-negative condition rises to its highest intensity, and the elements on sesqui-radius 1 (lithium, sodium, potassium, rubidium, and cæsium) which are the most electro-positive known.

The paper above referred to was not printed by the Royal Society; but while it was *sub judice* the Bath meeting of the British Association was held, at which, with the permission of the Secretaries of the Royal Society, I gave an account of the investigation and exhibited on a large scale two of the diagrams *, one of them that which is here reproduced in Pl. IV., and the other a diagram illustrating the laws of the deviations. I also distributed either at the meeting or since some hundreds of copies of the diagram which accompanies this letter, which I had had printed for the purpose, as well as the following "Observations" in explanation of it.

These have recently been referred to by more than one scientific man †, and it has been suggested to me that they ought to be more satisfactorily published. I therefore venture to request you to admit them into the Philosophical Magazine, so as to ensure their being accessible to everyone interested in the matters discussed in them, as these are likely to attract more attention now than they did fourteen years ago.

I am, Gentlemen,
Faithfully yours,
G Johnstone Stoney.

30 Ledbury Road, W.,
August 16, 1902.

The following is a copy of the document which was circulated in 1888, with the diagram reproduced in Plate IV.

"*Observations on the accompanying Diagram illustrating the Logarithmic (or the Elliptic) Law of Atomic Weights*

"1. The accompanying diagram is sent in advance by the

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* One of these large diagrams I gave to Professor Hartley shortly after the meeting, and I have ascertained that it is still in existence in the collection of chemical diagrams in the Royal College of Science in Dublin.

† See Prof. Emerson Reynolds's Presidential Address to the Chemical Society in last March (Transactions of the Chemical Society 1892, vol. lxxxi. p. 614); and Dr. J. H. Vincent's paper in the Phil. Mag. of last July, p. 105.

Author to his scientific friends, with the permission of the Secretaries of the Royal Society.

"2. The curve of the diagram is the Logarithmic Spiral described in a memoir that is referred to in the heading to the diagram.

"OBSERVATION.—Another spiral, nearly coincident with that of the figure, may be derived from an elliptic law. The Logarithmic Law appears the more probable, but for the present use of chemists it is immaterial whether the curve be derived from the logarithmic or the elliptic law. What they are chiefly interested in are the properties enumerated below, which, with the exception of the *amount* of the deviations, are common to both curves.

"3. The cardinal feature of the diagram is that it represents atomic weights by volumes, not by lines.

"The *volume* of the globe in the centre represents the atomic weight of hydrogen.

"The atomic weights of the other elements are represented on the same scale by the *volumes* of concentric spheres extending out to the points intended to be indicated by the symbols of the elements.

"4. These points lie along the radii, and so near to their intersections with the logarithmic spiral that they are *within* a millimetre of that curve in fifty-nine instances. Such deviations are too small to be conveniently represented on the diagram; but the deviations of the other six elements—H, Li, Ca, Fe, Te, W—are indicated. The deviations of these six elements on the scale of the figure amount respectively to +2·92, −1·32, −1·51, −1·08, +1·00, −1·14 'millimetres.'

[The original of Plate IV. being of inconvenient size has been reduced in about the ratio of 8 to 9. Accordingly, the values of the maximum deviations given above are too large, and require to be diminished in that ratio to reduce them to the same scale as Plate IV.]

"5. The deviations (of which the foregoing are the largest) follow definite laws which are in part investigated in the memoir. The dotted spiral and the little curved lines of the figure have reference to these laws.

"6. The atomic sphere of hydrogen is drawn upon the diagram, and the others are so easily conceived, that the diagram represents the atomic weights in a form which the mind can effectually grasp.

"This is the chief peculiarity of the diagram.

"7. The quadrants are alternately electro-positive and electro-negative. The transition between these states is gradual elsewhere, but *becomes abrupt between sesqui-radius*

15 *and sesqui-radius* 1. Between these lies the vacant sesqui-radius 16.

"NOTE.—By a sesqui-radius is meant a radius along with the inner part of the opposite radius.

"8. It is proved in the memoir that the unoccupied sesqui-radius is not arbitrarily introduced into the diagram, but has a real existence in nature.

"9. The natural chemical groupings of the elements come out with conspicuous distinctness, *e. g.*, F, Cl, Br, I, on sesqui-radius 15.

"10. Shaded prominences are introduced to point out the elements of greatest atomic volume in the solid state, and shaded sectors to indicate those of least atomic volume. It is easily seen that the diagram can be made to convey other useful information in a similarly convenient form.

"11. If, as seems probable, the Logarithmic Law is the law of nature, there appear to be three elements lighter than hydrogen, which may be called infra-fluorine, infra-oxygen, and infra-nitrogen. Again, whether the real law be the logarithmic or the elliptic law, there are six missing elements between hydrogen and lithium. Infra-nitrogen has a conjectured atomic weight of about one-sixty-fourth the atomic weight of hydrogen. This estimate is arrived at by computing the deviation by the law referred to above in section 5, and applying it to the *logarithmic* curve.

"12. It will be found convenient to number the radii from 1 to 16, and to letter the coils from *a* to *g*, using for coil *a* —the innermost coil—only three-quarters of a complete coil. By this arrangement the numbering of the radii will be that which is most convenient to chemists.

"Thus thallium, being on radius 11 and coil *f*, may be briefly designated 11*f*, or *f* 11. Uranium is *g* 6. Infra-nitrogen, infra-oxygen, and infra-fluorine, are *a* 5, *a* 6, and *a* 7.

"13. The best determinations of atomic weights that could be procured were used in the investigation, but those entered on the diagram are only the rough values in common use.

"August 1888." "G. JOHNSTONE STONEY."

[*Note added August* 1902.—No. 11 of the above 'Observations' contains conjectures depending on *extrapolation*, which I am unwilling to put forward again without a caution that they are now more doubtful than they seemed to be fourteen years ago. They depend on the probability, whatever it is, that the logarithmic curve is to be employed for elements with less atomic weight than lithium, rather than the elliptic curve, or any other, if other there be, which can, like these, thread its way amid all observed atomic weights from lithium up to uranium. This seemed probable in 1888; but the position of helium upon the diagram, which has since been determined, appears to make it now less probable.

On the other hand, the existence of sesqui-radius 16 was an inference from premisses *upon which full reliance was justifiable.*—G. J. S.]

XLV. *Notices respecting New Books.*

Science Abstracts.

'SCIENCE ABSTRACTS' continues to appear regularly under the editorship of Mr. G. W. de Tunzelmann, and seems to maintain its character as a carefully prepared epitome of contemporary work in Physics, Physical Chemistry, Electrical Engineering, and allied matters. We have received from the editor the subjoined list of Journals recently added to those from which the Abstracts are prepared.

Journal of the Russian Physico-Chemical Society (Russian). Proceedings of Academy of Sciences, Amsterdam (Dutch). Proceedings of Academy of Sciences, Stockholm (Swedish). Proceedings of Academy of Sciences, Christiania (Norwegian). Proceedings of Academy of Sciences, Copenhagen (Danish). Also: Zeitschrift für anorganischen Chemie. Royal Society of Edinburgh, Transactions and Proceedings. British Optical Journal. Elettricistà (Rome). Iron and Steel Institute, Transactions. American Society of Mechanical Engineers. Engineering and Mining Journal (New York). Power (New York). American Telephone Journal. La France Automobile. Der Motorwagen. Automobile Review (Chicago). Archives of the Röntgen Ray. Washington Philosophical Society, Bulletin.

XLVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 176.]

January 22nd, 1902.—J. J. H. Teall, Esq., M.A., V.P.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Fossiliferous Silurian Beds and Associated Igneous Rocks of the Clogher Head District (County Kerry).' By Prof. Sidney Hugh Reynolds, M.A., F.G.S., and Charles Irving Gardiner, Esq., M.A., F.G.S.

After a brief account of the bibliography of the district, the authors proceed to give a detailed description of the coast from Dunquin past Clogher Head to Coosglass (south of Sybil Point), and of the western side of Smerwick Harbour. They next deal with the inland exposures, which are not very frequent, but include considerable rock-masses at Croaghmarhin and Minaunmore Rock. The rocks consist of sandstones, slates, calcareous flags, ashes and ashy conglomerates, rhyolitic lava-flows, and various intrusive rocks. The general structure is an S-shaped fold, inverted towards the north so that the dip of the beds is approximately south-easterly, and the oldest beds occur to the north, at Coosglass. Both anticline and syncline are faulted, and a patch of Old Red Sandstone is caught in under the synclinal thrust at Coosmore. Fossils, mainly corals, brachiopods, lamellibranchs, and gasteropods, are fairly abundant; but trilobites are rare and graptolites absent. The whole of the fossiliferous rocks are of Silurian age; the majority of those exposed on the coast are of Wenlock or Wenlock-Llandovery age, while the majority of those exposed inland are of Ludlow age. The general classification is as follows:—

		Feet.
Lower Devonian ...	Dingle Series.	
Ludlow	5. Croaghmarhin Beds: calcareous sandstones and flags of Ludlow age	? 1000
Wenlock	4. Drom Point Beds .... about	600
	3. Red sandstones and ashes, with green ash at the top	350
	2. Clogher Head Series: calcareous flags and slates, with abundant contemporaneous igneous rocks	550
Wenlock-Llandovery.	1. Ferriter's Cove Beds: chiefly calcareous flags, with a subordinate development of contemporaneous igneous rocks	2300
?	Smerwick Beds.	

Contemporaneous volcanic rocks are first met with low down in the Wenlock-Llandovery Series, and reach their maximum in the Wenlock Series, especially in the southern part of the area. There are ashes but no lavas in the Ludlow. The volcanic rocks are all of acid character, and include nodular, banded, and non-banded rhyolites, with tuffs and ashes both coarse and fine. The Dingle Beds appear to be conformable, but movement occurred before the Old-Red-Sandstone Conglomerate was laid down, and the overfolding and thrusting probably took place during the post-Carboniferous period of earth-movement. Before the last movement fine-grained diabasic rocks ('greenstones') appear to have been intruded. The thickening of the volcanic rocks to the southward seems to indicate that the vents must have been situated in this quarter. The beds as a whole were deposited in shallow water in the proximity of land, and they point to the existence of rocks, such as granites, not now known at the surface in the district.

2. 'A Process for the Mineral Analysis of Rocks.' By William Johnson Sollas, D.Sc., LL.D., F.R.S., F.G.S., Professor of Geology in the University of Oxford.

The method proposed is to obtain a quantitative estimation of the mineral composition of a rock, and from the known composition of the minerals to calculate the percentage-composition of the rock. The specific gravities of the minerals are first determined by means of a diffusion-column of methylene-iodide and beads of known specific gravity, and the presence or absence of particular minerals settled for a certainty. Next, the separation of the minerals in a weighed quantity of the powdered rock is undertaken by means of a special separator: the method being illustrated by the example of a rock containing orthoclase (sp. gr. 2·56), quartz (2·65), andesine (2·67), biotite (3·1), pyroxene (3·3), and magnetite. The first separation would be with a liquid of sp. gr. 2·885, the mean of that of andesine and biotite; the next with a liquid of sp. gr. 2·66; the next 2·605, and so on for the other constituents. The separated minerals are dried and weighed, the loss distributed, and the analysis checked by comparing the specific gravity of the rock in bulk with that calculated from the specific gravity and proportion by weight of its constituents. In making choice of particular mineral-analyses for calculating the chemical composition, there are three guiding principles: the analysis should be that of a mineral obtained from the same kind of rock as the one under investigation; if possible, from the same locality; and with the same specific gravity. The process was tested on specimens of kentallenite supplied by Mr. Teall and of gabbros from Skye by Mr. Harker, and in both cases the results compared closely with those obtained from bulk-analysis of the same rocks. A further test was the comparison of the mineral analysis by Miss Davies of a specimen of Devonshire granite with Phillips's published analysis; also of syenite from the Plauenschergrund, and of tonalite from Adamello, with published analyses.

February 5th.—J. J. H. Teall, Esq., M.A., V.P.R.S., President, in the Chair.

The following communications were read:—

1. 'The Matrix of the Suffolk Chalky Boulder-Clay.' By the Rev. Edwin Hill, M.A., F.G.S.

The author has been examining with the microscope washed residues from Boulder-Clays. He is able to group together the specimens from localities along a belt of country from Lowestoft to Bury St. Edmunds, as containing granules of Secondary clays and limestones. Other specimens contain granules which may be the same kind decomposed, others granules of other kinds; all these lie outside the belt occupied by the group, though some are very near it. The granules of the group, derived from Secondary rocks, may all have come from the west.

Certain peculiar round grains, found generally, except in the extreme east and north, are also probably from Secondary rocks, and they too point to a western origin.

The clays of the group, though some occupy the coast-cliffs, contain so little sand, that they cannot be supposed to have been brought from the side of the sea, that is from the east.

All the residues have been examined for coal-dust. Though this is contained in Glacial clays along the eastern coast of England as far south as the Wash, and probably farther, it is either altogether absent from the group, or present only on its eastern edge. It appears to be absent from the clays which border the group on the north.

These results combined lead to the conclusion that the materials of the matrix in the Suffolk Chalky Boulder-Clay were not brought from the east or north, but from inland; and not from so far inland as the Coalfields. Their sources therefore lie on a limited belt, bordering the Boulder-Clay area.

With this agrees the evidence of the included boulders as a whole.

2. 'On the Relation of certain Breccias to the Physical Geography of their Age.' By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S.

The author has endeavoured in this paper to collect from published accounts and his own observations the evidence which certain well-known and important beds of breccia afford, as to the physical conditions prevalent when they were formed. First come sketches of the principal breccias in the Rothliegende, the brockrams of the North-west of England and similar deposits in Armagh, the breccia-beds of the Midlands and of Devon, and those of the Thüringerwald. The fragments in these vary from angular to subangular, are sometimes interstratified with beds of finer material, sometimes are themselves slightly stratified. They form marginal fringes to old land-masses, from which we may, with more or less certainty, infer them to have been derived, and are sometimes found to extend outward from them, wedge-fashion, for a few miles. They appear, for reasons given, to have been the products of bare rocky hill-slopes rather than of mountain-torrents. Floating ice has been suggested as a means of transport, though the idea that the Clent and Enville breccias indicate the former existence of glaciers is not now generally accepted, Mr. Wickham King having shown the materials to have been derived from land-masses in the neighbourhood, and Mr. R. D. Oldham having pointed out their resemblance to certain Indian breccias.

The so-called Dolomitic Conglomerate of the South-west of England, which exhibits similar characters, though on a smaller scale, and the remarkable breccias in the Upper Oolite of Caithness described by Prof. Judd are next noticed, after which the author passes on to the breccia-beds in the Alpine Flysch, taking as examples those of the Habkerenthal and of the Val des Ormonts. The former apparently are more sporadic in character, and are suggestive of the intervention of floating ice; the latter are more regularly interbanded, and that with true marine deposits: their occurrence is extremely difficult to explain, without assuming the existence of a mountain-range or a great highland district in their immediate neighbourhood.

When we seek for parallels to these breccias in deposits of late date or in process of formation, we find some resemblances to them in the breccias of Gibraltar described by Sir Andrew Ramsay and Prof. James Geikie, in the stone-rivers of the Falkland Isles described by Sir Wyville Thomson, and in the breccias of Persia and other parts of Central Asia described by Dr. Blanford. The author accordingly infers the Rothliegende (and probably the Triassic) breccias to be indicative of a Continental climate, due to a great extension of land or more probably the existence of a mountain-region on the west—winters with severe cold and snow, but rather hot and arid summers.

The Caithness breccias were perhaps more analogous to the stone-rivers of the Falkland Islands, but they also indicate a rather low temperature; while the Flysch-breccias land us in the following dilemma, namely, that either similar temperatures existed in Switzerland, and that there was also an important highland district, of which no remnant can be found, within a short distance of the breccia-beds; or they must be the product of a range not inferior to the present Alps, which also has completely disappeared, and would be (for reasons given) very difficult to locate. But, even in the latter case, we seem forced to admit that a temperature if not lower, at any rate not higher than the present, prevailed in Central Europe late in the Eocene Period.

February 26th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'On some Gaps in the Lias.' By Edwin A. Walford, Esq., F.G.S.

The author's endeavour is to prove gaps in the stratigraphical succession of the Lias, involving the removal of zones or parts of zones, and also to prove palæontological gaps by the abrupt appearance of many new genera of mollusca.

The Middle Liassic ferruginous limestone of the zone of *Ammonites spinatus* he states to be mainly made up of a kind of crinoid (ferrocrinoid). The zone may be divided into

2. The Ferrocrinoid bank—upper. 30 feet.
1. The *Spirifer-oxygona* beds—lower. 20 feet.

The upper division varies from 30 feet at an altitude of 700 feet to 6 feet at the altitude of 350 feet on the edges of the Cherwell Vale, owing to waste by drainage. The upper zone is of great thickness and importance in Oxfordshire and Yorkshire (Cleveland), but almost absent in Dorset, Somerset, and Gloucestershire, where the fauna of the lower *Spirifer-oxygona* beds prevails. The ironstone is thickest towards the escarpment on the west of the Cherwell Vale; on the east side of the vale, it loses both in type and importance. At Bloxham a course of ferruginous limestone is made up of stems of the ferrocrinoid in great part, but near the top it becomes a pink compact limestone, full of fossils of the zone of *Ammonites communis*: the intermediate transition-bed and zone of *Ammonites serpentinus* having been removed by inter-waste rather than by contemporaneous erosion.

A transition-bed between the Middle and Upper Lias shows a great incoming of new forms. They are no doubt developed outside lines of known strata.

A third gap, measured by the occurrence of a thin bed of Pentacrinite-limestone, is in the zone of *Ammonites communis*.

The '*spinatus*-ironstone' is believed to lose in thickness on the side of a divide away from the main west-to-east dip. On the Northamptonshire side of the Cherwell, where the slope is to the west, and hence opposite to the general dip, the beds are thin, although the argillaceous beds are better preserved.

2. 'On the Origin of the River-System of South Wales, and its Connection with that of the Severn and Thames.' By Aubrey Strahan, Esq., M.A., F.G.S.

The southerly courses of some rivers from the Usk to the Ogmore are described, and shown to be independent of both the east-and-west folding and the north-north-westerly faulting of the rocks on which they lie. Farther west the drainage-system takes a different direction, the rivers coinciding so closely with a set of west-south-westerly disturbances as obviously to have been determined in direction by them.

Of the three systems of disturbance alluded to, the east-and-west (Armorican) folding was pre-Triassic; it marks a period of compression with impulse from the south, and though it reached great intensity in Devon, Somerset, and South Wales, it died away in Central Wales. The north-north-westerly (Charnian) faulting, though partly of pre-Triassic age, was renewed in post-Eocene times, and is manifested over much of the British Isles. It marked periods of relief from pressure, and of subsidence. The west-south-westerly (Caledonian) folding was the latest; it marked a period of compression, with impulse from the north, and displayed greater energy in Central than in South Wales. It gave rise to a series of subsidiary disturbances in the latter region, and initiated and controlled the river-system. The ignoring by the rivers of the structures due to the earlier disturbances is attributed to the Palæozoic areas having been overspread by Upper Cretaceous rocks at the time of the initiation of the river-system.

The eastward course of the Upper Severn is attributed to the upheaval of a main axis (now the main water-parting) in Central Wales. Its deflection to the south and south-west was due to the formation of an anticline in the Chalk, which must have been parallel to, but a little west of, the present Chalk-escarpment, and which was parallel to, and contemporaneous with, the Caledonian disturbances in Wales.

This anticline, acting in combination with the Armorican folding displayed in the London and Hampshire basins initiated the systems of the Thames and Frome. Those systems were initiated in post-Oligocene and pre-Pliocene times, and the same age is inferred for the systems of South Wales and of the Severn.

March 12th.—Sir Archibald Geikie, D.C.L., LL.D., F.R.S., Vice-President, in the Chair.

The following communications were read:—

1. 'The Crystalline Limestones of Ceylon.' By Ananda K. Coomáraswámy, Esq., B.Sc., F.L.S., F.G.S.

The crystalline rocks of Ceylon may be divided into three series:—

(1) The Older Gneisses.
(2) The Crystalline Limestones.
(3) The Granulites (Charnockite Series)—pyroxene-granulite, leptynite, etc. A local subdivision of this series is the Point de Galle Group—wollastonite-scapolite-gneisses, etc.

The crystalline limestones of Ceylon are intimately associated with the banded pyroxene- and acid granulites (Charnockite Series). They form bands with outcrops from a few feet to over a quarter of a mile in width, interbedded with the granulites. The limestones themselves have a banded structure (foliation) parallel to that of the granulites and to the boundaries. This foliation of the limestone depends on variations in structure, amount of accessory minerals, and relative proportion of calcite and dolomite. The grain is coarse, sometimes exceedingly so. Parallel and graphic intergrowths of calcite and dolomite are very characteristic. The most abundant accessory minerals are olivine, phlogopite, pink or violet spinel, diopside, pyrite, and blue apatite; less common are amphiboles, clinohumite, green spinel, etc. The most characteristic contact-minerals are diopside, amphibole, green spinel, and greenish micas; and, rather in the granulite than the limestone, scapolite, phlogopite, diopside, sphene. There occur also in the limestones, nodular mineral aggregates composed of characteristic minerals such as diopside, phlogopite, blue apatite, and spinel.

There are often transitions between the limestones and granulites. In some other cases a zone of green rocks (with diopside, dark mica, amphibole, and green spinel) intervenes. Bands (sills) of granulite of various width, down to less than a foot, may occur in the limestone, and are parallel to the foliation and general strike. These show peripheral transitions to the limestone by incoming of original calcite and the appearance of lime-silicates, or are separated from it by a zone a few inches wide, in which the minerals diopside, amphibole, and green spinel are characteristic.

Some interrupted sills are described, and compared with the interrupted dykes of nepheline-syenite in the crystalline limestones of Alnö, described by Prof. Högbom. A sill may thus be continued along the strike as a series of lenticles. Elsewhere quite isolated masses of pyroxene-granulite occur as inclusions in the limestone.

Although the relation of the granulites to the limestones is on the whole intrusive, the two rocks in their present condition are essentially contemporaneous, and seem alike to have consolidated from a molten magma. The calcite occurring in the granulites near the contact has all the appearance of an original mineral. The foliation of the limestones is regarded as a sort of flow-structure, and corresponds with that of the granulites to which it is always parallel. That the foliation does not result from the action of earth-movements on a solid rock is shown by this, that the very minerals whose variable distribution is one of its chief causes, have certainly not been affected by deforming earth-movements, nor are they such as to have been produced by these; moreover, in this respect a distinction cannot be made between the limestones and granulites, which would necessarily have suffered alike had they been subjected to deforming strains since the consolidation of the latter, The original nature of the limestones is less evident: they may have been sedimentary or tufaceous, and, if so, subsequently softened and metamorphosed; or possibly *ab initio* truly igneous rocks, and related to the charnockite-magma. Reasons for and against these views are given. The relations between the crystalline limestones and nepheline-syenites of Alnö have suggested to Prof. Högbom that perhaps the limestone may have been a product of the nepheline-syenite magma there.

The author feels sure that the crystalline limestones of Ceylon have not arisen by the alteration of the basic lime-silicates of the pyroxene-granulites, although Prof. Judd has advanced this theory in connection with the crystalline limestones of Burma, which seem to resemble those of Ceylon in many ways.

2. 'On Proterozoic Gasteropoda which have been referred to *Murchisonia* and *Pleurotomaria*, with Descriptions of New Subgenera and Species.' By Miss Jane Donald.

March 26th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'On a remarkable Inlier among the Jurassic Rocks of Sutherland, and its Bearing on the Origin of the Breccia-Beds.' By the Rev. John Frederick Blake, M.A., F.G.S.

On the coast of Sutherland due south of Port Gower is seen on the scars at low water a long rocky crest of Old Red Sandstone, with its flaggy beds dipping at a high angle. It is of considerable height, and is surrounded by nearly horizontal Jurassic beds containing large blocks of rocks similar to those of the crest, irregularly placed. The size, outline, and relation to the surrounding rocks show that this cannot be a transported block, but must have been part of, or directly derived from, a neighbouring coast—like the modern sea-stacks of the present coast at Duncansby.

The relations of the Jurassic rocks to the Old Red Sandstone are seen in the Gartymore Burn. The fragments of the latter contained in beds of the former become more numerous as the junction is approached, and ultimately form the whole mass—as would happen in the case of a cliff-talus. It is concluded that the breccia-beds may in part have originated on the spot.

The distribution of the breccia-beds in the Jurassic Series is then considered in detail. Three horizons can be traced in this series, namely, the zones of *Cardioceras alternans*, *Hoplites eudoxus*, and *Perisphinctes Pallasi*. No breccia-beds are found in the first of these, but there are sporadic ones in the second, within which the inlier occurs, and they become very numerous in the third. The ordinary autochthonous fossils, including plant-remains, occur in the intervening shales, but the breccia-beds themselves contain only large heterochthonous fossils, including Rhynchonellas and corals, and where these occur intermediate beds are found, composed of crushed organisms. North of Helmsdale one breccia-bed has apparently squeezed up the underlying shale into an anticlinal arch, against another boss of Old Red Sandstone.

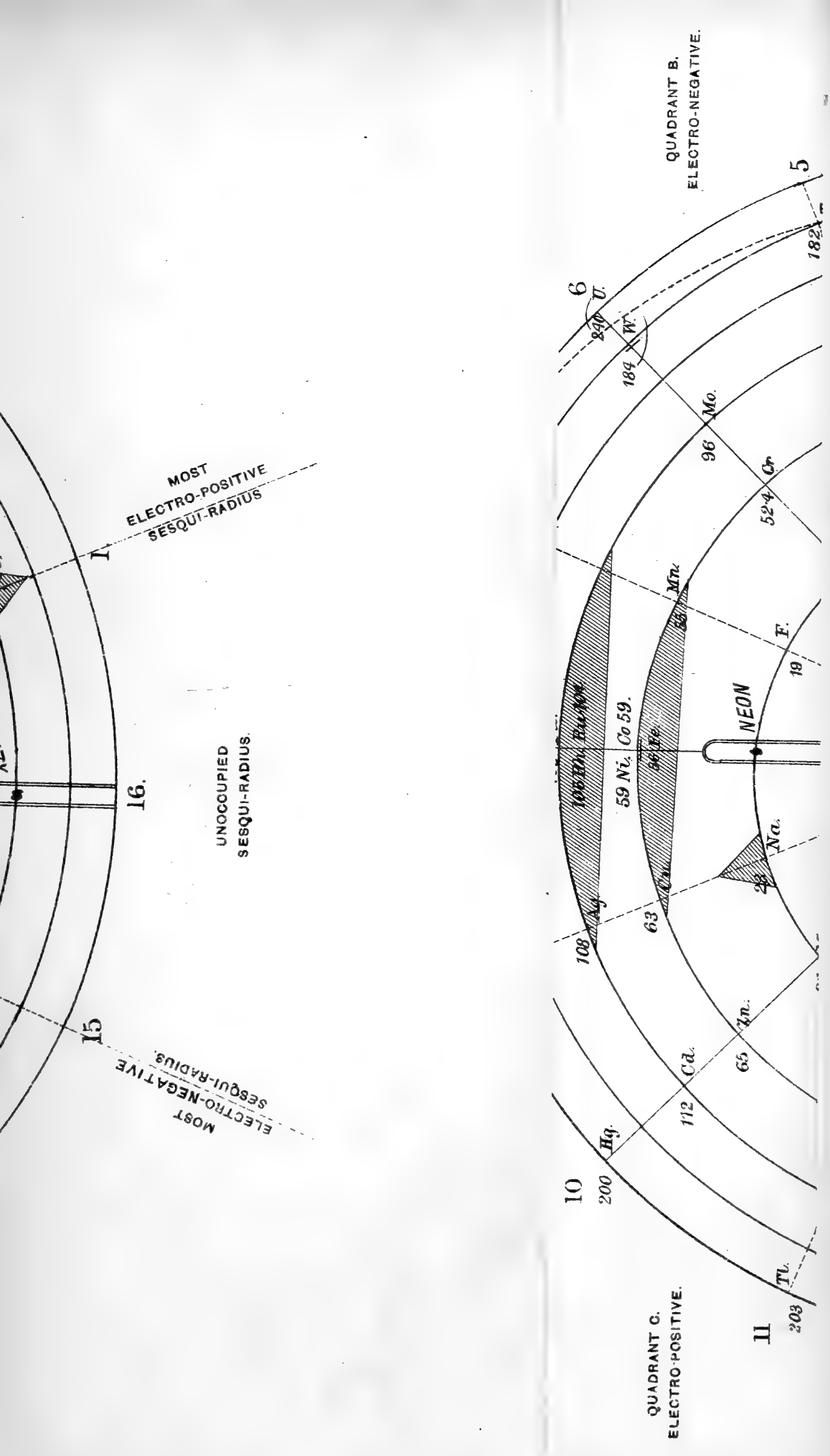
The phenomena thus described are then compared with those which have been actually seen—or which may be inferred to occur in the case of deposits from an ice-foot—and they are found to correspond in a remarkable degree. And it is therefore concluded that the breccia-beds are the product of an ice-foot of Upper Jurassic age, which invaded the normal deposits of that period.

2. 'On a Deep Boring at Lyme Regis.' By Alfred John Jukes-Browne, Esq., B.A., F.G.S.

During 1901 a boring was made near Lyme Regis in search of coal, and was carried to the depth of 1300 feet without reaching the base of the Upper Triassic Marls. The following abstract shows the formations passed through:—

			Thickness.		Depth.	
			Feet.	Inches.	Feet.	Inches.
SOIL AND GRAVEL			10	8	10	8
BLUE LIAS		probably	62	4	73	0
RHÆTIC BEDS.	White Lias	do.	22	1	95	1
	Black Shales	do.	38	7	133	8
	Grey Marls	do.	39	1	172	9
KEUPER MARLS, 1129 feet 6 inches.	Marls, without gypsum		124	7	297	4
	Marls, with veins of gypsum		118	10	416	2
	Marls, with beds of gypsum		313	10	730	0
	Gypsiferous marls, with three beds of sandstone		134	0	864	0
	Hard clays and marls, with gypsum.		297	7	1161	7
	Hard silty and micaceous clays, with some gypsum		140	5	1302	0

A full journal of the boring is given, and the beds are compared with those exposed along the cliffs from Lyme to Sidmouth. The exposures of the Rhætic Beds near Lyme are described, and the 'tea-green marls' are included in the Rhætic group, although no fossils have been obtained from them in Devon. Reference is made to the difficulty of measuring the Keuper Marls. The site of the boring is in the valley of the stream which enters the sea at Lyme, at a spot about 1 mile north-west of that town and about half a mile east of Uplyme, close to the boundary between Devon and Dorset. The Blue Lias in the borehole belongs to the zones of *Ammonites Bucklandi*, *A. angulatus*, and *A. planorbis*. Between the depths of 480 and 864 feet three beds of grey, calcareous sandstone were traversed, each from 12 to 15 inches thick, and separated by beds of red and grey, gypsiferous marl. Similar beds occur near Taunton and North Curry, in Somerset. Some of the lowest beds may be called 'siltstones'; they were originally silty muds. The author concludes that the boring did not reach the beds which near Sidmouth form a passage from the Keuper Marls to the Keuper Sandstones, and that the Keuper Marls proved by the boring are at least 1130 feet, and may amount to 1200 feet in thickness.


MOST
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QUADRANT B.
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U.
240
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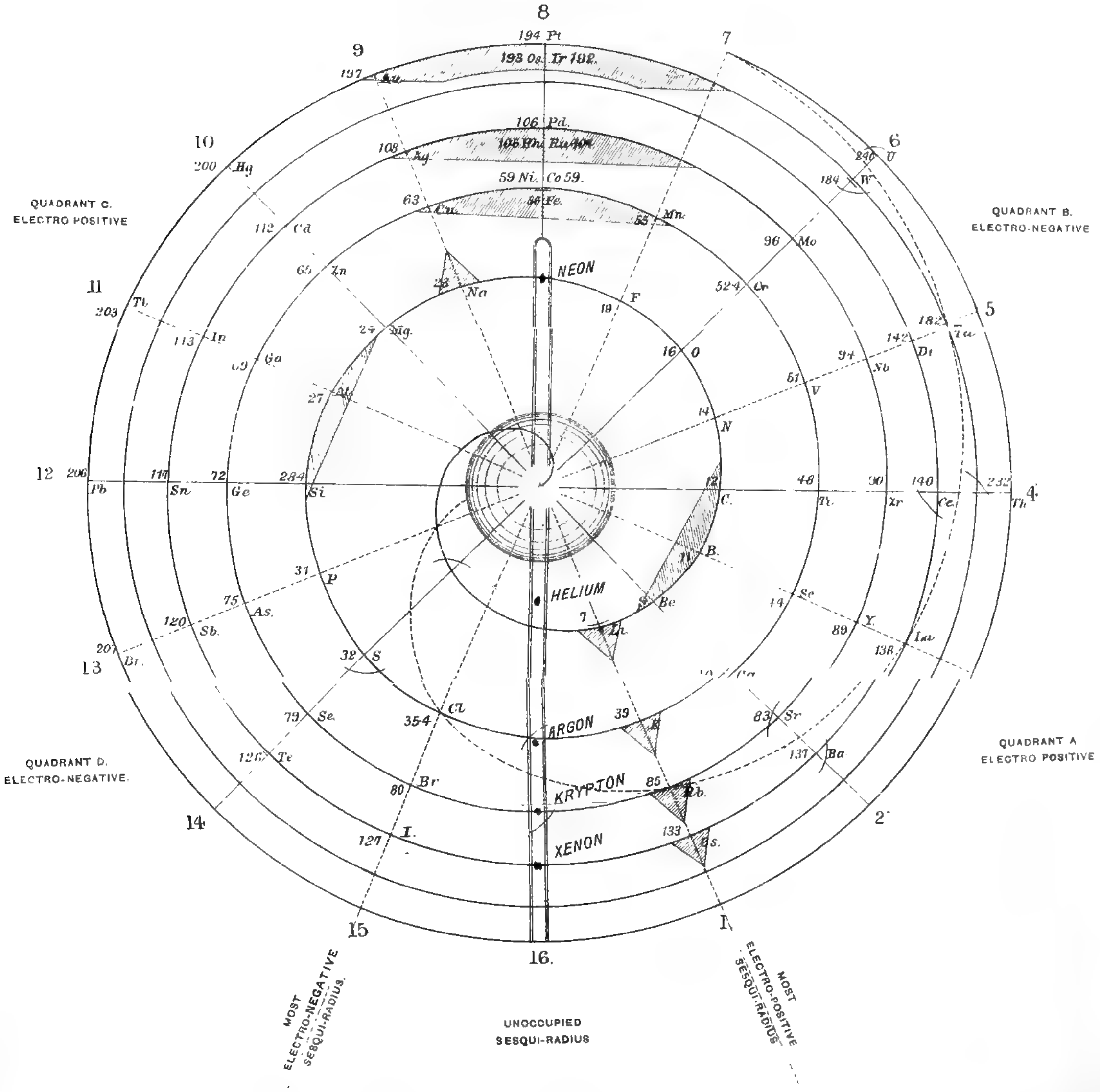
184
Mo.
96
Cr
52·4
Mn
55
F.
19
106 Rh. Ru 104
59 Ni. Co 59.
56 Fe
NEON
Ag.
108
Cu
63
Na.
23
Zn.
65
Cd.
112
Hg.
200
10
Tl.
203
11
QUADRANT C.
ELECTRO-POSITIVE.

[Copy of a diagram circulated at the Bath Meeting of the British Association in 1888. In this copy, the elements, since discovered, that occupy the sesqui-radius which was unoccupied in 1888, are inserted in their proper places.]

PLATE III. OF A PAPER "ON THE LAW

OF ATOMIC WEIGHTS," READ BEFORE THE ROYAL SOCIETY, APRIL 19, 1888,

BY G. JOHNSTONE STONEY, M.A., DSc., F.R.S



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LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

OCTOBER 1902.

V H.

XLVII. *On the Electrical Resonance of Metal Particles for Light-Waves—Second Communication. By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University*[*].

In a previous paper[†] I have shown that granular deposits of the alkali metals exhibit brilliant colours by transmitted light. These colours were referred provisionally to the electrical resonance of the minute particles for light-waves.

At the time of writing this paper, I was not acquainted with Prof. Threlfall's interesting work on the optical properties of metallic precipitates and his attempts to verify the polarization effects calculated by Prof. Thomson, to which I alluded. I feel sure that the colours observed by Prof. Threlfall, and those which I have observed, are to be referred to the same causes. It was found that the immersion of the particles in a liquid of high dielectric constant produced striking changes in the colour of the transmitted light, the change corresponding to a shift in the absorption-band towards the red end of the spectrum. It has been recently shown by Aschkinass and Shaefer[‡] that the length of electromagnetic waves to which a system of metallic resonators respond, is increased by immersing the resonator system in a liquid of high dielectric constant, which is obviously analogous to the behaviour of the sodium and potassium films. It is also well known that the position of the absorption-band of aniline dyes

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[*] Communicated by the Physical Society: read June 20, 1892.

[†] Proc. Physical Society, vol. xviii.; Phil. Mag. April 1902.

[‡] Drude's *Annalen der Physik*, vol. v. p. 489.

depends to a certain extent on the dielectric constant of the medium in which the dye is dissolved.

Continued investigation along the lines indicated in my previous paper has convinced me that it is impossible to refer the colours either to interference or diffraction, and it remains only to determine whether the resonance of the metal films is molecular, as in the case of the aniline dyes, or whether we are dealing with an electrical vibration of metallic masses, smaller than the light-waves though of the same order of magnitude. At the time of writing my first paper I had been successful in producing coloured films only with sodium, potassium, and lithium. Consequently, the only optical investigations that could be made were such as could be adapted to films formed on the walls of exhausted bulbs. Determinations of dispersion were practically impossible under these conditions, except by means of very elaborate apparatus, which it did not seem worth while to construct until further efforts had been made to obtain films of this nature which would be permanent in air, and could be examined with the interferometer. I have since succeeded in producing deposits of gold, which exhibit colours very similar to those shown by the potassium films. The deposit is formed by the discharge from a gold cathode in a moderately high vacuum, the colour depending on the distance of the glass plate from the electrode and the degree of exhaustion. Under certain conditions a green film is deposited, of a tint similar to that of gold leaf, while under other conditions blue, violet, and purple films can be obtained. The colour of the green film is doubtless to be ascribed to the same causes which operate in the case of gold leaf. The tint of the blue and purple films, however, is changed by moistening the plate with ligroin, precisely as is the case with potassium deposits. The mere approach of a glass rod, moistened with the liquid, is sufficient to produce a change of colour, the film apparently possessing the power of condensing the vapour upon its surface. Platinum and other metals in a fine state of division have this same property, consequently it seems extremely probable that the gold deposit is of this nature. Thus far I have only obtained two or three deposits which show this change. Most of the films are but slightly, if at all, affected by ligroin.

In the case of the gold films, the particles are too small to be seen under the microscope, with the facilities at my disposal; and I am inclined to the opinion that, in the case of the sodium and potassium films, particles which were actually seen with the microscope were only the moderately large ones, and may not have been instrumental in producing the colour. In continuing the work, I plan to make more exhaustive examinations with the microscope, using higher powers if possible, employing photography, and ultra-violet light if necessary, for I believe that only in this way can the nature of the resonator be determined. There will be no great difficulty in determining the dispersion, since the gold films are permanent, and can be examined with the interferometer, or they may easily be given a prismatic form. I feel confident that they will show anomalous dispersion, a phenomenon which, if observed, would be almost proof positive that the absorption-band was due to resonance. It would not, however, enable us to decide whether the resonance was within the molecule or not, for prisms built up of tinfoil strips were found by Garbasso and Aschkinass * to refract and disperse electromagnetic waves. Rubens and Nichols have examined the action on heat-waves of resonator systems formed by ruling crossed gratings on thin silver films, and found evidences of a higher reflexion percentage when the length of the resonators approaches a whole number of half wave-lengths.

Prof. Nichols and I are, at the present time, working in collaboration on the selective reflexion from a number of plates covered with resonators, very much smaller than any that have hitherto been employed. By depositing thin films of gold *in vacuo*, on glass, and ruling under oil, I have succeeded in producing resonators measuring $0{\cdot}8\,\mu$ by $1{\cdot}1\,\mu$, which should resonate in a part of the spectrum where there is plenty of energy. Some of the trial rulings were made on the blue and purple films which I have mentioned, and in examining them under the microscope I have detected numerous minute granules, of about the same size as the sodium particles which I described in my previous paper. Whether these are the particles deposited by the cathode discharge, or merely metallic dust cut off by the diamond point, I am unable to say. The fact that the coloured films of gold are produced when the glass plate is at some distance from the diamond point, seems to indicate that the gold vapour, if we may use the term, has time to condense into minute drops before reaching the plate. These films adhere much less firmly to glass than the green films which are formed when the distance between the cathode and the plate is small. In the latter the deposit is doubtless molecular, and the optical properties are similar to those of gold leaf. I have thus far been unable to obtain coloured deposits of platinum, which is the only other metal I have examined at the present time, which fact makes it seem as if the molecule was in some

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* Wiedemann's *Annalen*, vol. liii. p. 534.

way concerned with the colour. The variable nature of the colour, however, especially in the case of sodium and potassium, makes it appear improbable that the action is similar to that of aniline dyes; namely, a resonance within the molecule; for deposits of the same substance can be obtained showing an absorption-band almost anywhere in the visible spectrum, which is not the case with the more common types of coloured media.

The colour of the gold deposit varies, as I have said, with the conditions under which the deposition takes place. I have employed gold cathodes of two forms: a flat plate about 3 cms. square, and a thick wire, screening off the radiation from all but the tip with a mica screen. The most interesting deposits were obtained from the small source. In one instance the film showed a brilliant green surface colour, resembling fuchsine, the transmitted light having a purple tint. Owing to the transparency of the film a good deal of white light is mixed with the selectively reflected light; this can be cut off with a nicol, if the reflexion takes place at the polarizing angle for glass, and the coloured light from the film which is unpolarized then appears in great purity. One plate showed patches of brilliant carmine red, deep blue, and green, of an intensity and saturation which I have never seen equalled in any interference experiment. The colour of the selectively reflected light depended somewhat on the angle of incidence, a phenomenon observed also in the case of the sodium and potassium films. Increasing the angle of incidence changed the colour from green to blue; the period of vibration of the resonator system appears therefore to be less when the angle of incidence is large.

If the glass plate is placed near the tip of the gold wire, the green deposit, similar to gold leaf in its optical properties, is deposited at the centre. Surrounding this is a film appearing light yellow by transmitted light, and bluish by reflected light. This seems to be what we should expect, for the smallest particles, which will resonate for blue light, will be deposited when the distance from the cathode is a little greater than that at which the molecular deposit occurs. Increasing the distance, we get larger particles, and the point of maximum resonance moves up into the green, giving us a purple film with green surface colour. At a still greater distance we get particles large enough to resonate for red, and the film appears deep blue by transmitted light. All of these variously coloured films can be changed into the green structureless film by heating. We may regard the change as due to the fusing together of the resonators. If this is the case, the electrical resistance should be less after firing than before. This was found to be the case. The conductivity of the films is surprisingly good. A strip of a deep blue film measuring 10 by 5 mms. had a resistance of only a little over 2 ohms. After heating the film its resistance dropped to about half this value.

It is even possible to change the colours by heating without sending the film over to the gold-leaf stage. I have a yellow film which local heating has changed to blue and purple in spots. A similar temperature change was noticed with the sodium and potassium films, as I mentioned in my previous paper, which I was unable to explain satisfactorily, since it appeared to be the opposite to what we should expect, if it was due to evaporation, which was the only thing that occurred to me at the time. It now seems as if the changes in both instances could be referred to a partial coalescing of the resonators.

I find a difficulty in reconciling the assumed resonance of the films with their electrical conductivity, but the matter is perhaps less troublesome than the explanation of why gold-leaf transmits any light at all.

Coloured films of a similar nature can be made of silver, by pouring a solution of Carey Lea's soluble allotropic silver on a glass plate and evaporating it over a flame*. Ten parts of the ferrous sulphate solution are mixed with fourteen parts of the sodic citrate solution, to which is then added ten parts of the silver nitrate. The precipitate is allowed to settle, the liquid decanted, and the residue filtered. A small amount of distilled water is next poured into the filter and allowed to run through. More distilled water is now passed through the filter and collected. It will be found to have a very deep red colour, and if a small amount be spread over a clean glass plate and evaporated, it leaves a film which appears deep red, purple, and blue by transmitted light. The reflected light is of a complementary tint, the purple film reflecting green, and the red a greenish blue.

Ligroin changes the optical properties of the film, though the change is only to be seen when a nicol is used, and even then it is not very pronounced. I feel pretty certain that I have detected traces of a granular structure in these silver films with the microscope, and hope to confirm the observation as soon as a more perfect objective is at my disposal.

An investigation of the dispersion of the films, which I intend to take up next, and a more careful study with polarized light, will doubtless throw further light on the matter.

Baltimore, Md., U.S.A.,
May 30, 1902.

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* American Journal of Science, vol. xxxvii. p. 476 (1889).

XLVIII. *On the Magnetic Change of Length and Electrical Resistance in Nickel.* By W. E. Williams, *B.Sc.*[*]

IT is well known that the length of a nickel wire is diminished, while its electrical resistance is increased, by longitudinal magnetization. The first of these effects has been investigated by Bidwell[†], Nagaoka[‡], and Taylor Jones[§], and the second by Tomlinson[||] and Barlow[¶].

If these effects are represented in curves showing the change of length, or resistance, as a function of the magnetizing field, it will be found that the two curves bear a very striking resemblance to each other. This is well shown by the similarity in form of the hysteresis curves of the two effects given by Nagaoka and Barlow.

It was suggested by Prof. Taylor Jones that I should investigate further the relation between these two effects, and the experiments described below were undertaken for that purpose.

As both effects vary considerably for different specimens and even for the same specimen at different times, it was thought necessary to measure both changes in the same piece of wire, as nearly as possible at the same time and under the same conditions.

Apparatus.—The magnetizing field was furnished by a solenoid 1 metre long, giving a field of 50 C.G.S. units per ampere, the maximum field used being 420 units. This coil was fixed vertically in a wooden framework.

The experiments were made on a nickel wire ·12 mm. diameter and 80 cms. long. Its ends were soldered to two thick brass rods, the lower of which was firmly clamped to the wooden plank on which the coil rested, the other being held up by means of a lever. The tension of the wire could be altered by placing weights on the other end of this lever.

Between the brass rods and the inner tube of the solenoid were placed two brass tubes, which formed the terminals of the copper wire used for comparison of resistance, this wire also being within the solenoid. The coil was provided with a water-jacket through which a current of cold water was kept constantly flowing. The wires were further protected from the heating effect of the current by means of a glass tube, in which they were inclosed. The wires and terminals were, of course, well insulated from each other and from the coil, and

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[*] Communicated by Prof. E. Taylor Jones.

[†] Bidwell, Proc. Roy. Soc. vol lv. p. 228.

[‡] Nagaoka, Phil. Mag. vol. xxxvii. p. 131.

[§] Taylor Jones, Phil. Trans. 1897.

[||] Tomlinson, ibid. 1883, p. 1.

[¶] Barlow, Proc. Roy. Soc. 1902.

care was taken to prevent them touching each other, as this was found to impede the motion of the nickel wire, and to affect the accuracy of the measurement of the change of length.

The change of length was measured by the well-known lever and mirror method, the short arm of the lever pressing upwards against a projecting piece attached to the upper end of the nickel wire. The lever ratio was 15, and the total magnification 18,000. The maximum deflexion obtained on the scale was about 50 cms., which could be easily read to a millimetre.

The change of resistance was measured by means of a slide-wire bridge. The bridge-wire was of german-silver, 2·75 mm. diameter, with a resistance of ·000361 ohm per cm.

The resistance of the nickel wire was 2·5 ohms, and that of the copper wire used for comparison was 2·6 ohms. The nickel and copper wires were connected in the outer gaps of the bridge, and two auxiliary coils* of german-silver wire of about the same resistance were connected in the inner gaps. These were placed together in an oil-bath in order to maintain them at the same temperature. The connexions were made by thick copper rods, soldered to the brass terminals of the wires, except in the case of the free end of the nickel wire, where a short piece of flexible wire was used.

The change of resistance in nickel at the highest fields used is about one per cent., and this corresponds to a step of 40 cms. on the bridge.

The ends of the nickel wire being at opposite ends of the magnetizing coil the thermoelectric E.M.F. was generally very considerable. It is easily seen, however, that it does not produce an appreciable error in the measured change of resistance (owing to the relatively small value of the effect) provided that the E.M.F. is constant during the time of taking the two readings. In order to secure this it was found necessary to allow the current to flow constantly through the bridge circuit.

The error arising from this cause, and also from the heating effect of the magnetizing current, was further diminished by taking the readings rapidly. In order to facilitate this, two sliders were used on the bridge, connected to the galvanometer by a double key, so that either slider could be used at will. One slider was used to balance when the magnetizing current was on, and the other when it was off. In this way it was found possible to arrange so that the zero did not change appreciably during the time of taking a reading.

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* *Cf.* Gray and Taylor Jones, Proc. Roy. Soc. vol. lxvii. p. 208.

In all the experiments a curve of ascending reversals was first found, and then the residual effect was found separately, and the two added to get the curve of total change of length or resistance. This method has the advantage that the zero reading can be found before and after each separate reading, and it can be ascertained whether it has changed in the interval. The residual effect is comparatively small, and the curve is a straight line for the greater part of its length.

The magnetic change of resistance was calculated from the formula

$$\frac{\delta R}{R}=\frac{(S+R+100\sigma)\delta x}{R(S+x\sigma)},$$

where R is the resistance of nickel wire,
S is the resistance of copper wire,
σ is the resistance of bridge-wire per cm.,
x is the reading on the bridge.

The results obtained are shown in the following tables and the accompanying curves.

TABLE I.—Change of Resistance for Various Loads.

$\frac{dR}{R}\times 10^4$. Load in grammes.

H.	0.	50.	100.	300.	500.	700.
10	3·0	1·5	1·0	·8	·5	0·0
20	10·5	7·8	6·0	3·6	2·1	·4
30	18·5	15·7	13·5	7·5	4·5	·8
50	31·2	30·0	26·1	15·5	9·6	3·3
75	45·3	39·6	40 8	25·8	17·4	7·2
100	55·2	55·5	53·4	37·2	27·3	14·4
150	69·6	72·6	72·0	59·6	47·1	24·3
200	78·0	83·1	84·7	78·0	66·0	40·2
250	83·7	91·2	92·7	94·9	83·4	55·5
300	88·8	97·7	99·0	102·3	103·3	69·9
350	93·0	102·9	108·0	...	114·6	84·6
400	96·3	107·4	...	...	124·8	101·8

Table I. gives the change of resistance for different loads ranging from 0 to 700 grammes. The corresponding curves are shown in fig. 1, the ordinates being the change of resistance $\frac{dR}{R}\times 10^4$ and the abscissæ the magnetizing field in C.G.S. units. It will be noticed that these curves cross each other, which, as is well known, is not the case with the magnetization curves for these loads.

Fig. 1.

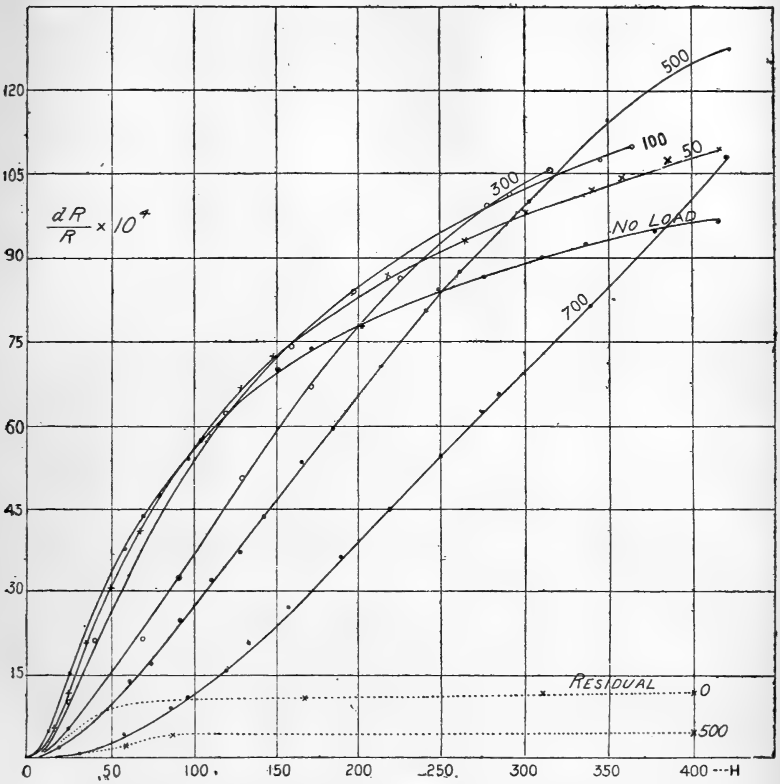
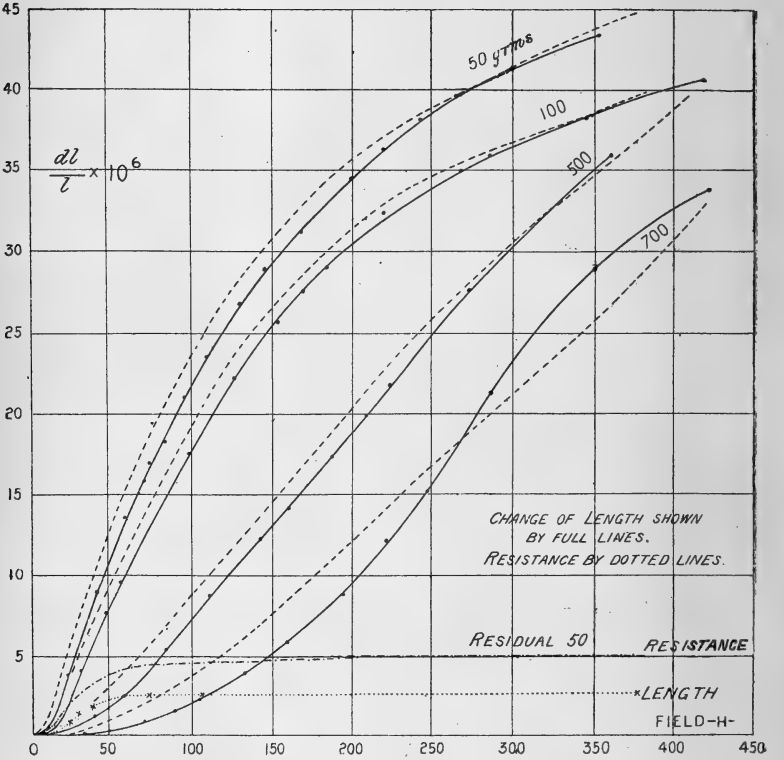


TABLE II.—Comparison of Change of Length and of Resistance for Various Loads.

H.	50 grammes.		100 grms.		500 grms.		700 grms.	
	*d*L.	*d*R × ·42.	*d*L.	*d*R × ·36.	*d*L.	*d*R × ·3.	*d*L.	*d*R × ·3.
10	·3	1·5	·1	·4	·0	·1	·0	·0
20	2·5	4·0	1·1	2·0	·1	·5	·0	·1
30	5·6	7·0	3·5	4·8	·5	1·4	·1	·3
50	10·9	12·5	8·1	10·4	1·9	3·0	·3	1·0
75	16·8	18·5	13·5	14·6	4·4	5·7	1·0	2·1
100	21·9	23·5	17·7	19·3	7·2	8·4	1·8	3·6
150	29·5	30·6	25·2	26·3	13·0	14·5	4·8	7·5
200	34·7	35·5	30·5	31·2	18·7	20·3	9·3	12·0
250	37·7	37·7	34·1	34·6	25·0	25·7	15·5	16·7
300	41·2	41·2	36·5	36·9	30·5	30·3	23	21·3
350	43·3	43·6	38·5	38·7	35·3	34·6	28·9	26·2
400	...	...	40·0	...	...	38·5	32·7	31·3

In Table II. the columns headed *d*L give the change of length in millionths of the length of the wire, and the adjacent columns headed dR give the change of resistance for the same loads, the numbers of Table I. being multiplied by a factor, as shown in the table. This factor is chosen so as to bring both changes into agreement for a field of about 300. These results are plotted graphically in fig. 2. The

Fig. 2.



full lines represent the change of length and the dotted lines the change of resistance. The two residual curves are given for a load of 50, and are on the same scale as the corresponding curves for the total effect.

It will be seen from the diagram that for the loads 50, 100, and 500 the two sets of curves very nearly coincide, and that the discrepancy between them may be regarded as arising almost wholly near the origin. The residual change of resistance is considerably greater than the residual change of length, but the general shape of the curves is the same in both cases.

It will be noticed, however, that the ratio of the change of resistance to the change of length is different for different loads, so that different factors have to be used in bringing them into agreement, showing that the effect of loading is different in the two cases. This is also seen by comparing the set of resistance-curves in fig. 1 with the length-curves in fig. 2.

As may be seen by a comparison of the curves given by Nagaoka and Barlow, there is no similarity between the curves of change of length and change of resistance in iron.

The change of length is in this case different in sign at high and at low fields, being a contraction in the former and an elongation in the latter case. There is no such change of sign in the change of resistance. It may be conjectured that this is in some way connected with the Villari reversal which occurs in iron, and this view is perhaps supported by the fact that there is a similar reversal in nickel at very low fields*, where, as mentioned above, the greater part of the discrepancy shown by the present experiments arises.

The experiments were made in the Physical Laboratory of the University College of North Wales, and I desire to express my best thanks to Prof. Taylor Jones for placing the necessary apparatus at my disposal, and also for many suggestions made in the course of the work.

Bangor, July 1902.

W. M. G.
V. T. G.

XLIX. *The Chemical and Geological History of the Atmosphere.* By JOHN STEVENSON, *M.A., F.I.C.*†

II.—*The Composition and Extent of the Atmosphere in very Primitive Times.*

IN my former paper (Phil. Mag., Sept. 1900, p. 312, and Oct. 1900, p. 399) it was shown that there was good reason to believe that there was no free oxygen in the primitive atmosphere of the earth, and even that reasons could be given in favour of the view that considerable quantities of hydrogen or of hydrocarbon gases were present in the primitive atmosphere. We estimated that if the crust of the earth contained on the average $\frac{1}{10}$ of 1 per cent. of carbonaceous matter, there would be as much of such oxidizable matter in each half-mile thickness of the crust of the earth belonging to the continental and transitional areas as

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* Heydweiller, Wied. *Ann.* vol. lii. p. 228 (1894).

† Communicated by the Author.

would be equivalent to the whole of our present free oxygen; and as the continental and transitional areas occupy only about one-half of the surface of the earth, it is obvious that there would be as much carbonaceous matter in each $\frac{1}{4}$-mile thickness of the whole of the earth's crust (or each shell or layer of the crust $\frac{1}{4}$ mile thick) as would be equivalent to the whole of our present free oxygen, if the rocks underlying the great oceans should also contain $\frac{1}{10}$ per cent. of carbonaceous matter. We know practically nothing on this last point, but as regards the continental and transitional areas it is highly probable that the average percentage of carbonaceous matter is greater than $\frac{1}{10}$, and that the rocks containing carbonaceous matter have a much greater thickness than $\frac{1}{2}$ mile. Further, there is a considerable quantity of sulphide of iron present in many rocks, and this has probably been formed by the reducing action of carbonaceous matter on sulphates. All these circumstances point (as was explained in the paper) to the probable existence of an atmosphere in very ancient times containing much hydrogen or hydrocarbon gases, and if we knew the exact quantity of carbonaceous matter derived from organic remains, and also of sulphide of iron produced by the reducing action of organic remains, we might hope to be able to make some estimate of the ancient atmosphere or of the quantities of hydrogen or hydrocarbon gases present in it. But the above data, even if they were ascertained with a fair degree of completeness, would still be insufficient for our purpose, as the question is complicated by other considerations. We must on the one hand allow for free oxygen that has been removed from the atmosphere and absorbed or fixed in the ground through the oxidation or peroxidation of various substances, especially the protoxide and the sulphide of iron; and on the other hand we ought to allow for carbonaceous matter which may have been destroyed in the course of geological history, but in such a way that its former existence would have an important bearing on our inquiry.

As regards the quantity of oxygen used up in oxidizing iron compounds, it was calculated by Ebelmen, about 1845, that if all the sesquioxide of iron on the earth was originally protoxide, there must have been at least as much oxygen abstracted from the atmosphere to effect the peroxidation as there still is of free oxygen in our atmosphere. This estimate is confirmed, and more than confirmed, by Messrs. Clarke and Hillebrand's series of rock-analyses published in Bulletin 148 of the United States Geological Survey (Washington, 1897), from which Mr. Clarke calculates that the average quantity of ferric oxide (sesquioxide of iron) in known rocks is 2·65 per cent. If this were all originally protoxide of iron it would require to effect its peroxidation for each half-mile thickness of the earth's crust belonging to the continental and transitional areas, or for each $\frac{1}{4}$-mile thickness of the whole of the earth's crust, a quantity of oxygen equal to the whole quantity in our present atmosphere. Also it may be noted that the oxygen required to produce 2·65 per cent. sesquioxide of iron from protoxide is very nearly equivalent to 0·1 per cent. of carbon, that is, there would require to be this amount of carbon or carbonaceous matter in the ground to balance the oxygen that has been removed from the atmosphere in the oxidation of the protoxide of iron.

Besides peroxide of iron, the binoxide of manganese found in the ground has probably been peroxidized by atmospheric free oxygen, but it may be passed over on account of its comparatively small quantity. But besides peroxides there is a very considerable quantity of sulphates found on the earth, and these have very probably been formed through the oxidation of sulphides by free oxygen. Clarke and Hillebrand estimate the quantity of anhydrous sulphuric acid (SO_3) which is found combined with lime and other bases in the crust of the earth at 0·06 per cent. of the total rocks present. The quantity of oxygen (viz. 0·036 per cent.) represented in this percentage, being only about one ninth of that required to produce the sesquioxide of iron (referred to above) from protoxide, may be passed over, but besides the sulphates found in the solid crust of the earth, there is a very considerable quantity found in the sea. Prof. Dittmar (see *Encyclopedia Britt.*, 9th ed.) estimated the sea to contain 2192×10^{12} tons $MgSO_4$, 1666×10^{12} tons $CaSO_4$, and 1141×10^{12} tons K_2SO_4, which are equivalent to a total quantity of 2994×10^{12} tons SO_3 (anhydrous sulphuric acid). The oxygen present in this, viz. 1776×10^{12} tons, is considerably greater in amount than the total free oxygen of the atmosphere (viz. 1200×10^{12} tons). It is no doubt possible that the sulphur present in the above sulphates may have always existed in combination with oxygen, but this is not very probable if there was originally a considerable excess of oxidisable elements relatively to oxygen itself on the earth. For the same reason we may infer that the sulphur of the sulphide of iron which has been formed from sulphates by the reducing action of organic matter has in the course of such a reaction only returned to its original form of combination, and should therefore be left out of account in calculations regarding the composition of the primitive atmosphere. In any case we must admit that the large quantities of sesquioxide of iron and of sulphates found on the earth form a very formidable counterpoise to the carbonaceous matter, and therefore weaken to a very considerable extent the position taken up in my first paper regarding the history of free oxygen. But on the other hand there are certain considerations which tend to strengthen the position very materially. It is quite possible that in the treatment of this question allowance should be made for carbonaceous matter which formerly existed on the earth, but which has been destroyed in the course of geological history, for notwithstanding its destruction, its former existence and the mode of its destruction might have an important bearing on the question before us.

It is obvious that coal and similar carbonaceous matters would undergo great changes if the strata containing them should become highly heated, and that they would even be destroyed or disappear if they should be highly heated in contact with oxide of iron and certain other metallic oxides. In that event the carbon would be converted into carbonic oxide or carbonic acid, and the metallic oxides would be reduced to the metallic condition, or at any rate to compounds containing a smaller proportion of oxygen than before. At first glance one would be inclined to say that this reaction cannot have taken place to any great extent in the course of geological history on account of the comparative rarity of native metallic iron and other free metals, but a little reflection will show that the reaction may quite possibly have taken place on a large scale in very early times, though little or none of the metallic iron then produced may be now visible. It is obvious that when the rocks became heated up to the point at which the metallic oxides present were reduced to the metallic condition the rocks would either be fused or would be not far from the fusing-point, and if reduction should sometimes have taken place before fusion, still the process of heating would probably, in most cases, be continued until fusion also took place, and in that case the metallic iron or other metals produced would sink down through the melted rock-mass. If this melted mass should be very great or deeply-seated within the crust of the earth, the metal might sink to such a depth that it would never afterwards be brought by geological changes sufficiently near the surface of the earth to come within the range of human observation.

Fortunately for the purposes of this inquiry there are sufficiently substantial data from which to make some inferences as to the probability of the reaction having taken place in very early times, and even roughly to estimate the extent to which it may have taken place, or at least there are certain observed facts which may be explained by means of the foregoing theory. These data or facts have reference to the chemical composition of rocks at varying depths of the earth's crust, or perhaps more properly the composition of very ancient rocks as compared with that of those which are regarded as being more modern. It is well known that the oldest rocks, or those which are regarded as the oldest, are much more basic than comparatively recent rocks, in fact the ancient rocks are frequently called "basic," and the more recent rocks "acidic." There is, so far as I am aware, no exact line of demarcation or exact definition of the terms, but, generally speaking, rocks or minerals which, like the supposed ancient rocks, contain about 55 per cent. of bases and only 45 per cent. of silica are called "basic," while rocks or minerals which, like the bulk of more recent rocks, contain about 60 per cent. or more of silica and only 40 per cent. or less of bases, are called "acidic." Now this difference in the composition of ancient and comparatively recent rocks may quite well have been brought about in the course of geological history. According to the usually accepted theory, the earth was so hot in very early times as to be in the liquid condition, and also according to accepted theories, the tides were very high and energetic in those early times. Under these circumstances, the materials which now constitute the crust of the earth must have been well mixed, and therefore the composition of the liquid mass (at any rate in its upper part, containing as it probably did materials that were mutually miscible or had sufficient chemical affinity to combine with each other and produce compounds that were mutually miscible) must have been fairly uniform throughout. Indeed it should have been quite comparable, as regards uniformity of composition, with the composition of the sea at the present day. There would therefore be no distinction of basic and acidic rocks at that period. The proportion of silica and of bases would be uniform throughout the mass. But when the earth cooled sufficiently to become solid, or to permit of the formation of a hard crust on the surface, natural operations might very well have brought about the great variety that is now observed in the composition of rocks. The primitive atmosphere, as we shall see in the course of this paper, most likely contained very large quantities of carbonic acid. This carbonic acid, acting along with water or aqueous vapour on the primitive crust, would soon decompose the rocks, forming carbonates, hydrates, and free silica or rock-forming materials containing a much higher proportion of silica than the original rock-mass of the earth. There may also have been a very considerable quantity of hydrochloric acid in the primitive atmosphere or ocean, which of course would also act on the crust with the formation of chlorides; but as the total quantity of chlorides on the earth is very small in comparison with that of carbonates, they may for our present purpose be left out of account. Now if we were to add to modern acidic rocks the bases (chemically speaking) of the rocks composed of carbonates, oxides, and hydrated oxides that are found interspersed with them, or if we were simply to imagine them all to be fused together, the resulting mass of silicate rocks would obviously be less acidic and more basic than it was previously, though possibly it might not be so basic as the deep-seated primordial rocks, which are technically called "basic." Indeed, we may be quite sure that it would not, for it is well known that sandstone or free silica is very much more abundant than limestone, and even in the English Oolitic system, which is comparatively rich in limestone, Prof. Phillips estimated that there was three feet of sandstone for one foot of limestone. If then the total limestone of the earth bears such a small proportion to the total sandstone, it is evident that if the materials composing the upper part of the crust of the earth were all fused together the composition of the resulting mass would still be acidic when compared with that of the older or primordial rocks lying lower down. Therefore, if the whole rock-mass of the earth was at one time uniform in composition or homogeneous throughout, a portion of the basic constituents must have been abstracted from the materials which now constitute the upper part of the crust. The principal bases in both basic and acidic rocks are alumina, lime, magnesia, oxide of iron, potash, and soda. Of these, oxide of iron is the base, the deficiency of which in acidic rocks is most pronounced when compared with its percentage in basic rocks. Indeed, it is possible that the other bases being so largely represented by carbonates, chlorides, and sulphates may not be deficient at all, though this is rather doubtful, as we shall see later on; but in any case there would be required a fuller knowledge of the subject than we at present possess to enable us to answer this part of the question definitely. In the case of iron, however, the difference is very marked. Basic rocks contain from about 5 to 30 per cent. of oxide of iron, the average amount being probably at least 8 per cent., and that principally in the form of protoxide of iron. Acidic rocks, on the other hand, contain on the average only some 2 or 3 per cent.

of oxide of iron, and that mostly or very largely in the form of sesquioxide of iron. We may therefore conclude that basic rocks contain on the average about 6 per cent. more of oxide of iron than the more recent acidic rocks.

Now this difference in composition may quite well have been brought about by the action of carbonaceous matter at a high temperature on basic rocks or on the materials derived from them by ordinary disintegration and denudation. The formation of metallic iron by volcanic or plutonic agency is not only conceivable but is very highly probable. The molten or heated materials lying beneath volcanoes no doubt consist in many cases to a large extent of what had been sedimentary rocks, containing among other things oxide of iron and carbonaceous matter, which, when heated together, would react on each other, forming carbonic acid (or carbonic oxide) and metallic iron. Even if the oxide of iron and the carbonaceous matter should not have been in direct contact with each other at first, they would be brought into contact by the agitation caused in the mass by the evolution of carbonic acid from carbonates, of steam from clays, shales, and other hydrated rocks, and of hydrocarbon gases and carbonic oxide from the carbonaceous matter itself, while in some cases the hydrocarbon gases and carbonic oxide might themselves be able to effect or at least to assist in the reduction of the oxide of iron. The production of metallic iron is therefore just what we might expect as one of the results of volcanic action, and if iron of volcanic origin has not yet been met with, or only to a very insignificant extent, this circumstance may be explained by the sinking of the iron down into inaccessible regions, or by its subsequent oxidation through exposure to the action of atmospheric free oxygen. Native iron in small quantities has been observed in many localities in both Europe and America, especially in granitic and basaltic rocks. Metallic iron has even been known to be produced in France by a fire in a coal-mine, from which we may infer that if the materials existing in that mine were heated up in a volcano, a considerable quantity of metallic iron would be produced. Further, when we reflect that there must be many coal-bearing regions in the world where the percentage of carbonaceous matter over large tracts of country, and down to very considerable depths, amounts to 1 per cent. and upwards, the reasonableness of our standpoint is quite apparent. In the deep bore at Paruschowitz, in Silesia, which is 2003 metres deep, 83 seams of coal, having a total thickness of about 90 metres, have been met with. This makes the thickness of the coal 4·5 per cent. of the total depth, and the weight of the coal about 2·25 per cent. of that of the total rocks present; and of course there might be a large quantity of thinly-disseminated carbonaceous matter in addition to the coal itself.

There is, therefore, nothing very fanciful or far-fetched in this theory about the production of metallic iron by volcanic action, but of course the question as to whether the reaction has taken place on a scale sufficiently great to affect the composition of the whole of the upper crust of the earth to a great extent is a very wide and somewhat difficult one, involving as it does a number of important considerations. In particular the occurrence of the reaction to such an extent would require a truly enormous quantity of coal or carbonaceous matter to effect the reduction of the oxide of iron. Let us suppose that the acidic or upper and altered part of the crust of the earth is on the average 10 miles thick, and that it is composed of rocks having an average specific gravity of 2·6. Its weight in that case would be about 20×10^{18} tons, and if 6 per cent. oxide of iron has been removed from it by reduction with carbonaceous matter, the quantity of oxide removed would be $1{\cdot}2 \times 10^{18}$ tons; and this would require for its reduction about $0{\cdot}1 \times 10^{18}$ tons carbon, or fully 200 times as much as would be required to combine with and use up the total free oxygen of our present atmosphere. It is obvious that such a quantity of carbonaceous matter would take an extremely long time to produce by the growth of vegetation and the deposition of coal or bituminous matter in the ground at anything like the rate at which these natural operations are carried on at present. If the average percentage of carbonaceous matter in the crust of the earth should be only $\frac{1}{10}$ of 1 per cent., and should have been only $\frac{1}{10}$ of 1 per cent. during the whole of geological history, it would take a series of sedimentary strata 50 miles in thickness all over the earth to give the amount required. Then if we assume (as is most probable) that the ordinary geological operations of denudation and deposition have been confined to the rocks that lie within a comparatively short distance from the surface of the earth, say a layer or outer crust not exceeding 10 miles in thickness, then the whole of the materials composing this crust would require to be denuded away, redeposited, and heated to fusing-point or thereby no less than five times in the course of geological history. This supposition is hardly credible, but still it is quite possible, not only that the proportion of carbonaceous matter is greater than $\frac{1}{10}$ per cent. in the present crust of the earth, but also that it was very much greater in very ancient times.

It is generally supposed that there was comparatively little coal deposited in pre-carboniferous epochs, but this is a mistaken idea ; at least there is a great abundance of carbonaceous or bituminous matter in the rocks of these epochs, though it may not be available for use as coal. In both Devonian and Silurian rocks in certain parts of America there are thick strata of bituminous shale and of limestone rich in bituminous matter and organic remains; and the Laurentian rocks of Canada contain so much graphite that (according to Sir W. Dawson) their average percentage of carbonaceous matter must be at least as high as that of the rocks of the carboniferous epoch. We have therefore no evidence to lead us to suppose that there was less vegetation growing or less coal deposited on the earth in the Laurentian epoch than in subsequent epochs, and we know from the presence of much ferric oxide in the rocks of that period that there must have been free oxygen in the earth's atmosphere. The conditions therefore as regards the presence of free oxygen on the earth, and (inferentially) the decay or eremacausis of vegetable remains, must have been similar to those of the present day, and probably only a small proportion of the vegetation of that epoch would be preserved in the form of coal or graphite. But, as is evident from Dr. Phipson's experiment on the growth of plants in various gases, vegetation might quite well have grown on the earth in the periods anterior to the existence of free oxygen.

In the absence of free oxygen the remains of the vegetation would not be subject to eremacausis, and would therefore be preserved (for a considerable time at any rate) in the form of coal or graphite or mineral carbonaceous matter of some description. Obviously then it would require a very much shorter time under these conditions to produce $0 \cdot 1 \times 10^{18}$ tons of coal than it would under modern conditions when probably less than 1 per cent. of vegetable remains is preserved as coal or carbonaceous matter. In fact the time required to produce our $0 \cdot 1 \times 10^{18}$ tons of coal would come within quite reasonable or credible limits, for it is surely not unreasonable to suppose that the ordinary geological operations of denudation and deposition have been going on for a period at least two or three times as long as the time that has elapsed since the earlier part of the Laurentian epoch, and a period of this extent is probably long enough under the conditions above specified to produce $0 \cdot 1 \times 10^{18}$ tons of coal or other carbonaceous matter as the result of vegetable growth. This quantity is equivalent to about 0·5 per cent. of the weight of the whole crust of the earth for the first ten miles of its thickness.

But another difficulty in the way of accepting our theory is raised by the question as to whether it is possible or probable that the whole crust of the earth for several miles of its thickness should be heated after its first solidification to a temperature sufficiently high to produce metallic iron from oxides and silicates and other compounds of iron through the reducing action of carbonaceous matter, and also to liquefy the rocks so as to allow the metallic iron to sink down to an inaccessible depth. We know sufficiently well that all through geological history down to the present day certain portions of the crust—the seats of volcanic action—have been heated to this extent, but as regards the area and depth of these portions or regions, and the quantity of material heated in each case, our information is very limited. However, judging from what we may roughly infer regarding the prevalence of volcanic action both in our own times and in past geological history, we should say that the total amount of volcanic action has probably *not* been sufficient to heat up the whole crust of the earth to the extent required for our theory. At any rate, we should say with a fair degree of certainty that the total volcanic action on the earth, as inferred from geological observation, would not be sufficient to heat up the whole crust of the earth (in portions at a time of course) *repeatedly* to the fluid condition, as would require to be the case if the amount of carbonaceous matter has always averaged considerably less than ½ per cent. But on the other hand it is quite possible that the conditions affecting the prevalence of volcanic action or heating operations were very different in very ancient times from what they have been during known geological epochs. When the surface of the earth first became solid the underlying rocks must have been very hot, perhaps liquid in many places; but even if they were solid they must have been near the fusing-point, and therefore volcanic effects must have been more easily produced then than now. Further, the low degree of conductivity for heat possessed by ordinary rocks has, at this point, an important bearing on the question before us. Lord Kelvin in his essay on the 'Age of the Earth' gives expression to the opinion that vegetation or some kind of organic life may quite well have begun very soon after the surface of the earth first became solid, and it is easy to see that any vegetable or other organic remains deposited in those very early epochs would not have much chance of remaining in a comparatively unaltered condition for a great length of time, as the sedimentary rocks of that epoch would be liable to be heated to a high temperature within a comparatively short period after their deposition. Also we should expect that the metallic iron produced by the heating of the organic or carbonaceous matter present in those deposits along with oxide of iron and other iron compounds also present would sink deep down—possibly as a rule to inaccessible depths. It should also be remembered when discussing the question of the production of the heat necessary for our theory, that the combination of the carbon or organic matter with the oxygen of the iron compounds would probably tend to raise the temperature of the mass to an appreciable extent, and that the long time during which the materials would be heated together, or even the long time during which the iron compounds would be heated in the presence of reducing gases derived from the destructive distillation of the organic matter, would be in favour of a more thorough reduction of the iron compounds to the metallic condition than we should expect to take place if the very same materials were heated for a short time in a modern blast-furnace. Another point worth noting is that the reduction of oxygenated iron compounds by carbonaceous matter may have taken place, at all epochs and on a very large scale, in the presence of sulphur compounds at quite ordinary temperatures, and it is also possible that a large quantity of the sulphide of iron produced in this way may have sunk down to an inaccessible depth when the rocks containing it were heated to fusion by volcanic action (or the causes which bring about volcanic action). Of course the disappearance of sulphide of iron in this way involves the question of heating up just as much as reduction to the metallic state would, but still enough has already been said to show that the question of heating does not, or at least need not, put insuperable difficulties in the way of our theory.

Questions regarding the nature of the vegetation or organic life in those very early epochs need not cause any serious difficulty, for organisms of the humblest type, such as diatoms or infusoria, would be sufficient for the purpose. The very obvious difficulty regarding the absence or comparative absence of light at the base of the great atmosphere which we have conjectured, and the probably adverse conditions for the growth of vegetation thereby produced, may be met by asking the question—Why do plants require light to promote their growth? Is it not to decompose carbonic acid and water in order to produce compounds containing a smaller proportion of oxygen? If compounds containing less oxygen were already present in the atmosphere and ocean in abundance, the conditions would be very different, and in these conditions it is quite possible that vegetable growth or organic growth of some kind might go on in the absence of light.

In addition to the difficulties which have just been discussed, there is one to which reference was made in connexion with the argument drawn from the composition of basic and acidic rocks. We stated that if the acidic rocks of the earth's crust, containing as they do 60 per cent. or more of silica, have been derived from a primordial basic rock-mass containing only 45 per cent. (or less) of silica, it is not easy to see what has become of all the missing bases. It should be noted that the quantity of missing bases is even greater than one may at first be apt to infer from the above percentage of silica.

In basic rocks containing 45 per cent. of silica and 55 per cent. of bases, there will be 122 parts by weight of bases to 100 parts of silica, while in acidic rocks containing 60 per cent. of silica and 40 per cent. of bases, there are only 66 parts by weight of bases for 100 parts of silica, or not much more than half the proportion of base relatively to silica found in the basic rocks. Acidic rocks would thus seem to have lost about half the quantity of base which was originally present. If then they have been derived from primordial basic rocks we should expect to find a very large quantity of carbonates, sulphates, chlorides, and hydrated oxides on the earth, or else we should infer that a very large quantity of oxide of iron has been removed, perhaps several times more than the 6 per cent. already postulated. As regards the amount of carbonates &c. we have already remarked that there seems not to be as much limestone (which is the principal carbonate present) as would be equivalent to the sandstone or free silica alone, while the sulphates, chlorides, and hydrated oxides are comparatively small in quantity. There might no doubt be large quantities of carbonates in the rocks underlying the great oceans and these might be accompanied by a comparatively small quantity of sandstone. It is quite reasonable at any rate to infer that considerable quantities of carbonates exist below the great oceans from observations made regarding the evolution of carbonic acid at the bottom of the sea, or at least the presence of carbonic acid in varying proportions at different places in the sea (see Prof. Dittmar's figures on this subject in vol. i. p. 219 *et seq.* (Physics and Chemistry) of the Reports issued in connexion with the 'Challenger' Expedition); and at the same time we should reasonably expect that there should not be much sandstone underlying the great oceans, or at any rate the abysmal regions of the great oceans, on account of the very long period during which they are supposed to have been in existence.

Also, as regards the quantity of oxide of iron removed from the rocks composing the crust of the earth, it is quite possible that it may have been much greater than the 6 per cent. postulated above. If the average composition of the earth as a whole is at all similar to that of the meteorites which fall upon it, and there is some reason to suppose that it is, the percentage of iron present should be very large, and therefore we should not be surprised if the rock-mass forming the earth's crust originally contained very much more than 8 or 10 per cent. oxide of iron. To postulate a considerable addition to the quantity of oxide of iron originally present would no doubt intensify some of the difficulties discussed in the preceding paragraphs, but it would not necessarily make them insurmountable. However, our information with regard to the various data required, viz., the composition of the primordial basic rocks or rock-mass of the earth, and the average composition and total quantity of the acidic and other derived rocks, is too indefinite to admit of them being used as the basis of a decisive verdict either one way or the other. At the same time, it is worth noting that the total quantities of water and carbonic acid (or carbonates) on the earth, so far as they can be estimated roughly, seem to accord fairly well with the requirements of our theory, at least in so far as the question of whether there is enough carbon and hydrogen on the earth to form the carbonaceous matter necessary for reducing the oxide of iron is concerned. The quantity of carbonic acid on the earth as inferred from Dr. Sterry Hunt's estimate of the carbonates present, viz. enough to form an atmosphere 200 times greater in extent than our present one, may be taken roughly at $1{\cdot}4 \times 10^{18}$ tons, which corresponds to about $0{\cdot}38 \times 10^{18}$ tons carbon. As we have already estimated that the quantity of carbonaceous matter which would be required to remove 6 per cent. of oxide of iron from a shell of the earth's crust ten miles in thickness would be $0{\cdot}1 \times 10^{18}$ tons, it is obvious that there is more than enough carbon on the earth, if it formerly existed in the unoxidized condition, to effect the reduction in question, and indeed that there is enough to remove fully 20 per cent. of oxide of iron from a shell of the earth's crust ten miles thick even if each particle of carbon took part only once in the reaction. And besides the carbonic acid there is a very large quantity of water on the earth, even larger than the quantity of carbonic acid as estimated above and containing a larger proportion of oxygen. If a large proportion of the hydrogen of the water originally existed in the unoxidized condition, either quite free or in combination with carbon or other elements, there would obviously be ample materials for reducing a very large quantity of oxide of iron to the metallic condition. No doubt we should hardly expect, even if there was a great deficiency of oxygen on the earth relatively to the other elements, that all the carbon and hydrogen would be originally unoxidized, but still after all it is only a comparatively small proportion of the total quantity of these elements that our theory requires to have been present originally in the unoxidized condition, something like $\frac{1}{4}$ or $\frac{1}{10}$ or even considerably less. We need not therefore go further into detail on this point, but it may be well to state again how we conceive that the hydrogen or other oxidisable gas, present by our hypothesis in the primitive atmosphere, gradually disappeared. We assume that vegetation or organic life of some description could grow and flourish in such an atmosphere, and that it may possibly even have derived nourishment from the hydrogen or hydrocarbon gases or perhaps also carbonic oxide (CO) which may have been present. The coal or carbonaceous matter formed from the remains of these vegetables or organisms would eventually become heated along with materials containing oxide of iron, with the resultant formation of metallic iron and carbonic acid. If the hydrocarbon gases and carbonic oxide of the primitive atmosphere were absorbed directly by vegetation (or the organic life of the time) they would gradually come to be used up and disappear, and after that period carbonic acid alone would supply the carbon required for vegetation or organic growth. The use of carbonic acid would involve the liberation of oxygen, but as long as free hydrogen existed in the atmosphere the oxygen liberated would be taken up by the hydrogen and water formed. If carbonic acid was necessary from the very first for the support of life, there would probably be oxygen evolved from the very earliest period, and this oxygen would for a long time be used up in oxidizing the hydrogen, hydrocarbon gases, and carbonic oxide or whatever oxidisable gases may have been present.

Whatever may be thought of the above theory and the arguments adduced in support of it, we may be tolerably sure that if the primitive atmosphere did not contain hydrogen, hydrocarbon gases, or carbonic oxide it must have contained a very large quantity of carbonic acid gas. It is quite obvious that if the rocks composing the crust of the earth were heated until they became liquefied, the limestone and other carbonates which are present in enormous quantities would be decomposed, with the result that silicates would be formed and carbonic acid set free. Similarly we may infer that if the earth was all highly heated and liquid in very ancient times, there could not be any carbonates present such as we find now, and therefore the carbonic acid now found in them in the combined condition must have existed at that time in the free condition, unless of course the carbon and oxygen composing it existed in some other forms of chemical combination. The total quantity of these carbonates is very great. Dr. Sterry Hunt, as already referred to, in his papers on the Geological Relations of the Atmosphere, calculated that there was enough CO_2 present on the earth in the form of carbonates to form, if set free, an atmosphere 200 times greater in extent than our present atmosphere. Now it is obvious that an atmosphere of CO_2 of this extent would have a very great influence on many terrestrial phenomena. The terrestrial radiation of heat would be much affected by it, and the temperature of the surface of the earth would be considerably higher than with our present atmosphere. Prof. Arrhenius, of Stockholm, calculates (Phil. Mag. April 1896, p. 268) that if the present small quantity of carbonic acid in the atmosphere (·03 per cent.) were increased 2·5 to 3 times, the temperature in the arctic regions would rise about 8° or 9° C., an amount sufficient to cause very great climatic changes. And if such a (comparatively) small addition of carbonic acid to the atmosphere is likely to cause such a change in the temperature, what are we to infer regarding the influence of a quantity several hundreds of thousands of times greater? Clearly an atmosphere containing such a quantity of carbonic acid or even a considerably less quantity, say one tenth or one hundredth of the above amount, would have a marked effect in retarding the radiation of heat from the earth, and it is therefore quite possible that the rate of the secular cooling of the earth was considerably lower in very early geological times than it is now.

Further, an atmosphere containing much carbonic acid must have had a much more powerful solvent or disintegrating action on siliceous rocks than our present one, and therefore the rate of the formation of carbonates and probably also the rate of general denudation must have been much greater than they are now. The rate of denudation would also be increased, as compared with that of modern times, by the much greater rainfall which we should expect to take place as a result of the greater extent of the atmosphere and the greater quantity of aqueous vapour that it would contain.

It is worth noting here, that the formation of carbonates from silicates (which are anhydrous, or nearly so, in the case of igneous and crystalline rocks) is usually accompanied by the formation of hydrated silicates, and so, in taking a general survey of geological history, we shall find that there has been a fixation, not only of much carbonic acid in the crust of the earth, but of a very large quantity of water as well. This quantity is so great as to represent a very considerable proportion of the total water existing on the earth. Taken along with the moisture or uncombined (hygroscopic) water present in the rocks it may amount to as much as $\frac{1}{3}$ or $\frac{1}{4}$ of the quantity of water present in the ocean itself. Mr. F. W. Clarke in his recent estimate of the average composition of the rocks forming the crust of the earth gives the water at 1·51 per cent., which for a ten miles' thickness of the earth's crust would give a total of about $0{\cdot}3 \times 10^{18}$ tons water. As this estimate seems not to include hygroscopic water, it may be well also to note his earlier estimate (which does include hygroscopic water), viz., 1·96 per cent., a percentage which in a ten miles' thickness of the earth's crust would give about $0{\cdot}4 \times 10^{18}$ tons water, or nearly one third of the water present in the ocean (say $1{\cdot}3 \times 10^{18}$ tons). It is obvious that if this water present in the rocks has been derived from the atmosphere and the ocean, the ocean must have contained considerably more water in ancient times than it does now, and probably covered a greater area of the earth. It is also worth noting that the combined and hygroscopic water present in rocks may be the real or the principal source of the steam which is evolved in such large quantities during volcanic eruptions.

A question of some interest which is naturally suggested here is that regarding the ratio of the quantities of terrestrial hydrogen and carbon to each other. It would be of very considerable interest if the quantities should be found to bear a ratio to each other that could be expressed by such a formula as CH_4, or that of some other hydrocarbon compound. However, if we accept Dr. Sterry Hunt's estimate of the quantity of carbonates on the earth, we shall find that there is not enough carbon to form methane (CH_4 the hydrocarbon which contains the largest proportion of hydrogen) with the hydrogen of sea-water alone. It is no doubt possible that carbon might be present in large quantities in the internal parts of the earth combined with iron and other metals, but of this we have no definite information, and in any case we would naturally expect, as already stated, that a large proportion of the hydrogen and the carbon would be present on the earth in the oxidized condition from an indefinitely early period.

In conclusion we may sum up the results of this paper by saying that the primitive atmosphere was most probably a very extensive one, perhaps a hundred or several hundred times greater in extent than our present atmosphere. It may have consisted principally of carbonic acid, or it may have contained, either in addition to or instead of carbonic acid, large quantities of hydrogen, hydrocarbon gases, and carbonic oxide. At present our information regarding the data bearing on this question is not definite enough to decide the point with certainty, but we may reasonably hope that sufficient evidence will sooner or later accumulate to give a fairly decisive verdict.

L. *On an Improved Form of Coal-Calorimeter.* *By* WALTER ROSENHAIN, *B.A.* (*Cantab.*), *B.C.E.* (*Melbourne*)[*].

THE author recently designed a coal-calorimeter for use in a Works laboratory[†]. In doing so, he was guided in the first instance by an instrument which was shown to him by the courtesy of Professor T. Hudson Beare[‡] at the Engineering Laboratory of University College, London, and the author wishes to acknowledge his indebtedness to Professor Hudson Beare in this matter. The instrument which the author saw at University College had the advantage of great simplicity, but on trial under the somewhat different conditions of a Works laboratory certain improvements suggested themselves, and, after a number of intermediate forms, the present instrument was arrived at. The author was greatly aided in this work by the Cambridge Scientific Instrument Co.

In the present form of coal-calorimeter the Thomson principle is retained[§], and the coal is burnt in a stream of oxygen while inclosed in a chamber immersed in the water of the calorimeter. The calorimeter therefore consists of two essential parts, a vessel for containing the water, and a chamber in which the combustion takes place. The former is a rectangular vessel of sheet-brass, containing about 2½ litres of water, while the latter is much smaller, and is made principally of glass and provided with a set of pipes and valves for the admission of the oxygen and the escape of the products of combustion. As the improve-

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[*] Communicated by Professor Ewing, F.R.S.

[†] Of Messrs. Chance Bros. & Co., Ltd., Glass Works, near Birmingham.

[‡] Prof. Hudson Beare states that this instrument was designed by Mr. Legros, A.M.Inst.C.E.

[§] Wm. Thomson, F.R.S., Journal Soc. Chem. Ind., 29th Nov. 1896.

ments which the author believes he has introduced into the present form of calorimeter are principally connected with the design of the various details of the instrument, a detailed description will be necessary.

The calorimeter-vessel is seen in section in fig. 1. The brass vessel is provided with two opposite windows, which allow of a full view of the interior of the vessel, so that the progress of the combustion in the glass combustion-chamber can be observed. When in use the calorimeter-vessel stands in a wooden casing, as a protection against radiation, and this casing is provided with slots to correspond with the windows in the vessel itself. On the base of the calorimeter-vessel is a lug which forms part of a bayonet-joint by which the combustion-chamber can be fixed in its place within the calorimeter.

Fig. 1.

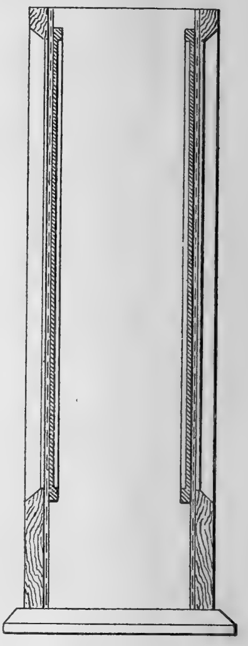

Fig. 2 shows the combustion-chamber in section, as seen in its place within the calorimeter, while fig. 3 is a plan of the same. Fig. 4 shows the combustion-chamber in elevation, placed upon an independent stand when removed from the calorimeter.

In fig. 2 (*a*) is the outer wooden case, (*b*) the brass calorimeter-vessel, (*c*) the bayonet-joint. The combustion-chamber itself is formed by a lamp-chimney—in practice a Jena incandescent gaslight chimney is used—which is closed at top and bottom by means of pairs of brass plates. In each case the outer plate is movable, and can be brought near to the other by means of a screw; a rubber collar is placed between each pair of plates, and this makes a tight joint with the glass when the screws are drawn tight[*]. These are shown in section at (*d d*) fig. 2. In each case the fixed inner plate carries the various attachments. These will be best understood by following the course of the oxygen that flows through the chamber when in use. The gas enters

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[*] It is proper to state that the use of a lamp-glass for this purpose is taken from Prof. Hudson Beare's instrument, but the author has substituted cylindrical gaslight glasses for the curved lamp-chimneys of the former instrument, as the cylindrical glasses are made of more regular shape.

the instrument at the tap (*e*), and flows down the tube (*f*) to the small "rose" nozzle (*g*). After taking part in the combustion of the coal, which is placed at (*h*), the gas leaves the

Fig. 2.

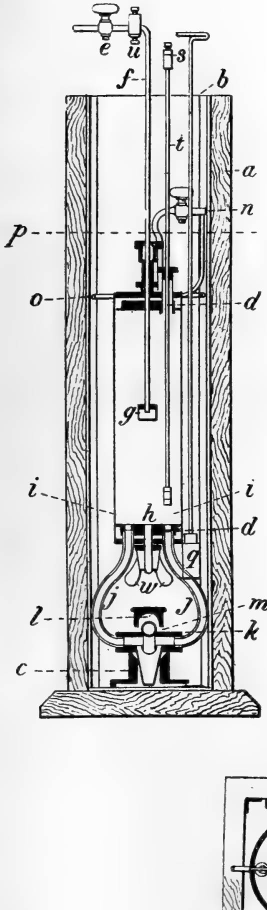


Fig. 4.

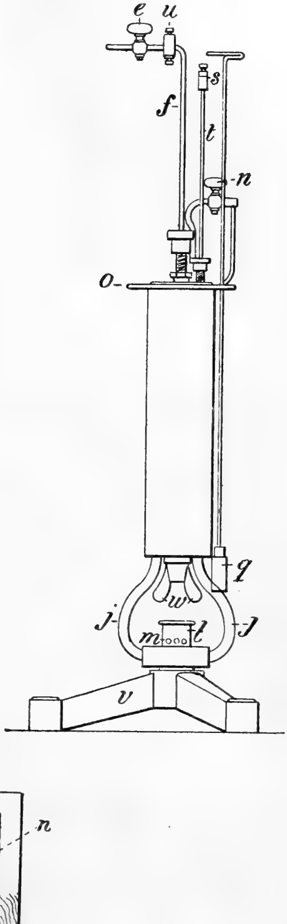
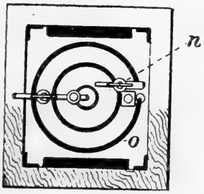


Fig. 3.



chamber by the openings (*i i*), and flows down the tubes (*j j*) to the ball-valve (*k*). Lifting this valve, the gas enters the small chamber (*l*), and escapes into the water of the calorimeter by the small holes (*m*) (see also fig. 4). This continues until the combustion is finished; then the supply of oxygen is cut off, and the tap (*n*) (figs. 2, 3, and 4) is opened. This establishes free communication between the gas in the combustion-chamber and the water of the calorimeter through the small pipe (*o*). As the water-level in the calorimeter when filled for use is at (*p p*), the tap (*n*) is only just above water-level, and the whole of the pipe (*o*) is immersed in the water; any gas escaping by this pipe is thus thoroughly cooled. When the tap (*n*) is open, the water is only prevented from entering the combustion-chamber by the ball-valve (*k*). Such a valve was found necessary to prevent the water from rushing into the combustion-chamber whenever the combustion slackened. At those times the gases in the combustion-chamber would cool and contract so rapidly that the oxygen supply could not keep up the pressure, and, in the absence of a valve, the water often entered and extinguished the combustion. The presence of the valve, however, necessitates a by-pass, which is provided by means of an opening (*q*) in one of the tubes (*j*), which is normally closed by a stopper with a long handle projecting above the water-level. It will be seen that no stirring arrangement is used, as it is found that the vigorous bubbling of the gas from the many small holes (*m*) stirs the water most efficiently.

The combustion is started in the first instance by means of a platinum wire heated electrically. An insulated wire passes down the tube (*t*) from the terminal (*s*); the other terminal is formed by the oxygen inlet-tube (*f*), whose upper end carries the terminal (*u*). Both the oxygen inlet-tube and the lead-tube (*t*) pass through the upper clamping-plates by means of stuffing-boxes which allow the heating-wire to be moved about and also admit of the adjustment of the position of the oxygen inlet.

The stand (*v*) (fig. 4) is provided with a bayonet-joint similar to that on the base of the calorimeter-vessel for the purpose of holding the combustion-chamber when removed from the calorimeter. For the introduction of the sample of coal at the commencement of an experiment, the chamber is placed on this stand and the wing-nut (*w*) is loosened; this allows the lamp-glass and its attachments to be lifted off and replaced when the coal has been put in place. The combustion-chamber, having been screwed up, is then removed from the stand and put into place within the calorimeter-vessel, the water being only poured in after this has been done.

The length of time occupied by a combustion varies with the conditions: with a sample of coal in the shape of a briquette, weighing about 1½ grammes, and containing 7 per cent. ash, the time of a combustion will be about six minutes, and the rise of temperature about $2\frac{1}{2}°$ C., but as the combustion takes place in full view, it can be readily retarded or accelerated by adjusting the oxygen.

In the author's opinion, the present form of coal-calorimeter has certain special advantages, and these will best appear by comparing it with the well-known Mahler-Berthellot "bomb" calorimeter. Certain chemists have stated that the latter form of instrument, in which the coal is burnt, practically instantaneously, in an atmosphere of oxygen under very high pressure (up to 180 lbs. per sq. in.) is alone reliable, as in their opinion * the combustion of coal in a current of oxygen under atmospheric pressure is never complete. Were it possible or necessary to determine the calorific value of coal to an accuracy of 0·1 per cent., then this objection would be perfectly valid, as such combustion is never *perfectly* complete, but such accuracy would in any case be merely imaginary, owing to the varying quality of the coal in various parts of even one truck-load, and the author has found that by observing certain precautions, the combustion in the present instrument can be rendered sufficiently complete for the degree of accuracy required. The most important of the special precautions which must be observed is to provide for a free access of the oxygen to the entire sample of fuel. When the coal is burnt as a powder lying in a platinum crucible, this condition is not fulfilled, as the carbon dioxide formed by the combustion tends to remain in the crucible and to dilute the inflowing oxygen. To avoid this, the author replaces the platinum crucible by a flat tray of porcelain, and uses the sample of coal in the shape of a small cylindrical briquette standing freely on the tray, the briquette being readily formed from the powdered sample by pressure in a mould. The author prefers a porcelain to a platinum tray on account of the feebler heat-conductivity of the former, which therefore does not cool down the layers of fuel in contact with it so rapidly towards the end of the combustion. The author finds that these modifications reduce the time occupied by a combustion to about one half, and at the same time cause a very nearly complete combustion to take place. The only residue is generally a very thin film of tarry matter deposited upon the porcelain tray close to the specimen. To determine the weight of this unburnt residue the following experiments were made. A series of samples of coal were burnt in the calorimeter under working conditions, except that larger quantities

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* Hempel, 'Gas Analysis,' p. 356.

of coal were used to render the measurements more exact; when the combustion itself was over, the sample was in each case removed from the calorimeter without having been brought into contact with the calorimeter-water; this "calorimeter ash" was then dried to constant weight at 130° C., and its weight determined; it was then exposed to oxidation in a muffle, also until constant weight was attained; the difference between the weight before and after the treatment in the muffle was taken to represent the weight of the unburnt residue left by the combustion in the calorimeter, and, as the following table will serve to show, this was in all cases found to be small.

Weight of coal used.	Ash from calorimeter.	Ash after muffle.	Difference (unburnt).	Percentage of "unburnt residue."
2·6019	·3651	·3572	·0079	·30 per cent.
3·4228	·4854	·4790	·0064	·19 "
2·5023	·3420	·3341	·0079	·31 "
1·7865	·2848	·2791	·0057	·32 "

It has also been suggested that in the present form of instrument there is a risk of a small quantity of carbon monoxide being formed and escaping unburnt in the gases leaving the calorimeter. To test this point the author made a number of analyses of the gases leaving the calorimeter during a combustion. For this purpose the valve in the base of the instrument was firmly screwed down by means of a piece of indiarubber packing, and the plug in the opening of the lower outlet-tube was replaced by a glass tube. The gases, therefore, instead of bubbling up through the water of the calorimeter, passed along this tube and through the apparatus arranged for the analysis. The gases were first passed through solutions of caustic potash, to absorb the carbon dioxide, and then through strong sulphuric acid; the only gases which would pass through would be oxygen and any carbonic oxide present; this mixture was then passed through a long tube filled with palladium asbestos, and kept hot during the experiment. Any monoxide present would be oxidized, and its presence and amount observed by the increase in weight of the soda-lime absorption-tubes through which the gases were passed after again drying them. As the entire arrangement was in action before the specimen was ignited, it will be seen that all the gases passed through the apparatus, so that any formation of carbon monoxide, even at the beginning or end of the combustion, would be detected.

The result of a number of such tests was entirely in favour of the instrument, as it was found that when the combustion was properly regulated no carbon monoxide whatever could be detected. Only in one case was any real increase of weight in the absorption-tube observed, and in that case the amount of carbon dioxide obtained corresponded to 0·33 per cent. of incompletely burnt carbon; but in this case the oxygen supply was very badly adjusted, and the combustion was obviously imperfect, a considerable amount of soot being deposited; the experiment was, however, continued in that way in order to test the efficiency of the analysing arrangement, and the result serves to show that the apparatus was quite satisfactory. The author therefore feels justified in stating that any loss of heat due to the escape of partially burnt gases may be disregarded when the combustion is properly conducted *.

As compared with the "bomb" type of coal-calorimeter, the present form of instrument has certain obvious advantages. One of these is greater simplicity and cheapness; no high pressures have to be resisted, and no explosions can possibly occur. Further, the combustion takes place in full view, and can be watched and regulated throughout, and the combustion takes place under conditions rather more like those of actual practice than explosive combination under great pressure. The operator has therefore a means of judging the behaviour of the coal as regards coking and clinkering which is not afforded by the other instrument. But the strongest objection to the "bomb" instruments is that in them the combustion takes place in a closed vessel having thick walls; the heat must therefore penetrate these walls and be transferred to the water of the calorimeter by conduction alone, and it is probable that a considerable time must elapse before the water has taken up sensibly the whole of the heat. In the present instrument the water is admitted at the end of the combustion to the interior of the combustion-chamber, and thus has every opportunity of taking up the whole heat quickly.

With the large bulk of water and the small rise of temperature used in the present instrument, the radiation correction is very slight; with a temperature-difference of 2° C. the rate of cooling is about 0°·001 C. per minute, and the value of the correction can be readily found in any of the

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* The thanks of the author are due to his senior assistant, Mr. W. J. Rees, for help with these experiments.

usual ways ; it is, however, necessary to ensure the constancy of temperature of the stream of oxygen passing through the instrument. When the supply is taken from a cylinder the gas is apt to be cold, and should be passed through a coil of tubing to attain the temperature of the room, and finally bubbled through a wash-bottle containing a thermometer to ascertain its temperature and to saturate it with moisture.

A certain amount of heat is introduced into the calorimeter by the electric ignition ; this may be kept constant by always using the same strength of current for the same length of time, and the correction may then be eliminated by using the same current when calibrating the instrument. The author prefers to do this by burning in it a known weight of a substance whose calorific value is known, and deducing the water-equivalent of the whole from the rise of temperature observed ; by slightly adjusting the water-contents the water-equivalent may then be brought to round numbers, thus saving much time in calculations. The substance used by the author is pure carbon, such as obtained from sugar, and the heating value is calculated from an elementary analysis. Cakes of such carbon may refuse to ignite in the instrument, but this can be overcome by adding a small but known weight of some such substance as stearic acid, which ignites readily and starts the combustion of the carbon. It has been suggested to calibrate these instruments by the combustion of such organic bodies alone, but the author finds that they will not burn satisfactorily in this instrument.

As an alternative method of calibration a known amount of heat may be introduced into the calorimeter by means of the electric ignition device, but the author does not regard this as anything more than a check upon the other calibration.

From the above account of the present instrument it will be seen that no novelty of principle is claimed for it ; but the author believes that the modifications of design and method of use which he has introduced will allow the old principles to be applied to greater advantage, and will render this type of calorimeter more convenient to use and more accurate and certain in its results.

LI. *Change of the Modulus of Elasticity of Ferromagnetic Substances by Magnetization.* By K. HONDA, *Rigakushi*, S. SHIMIZU, *Rigakushi, and* S. KUSAKABE, *Rigakushi* *.

IT has been generally admitted that magnetization has very little effect upon the elasticity of ferromagnetic substances. Wertheim † first measured with a micrometer the elongation of an iron wire due to tension in the magnetized and in the unmagnetized state with exactly the same result. Guillemin ‡ placed an iron bar horizontally and fixed it at one end and hung a small weight at the other, which was left free. The magnetization of the bar by a coaxial coil produced a small rise of the weight. Wartmann § used Chladni's figures to investigate the change of elasticity of magnetized iron and steel plates, and also examined the sound accompanying longitudinal and transversal vibrations of magnetized iron wires. No influence of magnetization was observed. Trèves || set in vibration two tuning-forks having the same period of vibrations. When one of them was placed in a coil and magnetized by a strong electric current, its vibration was accelerated producing beats; but when the current was broken the beats were no more to be heard, and the two notes were in unison. This experiment shows an increase of the modulus of elasticity by magnetization. H. Tomlinson ¶ found, on the contrary, that the elongation of an iron wire by loading is independent of magnetization. Bock ** found the effect to be smaller than ½ per cent., if there is any. By passing an electric current through a stretched pianoforte-wire, M. G. Noyes †† noticed an increase of elasticity, which was less than 1 per cent. Maurain ‡‡ also found a small increase of elasticity by means of tuning-forks placed in a very strong magnetic field. In the investigation on the effect of tension upon magnetic elongation of a pianoforte-wire, B. Brackett §§ observed a small increase

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* Communicated by Prof. Nagaoka.

† Wertheim, *Ann. de Chim. et de Phys.* [3] xii. p. 610 (1842).

‡ Guillemin, *Comp. Rend.* xxii. pp. 246, 432 (1846).

§ Wartmann, *Ann. de Chim. et de Phys.* xxiv. p. 360 (1848).

|| Trèves, *Comp. Rend* lxvii. p. 321 (1868); *Archives des Sci. Nat.* n. s. xxxiii. p. 74 (1868).

¶ Tomlinson, Proc. Roy. Soc. xl. p. 447 (1886).

** Bock, Wied. *Ann.* liv. p. 442 (1895); Phil. Mag. [5] xxxix. p. 548 (1895).

†† M. G. Noyes, Phys. Rev, [4] ii. p. 277 (1895); Phys. Rev. [6] iii. p. 432 (1896).

‡‡ Maurain, *Comp. Rend.* cxxi. p. 248 (1895).

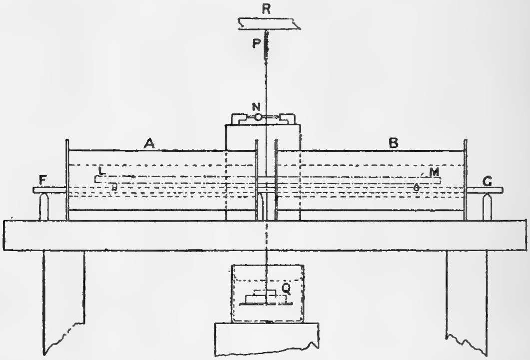
§§ B. Brackett, Phys. Rev. [5] v. p. 257 (1897).

of elasticity amounting to about ½ per cent. J. S. Stevens and H. G. Dorsey[*] used the method of flexure, and applied the interference-fringes to measure the amount of depression. The effect of magnetization upon a loaded iron and steel bar was found to be very small; it showed a minute increase of the modulus of elasticity by about $\frac{1}{300}$ per cent. for the strongest current used. In the next year, Stevens measured the magnetic elongation of steel wires under several loadings and found an increase of elasticity. Lately, Tangl[†] published his results on the same subject. He made use of the principle that the moment of a bifilar suspension increases with tension applied to its lower end. Besides iron, he also examined nickel wires. In fields ranging from 200 to 480 C.G.S. units the maximum increase of the modulus of elasticity amounted to about 1 per cent. for iron and nickel.

All of these experiments show that magnetization increases slightly the modulus of elasticity in iron and nickel, and that the change increases with magnetizing force, but its law is not clearly brought out.

2. The method of measurement in our experiment was similar to that of Stevens and Dorsey, as shown in fig. 1.

Fig. 1.



A and B are two magnetizing coils of the same dimensions, which rested horizontally in a coaxial line. F G is a stout brass rod of rectangular section extending between two fulcrums; it is also supported at the middle point by another fulcrum. The coils can therefore be moved independently of the bar. L M is a rod to be tested placed in the axial line

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[*] J. S. Stevens and H. G. Dorsey, Phys. Rev. [2] ix. p. 116 (1899); Phys. Rev. [2] xi. p. 95 (1900); *Zeitschr.* ii. p. 682 (1900).

[†] Tangl, *Ann. de Phys.* vi. p. 34 (1901).

of the coils. It is supported at L and M by two fulcrums; one of them is an ordinary wedge fixed to the brass rod, while the other consists of a cylinder which can rotate about its own axis. Q is the weight suspended from the middle of the bar. At the centre of the bar a fine copper wire, whose diameter is about 0·08 mm., is soldered and stretched vertically upwards by means of a weak spring P. This copper wire is wound once round a rotating cylinder to which a reflecting mirror is fixed, and stretched upwards, as used in Hertz's dynamometer. The rotation of the cylinder is observed by means of a vertical scale and a telescope.

The dimensions of each part of our arrangement are as follows:—

Length of each coil .... = 39·90 cm.
Its internal diameter.............. = 5·80 cm.
$4\pi n$ .... = 393·5 cm.
Distance between the coils in air-gap .... = 2·5 cm. for iron and steel.
= 2·0 cm. for nickel and cobalt.
Distance between two fulcrums L and M .... = 59·91 cm. for iron and steel.
= 21·95 cm. for nickel and cobalt.
Diameter of rotating cylinder ... = 0·172 cm.
Scale-distance........................ = 261·3 cm.

The sensibility of our apparatus was such that a displacement of one division of the image of the vertical scale in the field of the telescope corresponded to the change of depression of $1·72 \times 10^{-5}$ cm. at the middle of our ferromagnetic rod. It was necessary to protect the mirror and the thin copper wire from air-currents in order to get rid of minute vibrations of the mirror.

The measurement was conducted in the following way. The bar to be tested was placed in the axial line of the coils and then loaded by a weight. The tension of the fine copper wire was then suitably adjusted, and the mirror was directed to the observing telescope. This adjustment was performed as in the former experiment. To begin with, the bar was demagnetized and then the initial reading taken. A current was then passed through the coils and the corresponding deflexion noted. These processes were repeated with successively increasing currents.

Since the resistance of the coils did not exceed 3 ohms, no trace of heating effect due to current was observed during the time in which the deflexion was taken; we therefore dispensed with a water-jacketing arrangement. The lateral contraction or elongation, which necessarily accompanies the magnetization of a ferromagnetic rod, was at most of the order 2×10^{-6} cm. for iron and 7×10^{-6} cm. for nickel. Hence with our arrangement, the lateral change of dimension due to magnetization was within the limit of experimental errors. The disturbance of the results due to magnetic elongation or contraction in the longitudinal direction was eliminated by means of the rotating cylinder which served as one of the fulcrums.

The bar bent slightly downwards if loaded; hence when it was magnetized it would strive to make itself straight. This may cause an apparent increase of elasticity; but it was confirmed by direct experiments that the effect was negligibly small, because the reading obtained by inclining two coils with respect to the bar to a degree greater than the actual case was almost the same as in the case when the coils rested in a coaxial line.

Since the bar was considerably shorter than the whole length of the coils, it lay nearly in a uniform field except at the middle. The effect of the air-gap between the coils was also studied, varying its width by 1 or 2 cms.; however, such a change had no sensible effect on our results.

3. The dimensions of the specimens used in our experiments and their moduli of elasticity were as follows:—

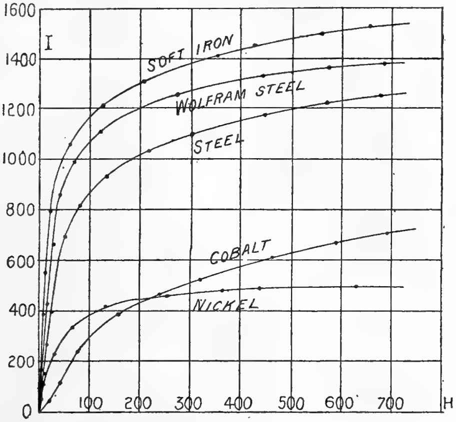
Metals:	Soft Iron.	Steel.	Wolfram Steel.	Nickel.	Cobalt.
Length	64·00 cm.	64·00 cm.	64·00 cm.	24·20 cm.	27·30 cm.
Breadth	0·903	0·920	0·948	0·510	Radius
Thickness ...	0·901	0·913	0·953	0·511	=0·680
Elasticity ...	$2{\cdot}02\times10^{12}$	$2{\cdot}01\times10^{12}$	$2{\cdot}05\times10^{12}$	$1{\cdot}96\times10^{12}$	$1{\cdot}79\times10^{12}$

The present arrangement was not suitable for the absolute measurement of the modulus of elasticity, since the yielding effect of several parts of the arrangement disturbs the result. Hence the modulus of elasticity was determined by the ordinary method of flexure with two reflecting mirrors.

The intensity of magnetization of the specimens was determined by the magnetometric method. The results are given in fig. 2. Ordinates represent the intensity of magnetization, and abscissæ the effective field.

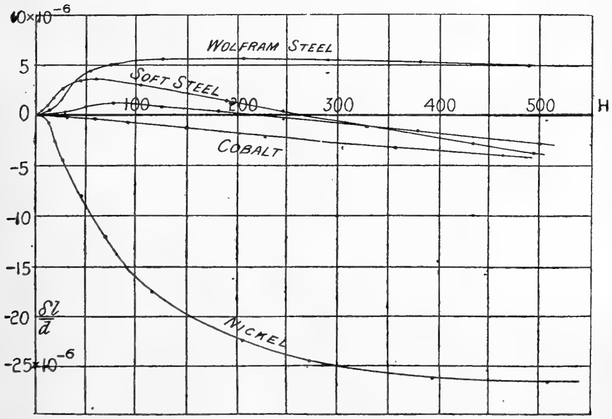
The magnetic change of length was found to have an intimate relation to the change of elasticity, so that it was measured for each specimen. To each end of the bar a brass rod of the same thickness and 15 cms. long was soldered. The bar was then vertically suspended coaxial with the magnetizing coil by means of a screw adjustment. From its lower end a weight of 1 or ½ kilogram was hung by a copper wire. The weight was dipped in water so as to avoid its vibratory disturbance. The rotating cylinder with a

Fig. 2.



reflecting mirror, described in the preceding paper, was brought in contact with the copper wire under slight pressure to prevent sliding. The magnetizing coil was so long that the bar lay in a nearly uniform field. The results of experiment are given in fig. 3. Here H denotes effective field

Fig. 3.

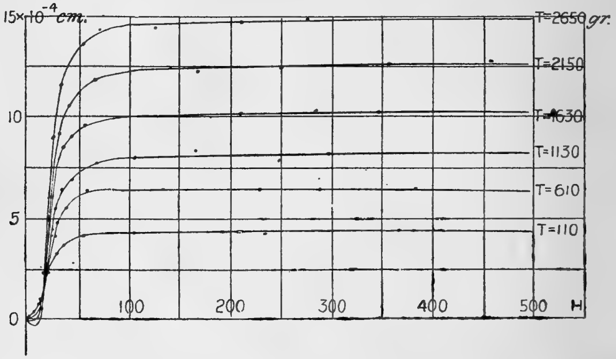


and $\frac{\delta l}{l}$ the magnetic change of length per cm. We observe that the elasticity of a substance undergoing a large change of length is also similarly affected by magnetization.

4. *Soft Iron.*—In observing the deflexion from our scale-reading by passing a current through the coils, we were first struck with the large effect contrary to the results of previous experimenters. The largest deflexions for soft iron and Wolfram steel amounted to about 9 cm. with a scale at 2·61 m. distant in a field of 500 c.g.s. units, while for a steel bar it was only one third. Even nickel, for which the distance between the two fulcrums was only 22 cm., showed a deflexion of 3 cm.

The curves for the change of depression corresponding to different loadings in soft iron are given in fig. 4. Ordinates represent in centimetres the amount of the change of depression, taken positive when it indicates an increase of elasticity, and taken negative when it indicates a decrease. Abscissæ represent the effective field, and T the suspended weight in grams.

Fig. 4.



The general course of these curves resembles that of magnetization. In weak fields, however, we notice a minute decrease of elasticity when the load exceeds about 1·5 kilograms. Iron contracts laterally when magnetized by weak currents, and this contraction may produce such an apparent decrease of elasticity; but the actual calculation shows that the initial depression is more than can be accounted for by the lateral contraction.

When the field increases beyond this region, the change of depression increases rapidly and soon reaches its asymptotic value, after which the increase takes place quite slowly. As the weight is increased the change of depression is also increased. The rate of increase is large with small loading and decreases as the load is increased, approaching to an asymptotic value.

From the change of depression we may calculate the ratio of the change of elasticity to the modulus itself. The depression due to the suspended weight as well as to its own weight in an unmagnetized bar is given by the approximate formula *

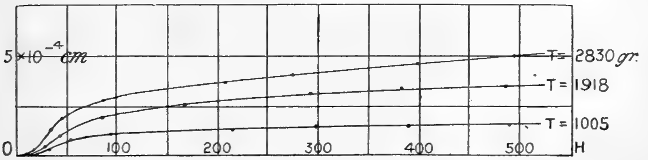
$$d=\frac{l^3g}{4Eab^3}(T+\tfrac{5}{8}W),$$

where l, a, b are the length, breadth, and thickness of the bar, T and W the suspended weight and the weight of the bar itself respectively. d and W refer to the part of the bar lying between two fulcrums. The observed change of depression divided by this depression is the ratio in question, that is, $\frac{\delta E}{E}$. Some of the results of our calculation are given in the following table. In the calculation the effect of the weak spring stretching the thin copper wire was corrected for.

H / $T+\frac{5}{8}W$.	329 gr.	829 gr.	1349 gr.	1849 gr.	5869 gr.
20	$1{\cdot}64\times10^{-2}$	$0{\cdot}77\times10^{-2}$	$0{\cdot}50\times10^{-2}$	$0{\cdot}47\times10^{-2}$	$0{\cdot}44\times10^{-2}$
30	2·79	1·47	1·09	1·08	0·88
50	3·15	1·84	1·35	1·28	1·16
100	3·36	1·92	1·48	1·37	1·28
250	3·40	1·93	1·51	1·40	1·32
400	3·40	1·93	1·51	1·40	1·32

These numbers show that the value of $\frac{\delta E}{E}$ becomes greater as the field is increased, and that it becomes less as the weight is increased.

Fig. 5.



5. *Steel.*—The general character of the change of depression is similar to that of soft iron, as given in fig. 5; but the

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* Clebsch's *Elasticität*, p. 375; Winkelmann's *Physik*, i. p. 266.

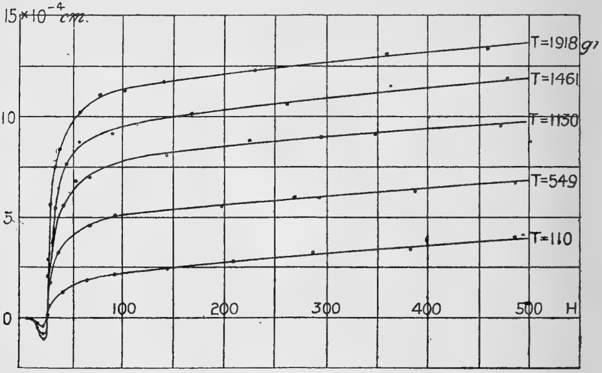
initial decrease is not observed. Some of the values of $\frac{\delta E}{E}$ are given in the following table:—

H/T+$\frac{5}{8}$W.	1251 gr.	2184 gr.	3096 gr.
50	$0{\cdot}14\times10^{-2}$	$0{\cdot}15\times10^{-2}$	$0{\cdot}17\times10^{-2}$
100	0·22	0·25	0·25
200	0·27	0·33	0·31
300	0·28	0·37	0·35
400	0·30	0·40	0·39

This steel bar shows a comparatively small increase of elasticity. With the present specimen, the value of $\frac{\delta E}{E}$ under a given field reaches a maximum with a load lying between 1270 and 2200 grams.

6. *Wolfram Steel.*—The change of depression for Wolfram steel bar by magnetization is similar to that for soft iron, as shown in fig. 6. It is still greater, and the curve does not tend to become asymptotic. The initial decrease of elasticity is more marked in the metal than in soft iron and occurs even with the smallest load. The following table contains the values of $\frac{\delta E}{E}$ for different fields and loadings:—

Fig. 6.

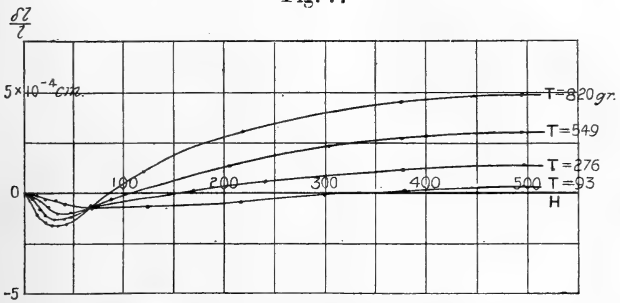


H/T+$\frac{5}{8}$W.	358 gr.	797 gr.	1378 gr.	2206 gr.
70	$1{\cdot}79\times10^{-2}$	$1{\cdot}88\times10^{-2}$	$1{\cdot}67\times10^{-2}$	$1{\cdot}56\times10^{-2}$
100	2·05	2·02	1·79	1·64
200	2·55	2·27	2·00	1·80
300	2·93	2·42	2·10	1·89
400	3·26	2·60	2·18	1·92
500	3·54	2·68	2·23	1·97

The above table shows that the increase of elasticity under a given field becomes generally less as the load is increased. In weak fields, however, a maximum is observed as in the case of steel. It also increases first rapidly and then slowly as the field is increased.

7. *Nickel.*—Nickel rod shows an abnormal behaviour as regards the change of elasticity by magnetization. The results of observation are graphically shown in fig. 7, and the values of $\frac{\delta E}{E}$ are given in the following table:—

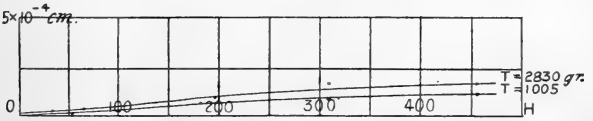
Fig. 7.



$H / T+\frac{5}{8}W.$	105 gr.	287 gr.	561 gr.	832 gr.
30	$-1{\cdot}80\times10^{-2}$	$-1{\cdot}60\times10^{-2}$	$-1{\cdot}30\times10^{-2}$	$-1{\cdot}08\times10^{-2}$
70	−4·08	−1·40	−0·70	−0·38
100	−3·84	−0·92	−0·21	+0·30
200	−2·50	+0·46	+1·20	+1·80
300	−0·88	+1·47	+2·07	+2·52
400	+0·42	+2·17	+2·56	+2·83
500	+1·34	+2·67	+2·84	+3·03

Thus the modulus of elasticity considerably decreases in weak fields and increases in the strong. The field of no change decreases as the load is increased. In a given field the amount of decrease becomes less as the load is increased; in strong fields, however, the increase becomes gradually greater as the load is increased.

Fig. 8.



8. *Cobalt.*—Our cobalt bar was too thick and the maximum deflexion in the field of the telescope was only 1·5 divisions,

so that we cannot claim for cobalt the same accuracy as in iron, steel, and nickel. But we notice a distinct increase of elasticity, as shown in fig.8 and the following table:—

H/T.	1005 gr.	2830 gr.
100	$0{\cdot}24\times10^{-2}$	$0{\cdot}08\times10^{-2}$
200	0·48	0·22
300	0·59	0·33
400	0·70	0·39

The total depression d due to a suspended weight T is calculated by the formula, neglecting the weight of the bar itself,

$$d=\frac{1}{12\pi}\frac{\mathrm{T}l^3}{\mathrm{E}\mathrm{R}^4},$$

where R is the radius of the bar.

Generally speaking, the above results for iron, steel, and nickel are far greater than those given by former experimenters. That the modulus of elasticity of nickel decreases in weak fields has not yet been observed. Moreover, no experiment has ever been tried with cobalt.

We have to express our cordial thanks to Profs. H. Nagaoka and A. Tanakadate for valuable suggestions in carrying out the present experiments.

LII. *On the Velocity of Reaction before Complete Equilibrium and the Point of Transition are reached, &c.*—Part III. *By* Meyer Wilderman, *Ph.D.*, *B.Sc.* (*Oxon.*) *.

Contents.

I. The general laws concerning all kinds of equilibrium in heterogeneous systems, and velocity of reaction before any one of them.
II. The true meaning of the equations for chemical equilibrium in heterogeneous systems. The laws of chemical velocity of reaction in heterogeneous systems.
III. On the real and apparent points of chemical equilibrium in heterogeneous systems.

I. *General Laws.*

We now pass to the determination of the general laws which concern all three kinds of equilibrium in heterogeneous systems and the velocity of reaction before any one of the three kinds is reached.

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* Communicated by the Author.

A. *In Complete Equilibrium.*—Let us take the most general equation for the velocity of reaction; for this let our reaction be

$$\nu_1 a_1 + \nu_2 a_2 + \ldots n_1 \mathrm{A}_1 + n_2 \mathrm{A}_2 + \ldots \leftrightarrows \nu_1' a_1' + \nu_2' a_2' + \ldots, n_1' \mathrm{A}_1' + n_2' \mathrm{A}_2' \ldots,$$

where $a_1, a_2, \ldots a_1', a_2'$ are solid or liquid substances, and A_1, $\mathrm{A}_2 \ldots$, A_1', $\mathrm{A}_2' \ldots$ gaseous substances (or substances in solution); $\nu_1, \nu_2 \ldots \nu_1', \nu_2' \ldots n_1, n_2 \ldots n_1', n_2' \ldots$ are the number of molecules with which every substance takes part in the equation of the reaction. Since every solid or liquid substance has a vapour- or solution-pressure, our general equation for equilibrium is according to Van't Hoff

$$k\pi_1^{\nu_1}\pi_2^{\nu_2} \ldots p_1^{n_1}p_2^{n_2} \ldots \overset{\rightarrow}{\underset{\leftarrow}{=}} k'\pi_1'^{\nu_1'}\pi_2'^{\nu_2'} \ldots p_1'^{n_1}p_2'^{n_2}, \quad . \quad . \quad \text{(i.)}$$

where $\pi_1', \pi_2' \ldots \pi_1, \pi_2 \ldots$ are the partial vapour-pressures (or concentrations in solution) of the solid or liquid substances, and $p_1, p_2 \ldots p_1', p_2' \ldots$ those of the gaseous substances. Since, according to the law of Dalton, the vapour-pressure (or solubility) of a solid or of a liquid has for every temperature a certain constant value, we have instead of (i.):

$$\mathrm{K}p_1^{n_1}p_2^{n_2} \ldots \overset{\rightarrow}{\underset{\leftarrow}{=}} \mathrm{K}'p_1'^{n_1'}p_2'^{n_2'}, \ldots \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

i. e., "the active mass of a solid (or liquid) substance is," as Guldberg and Waage found empirically, "necessarily constant, independent of the quantity of the solid." Thus, what Guldberg and Waage found empirically, Van't Hoff explained to be a necessary consequence of the law of action of mass. The mutual chemical action between the solid or liquid and gaseous substances is, however, conceived by Van't Hoff in the same light as it was by Guldberg and Waage, namely, as of a reciprocal nature (and he extends this even to physical reactions), representing them all as follows: *before equilibrium,* when a reaction is still going on, water $\leftrightarrows$ aqueous vapour, K (solid substance) $\leftrightarrows cp_1^{n_1}p_2^{n_2}$ (gaseous substance or substances in solution); *at equilibrium,* water $\overset{\rightarrow}{\underset{\leftarrow}{=}}$ saturated aqueous vapour, $\mathrm{K} \overset{\rightarrow}{\underset{\leftarrow}{=}} cp_1^{n_1}p_2^{n_2} \ldots$, i. e., *at equilibrium the two opposite reactions still continue, but become equal,* i. e., *just as much (counting in mass or in molecules) of every one of the substances is formed in the unit of time as disappears.* No variation in the quantities of the substances is thus taking place, but the equilibrium is nevertheless of a *dynamic* nature. In other words the above equation (ii.) is to be understood in this way: we have *partial* velocities of each of the *two* opposite reactions:

$$\left(\frac{dt}{d\tau}\right)=\mathrm{K}p_1^{n_1}p_2^{n_2}\ldots,\ \left(\frac{dt}{d\tau}\right)'=\mathrm{K}'p_1^{\prime n_1'}p_2^{\prime n_2'}\ldots;$$

the *total* velocity *before* equilibrium is:

$$\frac{dt}{d\tau}=\mathrm{K}p_1^{n_1}p_2^{n_2}\overset{\rightarrow}{\underset{\leftarrow}{-}}\mathrm{K}'p_1^{\prime n_1'}p_2^{\prime n_2'}\ldots,$$

and *at* equilibrium we have $\left(\frac{dt}{d\tau}\right)=\left(\frac{dt}{d\tau}\right)'$ or

$$\frac{dt}{d\tau}=\mathrm{K}p_1^{n_1}p_2^{n_2}\ldots\overset{\rightarrow}{\underset{\leftarrow}{-}}\mathrm{K}'p_1^{\prime n_1'}p_2^{\prime n_2'}=0,\quad .\quad .\ \text{(iv.)}$$

and

$$\frac{p_1^{n_1}p_2^{n_2}}{p_1^{\prime n_1'}p_2^{\prime n_2'}}=\frac{\mathrm{K}'}{\mathrm{K}}=\text{const.*}\quad .\quad .\quad .\quad .\quad .\ \text{(iv}'\text{.)}$$

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* *I. e., at* equilibrium the substances taking part in the *two opposite* reactions are *all present, as before* equilibrium, being regulated by iv. or iv.', and none of the substances can disappear because none of the velocity-constants K or K' equals zero. It should be remarked, reversing the argument, that the same two reactions, which take place *at* equilibrium, take place *before* equilibrium, with the same velocity constants K and K', $\left(\frac{dt}{d\tau}\right)$ being either > or < $\left(\frac{dt}{d\tau}\right)'$. *At equilibrium neither* $\left(\frac{dt}{d\tau}\right)=0$, *nor* $\left(\frac{dt}{d\tau}\right)'=0$, *but* $\left(\frac{dt}{d\tau}\right)-\left(\frac{dt}{d\tau}\right)'=0$. This conception can be shown to be true in *homogeneous* systems, and not to be a mere theoretical (dynamical) *conception* which can just as well be replaced by another one, for the reason that it can be shown to be true in all its details experimentally: in cases of chemical equilibrium in homogeneous systems, each of the two opposite reactions can be isolated and studied separately so as to get the constants K or K' separately. For this it is enough to start with a system in which the reacting substances of one reaction are in great preponderance over the substances of the opposite reaction, so that $\left(\frac{dt}{d\tau}\right)-\left(\frac{dt}{d\tau}\right)'$ can for a sufficient time be taken to be equal to $\left(\frac{dt}{d\tau}\right)$ or to $\left(\frac{dt}{d\tau}\right)'$ respectively, and the values K and K' separately determined. We find then that equilibrium actually takes place just when $\frac{p_1^{n_1}p_2^{n_2}}{p_1^{\prime n_1'}p_2^{\prime n_2'}}$ becomes $=\frac{\mathrm{K}'}{\mathrm{K}}=\mathrm{C}$, *i. e.*, the whole conception in all its elements from the beginning to the end can be tested (in homogeneous systems) experimentally, and proves to be correct.

The present conceptions of the velocity of chemical reaction in heterogeneous systems, and of chemical equilibrium in heterogeneous systems, can thus be summed up in the following few general statements:

The active mass of a solid (or liquid) substance is, before and at the equilibrium constant (K), independent of the quantities of the solid (or liquid) substance. The velocity with which one or more gases (or substances in solution) combine to form a solid substance is $K'p_1^{\prime n_1'}p_2^{\prime n_2'} \ldots$, where p_1', $p_2' \ldots$ are *the concentrations of the gaseous substances (or of the substances in solution) at the time* τ, *and* n_1', n_2' *are the number of molecules with which each gaseous substance takes part in the reaction; this velocity is independent of the quantity of the solid. When both opposite reactions become equal, a dynamic equilibrium is present.*

In this way we are able to explain or interpret the experimental data observed for chemical *equilibrium* in *heterogeneous* systems. But on the other hand there are almost no experimental observations concerning the *velocity of reactions* in *heterogeneous* systems, and we are therefore necessarily compelled to be very cautious in drawing conclusions from facts observed at equilibrium for the velocity of reaction in the system before equilibrium has taken place; the more so as *the above is not the only interpretation possible.* Another, which is more in conformity with the facts concerning the velocity of reaction as far as they are known to the chemist at present, may be formulated thus: ***The active mass of a solid (or liquid) substance is at the time*** τ ***before and at the equilibrium directly proportional to its surface*** Σ_τ. ***The velocity with which one or more gases (or substances in solution) combine to form a solid (or liquid) substance at the time*** τ ***is*** $K'p_{1\tau}^{\prime n_1'}p_{2\tau}^{\prime n_2'} . \Sigma_\tau$, i. e., ***is at the time*** τ ***a function of their concentrations as well as of their surface of contact with the solid, which is also*** Σ_τ. ***The total velocity*** BEFORE ***equilibrium is***

$$\frac{dt}{d\tau} = K . \Sigma_\tau \overset{\rightarrow}{\underset{\leftarrow}{-}} K'p_{1\tau}^{\prime n_1'}p_{2\tau}^{\prime n_2'} . \Sigma_\tau = \Sigma_\tau\left(K \overset{\rightarrow}{\underset{\leftarrow}{-}} K'p_{1\tau}^{\prime n_1'}p_{2\tau}^{\prime n_2'}\right),$$

AT *equilibrium*

$$\left(\frac{dt}{d\tau}\right) = \Sigma_\tau\left(K \overset{\rightarrow}{\underset{\leftarrow}{-}} K'p_1^{\prime n_1'}p_2^{\prime n_2'}\right) = 0 = K \overset{\leftarrow}{\underset{\rightarrow}{-}} K'p_1^{\prime n_1'}p_2^{\prime n_2'}.$$

These general statements explain just as well as those given before all the facts observed *at* equilibrium of heterogeneous systems, and give at the same time a more correct form for the equations for the *velocity* of reaction. It is well known that when an acid solution, for example, is acting upon a solid, the reaction is very much quicker when the solid is taken in the form of a powder instead of in big lumps, *i. e.*, the velocity of chemical reaction in heterogeneous systems *is* dependent on the surface of the solid substance. In attempting to conceive chemical equilibrium in heterogeneous systems in the same manner as we conceive it in homogeneous systems, *i. e.*, as two opposite reactions which at equilibrium become constant, the above modification of the existing conceptions becomes *à priori* inevitable, because we have to view equilibrium here, as we did in homogeneous systems, in the light of velocity of reaction. We shall, however, have first to see more carefully what is the advance made in this manner, and *whether it is possible or not on this modified basis* to bring all kinds of equilibrium, complete equilibrium, points of transition, and incomplete equilibrium, as well as velocity of reaction in all these regions, under one general law, under one general principle. If this does not prove possible, we shall have to look out for other ways and methods to arrive at such general principles or laws, if possible.

B. Let us again consider the equation concerning *complete equilibrium* as well as the *points of transition.*

The general equations for the velocity of reaction I found to be

$$\left(\frac{dt}{d\tau}\right)=c'(t_o-t)(t-t_{ov}+\mathrm{K}), \quad . \quad . \quad . \quad . \quad (a)$$

i. e., the velocity of reaction is, in all cases of complete equilibrium and of the points of transition, directly proportional to the remoteness from the point of equilibrium, $\mathrm{T}_o-\mathrm{T}$, to the surface of contact of the parts of the heterogeneous system which act one upon another, $\mathrm{T}-\mathrm{T}_{ov}$, + the instability constant K. Let us start with a supersaturated solution.

Equation (a) may in this case be written :

$$\left(\frac{dt}{d\tau}\right)=c'(\mathrm{C}_o-\mathrm{C}_\tau)(\Sigma_\tau+\mathrm{K}), \quad . \quad . \quad . \quad . \quad (a')$$

where C_o is the concentration of the solutions at the point of equilibrium, C_τ, Σ_τ are the concentration of the solution and the surface of contact of the reacting parts at the time t.

Equation (a') can be written :

$$\frac{dt}{d\tau}=c'\mathrm{C}_o(\Sigma_\tau+\mathrm{K})-c'\mathrm{C}_\tau(\Sigma_\tau+\mathrm{K})\,; \quad . \quad . \quad . \quad (a'')$$

this equation (a'') can be conceived as the total velocity of reaction of two partial reaction velocities :

$$\left(\frac{dt}{d\tau}\right)=c'\mathrm{C}_o(\Sigma_\tau+\mathrm{K}) \quad \text{and} \quad \left(\frac{dt}{d\tau}\right)'=c'\mathrm{C}_\tau(\Sigma_\tau+\mathrm{K}).$$

At equilibrium C_τ becomes C_0:

$$\frac{dt}{d\tau} = c'C_0(\Sigma_0 + K) \overset{\rightarrow}{\underset{\leftarrow}{-}} c'C_0(\Sigma_0 + K) = 0.$$

Thus we could understand the equation (a) or (a'), taking as an instance for consideration the separation of salt from supersaturated solution, in this way:

$$\left(\frac{dt}{d\tau}\right) = c'C_0(\Sigma_\tau + K),$$

and the resulting equation from it

$$\left(\frac{dt}{d\tau}\right) = c'C_0(\Sigma_0 + K),$$

give the velocity with which the solid salt is passing into the solution before and at equilibrium, C_0 being the active mass of the solid per unit surface *expressed in the value of concentration of the solution at equilibrium*; and

$$\left(\frac{dt}{d\tau}\right)' = c'C_\tau(\Sigma_\tau + K),$$

and the equation resulting from it

$$\left(\frac{dt}{d\tau}\right)' = c'C_0(\Sigma_0 + K),$$

give the velocity of separation of salt from the supersaturated solution before and at equilibrium. This means that the velocity of solution of the solid is directly proportional to its surface at the time τ* (+ the instability constant K); the velocity with which the dissolved salt transforms into solid salt is directly proportional to its concentration in the solution and to the surface of contact of the solid with the solution at the time τ* (+ the instability constant K); equilibrium is

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* It should be remarked that the instability constant K cannot be disposed of and explained as an increase of the surface produced by the crystal of ice or salt which is introduced into the overcooled or oversaturated solution in order to start the reaction. In cooling down in my experiments, *e.g.*, 4½ litres of water 0°·4 below 0°, 22·5 c. cm. H_2O separated in form of ice; the introduced small crystal cannot possibly amount even to 0°·01 c. cm. water or ice, *i. e.*, it cannot amount to 1/2250 part of the total amount of ice separated. The value of K, however, is found not to be so small, but in the above experiment $=1/10$ part of $t_o - \tau_{ov}$ or of the total amount of ice separated during the reaction, and much exceeds the value $t - t_{ov}$ at the beginning of the reaction. It should also be remarked that the instability constant shows an additional strain in the liquid removed from the point of equilibrium, which forces the same to strive at a state of equilibrium, it therefore always *increases* the velocity of reaction and K is always positive.

taking place when the velocities of the two opposite reactions become equal. Thus we apparently arrive in this case at the same general statement made before in modifying the generalizations concerning the velocity of chemical reaction and chemical equilibrium in heterogeneous systems by the introduction of the surface of contact Σ_τ into the equations. Such decomposition of the equation

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K})$$

cannot, however, be regarded as satisfactory, if the intrinsic meaning of this decomposition cannot give us satisfaction and cannot be generally adopted in all cases. Let us see what this decomposition of the general equation means? It means that above as well as below the point of equilibrium the same two reactions (solution of the solid and separation of the solid) take place. Below the point of equilibrium the velocity of separation of the solid is preponderating over the velocity of solution of the solid, and above the point of equilibrium the velocity of the solution of the solid is greater than the velocity of separation of the solid. The velocity constant of the solution of the solid is further assumed to be at the same time, at any temperature, equal to the velocity-constant of separation of the solid, be this temperature above or below the point of equilibrium. It further assumes that at equilibrium both reactions (separation and solution, condensation or evaporation, &c.) continue, only both opposite velocities of reaction become equal to one another, so that just as much of each substance is formed in the unit of time as disappears. To start with, we have no right whatever to assume that given the same surface of contact of the reacting parts, the velocity-constant of separation of salt or of ice from a supersaturated solution or from overcooled water is equal to the velocity-constant of solution of salt or of melting of ice in an unsaturated solution, or in water above 0°. There is no evidence for such an assumption; if anything, there is evidence to the contrary. If an ice-crystal is brought into supercooled water, ice separates with a certain speed and we get a velocity-constant. Now introduce, by means of a pipette, some warm water to the bottom layers of the solution, stir rapidly, and use the same separated ice for the melting process, and the velocity-constant of melting is not found to be the same. The difference is too great to be attributed to experimental errors. It takes further a very few minutes to separate the salt from a supersaturated solution, and you may take even 10 or 100 times as much salt (powdered) and bring it in contact with water, and you will never get a saturated solution in the time of a very few minutes. A further question is, Why should C_0 of the solid not change during the reaction with temperature, while C_τ of the solution does change with the same? But let us pursue the same conception further. When a solid transforms into a liquid, or liquid into a solid, or solid into a solid and liquid into a liquid, *e. g.*, in a system of ice and water, we might (as in case of solution of solid salt) according to this conception have for both opposite reactions separately the same equations

$$\left(\frac{dt}{d\tau}\right) = c'.\,C_0(\Sigma_\tau + \mathrm{K}) \text{ and } \left(\frac{dt}{d\tau}\right)' = c'C_0(\Sigma_\tau + \mathrm{K}),$$

and since according to the above conception, above, below, and at equilibrium both opposite reactions take place simultaneously, the total velocity

$$\frac{dt}{d\tau} = \left(\frac{dt}{d\tau}\right) - \left(\frac{dt}{d\tau}\right)'$$

ought to be

$$= c'C_0(\Sigma_\tau + \mathrm{K}) - c'C_0(\Sigma_\tau + \mathrm{K}),$$

i. e., not only at the point of equilibrium, but also above or below the point of equilibrium, no separation or solution of the solid (in case of the system water $\leftrightarrows$ ice, no separation of ice below zero, and no melting of ice above zero) would be possible. Let us now assume that the velocity-constants of the two opposite reactions (of ice melting and of ice separation) are different, which, however, does not follow from the decomposition of equation (a'), still we ought to get in this case with the above conception in case water $\leftrightarrows$ ice for the total velocity above, below, and at equilibrium,

$$\frac{dt}{d\tau} = c'C_0(\Sigma_\tau + \mathrm{K}) - c''C_0(\Sigma_\tau + \mathrm{K}) = (\mathrm{K}' - \mathrm{K}'')(\Sigma_\tau + \mathrm{K}) = \mathrm{K}'''(\Sigma_\tau + \mathrm{K})$$

instead of the actually found equation

$$\frac{dt}{d\tau} = c(t_0 - t)(\Sigma_\tau + \mathrm{K}).$$

Now let us assume for a while that since the velocity-constants change with temperature, we get for ice $\leftrightarrows$ water the equation

$$\frac{dt}{d\tau} = c(t_0 - t)(t - t_{00} + \mathrm{K}), \text{ or } \frac{dt}{d\tau} = c(t_0 - t)(\Sigma_\tau + \mathrm{K}),$$

because K''' is to be put $= c(t_0 - t)$. Should we assume that

K''' can be put $=c(t_o-t)$ we shall get above, below, and at equilibrium

$$\left(\frac{dt}{d\tau}\right)=c'(t_o-t)(\Sigma_\tau+K) \text{ and } \left(\frac{dt}{d\tau}\right)=c''(t_o-t)(\Sigma_\tau+K)$$

for the partial velocities of ice melting and ice separation, *i. e.*, we shall get the result that the velocity-constants of each reaction $c'(t_o-t)$, $c''(t_o-t)$ *decrease with rise of temperature below the point of equilibrium, become = zero at equilibrium, and then increase with the rise of temperature above the point of equilibrium.* No such conceptions can be entertained for one moment. It is a thermodynamic impossibility that the velocity-constant of a reaction should change in this manner and become zero at any temperature. If such an interpretation of $c(t_o-t)$ should be made here, it is to be made in all cases of complete equilibrium, &c., where a similar equation holds good. Now I found on the basis of careful experiments that the velocity of separation of salt from a supersaturated solution becomes greater the higher the temperature, and it is a very well-known fact that the velocity of solution of a salt in water or unsaturated solution becomes greater the higher the temperature. But granting even that such interpretation of K''', K' K'', were possible, what is the result? Since at equilibrium K' or $c'(t_o-t)=0$, and K'' or $c''(t_o-t)=0$, and therefore also K''' becomes $=$zero, we get the result that the constant of equilibrium K''', which is to regulate the two opposite reactions at equilibrium, does not exist at all —is zero —the two opposite reactions, which are to explain equilibrium dynamically as counterbalancing each other, do not exist at equilibrium at all, and with it the whole foundation for such a conception falls to pieces. Now, if there are no two opposite reactions at equilibrium, why should we assume the same before equilibrium, and under assumptions which seem to us quite unnatural. Indeed, while in the case of chemical reactions it seems quite natural to assume that two opposite reactions are taking place simultaneously, it is difficult to assume the same for complete equilibrium and for the point of transition; it is difficult to think that below 0° ice melts, above 0° ice separates, that an unsaturated solution can separate salt or that an unsaturated vapour has the property to condense to a liquid; in the notion of an unsaturated solution or vapour, moreover, the idea is contained that the solid salt or the liquid cannot co-exist with them together, can not only not be formed, but must go first into solution or evaporate, and the solution must first become saturated, or the vapour saturated, before such a co-existence becomes possible. *Thus we arrive at the necessary conclusion that above and below the point of complete equilibrium or the point of transition only one of the two opposite reactions is taking place; that the velocity of reaction is determined here not by the masses or the total concentrations and the surface of contact, but by the remoteness of the system from the point of equilibrium and the surface of contact* $\Sigma +$ *an instability constant* K. *All three elements of the equation* $t_0 - t$, Σ, K *are quite new and none of them are contained in the equations for the velocity of reaction in homogeneous systems, and the latter cannot be retained and applied for formulating the nature of the phenomena in these regions. We further arrive at the necessary conclusion that when the remoteness from the point of equilibrium becomes equal to zero, no more reaction is taking place, and the complete equilibrium as well as the point of transition are of a* STATIC NOT OF A DYNAMIC *nature.*

C. *The connexion between the three kinds of equilibrium and between the velocities of reaction in the three kinds of heterogeneous systems.*

We are thus unable even after the modifications made in the laws of action of mass in heterogeneous systems (by the introduction of the surface of contact of the reacting parts) to connect all kinds of equilibrium and all kinds of velocity of reaction under one general law. At the most we may assume (neglecting even the very probable difference in the values of the velocity constants for solution or separation of salt or ice, &c.) that the only general result arrived at up to the present in the above manner (by the introduction of the surface of contact into the old conceptions) is that there are in heterogeneous systems two great classes of phenomena, which seem to be essentially different without, however, any apparent reason: complete equilibrium and the point of transition are of a *static* nature; incomplete equilibrium in heterogeneous systems is of a *dynamic* nature. In the first only *one* of the two opposite reactions is taking place, before equilibrium is arrived at, according as the system is above or below the point of equilibrium, and non-action occurs at equilibrium; in the second, on the contrary, *two* opposite reactions take place simultaneously before equilibrium is arrived at, and both reactions still continue at equilibrium. It remains now to see whether we cannot succeed in connecting all kinds of equilibrium and all kinds of velocities of reaction in heterogeneous systems under one general principle, if we undertake this work of classification anew, putting aside from our present conceptions everything which forms only an interpretation of observed results, and retaining only what is sure to be correct. We may safely regard as experimentally verified and correct: (1) That every solid or liquid has a vapour or solubility pressure. (2) That the laws of action of mass are established for homogeneous systems. (3) That the equation

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K})$$

regulates the velocity of reaction and equilibrium in case of perfect equilibrium and the point of transition.

If now we make an extended use of the very original and happy idea of Van't Hoff of taking into account the fact that solids or liquids have a vapour or solution pressure, we can not only bring all three kinds of equilibrium and all kinds of velocities of reaction in heterogeneous systems under one general principle, but for the first time we arrive at the true meaning of chemical equilibrium in heterogeneous systems, and we are at last able to derive the equations for the velocity of chemical reactions in heterogeneous systems, which experiments have always failed to elucidate owing to the fact that the phenomena in question are much more complicated than was usually assumed.

Let us first write down every chemical reaction and every kind of chemical equilibrium in heterogeneous systems in a scheme. Care should be taken that this is done in a most detailed manner, and that to every part of the scheme the proper attention should be given. Let us start, say, with the case of decomposition of solid NH_4Cl into gaseous NH and HCl:

$$\begin{tikzcd}
\mathrm{NH_4Cl\ gas} \arrow[r, shift left, leftarrow] \arrow[r, shift right] \arrow[d, shift right, leftarrow] \arrow[d, shift left] & \mathrm{NH_3\ gas + HCl\ gas.} \\
\mathrm{NH_4Cl\ solid.} &
\end{tikzcd}$$

An analogous case to this will be

$$\begin{tikzcd}
n\mathrm{A_1\ in\ solution} \arrow[r, shift left, leftarrow] \arrow[r, shift right] \arrow[d, shift right, leftarrow] \arrow[d, shift left] & m\mathrm{B_1\ in\ sol.} + m'\mathrm{C_1\ in\ sol.} \\
\mathrm{A_1\ solid\ (or\ liquid).} &
\end{tikzcd}$$

We have to consider this kind of scheme *not only in case of equilibrium*, but *also in case of velocities of reaction.* Moreover it is of real importance and use, chiefly for the latter: because in case of equilibrium we are always entitled to consider that the solid NH_4Cl, which is in equilibrium with gaseous NH_4Cl, is at the same time in equilibrium with NH_3 and HCl as well; this, properly speaking, is implied by the notion of the equilibrium of a system, but we cannot make the same assumption for the velocity of reaction. Giving proper attention to the above, we see at once that what we were always accustomed to consider "as chemical action between solids (or liquids) and gases (or substances in solution)" does not exist at all, but that these reactions are of a complicated nature, *always consisting of two different kinds of reaction. The first,* solid $NH_4Cl \leftrightarrows$ gaseous NH_4Cl (or A_1 solid $\leftrightarrows n'A_1$ in solution), represents either the evaporation or solution of a solid, or the condensation of the vapour to the solid or the separation of the salt from an oversaturated solution. *The second,* gaseous $NH_4Cl \leftrightarrows NH_3$ gas $+ HCl$ gas (or nA_1 in solution $\leftrightarrows mB_1$ in sol. $+ m'C_1$ in sol.), represents a chemical reaction in the homogeneous system (gaseous or in solution). The first kind of reaction is regulated by the equation

$$\frac{dt}{d\tau} = c(t_o - t)(t - t_{ov} + \mathrm{K})$$

as shown above, the second by the law of action of mass. Consequently we have not to deal here with different laws for the different kind of equilibrium in heterogeneous systems, but the equation found for the complete equilibrium and the point of transition forms at the same time the basis of incomplete equilibrium in heterogeneous systems, the basis for the so-called chemical velocity of reaction and chemical equilibrium in heterogeneous systems. We have, therefore, arrived at the following very clear discrimination:—

Chemical action between substances is restricted only to homogeneous systems. The law of action of mass is the regulating principle here. Two opposite reactions are here taking place simultaneously, since the molecules of each kind have in the vapour-space, or in solution, the same kind of free movement, the same possibility of meeting together and acting one upon another.

In the same way the mutual action between different parts of the heterogeneous systems is in all kinds of equilibrium restricted solely to the transportation of the substance (possibly molecular, but no chemical transformation) from one part of the system to the other. This is regulated by the equation

$$\frac{dt}{d\tau} = c(t_o - t)(t - t_{ov} + \mathrm{K}),$$

i.e., *the surface of contact of the reacting parts of the system and the remoteness from the point of equilibrium are here the regulating principle.*

II. *The true meaning of the equations for chemical equilibrium in heterogeneous systems. The laws of chemical velocity of reaction in heterogeneous systems.*

We return to the system given above: NH_4Cl solid, NH_3 gas, HCl gas.

At equilibrium no reaction takes place between solid NH_4Cl and gaseous NH_4Cl, as is seen from the equation

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K}).$$

This means generally: *chemical equilibrium in heterogeneous systems depends only upon the reactions which are taking place in the homogeneous parts,* since at equilibrium no further reaction occurs between the different parts of the heterogeneous system. This also explains the fact why "chemical equilibrium in heterogeneous systems is independent of the mass of the solid":

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K}) \text{ is} = 0, \text{ when } t_o-t=0$$

for all values of $t-t_{ov}+\mathrm{K}$. On the other hand the vapour-pressure of a solid for every temperature is at equilibrium of a definite value, is constant. If the vapour-pressure of the solid NH_4Cl at equilibrium is p_o, that of the gaseous NH_3 or HCl is p,

$$\frac{dt}{d\tau}=\mathrm{K}'p^2 \underset{\leftarrow}{\overset{\rightarrow}{-}} \mathrm{K}''p_o=0;\ i.e.,\ p^2=\frac{\mathrm{K}''p_o}{\mathrm{K}'}=\mathrm{K}'''$$

(observations of Horstman in 1877 for the quite analogous case of solid $NH_4SH \leftrightarrows NH_3+SH_2$.) *The constant* K''' *is therefore not the "active mass of the solid," as assumed, but the ratio of the velocity constants of the two opposite reactions in the homogeneous part.* We cannot therefore assume that a phenomenon expressed by

$$\frac{dt}{d\tau}=\mathrm{K}'p^2 \underset{\leftarrow}{\overset{\rightarrow}{-}} \mathrm{K}^{\mathrm{iv}}=0$$

exists where K^{iv} is the active mass of the solid, but we are very well justified in thinking that

$$\frac{dt}{d\tau}=\mathrm{K}'p^2 \underset{\leftarrow}{\overset{\rightarrow}{-}} \mathrm{K}''p_o=0$$

gives the existing relations at equilibrium where p_o is the pressure of NH_4Cl gas at equilibrium.

Reverting to "*the velocity of chemical reaction in heterogeneous systems*," by such an expression we now understand the velocity with which one or more substances of one part of the heterogeneous system transform indirectly (by means of its vapour or dissolved molecules) into other substances of another part of the heterogeneous system. In the above system NH_4Cl, NH_3, HCl we see two reactions taking place simultaneously: The *first* reaction is solid $NH_4Cl \rightarrow$ or $\leftarrow$ gaseous NH_4Cl is regulated by the equation

$$\left(\frac{dt}{d\tau}\right) = c\Sigma_\tau (p_o - p_\tau)$$

(we omit for convenience' sake the instability constant; we ought in more strict calculations to always write $\Sigma_\tau + K$ instead of Σ_τ), where Σ_τ is the surface of the solid NH_4Cl, p_o is the vapour-pressure of the solid NH_4Cl at the real point of equilibrium, p_τ is the vapour-pressure at the time τ. The *second* reaction is gaseous $NH_4Cl \leftrightarrows NH_3$ gas + HCl gas; it is regulated by the equation

$$\left(\frac{dt}{d\tau}\right)' = c'p_\tau \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p_\tau'^2$$

where p_τ' is the vapour-pressure of NH_3 gas as well as of HCl gas at the time τ.

If the reaction is now begun, e. g., *with solid* NH_4Cl, *a state will soon be arrived at in the system at which in the unit of time as much of the solid* NH_4Cl *is transformed into* NH_4Cl *gas as the gaseous* NH_4Cl *dissociates into* NH_3 *and* HCl; because the gaseous NH_3 and HCl can be formed continuously from gaseous NH_4Cl only because gaseous NH_4Cl is simultaneously formed from solid NH_4Cl. Now the quantity of gaseous NH_4Cl which is transformed in the unit of time into NH_3 and HCl is given by the *total* velocity of reaction in the homogeneous system, *i. e.*, by $\left(\frac{dt}{d\tau}\right)'$; therefore

$$c\Sigma_\tau (p_o - p_\tau) = c'p_\tau - c''p_\tau'^2,$$

and from this

$$p_\tau = \frac{c\Sigma_\tau p_o + c''p_\tau'^2}{c' + c\Sigma_\tau}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(i.)}$$

i. e., *before equilibrium has been arrived at, the concentration of the gaseous* NH_4Cl *is of no constant value, as it is a function of the surface of the solid* NH_4Cl *and of the concentrations of the gaseous* NH_3 *and* HCl *at the time* τ; *since these vary during the reaction,* p_τ *must also change* (*as given by* i.).

This can be clearly understood also from the following: should at the time τ more of the gaseous NH_4Cl dissociate into NH_3 and HCl in the unit of time, than solid NH_4Cl transforms into gaseous NH_4Cl, p_T would become smaller and $p_o - p_T$ greater, *i.e.*, the reaction of the dissociation of the gaseous NH_4Cl into NH_3 and HCl would become slower and the reaction of evaporation of the solid NH_4Cl quicker. Again, should in the unit of time at the time τ more of the solid NH_4Cl evaporate than of the gaseous NH_4Cl dissociate into NH_3 and HCl, p_T will become greater and the $p_o - p_T$ smaller, *i. e.*, the reaction of evaporation will become slower and that of dissociation quicker. *The vapour-pressure of the solid* NH_4Cl *has thus the function of a regulator which keeps the velocities of the two reactions equal.* As to the mode in which the reaction takes place it may be further added that if we start the reaction with solid NH_4Cl, p_T is $< p_o$, the concentration of the gaseous NH_4Cl is smaller than that of its saturated vapour at equilibrium, *i. e.*, only the process of evaporation of the solid NH_4Cl is possible. On the contrary, if we start the reaction with NH_3 and HCl, solid NH_4Cl can be formed from the gaseous NH_4Cl only when the latter is in a supersaturated state, consequently, $p_T > p_o$ and only the reaction of condensation of the gaseous NH_4Cl to solid NH_4Cl can occur.

If we put the above value of p_τ from equation (i.) into

$$\left(\frac{dt}{d\tau}\right) = c\Sigma_\tau (p_o - p_\tau) \text{ or into } \left(\frac{dt}{d\tau}\right)'$$

we get

$$\frac{dt}{d\tau} = c\Sigma_\tau \left(p - \frac{c\Sigma_\tau p_o + c'' p_\tau'^2}{c' + c\Sigma_\tau} \right) = c\Sigma_\tau \left(\frac{p_o c' - c'' p_\tau'^2}{c' + c\Sigma_\tau} \right), \quad . \quad \text{(i'.)}$$

i. e., *the velocity with which solid* NH_4Cl *evaporates or gaseous* NH_3 *and* HCl *are indirectly formed from solid* NH_4Cl *is a function of the surface of the solid* NH_4Cl (*of the surface of contact of reacting parts of the system*) *and of the concentrations of the gaseous* NH_3 *and* HCl. *The same is the case with the indirect formation of the solid* NH_4Cl *from* NH_3 *and* HCl.

If the surface of the solid NH_4Cl remain during the whole time of the reaction constant, we have instead of (i.′)

$$\frac{dt}{d\tau} = K\left(p_o - \frac{K p_o + c'' p_\tau'^2}{c' + K} \right) = K'' - K''' p_\tau'^2, \quad . \quad . \quad \text{(i.'')}$$

i. e., the velocity of reaction is a function of the concentrations of NH_3 and HCl.

If one of the products of dissociation be introduced, *e. g.*, if in the air-space A mol. NH_3 or HCl are present, and we start the reaction with the solid NH_4Cl, then (i.) becomes

$$p_\tau = \frac{c\Sigma_\tau p_o + c'' p_\tau' (p_\tau' + \mathrm{A})}{c' + c\Sigma_\tau}$$

and (i.′) becomes

$$\frac{dt}{d\tau} = c\Sigma_\tau \left(p_o - \frac{c\Sigma_\tau p_o + c'' p_\tau' (p_\tau' + \mathrm{A})}{c' + c\Sigma_\tau} \right) = c\Sigma_\tau \left(\frac{c' p_o - c'' p_\tau' (p_\tau' + \mathrm{A})}{c' + c\Sigma_\tau} \right), \text{(i.‴)}$$

i. e., *the velocity of dissociation of solid* NH_4Cl *becomes smaller when one of the products of dissociation is introduced.*

As is to be already seen from this comparatively simple case, there is no wonder that to the present the equations for the velocity of chemical reaction in heterogeneous systems could not be found. It is only natural that a simple connexion between the velocity of reaction and the concentrations, or the concentrations and the surface of the solid, has always been sought for; the processes which are taking place here and the remoteness of p_τ from p_o escaped the attention of the experimenters, since the equations for the velocity of evaporation or condensation, &c., were quite unknown to them, and without them there is no possibility of getting to the true equations in this very complicated region of phenomena.

As we shall see in some other examples, the equations for the velocity of chemical reaction in heterogeneous systems easily become of a very complicated form; we now know them, nevertheless, with complete certainty, since they follow directly from well-established and known equations, so that the investigation of the former is reduced to the investigation of the latter.

Let us now take another system in order that we may further follow up the points which come into consideration in the solution of the problems of this kind:—

$$\begin{array}{lll} n\mathrm{A}_1 \text{ gas} \leftrightarrows & m\mathrm{B}_1 \text{ gas} + m'\mathrm{C}_1 \text{ gas.} \\ \downarrow \text{or} \uparrow & \downarrow \text{or} \uparrow \\ \mathrm{A}_1 \text{ solid} & \mathrm{B}_1 \text{ solid,} \end{array}$$

and

$$\begin{array}{lll} n\mathrm{A}_1 \text{ in sol.} \rightleftarrows & m\mathrm{B}_1 \text{ in sol.} + m'\mathrm{C}_1 \text{ in sol.} \\ \downarrow \text{or} \uparrow & \downarrow \text{or} \uparrow \\ \mathrm{A}_1 \text{ solid} & \mathrm{B}_1 \text{ solid,} \end{array}$$

e. g., the dissociation of CaO_3 into CaO and CO_2,

$$\begin{array}{ll} CaCO_3 \text{ gas} \leftrightarrows & CaO \text{ gas} + CO_2 \text{ gas} \\ \downarrow \text{or} \uparrow & \downarrow \text{or} \uparrow \\ CaCO_3 \text{ solid} & CaO \text{ solid.} \end{array}$$

At equilibrium only the reaction in the homogeneous part $CaCO_3 \rightleftarrows CaO_2 g. + CO_2$ is to be considered, *i. e.*,

$$\frac{dt}{d\tau}=c'p_o \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p_o'p''=0,$$

where p_o and p_o' are the vapour-pressure of the solid $CaCO_3$ and CaO, p'' is the pressure of CO_2. We consequently get

$$p''=\frac{c'p_o}{c''p_o'}=K,$$

i. e., p'' is independent of the quantity $CaCO_3$ or CaO taken (observations of Debray, 1867). If CO_2 be introduced we have

$$\left(\frac{dt}{d\tau}\right)=c'p_o \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p_o'(p'''+A)=0, \text{ and } (p'''+A)=\frac{c'p_o}{c''p_o'}=K,$$

i. e., the pressure of CO_2, which is ultimately obtained over the solid $CaCO_3$ and CaO, will remain the same whether CO_2 is introduced or not (observations of Debray).

For the velocity of decomposition of solid $CaCO_3$ into solid $CaO + CO_2$, or of the formation of solid $CaCO_3$ from CaO and CO_2 we have

For $CaCO_3$ solid→ or ←$CaCO_3$ gas:—

$$\text{the equation } \left(\frac{dt}{d\tau}\right)=c\Sigma_\tau(p_o-p_\tau).$$

For $CaCO_3$ gas $\leftrightarrows$ CaO gas + CO_2 gas :—

$$\text{the equation } \left(\frac{dt}{d\tau}\right)'=c'p_\tau \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p_\tau'p_\tau''.$$

For CaO gas→ or ←CaO solid :—

$$\text{the equation } \left(\frac{dt}{d\tau}\right)''=c'''\Sigma_\tau'(p_o'-p_\tau').$$

Now just as much of the solid $CaCO_3$ transforms in the unit of time into gaseous $CaCO_3$ as gaseous CaO and CO_2 are formed from gaseous $CaCO_3$. Therefore

$$p_\tau=\frac{c\Sigma_\tau p_o+c''p_\tau'p_\tau''}{c'+c\Sigma_\tau}$$

and

$$\left(\frac{dt}{d\tau}\right)=c\Sigma_\tau\left(p_o-\frac{c\Sigma_\tau p_o+c''p_\tau'p_\tau''}{c'+c\Sigma_\tau}\right)=c\Sigma_\tau\left(\frac{p_oc'-c''p_\tau'p_\tau''}{c'+c\Sigma_\tau}\right).$$

On the other hand we have that the number of molecules of the solid CaO (if we neglect the quantity of the gaseous CaO) which are formed in the unit of time is equal to the number of molecules of the solid $CaCO_3$ which have disappeared in the same time. Therefore

$$\left(\frac{dt}{d\tau}\right)=c\Sigma_\tau\left(p_o-\frac{c\Sigma_\tau p_o+c''p_\tau'p_\tau''}{c'+c\Sigma_\tau}\right)=\left(\frac{dt}{d\tau}\right)''=c'''\Sigma_\tau'(p_o'-p_\tau'),$$

and from this follows :—

$$p_\tau'=\frac{cc'\Sigma_\tau p_o-(c'+c\Sigma_\tau)c'''\Sigma_\tau'p_o'}{cc''\Sigma_\tau p_\tau''-(c'+c\Sigma_\tau)c'''\Sigma_\tau'}, \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

and

$$\left(\frac{dt}{d\tau}\right)=c\Sigma_\tau\left[p_o-\frac{c\Sigma_\tau p_o+c''p_\tau''\left(\frac{cc'\Sigma_\tau p_o-(c'+c\Sigma_\tau)c'''\Sigma_\tau'p_o'}{cc''\Sigma_\tau p_\tau''-(c'+c\Sigma_\tau)c'''\Sigma_\tau'}\right)}{c'+c\Sigma_\tau}\right]$$

$$=c\Sigma_\tau\left[\frac{p_oc'-c''p_\tau''\left(\frac{cc'\Sigma_\tau p_o-(c'+c\Sigma_\tau)c'''\Sigma_\tau'p_o'}{cc''\Sigma_\tau p_\tau''-(c'+c\Sigma_\tau)c''\Sigma_\tau'}\right)}{c'+c\Sigma_\tau}\right], \quad \text{(ii'.)}$$

i. e., *the velocity of decomposition of solid* $CaCO_3$ *into solid* CaO *and* CO_2 *gas is at the time* τ *a function of the surface of the solid* $CaCO_3$, *of the surface of the formed solid* CaO, *and of the concentration of the* CO_2 *at the time* τ.

If the evaporating surface of the solid $CaCO_3$ be kept constant during the whole time of the reaction, we have

$$\left(\frac{dt}{d\tau}\right)=\mathrm{K}-\mathrm{K}'p_\tau''\left(\frac{\mathrm{K}''-\mathrm{K}'''\Sigma_\tau'}{\mathrm{K}^{\mathrm{iv}}p_\tau''-\mathrm{K}^{\mathrm{v}}\Sigma_\tau'}\right). \quad . \quad . \quad \text{(ii.'')}$$

Let us now take another system :—

$$\begin{array}{llll} n'\mathrm{A}_1\text{ gas or in sol.}+ & n''\mathrm{A}_{11}\text{ gas or in sol.}\leftrightarrows & m'\mathrm{B}_1\text{ gas or in sol.}+ & m''\mathrm{B}_{11}\text{ gas} \\ & \downarrow\text{ or }\uparrow & \uparrow\text{ or }\downarrow & \text{[or in sol.} \\ & \mathrm{A}_{11}\text{ solid.} & \mathrm{B}_1\text{ solid.} & \end{array}$$

$$\begin{array}{llll} \textit{e.g.}\ \mathrm{K_2CO_3}\text{ in sol.}+ & \mathrm{BaSO_4}\text{ in sol.}\leftrightarrows & \mathrm{BaCO_3}\text{ in sol.}+ & \mathrm{K_2SO_4}\text{ in sol.} \\ & \downarrow\text{ or }\uparrow & \uparrow\text{ or }\downarrow & \\ & \mathrm{BaSO_4}\text{ solid.} & \mathrm{BaCO_3}\text{ solid.} & \end{array}$$

At equilibrium the reactions $BaSO_4$ solid→or←$BaSO_4$ in solution and the reaction $BaCO_3$ solid→ or←$BaCO_3$ in solution do not take place; only the reaction K_2CO_3 in solution $+BaSO_4$ in solution $\rightleftarrows$ $BaCO_3$ in solution $+K_2SO_4$ in solution is to be considered. We have therefore

$$\frac{dt}{d\tau}=c'p_0'p\overset{\rightarrow}{\underset{\leftarrow}{-}}c''p_o'''p^{\mathrm{iv}}=0,$$

and since p_o', p_o''' are constant, we have

$$\frac{p^{\mathrm{iv}}\ \text{(concentration of } \mathrm{SO_4K_2} \text{ in solution)}}{p'\ \text{(concentration of } \mathrm{CO_3K_2} \text{ in solution)}}=\mathrm{K}$$

(Guldberg and Waage).

For the velocity of reaction we have :—

For $BaSO_4$ solid→or←$BaSO_4$ in sol. :—

$$\left(\frac{dt}{d\tau}\right)=c\Sigma_\tau(p_o-p_\tau).$$

For K_2CO_3 in sol. + $BaSo_4$ in sol. $\underset{\rightarrow}{\leftarrow}$ $BaCO_3$ in sol. + K_2SO_4 [in sol. :—

$$\left(\frac{dt}{d\tau}\right)'=c'p_\tau \,.\, p_\tau' \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p_\tau''' \,.\, p_\tau^{\text{iv}}.$$

For $BaCO_3$ solid→or←$BaCO_3$ in sol.:—

$$\left(\frac{dt}{d\tau}\right)''=c'''\Sigma_\tau'(p_o'-p_\tau''').$$

Now in a unit of time just as many molecules of solid $BaCO_3$ or of K_2SO_4 in solution are formed as molecules of $BaSO_4$ have disappeared. Consequently

$$\left(\frac{dt}{d\tau}\right)=\left(\frac{dt}{d\tau}\right)'=\left(\frac{dt}{d\tau}\right)''.$$

From $\left(\frac{dt}{d\tau}\right)$ and $\left(\frac{dt}{d\tau}\right)'$ the value of p_τ can be eliminated and $\left(\frac{dt}{d\tau}\right)$ can be represented as a function of Σ_τ, p_τ', p_τ''', p_τ^{iv}; *i. e.*, from this equation and $\left(\frac{dt}{d\tau}\right)''$ we can further eliminate p_τ''' and so ultimately get $\left(\frac{dt}{d\tau}\right)$ as a function of Σ_τ, Σ_τ', p_τ', p_τ^{iv}, *i. e.*, as a function of values which can all be directly observed and can be conveniently verified experimentally. Thus we see that in every system we have always $n+1$ equations if there are n terms, of which each is common to two equations, *i. e.*, we are always able to eliminate these terms, very often inaccessible for quantitative measurements.

It is evident that the laws of chemical velocity of reaction in heterogeneous systems can be best verified experimentally in cases where the vapour-pressure or the solution-pressure of the solid (or liquid) is not too small; then every one of the equations

$$\left(\frac{dt}{d\tau}\right),\quad \left(\frac{dt}{d\tau}\right)',\quad \left(\frac{dt}{d\tau}\right)'',\ \&c.,$$

can be directly investigated and the velocity constants determined.

In conclusion, those few experiments which have been undertaken at different times by different investigators with the object of finding out the laws of the velocity of chemical reaction in heterogeneous systems may be mentioned. De la Rive (1830), Boguski (1876), Kajander (1881), have investigated the velocity of solution of metals in acids, but could not arrive at any simple relations. Boguski attempted then to solve the same problem by an investigation of the velocity of reaction of acids (HCl, HBr, NO_3H) upon Carrara marble (1877), and he found that the equation

$$\frac{dt}{d\tau} = \mathrm{KO}(a-x)$$

holds tolerably well (where O is the surface of the solid marble, $a-x$ is the concentration of the acid). His formula cannot be true, not only for reasons given above, but it contradicts the laws of action of mass. Our system in this case is :—

$$\begin{array}{lll} \mathrm{Zn} \text{ in sol.} + 2\mathrm{HCl} & \leftrightarrows \mathrm{ZnCl_2} \text{ in sol.} + & \mathrm{H_2} \text{ in sol. (saturated)} \\ \downarrow \text{ or } \uparrow & & \downarrow \\ \mathrm{Zn} \text{ solid.} & & \mathrm{H_2} \text{ gas (escapes).} \end{array}$$

$$\begin{array}{lll} \mathrm{CaCO_3} \text{ in sol.} + 2\mathrm{HCl} & \leftrightarrows \mathrm{CaCl_2} \text{ in sol.} + & \mathrm{CO_2} \text{ in sol. (saturated).} \\ \downarrow \text{ or } \uparrow & & \downarrow \\ \mathrm{CaCO_3} \text{ solid.} & & \mathrm{CO_2} \text{ gas (escapes).} \end{array}$$

For solid $CaCO_3$ (solid Zn)→or←$CaCO_3$ in solution (or zinc in solution) we have :—

$$\left(\frac{dt}{d\tau}\right) = c\Sigma_\tau(p_o - p_\tau).$$

For $CaCO_3$ in solution $+ 2HCl$ in solution $\leftrightarrows CaCl_2$ in solution $+ CO_2$ in solution, as well as for Zn in solution $+ 2HCl$ in solution $\leftrightarrows ZnCl_2$ in solution $+ H_2$ in solution, we have :—

$$\left(\frac{dt}{d\tau}\right)' = c'p_\tau \,.\, p'^2 \overset{\rightarrow}{\underset{\leftarrow}{-}} c''p'' \,.\, \mathrm{K},$$

or if the opposite reaction be neglected :—

$$\left(\frac{dt}{d\tau}\right)' = c'p_\tau \,.\, p'^2.$$

Now just as many molecules Zn in solution (or $CaCO_3$ in solution) must in the unit of time transform into $ZnCl_2$ (or $CaCl_2$) and H_2 (CO_2) as molecules of the solid Zn ($CaCO_3$)

are passing into the solution ; therefore :—

$$c\Sigma_\tau(p_o - p_\tau) = c' p_\tau \,.\, p'^2 \;;\; p_\tau = \frac{c\Sigma_\tau p_o}{c' p_\tau'^2 + c\Sigma_\tau}, \quad . \quad . \quad \text{(iii.)}$$

and
$$\frac{dt}{d\tau} = c\Sigma_\tau\left(p_o - \frac{c\Sigma_\tau p_o}{c' p_\tau'^2 + c\Sigma_\tau}\right) = c\Sigma_\tau\left(\frac{p_o c' p_\tau'^2}{c' p_\tau'^2 + c\Sigma_\tau}\right), \quad . \quad \text{(iii.')}$$

i. e., the velocity of solution of zinc or marble in acids, such as HCl, HBr, NO_3H, must be a function of the surface of the solid and of the *square* of the concentration of the acid. The equation for the velocity of solution of marble or zinc in acids belongs to the comparatively very simple cases, but is nevertheless of quite a different form from that which De la Rive or Boguski could, under their circumstances, suppose, since the form and kind of the processes which come into consideration, as well as the laws of evaporation, solution, &c., were not known to them when they carried out their experiments.

It must further be remarked that the equations $\left(\frac{dt}{d\tau}\right)$, $\left(\frac{dt}{d\tau}\right)'$, *&c., must be taken as they actually are*, with all the additional terms for the deviations and abnormalities of whatever kind they may be, should any such complicate or limit the phenomena. For instance, the laws of action of mass are applicable chiefly to dilute solutions or to gases in the dilute state, they cease to hold good as we pass to greater concentrations or to higher pressures. Often the products of the reaction influence the velocity of the reaction and complicate the phenomenon. Reactions of a higher order often occur as if they were reactions of a lower order, &c.

It may be well to emphasize again that the equations derived here for the velocity of chemical reaction in heterogeneous systems hold good only from the time when the velocities become equal and they give no information as to the velocity of reaction before this takes place. For this reason it may happen, though under very exceptional conditions, that one or more of the reactions in the system may first have to almost complete themselves before they can become equal to the rest of the reactions in the system, *i. e.*, that so far as these reactions of great speed are concerned only a small region of their individual curves will be governed by the above equations.

III. *On the real and apparent points of chemical equilibrium in heterogeneous systems.*

It was shown before (Part II.) that all physical reactions between the same substance in the different parts of the heterogeneous system never reach, because of the nature of the equation, the point of equilibrium, and especially that, owing to the interference of external factors such as the surrounding temperature, &c., the obtained points of equilibrium are not the real ones but only apparent points of equilibrium. *It is evident that chemical equilibrium in heterogeneous systems has also only one point where it is real, and this is where equilibrium is real for all its constituent reactions.* Since now the real point of equilibrium is certainly not reached by the physical reactions, it follows that chemical equilibrium in heterogeneous systems is *also* only an *apparent* one, and the obtained results concerning equilibrium will, according to the arrangements of the experiment, always differ from one another, and always only approximate more or less to those results which are the correct ones. Having, namely, for equilibrium of the physical reactions the equation

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K})-c'(t_g-t)=0$$

instead of

$$\frac{dt}{d\tau}=c(t_o-t)(t-t_{ov}+\mathrm{K})=0,$$

the values of p_τ, p_τ' at equilibrium will always differ from P_o, P_o', and, according to the laws of action of mass, there will always be a redistribution between the quantities of each kind of molecules constituting the system in the homogeneous part, so as to correspond to the given values p_τ, p_τ'. Looking thus away from the form of the equations for velocity of reaction themselves, which show that a system can arrive at its point of real equilibrium only in an infinite time, and giving our attention to the more serious source of error arising from external influences, it is evident that to secure success in this region of research all the steps necessary to secure correct equilibrium for the physical reactions must be taken in the first instance. Only after this is done shall we be able from the equations concerning the velocity of reaction to calculate *how far* we succeeded in *approaching* the real point of equilibrium after a given time $\tau_2-\tau_1$. Should the nature of the phenomenon, or of the problem, on some occasions require very great accuracy in the method employed, we shall have here, as in the case of delicate freezing-points, or of solubility measurements, to make also detailed investigation of the values C, c'', t_o-t, $t-t_{ov}+\mathrm{K}$, t_g-t, &c., as this alone will enable us here as there to discriminate between correct and incorrect results, independently of the assertions of every investigator.

Davy Faraday Laboratory,
Royal Institution, May 1902.

V.H. - 1901/2

LIII. *On Conditions controlling the Drop of Potential at the Electrodes in Vacuum-tube Discharge.*—(Second Paper*).

By Clarence A. Skinner, *Adjunct Professor of Physics, University of Nebraska*†.

THE results of experiments described in a former communication seem to indicate that the drop of potential at the electrodes in vacuum-tube discharge is caused by a resistance to discharge of the gas ion to the metal electrode, this resistance increasing with the velocity with which the ion impinges on the electrode. To explain this it is conceived that the discharging ion must give up its kinetic energy with—or before it can give up—its charge. Different physicists have suggested that at least a momentary chemical combination takes place between the carrier and the electrode. It is very plausible then that the elastic reaction of the ion impinging on the electrode introduces a force resisting discharge, the resistance increasing with the velocity of impact. This being true, the ions approaching the electrode will accumulate at its surface until the thereby increased electric intensity becomes sufficient to cause as many to discharge in a given interval as arrive at the electrode during the same interval. From this standpoint the drop of potential will depend on the time required for the discharging ions, arriving with a definite velocity, to come to rest at the electrode—their kinetic energy being first given up by collision with both the neighbouring gas molecules and the electrode.

This being a mechanical explanation of the phenomena the laws of mechanics should be applicable in deducing and in predicting experimental results. The complicated nature of the problem, however, presents at present a discouraging barrier to any rigid mathematical discussion, but a simplified case may be considered in order to test the applicability of the view.

Suppose perpendicular to the plane of the figure (fig. 1) a plane electrode OA. Moving *freely* in the direction aO perpendicular to the electrode is a particle of mass m carrying a positive charge e. This particle is supposed to be driven towards the electrode by a uniform field equal to

$$\frac{V_a - V_0}{a\mathrm{O}} = \frac{V}{s},$$

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* The first paper under this title was published in the Phil. Mag. of Dec. 1901.

† Communicated by the Author, having been read before the American Association for the Advancement of Science, June 1902.

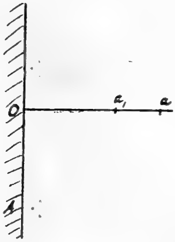
where V is the fall of potential from a to O, and s the distance. The force accelerating the particle is

$$\frac{V}{s}e,$$

and the acceleration produced

$$\frac{Ve}{sm}.$$

Fig. 1.



The kinetic energy of the mass when it reaches O is given by the expression

$$(\tfrac{1}{2}mu^2 + Ve),$$

where u is the velocity of the particle at a, and Ve the work done by the field on the charge e in moving from a to O.

The energy with which the particle rebounds is

$$(\tfrac{1}{2}mu^2 + Ve)k^2,$$

where k is the coefficient of restitution*, $0 < k < 1$. Under the energy of rebound it moves against the field with a decreasing velocity, coming to rest say at a_1 from which position it is again driven by the field to the electrode, reaching it with the same energy with which it left it. The energy with which it rebounds in the second case must be

$$(\tfrac{1}{2}mu^2 + Ve)k^4,$$

likewise for the third

$$(\tfrac{1}{2}mu^2 + Ve)k^6,$$

and so on.

We wish to find the time required for the particle to come to rest at the electrode—it being conceived as the time of discharge. This may be obtained by summing the intervals between successive impacts, considering the time of impact as relatively negligible.

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* See Tait and Steele, 'Dynamics of a Particle,' p. 345.

The time t_1 elapsing between the first and second impacts may be readily obtained by combining the equation of uniformly accelerated motion

$$s_1 = \frac{1}{2}\frac{Ve}{sm}\left(\frac{t_1}{2}\right)$$

(where $s_1 = Oa_1$, and $t_1/2$ the time required to pass over that space) with that of energy,

$$\frac{Ve}{s} \cdot s_1 = (\tfrac{1}{2} mu^2 + Ve)k^2,$$

which gives

$$t_1 = 2s\left[\left(\frac{m}{e}\right)^2 \frac{u^2}{V^2} + \frac{m}{e}\frac{2}{V}\right]^{\frac{1}{2}} k.$$

Likewise we obtain the interval t_2 between the second and third impacts,

$$t_2 = 2s\left[\left(\frac{m}{e}\right)^2 \frac{u^2}{V^2} + \frac{m}{e}\frac{2}{V}\right]^{\frac{1}{2}} k^2;$$

between the third and fourth,

$$t_3 = 2s\left[\left(\frac{m}{e}\right)^2 \frac{u^2}{V^2} + \frac{m}{e}\frac{2}{V}\right]^{\frac{1}{2}} k^3,$$

and so forth.

The time T required for the particle to come to rest at the electrode is given by the infinite series

$$\begin{aligned} T &= t_1 + t_2 + t_3 + \ldots \\ &= 2s\left[\left(\frac{m}{e}\right)^2 \frac{u^2}{V^2} + \frac{m}{e}\frac{2}{V}\right]^{\frac{1}{2}} \{k + k^2 + k^3 + \ldots\}, \end{aligned}$$

which, the series for $0 < k < 1$ being convergent and equal to $\frac{k}{1-k}$, gives

$$T = \frac{2sk}{1-k}\left[\left(\frac{m}{e}\right)^2 \frac{u^2}{V^2} + \frac{m}{e}\frac{2}{V}\right]^{\frac{1}{2}}.$$

Since T must be positive, $0 < k < 1$, and the other quantities chosen positive, the quantity in brackets $[\;]^{\frac{1}{2}}$ must be positive. Assuming this latter has a finite value we have

$$\begin{aligned} &\text{for} && k = 0, \quad T = 0, \\ &\text{and for} && k = 1, \quad T = \infty, \end{aligned}$$

as we should expect—there being no elastic reaction, the particle by first impact sticks to the electrode, while, on the other hand, if there be no loss of energy by impact it will not come to rest at all.

Considering now V as the drop of potential at the electrode, and u the velocity with which the ion enters the space over which this drop takes place, it is evident that

(*a*) for u=const., T decreases with increasing values of V —that is, by increasing the drop at the electrode the discharge of the ion is accelerated;

(*b*) for T=const., V increases with u, which means that to maintain the time of discharge the same the drop at the electrode must increase with the velocity with which the ions move into its field;

(*c*) for T=const. and u=const., V must increase with (m/e)—that is, other conditions being the same, the greater the ratio of the mass of the ion to its charge the greater must be the electrode drop.

Referring to (*a*) we explain the existence of a drop of potential wherever the ions move up to and discharge to a conductor. It also explains the fact that a conductor assumes the potential of the conducting gas, in that for $u=0$, T only approaches infinity as V approaches a zero value. (*b*) explains the simultaneous increase in drop at the two electrodes, in vacuum-tubes, if with the anode in the cathode dark space they are made to approach each other. For, in this case, the ions reaching one electrode are supposed to have emerged from the space covered by the drop at the other, hence a greater drop at the first producing a greater velocity u at the second necessitates thereby a greater drop at the second. The second acts in the same way on the first, so that there is a mutual increase in the drop at the two electrodes. By (*c*) the great difference in anode and cathode drops in vacuum-tubes may be explained under the view that the ratio (m/e) for the positive ions is much larger than for the negative, and hence the cathode drop (for the same velocity of approach u at the two electrodes) necessarily much larger at the cathode than at the anode. It is very likely that the difference would be much greater if the gradient (in the negative glow) driving the positive ions into the cathode field were not much smaller than that (in the positive column) driving the negative ions into the anode field.

We find in these examples that the above equation for T, though deduced from an ideal case, furnishes an explanation for many of the phenomena, and we may therefore conclude that it contains the controlling factors, those ignored entering as correcting factors. It is very likely that the electric intensity is not constant within the space covered by the drop at the electrodes, but in using the total drop we assume a mean value for this intensity which should not make a vital difference in the results. The presence of the neutral gas molecules by impeding the motion of the ions should be marked, especially at the higher gas pressures. On the one hand it should aid in destroying the kinetic energy of the ion, on the other it should increase the time between impacts on the electrode; the former would accelerate the discharge, the latter tend to impede it. There is another important factor which is not introduced in the equation, namely, the attraction of the metal used as electrode for the charge on the ion. As pointed out in the first paper, the discharge is facilitated by this attraction, in that on comparing different metals under the same conditions it is found that the drop decreases as the attraction of the metal for the charge carried by the ion increases.

To further test the above view of the cause of the electrode drop the following experiments were performed. The details of the apparatus are given in the first paper.

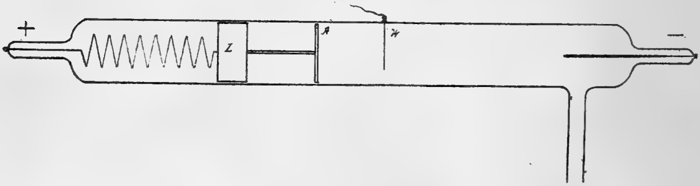
Drop at Anode with Potential Gradient in Neighbouring Gas.

The writer has already called attention (*l. c.*) to the fact that the increase in anode drop with gas pressure may be simply due to the simultaneous increase in the potential gradient in the positive column—in that with increased gradient the ions must be driven into the anode field with a greater velocity.

By using discharge-tubes of different diameters, in which the potential gradient in the positive column increases as the diameter decreases*, the variation of the anode drop with the potential gradient alone may be obtained.

Three tubes of form shown in fig. 2, having diameters of 18, 12, and 8 mm. respectively, were joined together in open connexion, very carefully prepared by repeated evacuations and drying, then filled to the desired pressure with atmospheric nitrogen obtained and purified in the usual manner.

Fig. 2.



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* A. Herz, Wied. *Ann.* liv. p. 244 (1895).

The disk anode A of polished aluminium (diameter to fit the tube) could be moved to any desired position by the action of a magnet on the iron lug L. By measuring the difference of potential between the inserted wire W and the anode at definite distances, the anode drop and potential gradient in the gas could both be obtained. In seeking the variation of the drop with the force driving the ion into the electrode field, it is obviously necessary that the conditions be so chosen that the potential gradient in the gas possess if possible a constant value up to the boundary of the electrode field. It has been found* that this is not the case at low gas pressures, even though the positive column be unstriated, but that to a certain short distance from the anode the gradient may be very small. This condition is, however, approached as the gas pressure increases, so that at the pressure chosen, 2 mm., the gradient rises to a constant value within a very short distance from the anode. The results obtained, given in Table I. and plotted in fig. 3 (p. 496), show, as expected, a marked increase in the anode drop with the potential gradient.

TABLE I.—Variation of Anode Drop with Potential Gradient in Positive Column.
Gas Pressure constant, 2 mm.

	Distance from anode to exploring wire (mm.).	Corresponding P.D. (volts).	Drop at Anode.	Pot. Grad. in Gas (volts/cm.).
1st Tube (diam. 18 mm.)...	0	28·4	28·4	
	10	95·3	...	66·9
	20	160·7	...	65·4
2nd Tube (diam. 12 mm.) .	0	29·9	29·9	
	20	168·2	...	69·2
3rd Tube (diam. 8 mm.) ...	0	33·5	33·5	
	10	108·9	...	75·4
	20	182·7	...	73·8

Anti-cathode Effects.

The phenomena attendant upon the crowding of the negative glow by the walls of the discharge-tube, or other obstruction, are on the whole complicated. Hittorf† found that when the negative glow is restricted in its natural expansion it is accompanied by an increased resistance to the passage of a current through the tube. The idea suggested itself to the writer that this increased resistance is caused by

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[*] C. A. Skinner, Wied. *Ann.* lxviii. p. 752 (1899).

[†] See J. J. Thomson, Rec. Res. in Elect. and Mag. p. 162.

reduced ionization in the negative glow, which in turn necessitates (for the same current passing) an increased velocity of the ions moving up to the cathode, and hence an increased cathode drop.

Fig. 3.

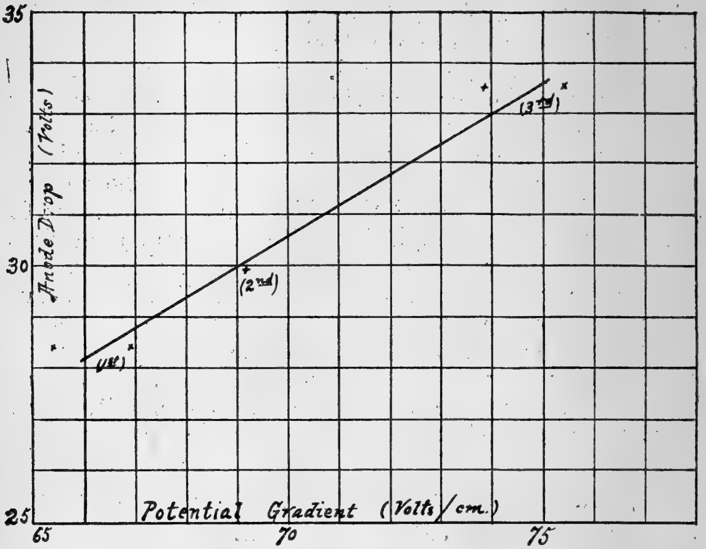
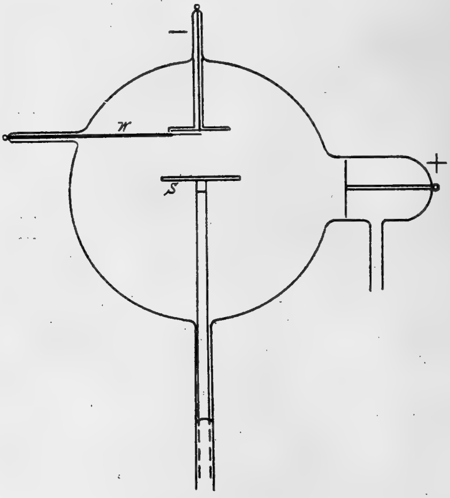


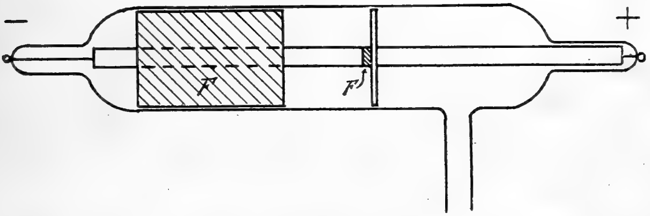
Fig. 4.



To study this a tube of form shown in fig. 4 was first tried. The cathode was inlaid in guttapercha, its stem sheathed in glass tubing. An inserted wire W was used to obtain the cathode drop. A guttapercha screen S parallel to and slightly larger than the cathode was mounted on a glass tube entering through a barometer column. This screen could be shifted to any desired distance from the cathode and its effect on the drop noted. It was found in this case, however, that the negative glow was simply reflected by the screen without any change in the cathode drop. Had the screen been replaced by an anode of the same form the drop would have increased greatly, as previously shown. Though this form of tube was evidently useless for making the desired study, the above experiment is important in that it shows that the increased drop at the cathode when the anode is brought near * is not, as might be supposed, due to an obstruction.

Tubes as shown in fig. 5 were then tried. To vary the conditions three of different diameters (11, 7, and 5·5 mm. resp.) were used. In each a steel cathode (diam. 2 mm., exposed length 6 mm.) passed through a guttapercha cylinder, and was capped by a piece of the same material F. The anode was a steel disk (fitting the tube) placed practically in the negative glow, where its drop is a vanishing quantity. The difference of potential between the terminals of the tube gave, therefore, the cathode drop. The results obtained were puzzling, and it was thought that the three tubes were not operating under similar conditions. They were taken apart, cleaned, and reconstructed with some slight modification in design, and were tried again with similar results, which are given in Table II. and plotted in fig. 6 (p. 499). The curves show at various gas pressures the variation of cathode drop with current.

Fig. 5.



At a pressure 3·6 mm. the drop in the two larger tubes was practically the same, while the smaller gave a higher value. This was to be expected, for the walls of the smaller tube were already confining the negative glow. At 1·2 mm.

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* See first paper.

TABLE II.—Effect of Diameter of Discharge Tube on the Drop at a Co-axial Cylinder Cathode.
Drop at Cathode in Volts.
Diameters :—1st Tube 11·0, 2nd 7, 3rd 5·5 mm.

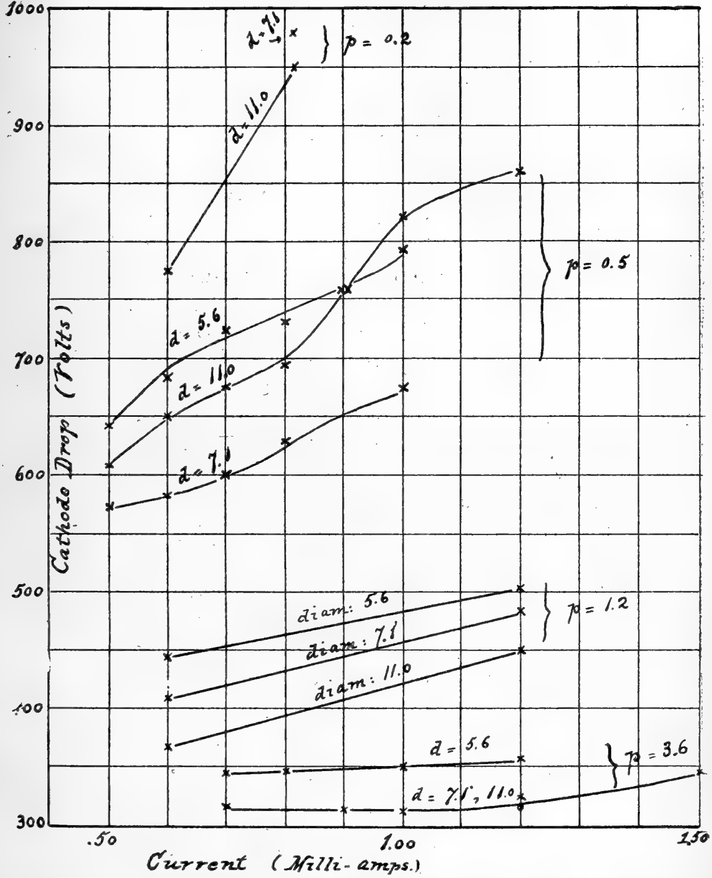
Gas Pressure (mm.).	3·6			1·2.			0·5.			0·2.	
Current.	1st Tube.	2nd Tube.	3rd Tube.	1st Tube.	2nd Tube.	3rd Tube.	1st Tube.	2nd Tube.	3rd Tube.	1st Tube.	2nd Tube.
0·50	...	...	...	...	...	...	605	573	645		
0·60	...	...	...	367	408	445	650	582	685	776	
0·70	316	317	344	...	...	...	672	600	723		
0·80	...	...	345	...	...	...	695	630	732		
0·82	...	...	...	...	...	...	...	...	...	950	980
0·90	316	316	348	...	...	...	755	...	755		
1·00	...	316	350	...	...	...	820	675	795		
1·20	324	318	355	450	485	502	860				
1·50	345										

the negative glow in the two smaller tubes, expanding with decreased pressure, touched the walls, while that in the largest remained still unconfined. At 0·5 mm. the curves are all irregular, but interest centres on the fact that the drop for the largest tube is for all currents above that for the one of intermediate size, while at the higher currents it rises above that for both. Now at this pressure (0·5 mm.) the negative glow in the largest tube just begins to touch the walls, and to the expansion of the glow with increasing current the form of the curves is probably to be attributed. At lower gas-pressures the battery could not maintain a current sufficient for making a complete set of observations, but it was found on decreasing the pressure that at a certain point the cathode drop for the different tubes gave again normal sequence, the smaller tube in each case possessing the greater drop, as shown by the observations taken at 0·2 mm.

These results are explicable when we consider as the ionizing agent the negative ion shot forth with a high velocity from the immediate vicinity of the cathode. The ionization from which the cathode draws its current is largely produced in the negative glow. Beyond the negative glow the ion does not possess sufficient velocity to further ionize the gas. If now in its course the ionizing particle impinges on the wall of the tube it must rebound with a loss of energy. With an incident velocity sufficiently large it should, after impact on the wall, possess a velocity such as to produce ionization, as is probably the case in the cathode dark space ;

if not, as is probably the case in the negative glow, the presence there of the walls of the tube will cause with the

Fig. 6.



same current a smaller degree of ionization, and hence through the thereby increased velocity of the discharging ions a greater cathode drop than either when the walls are brought into the cathode dark space or lie beyond the negative glow.

Effect of Tinfoil-coating on Tube surrounding the Cathode.

The cathode drop in the foregoing experiments was found under certain conditions to be very greatly increased when a sheet of tinfoil was wrapped around the tube opposite the discharging-surface of the cathode. The effect is inappreciable until the negative glow expands to, and is confined by the walls of the tube. It increases then very rapidly with decreasing gas-pressure, so that with a source of limited P.D. it soon prevents the passage of a current through the tube. Under these conditions the tube emits a hissing tone when the current is passing, and the cathode surface rapidly disintegrates, as shown by the deposit on the walls of the tube. If the current be reversed so that the disk serves as cathode, the presence of the tinfoil does not produce the slightest effect.

These phenomena may be explained by assuming a condenser-effect in which the cylinder cathode surface and the tinfoil surrounding the tube are the two surfaces of the condenser. With unconfined negative glow the highly conducting gas screens off the electrostatic forces which would otherwise act between the condenser-surfaces. When, however, by confining the glow the ionization is reduced, the condenser-effect enters, increasing the velocity with which the positive ions move up to the cathode, and thereby increasing their resistance to discharge causes for the same terminal P.D. a decreased current, as observed. With the current reversed the negative glow is not only unconfined in its expansion, but the condenser-effect acts on the ions moving up to the anode instead of the cathode, either of which would prevent any observable change due to the presence of the coating.

Effect of a Magnetic Field on the Electrode Drop.

The effect of a magnetic field on the discharge has been studied by different observers. The following experiments were made to gain a more definite knowledge of the effect of a magnetic field on the electrode drop.

A tube of form shown in fig. 7 was used. A disk-electrode A, of aluminium, was inlaid in guttapercha. The drop at this could be obtained by means of an adjustable wire W. A ponderous magnet being used, the tube was provided with a ground-joint T, so that without shifting it the electrode could be rotated to any desired direction with respect to that of the magnetic field.

At the Cathode.—In Table III. the effect of the field on the cathode drop (the P.D. between the cathode and the negative glow) is given, and the results plotted in fig. 8 (p. 502). They are independent of the direction of the field, and were taken at those pressures at which the field appears to have no influence on the distribution of current at the cathode. At a pressure of 1·8 mm. a field of 760 lines per sq. cm. produces an inappreciable effect; at 0·5 mm. a field of 650 lines reduces the drop about 8 volts; at 0·2 mm., 20 volts; at a much lower pressure about 200 volts. The decrease seems

Fig. 7.

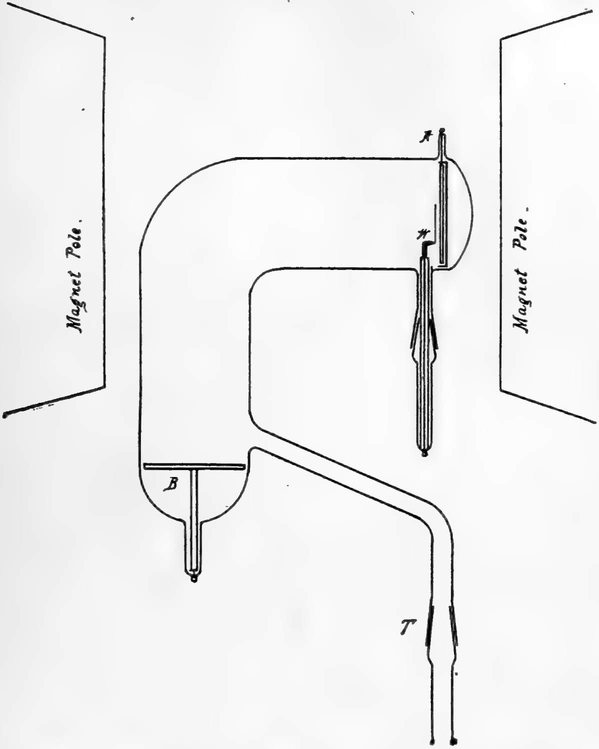


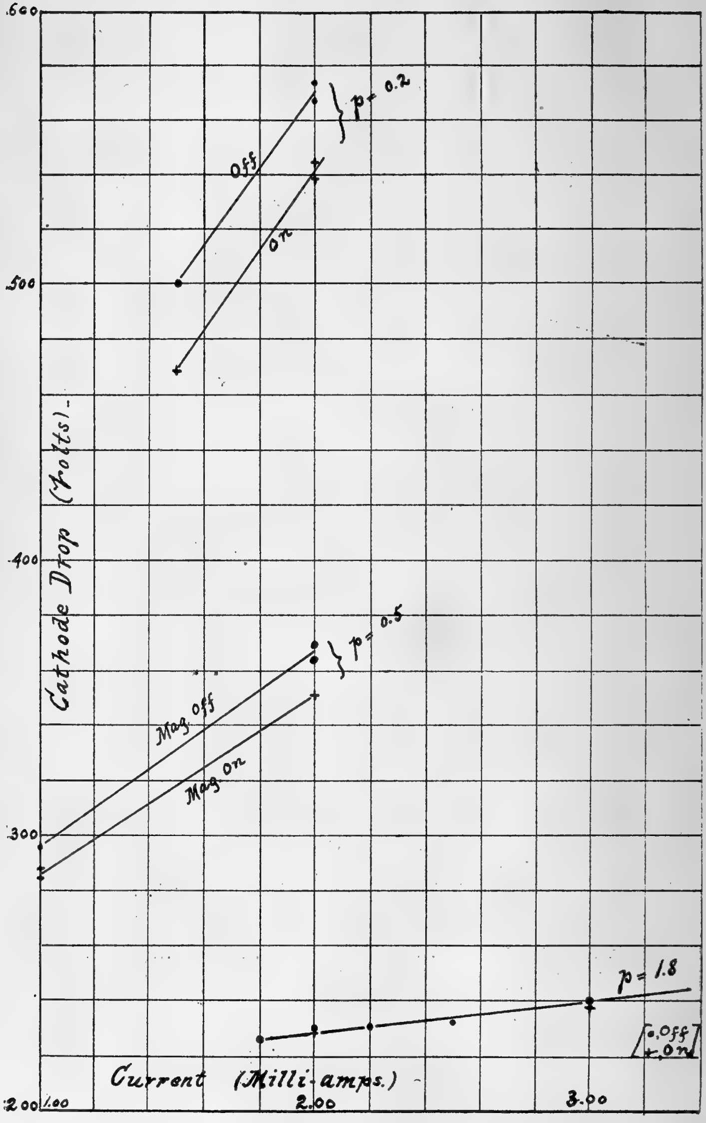
Table III.—Effect of a Magnetic Field on Cathode Drop at various Gas-Pressures.

Gas-pressure in mm.	1·8		0·5		0·2		Very low.	
Current (milli-amps.).	Without Field.	With Field. 760 lines.	Without Field.	With Field. 650 l.	Without Field.	With Field. 650 l.	Without Field.	With Field. 420 l.
0·20	...	...	...	...	...	...	555	355
1·00	...	...	296	289 286				
1·50	...	...	...	...	500	468		
1·80	227							
2·00	230	229	365	352	574 567	544 538*		
2·20	230							
2·50	232							
3·00	240	238						
4·00	252							

* At this pressure the gas deteriorates with currents of the given magnitude more or less rapidly.

very nearly independent of the current, a comparatively slight increase with current being registered.

Fig. 8.



Owing to the limited battery available the observations here are not as complete as could be desired, yet they show beyond a doubt that the effect of a magnetic field on the cathode drop increases without limit as the gas-pressure is reduced.

At the Anode.—The effect of the magnetic field on the anode drop seems, as in other cases, to be controlled by its effect on the gas-gradient. The results given in Table IV. are typical. They are intended to show the relation between anode drop and the gradient in the gas, but on account of the form of the tube being unsuitable for conclusive results on this point, only a few observations were taken. With the current passing from A as anode, the anode drop was obtained with and without magnetic field in the sequence recorded. The current was then reversed, and the difference of potential between the anode B and the negative glow at W measured. The difference between this value and the corresponding anode drop, with and without field, gives the total drop in the gas in each case. Without making a gross error we may assume this to be proportional to the gradient near the anode which drives the negative ion into the anode field, in that this is proportional to the drop in the positive column. Referring to the Table it is observed that the values of the anode drop, 52·8 (mean value) and 37, with and without field respectively, bear exactly the same ratio to each other as the corresponding values of the P.D. 212 and 148 in the gas. The accuracy of this ratio is considered accidental.

TABLE IV.—Effect of Magnetic Field on Anode Drop.

Gas-pressure 0·5 mm. Field-intensity 600. Current 3 m.a.

	Drop at Anode.	P.D. between Anode and Neg. Glow.	P.D. in Gas.
Mag. on	50·6		
Mag. off	37·0		
Mag. on	55		
Mag. off	...	185	148
Mag. on	...	265	212

The very large effect of the magnetic field on the P.D. in gases at low pressures, as observed by Almy[*], is most likely to be attributed to the effect on the cathode drop greatly overshadowing that on the rest of the path.

It is probable that the direct effect of the field on the

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[*] J. E. Almy, Proc. Camb. Phil. Soc. vol. xi. pt. iii.

anode drop is, as at the cathode, to slightly reduce it, but this is greatly overweighed by the indirect effect produced by the increased potential gradient in the gas.

The effect of a magnet on the cathode drop is probably to be ascribed to a factor which has been ignored in the foregoing considerations, namely, to the electromagnetic inertia of the ions, in that the magnetic field in constraining the oscillations of the ions facilitates their discharge.

Physical Laboratory,
University of Nebraska, Lincoln.

LIV. *On the Law of Atomic Weights. A forecast.*

To the Editors of the Philosophical Magazine.

Gentlemen,

THE letter on the Law of Atomic Weights which you were so good as to publish last month, was necessarily limited to a description of results arrived at several years ago, along with the insertion upon a diagram which had been constructed in 1888, of a series of elements since discovered.

To those earlier results I request you to allow me to add a forecast, which I desire to put forward in the hope that the appropriate laboratory tests may be applied to it.

In the diagram reproduced in Plate IV. of last month's magazine, shaded prominences were introduced to point out the elements of greatest atomic volume in the solid state, and shaded sectors to indicate those of least atomic volume. In 1888, when that diagram was designed, it was the elements on sesqui-radius 1 that were preeminent in atomic volume amongst the elements then known. But now that sesqui-radius 16 is occupied, the diagram suggests, and appears to suggest with considerable emphasis, if we recognize that the physical properties of the elements are controlled by general laws, that the column of shaded prominences on sesqui-radius 1 should be shifted to sesqui-radius 16. This would mean that it is the new elements on sesqui-radius 16, and not the elements on sesqui-radius 1, which possess the greatest atomic volume in the solid state.

To ascertain by experiment whether this is so in the case of helium would probably overtask the most refined methods of low-temperature research yet known. But it ought to be possible to determine the specific gravity in the solid state of xenon, krypton, argon, and neon; and if the forecast is found to be correct in regard to these four elements, its fulfilment will add strength to the evidence that the physical properties of the elements are the result of general laws, the truth of which proposition is the basis of the present forecast, and was the conclusion to which the original investigation led.

What that investigation claims to have established may be put briefly. Evidence that seemed conclusive was adduced that the atomic weights of the elements of even and of odd atomicity conform to two slightly divergent laws, the cause of which is obscure, and which, therefore, we can only grope for empirically.

They both, if fully worked out, would furnish values that lie close to the positions fixed by a simpler law, which is either the logarithmic law plotted down upon Plate IV. of last month's Phil. Mag., or the law represented by some other curve which throughout a considerable extent—from lithium to uranium—keeps close to that logarithmic curve.

Of such curves it is mathematically known that the number is unlimited. All but a few of these will represent laws that are so improbable that they may at once be rejected. This, however, may be the most we can do: between the few curves that remain we have not the data for discriminating with certainty so long as we can only investigate the laws of atomic weights empirically.

Under these circumstances, what we seem justified in regarding as established is, that there exist *two definite laws which control the atomic weights of the elements of even and of odd atomicity*; and that these laws *are adequately represented by the law presented by some one of the above family of curves* supplemented by one set of regulated small deviations for the artiads and another set for the perissads: with all the consequences of this suggestive fact. The laws of the deviations were less satisfactorily worked out; enough, however, to show the marked difference between them, and some of their main features, including a predominance in both of a period of 18 places of the Mendeléeff series.

Persons making use of the diagram in last month's Phil. Mag. are requested to insert upon it the following approximate atomic weights.

Neon	20		
Helium	4	Krypton	81
Argon	39·6	Xenon	127

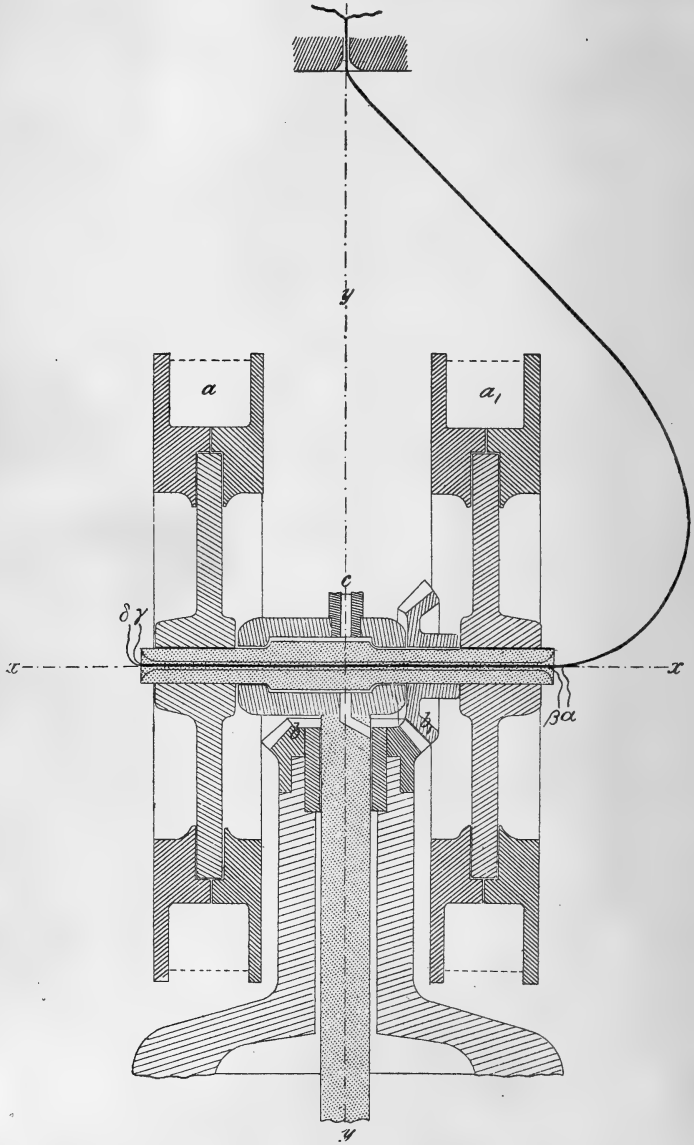
I remain, Gentlemen,
Faithfully yours,
G. Johnstone Stoney.

30 Ledbury Road, W.
September 1902.

LV. *Rotating Earth-Inductor without Sliding-Contacts.*

By J. J. TAUDIN CHABOT*.

THE solenoid of the earth-inductor is divided into two parts, shown at *a* and a_1. Both these parts are mounted on an axis *x x*, the middle portion of which rests in a bearing which



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[*] Communicated by the Author.

is rigidly connected with the end of the axis $y\,y$. At b there is a bevel-wheel connected to the stationary base of the instrument; at b_1 there is a similar wheel, having an equal number of teeth, fixed to the axis $x\,x$. At c there is an oil-reservoir for lubricating the bearings. A flexible thin-wire cable is used as a connector; this is at one end joined to a point in the prolongation of $y\,y$, and at the other, after being led through the hollow axis $x\,x$, is connected at α, β, γ, δ to the windings in a_1 and a.

If now the axis $y\,y$ is made to rotate, then the axis $x\,x$ must, on account of its being geared through $b\,b_1$, make one revolution for each revolution of $y\,y$, so as to leave the flexible cable *untwisted.* Hence if the $y\,y$ axis be placed vertically or horizontally in the magnetic equatorial plane of the earth's field, its rotation will induce currents in the a and a_1 windings; the simultaneous rotation about $x\,x$ does not in any way affect the results.

As will be seen, the uncertain sliding-contacts are by this means entirely eliminated.

Degerloch (Wttbg.), June 27, 1902.

LVI. *The Jacobian of the Primary Minors of an Axisymmetric Determinant with reference to the corresponding elements of the latter.* By Thomas Muir, *C.M.G., F.R.S.*[*]

(1) It would appear that in certain recent work of Professor Karl Pearson's he had occasion to make use of a determinant $|\, r_{1n} \,|$ in which $r_{ij} = r_{ji}$ and $r_{ii} = 1$, and from which was formed another determinant $|\, \rho_{1n} \,|$ such that in every case $\rho_{ij} = \mathrm{R}_{ij} / \sqrt{\mathrm{R}_{ii}\,\mathrm{R}_{jj}}$, the special problem which presented itself being the evaluation of the Jacobian

$$\frac{\partial(\rho_{12}, \rho_{13}, \ldots, \rho_{n-1,\,n})}{\partial(r_{12}, r_{13}, \ldots, r_{n-1,\,n})}.$$

Mr. Arthur Berry, to whom the problem was transferred, successfully solved it, and communicated the result to the Cambridge Phil. Soc. in October 1898[†]. His process consisted in showing that the Jacobian required was obtainable from two other Jacobians of lower order

$$\frac{\partial(\rho_{12}, \rho_{13}, \ldots, \rho_{n-2,\,n-1})}{\partial(r_{12}, r_{13}, \ldots, r_{n-2,\,n-1})}, \qquad \frac{\partial(r_{1n}, r_{2n}, \ldots, r_{n-1,\,n})}{\partial(\rho_{1n}, \rho_{2n}, \ldots, \rho_{n-1,\,n})},$$

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[*] Communicated by the Author.

[†] Pearson and Filon, "On the Probable Errors of Frequency Constants," Phil. Trans. A. cxci. pp. 229–311 (1898); Berry A., "On the Evaluation of a certain Determinant," Proceedings Cambridge Phil. Soc. x. pp. 2–10; Crawford L., "On the Evaluation of a certain Determinant," Proceedings Edinburgh Math. Soc. xviii. pp. 25–27.

being in fact the quotient of the former by the latter, and then of course evaluating these and performing the division. The expressions which he arrived at for his subsidiary Jacobians are not very pleasing in form, viz.:

$$(-1)^{\frac{1}{2}(n-1)(n-2)}\prod_{i=1}^{i=n-1}(1-r_{in}^2)\cdot|\,r_{1n}\,|^{\frac{1}{2}n(n-3)}\left\{\prod_{i=1}^{i=n-1}\mathrm{R}_{ii}\right\}^{-\frac{1}{2}n},$$

$$(-1)^{n-1}\prod_{i=1}^{i=n-1}(1-r_{in}^2)\,.\,|\,r_{1n}\,|^{-(n-1)}\mathrm{R}_{nn}^{\frac{1}{2}n}\left\{\prod_{i=1}^{i=n}\mathrm{R}_{ii}\right\}^{\frac{1}{2}},$$

but the quotient to which they lead is less forbidding, viz.:

$$(-1)^{\frac{1}{2}n(n-1)}\left\{|\,r_{1n}\,|^{n-2}\Big/\prod_{i=1}^{i=n}\mathrm{R}_{ii}\right\}^{\frac{1}{2}(n+1)}.$$

A glance at this suffices to suggest that a loss of simplicity may have occurred through specialization; and a little examination of the form of the elements of the derived determinant $|\,\rho_{1n}\,|$ makes clear that the more appropriate and more promising object of investigation is that which is indicated in the title of the present paper.

(2) In a general axisymmetric determinant of the nth order there are $\frac{1}{2}n(n+1)$ different elements, and the same number of different primary minors; consequently the Jacobian of the latter with respect to the former must be a determinant of the order $\frac{1}{2}n(n+1)$. Further, as each primary minor is of the $(n-1)$th degree in the elements involved in it, its differential-quotient with respect to any one of the latter will be of the $(n-2)$th degree, and therefore the degree of the Jacobian in question will be not higher than $\frac{1}{2}n(n+1)(n-2)$. It will be seen presently that this degree is attained by the Jacobian containing as a factor the $\frac{1}{2}(n+1)(n-2)$th power of the original determinant.

(3) For the purposes of proof it is necessary to draw attention to two results regarding determinants of special form. The one, given by Ferrers* about the year 1857, is almost self-evident, viz.:

$$\begin{vmatrix} 1+a_1 & 1 & \dots & 1 \\ 1 & 1+a_2 & \dots & 1 \\ \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot \\ 1 & 1 & \dots & 1+a_n \end{vmatrix} = a_1a_2\dots a_n\left(1+\frac{1}{a_1}+\frac{1}{a_2}+\dots+\frac{1}{a_n}\right).$$

The other is not so easily stated. It concerns a determinant of the order $\frac{1}{2}n(n+1)$ whose elements are derivable in a peculiar way from those of a determinant of the nth order,

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* Ferrers, N. M., "Two Elementary Theorems in Determinants," Quarterly Journ. of Math. i. p. 364.

every row

$$h_1,\ h_2,\ \ldots,\ h_n$$

of the latter taken along with itself producing the row

$$h_1^2,\ h_2^2,\ \ldots,\ h_n^2,\ 2h_{n-1}h_n,\ 2h_{n-2}h_n,\ \ldots,\ 2h_1h_2$$

of the former, and, taken along with any one

$$k_1,\ k_2,\ \ldots,\ k_n$$

of its fellows, the row

$$h_1k_1,\ h_2k_2,\ \ldots,\ h_nk_n,\ h_{n-1}k_n+h_nk_{n-1},\ \ldots,\ h_1k_2+h_2k_1\ ;$$

and the result in question is that the determinant thus derived is equal to the $(n+1)$th power of the original. A case of this, viz.:

$$\begin{vmatrix} x_1^2 & x_2^2 & x_3^2 & 2x_2x_3 & 2x_3x_1 & 2x_1x_2 \\ y_1^2 & y_2^2 & y_3^2 & 2y_2y_3 & 2y_3y_1 & 2y_1y_2 \\ z_1^2 & z_2^2 & z_3^2 & 2z_2z_3 & 2z_3z_1 & 2z_1z_2 \\ y_1z_1 & y_2z_2 & y_3z_3 & y_2z_3+y_3z_2 & y_3z_1+z_3y_1 & y_1z_2+z_1y_2 \\ z_1x_1 & z_2x_2 & z_3x_3 & z_2x_3+x_2z_3 & z_3x_1+x_3z_1 & z_1x_2+x_1z_2 \\ x_1y_1 & x_2y_2 & x_3y_3 & x_2y_3+y_2x_3 & x_3y_1+y_3x_1 & x_1y_2+y_1x_2 \end{vmatrix} = |\,x_1y_2z_3\,|^4$$

occurs in a paper by Brill[*] published in 1870. The proof of the general theorem may stand over for the present.

(4) Beginning with the axisymmetric determinant of the third order

$$\begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix} \quad \text{or } \Delta,$$

and agreeing to take the six independent variables in the order a, b, c, f, g, h, the Jacobian sought is

$$\frac{\partial(\mathrm{A},\ \mathrm{B},\ \mathrm{C},\ \mathrm{F},\ \mathrm{G},\ \mathrm{H})}{\partial(a,\ b,\ c,\ f,\ g,\ h)} \quad \text{or J},$$

where A, B, ... denote the *signed* complementary minors of a, b, ... As first obtained it takes the form

$$\begin{vmatrix} \cdot & c & b & -2f & \cdot & \cdot \\ c & \cdot & a & \cdot & -2g & \cdot \\ b & a & \cdot & \cdot & \cdot & -2h \\ -f & \cdot & \cdot & -a & h & g \\ \cdot & -g & \cdot & h & -b & f \\ \cdot & \cdot & -h & g & f & -c \end{vmatrix}$$

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[*] Brill A., "Ueber diejenigen Curven eines Büschels," *Math. Annalen*, iii. pp. 459–468.

Multiplying this columnwise by Δ^4 in the form

$$\begin{vmatrix} a^2 & h^2 & g^2 & hg & ga & ah \\ h^2 & b^2 & f^2 & bf & fh & hb \\ g^2 & f^2 & c^2 & fc & cg & gf \\ 2hg & 2bf & 2fc & bc+f^2 & hc+fg & hf+bg \\ 2ga & 2fh & 2cg & hc+fg & ac+g^2 & af+gh \\ 2ah & 2hb & 2gf & hf+bg & af+gh & ab+h^2 \end{vmatrix}$$

we obtain

$$\begin{vmatrix} a\mathrm{A}-\Delta & a\mathrm{B} & a\mathrm{C} & a\mathrm{F} & a\mathrm{G} & a\mathrm{H} \\ b\mathrm{A} & b\mathrm{B}-\Delta & b\mathrm{C} & b\mathrm{F} & b\mathrm{G} & b\mathrm{H} \\ c\mathrm{A} & c\mathrm{B} & c\mathrm{C}-\Delta & c\mathrm{F} & c\mathrm{G} & c\mathrm{H} \\ 2f\mathrm{A} & 2f\mathrm{B} & 2f\mathrm{C} & 2f\mathrm{F}-\Delta & 2f\mathrm{G} & 2f\mathrm{H} \\ 2g\mathrm{A} & 2g\mathrm{B} & 2g\mathrm{C} & 2g\mathrm{F} & 2g\mathrm{G}-\Delta & 2g\mathrm{H} \\ 2h\mathrm{A} & 2h\mathrm{B} & 2h\mathrm{C} & 2h\mathrm{F} & 2h\mathrm{G} & 2h\mathrm{H}-\Delta \end{vmatrix}$$

which, it is evident, equals

$$a\mathrm{A}\,.\,b\mathrm{B}\,.\,c\mathrm{C}\,.\,2f\mathrm{F}\,.\,2g\mathrm{G}\,.\,2h\mathrm{H}$$

$$\times\begin{vmatrix} 1-\dfrac{\Delta}{a\mathrm{A}} & 1 & 1 & \cdots \\ 1 & 1-\dfrac{\Delta}{b\mathrm{B}} & 1 & \cdots \\ 1 & 1 & 1-\dfrac{\Delta}{c\mathrm{C}} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}$$

This last determinant, however (§3),

$$=\frac{\Delta^6}{a\mathrm{A}\,.\,b\mathrm{B}\,.\,c\mathrm{C}\,.\,2f\mathrm{F}\,.\,2g\mathrm{G}\,.\,2h\mathrm{H}}\left\{1-\frac{a\mathrm{A}+b\mathrm{B}+c\mathrm{C}+2f\mathrm{F}+2g\mathrm{G}+2h\mathrm{H}}{\Delta}\right\};$$

consequently we have

$$\mathrm{J}\Delta^4=\Delta^6\left\{1-\frac{3\Delta}{\Delta}\right\}$$

and therefore $\mathrm{J}=-2\Delta^2.$

(5) In the case of the axisymmetric determinant of the

fourth order

$$\begin{vmatrix} a_1 & a_2 & a_3 & a_4 \\ a_2 & b_2 & b_3 & b_4 \\ a_3 & b_3 & c_3 & c_4 \\ a_4 & b_4 & c_4 & d_4 \end{vmatrix}, \text{ or } \Delta \text{ say,}$$

the Jacobian

$$\frac{\partial(A_1,\ B_2,\ C_3,\ D_4,\ C_4,\ B_4,\ B_3,\ A_4,\ A_3,\ A_2)}{\partial(a_1,\ b_2,\ c_3,\ d_4,\ c_4,\ b_4,\ b_3,\ a_4,\ a_3,\ a_2)}$$

(where the order of the independent variables deserves notice) is equal to

$$\begin{vmatrix} \cdot & c_3d_4-c_4^2 & b_2d_4-b_4^2 & \cdots & \cdot \\ c_3d_4-c_4^2 & \cdot & a_1d_4-a_4^2 & \cdots & \cdot \\ b_2d_4-b_4^2 & a_1d_4-a_4^2 & \cdot & \cdots & 2(a_4b_4-a_2d_4) \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & a_4b_4-a_2d_4 & \cdots & c_4^2-c_3d_4 \end{vmatrix}$$

Multiplying this by Δ^5 in the form

$$\begin{vmatrix} a_1^2 & a_2^2 & a_3^2 & \cdots & a_1a_2 \\ a_2^2 & b_2^2 & b_3^2 & \cdots & a_2b_2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 2a_1a_2 & 2a_2b_2 & 2a_3b_3 & & a_1b_2+a_2b_1 \end{vmatrix}$$

we obtain

$$a_1A_1 \,.\, b_2B_2 \,.\, c_3C_3 \,.\ \ldots\ .\, 2a_3A_3 \,.\, 2a_2A_2$$

$$\times \begin{vmatrix} 1-\dfrac{\Delta}{a_1A_1} & 1 & \cdots & 1 \\ 1 & 1-\dfrac{\Delta}{b_2B_2} & \cdots & 1 \\ \cdot & \cdot & \cdot & \cdot \\ 1 & 1 & \cdots & 1-\dfrac{\Delta}{2a_2A_2} \end{vmatrix}$$

so that we have

$$J\Delta^5 = \Delta^{10}\left\{1-\frac{a_1A_1+b_2B_2+\ldots+2a_2A_2}{\Delta}\right\};$$

and as

$$\begin{aligned} a_1A_1+b_2B_2+\ldots+2a_2A_2 &= a_1A_1+a_2A_2+a_3A_3+a_4A_4 \\ &\quad +a_2A_2+b_2B_2+b_3B_3+b_4B_4 \\ &\quad +a_3A_3+b_3B_3+c_3C_3+c_4C_4 \\ &\quad +a_4A_4+b_4B_4+c_4C_4+d_4D_4 \\ &= 4\Delta, \end{aligned}$$

the final result is

$$J=\Delta^5(1-4).$$

(6) The process, it is not difficult to see, is perfectly general, the fundamental part of it being the multiplication of the Jacobian by Δ^{n+1} expressed in a particular form, and the transformation of the product into $\Delta^{\frac{1}{2}n(n+1)}\left(1-\frac{n\Delta}{\Delta}\right)$. This gives the equation

$$J\Delta^{n+1}=\Delta^{\frac{1}{2}n(n+1)}\left(1-\frac{n\Delta}{\Delta}\right),$$

whence there follows

$$J=(1-n)\Delta^{\frac{1}{2}(n+1)(n-2)}.$$

Since $|A_{1n}|=|a_{1n}|^{n-1}$, and therefore

$$|A_{1n}|\div|a_{1n}|=|a_{1n}|^{n-2}$$

the theorem may be more neatly enunciated thus :—*If* $|a_{1n}|$ *be an axisymmetric determinant, then*

$$\frac{\partial(A_{11}, A_{22}, \ldots, A_{nn}, A_{n-1,n}, \ldots, A_{12})}{\partial(a_{11}, a_{22}, \ldots, a_{nn}, a_{n-1,n}, \ldots, a_{12})}=(1-n)\left\{\frac{|A_{1n}|}{|a_{1n}|}\right\}^{\frac{1}{2}(n+1)}.$$

(7) Putting $n=3$ we obtain a result in which both Sylvester and Cayley were interested from a totally different point of view*, and which on account of its seemingly unique character has attracted considerable attention since their time.

Capetown, South Africa,
16th July, 1902.

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* Sylvester J. J., "Examples of the Dialytic Method of Elimination as applied to Ternary Systems of Equations," Cambridge Math. Journ. ii. pp. 232–236 (1841); Cayley A., "Note upon a Result of Elimination," Phil. Mag. [4] xi. pp. 378–379 (1856).

LVII. *Notices respecting New Books.*

The Scientific Writings of the late GEORGE FRANCIS FITZGERALD. Collected and Edited with a Historical Introduction by JOSEPH LARMOR, Sec. R.S., Fellow of St. John's College, Cambridge. Dublin: Hodges, Figgis, & Co.; London: Longmans, Green, & Co. 1902.

IT will be long before the painful impression created by FitzGerald's early death wears out among his contemporaries. A regret, less personal perhaps, will at all times be evoked by the perusal of these papers that their brilliant author should have been taken from the harvest time of life.

Although there are but a few—among whom the distinguished editor of this book is one of the foremost—who can enter fully into FitzGerald's ideas in all their varied scope, there are few also who will not find in this collection of scientific writings something in their particular line of study which they may listen to as students to the words of a master. For it may safely be asserted that no scientist of his times was more extensively acquainted with contemporary scientific thought than was FitzGerald; and being of a fertile invention and always desirous of assisting others his ideas ranged over the whole extent of physical science, and often well over its boundaries into other divisions of scientific thought. But the salient feature of his writings is, undoubtedly, his work in the field opened more especially by Maxwell, and perhaps the chief event in his scientific career his connexion with, and participation in, the work of Hertz. Far the larger part of this volume of scientific papers is devoted to his papers on electromagnetic theory. To the last days of his life this subject occupied his thoughts. In the twenty-five years preceding his death—dating from his paper on the Kerr effect (in which FitzGerald first experienced the highest pleasure of the investigator, that of predicting the result)—FitzGerald was one of the foremost in this field; and those of his contemporaries who have worked along with him will be chiefly glad of this collection of his writings and of their careful editing by Prof. Larmor.

Any analysis of these several memoirs here would be superfluous—even did the present writer feel qualified for the task—in view of the very complete review which the editor has supplied as an introduction to the collected papers. Indeed this introductory account of the life and thought of FitzGerald by Prof. Larmor (reprinted with additions from the 'Physical Review') might be taken as a model of what the editor's work should be in such a case, and adds greatly to the value of the book. Here the student of his papers may find not only a synopsis of the paper he desires to peruse, but also an account of its bearing on preceding and contemporary thought and its influence on scientific advance.

But, as already said, papers appear here on many branches of Physical Science. FitzGerald's attention to the physics of the æther by no means resulted in neglect of other branches of scientific thought.

In molecular physics his papers on ionic theory and the nature of ions, and more especially a very original note communicated to 'Nature' "On the size at which Heat Movements are Manifested in Matter," are specially characteristic of the suggestiveness of the writer and of his brevity of expression; although in these, as in some others of his more speculative papers, suggestions appear to be made often more with a view to provoke inquiry than as intended to be in themselves any advance into Mr. Heaviside's "bottomless pit" of truth. This last paper may be cited as exemplifying a remark already made. It was in discussing with the present writer the difficulties of the problem of the Brownian movement or Pedesis and endeavouring to assist him in his work that the idea of this source of possible energy occurred to FitzGerald, although the applicability of the idea to pedetic phenomena is not strongly pressed by its originator.

Even to enumerate the various subjects dealt with in the collected papers would be impossible within the bounds of a short notice. Cathode Rays; the Kinetic Theory of Gases; Surface-tension Phenomena; The Zeeman Effect; Crookes's Force; Fluorescence; A Theory of Auroræ (an interesting paper not hitherto published); and various subjects in Thermodynamics, have evoked new and striking ideas from FitzGerald. But in no part of FitzGerald's writings is his universality so impressed upon the reader as in his reviews and memoirs. Of these many came from his pen; the best known being the Helmholtz Memorial Lecture; the summary of Lord Kelvin's researches; the Obituary Notice of Clausius; the review of Boltzmann's account of Maxwell's electromagnetic theory; of Hertz's Principles of Dynamics and of his Miscellaneous Papers; of Mr. Heaviside's papers; and of Professor Larmor's 'Æther and Matter.' What could be more admirable? It has been said that in proportion to the great intellectual grasp of FitzGerald his papers are few. Doubtless this is true, and yet he who knows what is in this volume will feel that to have written even but a couple of the best of the writings therein were a sufficient apology for a longer life-time than was allotted to George Francis FitzGerald.

FitzGerald lived too completely in touch with the best thinkers of his time not to realise the vital importance of educational questions. No one was better acquainted with the necessities and difficulties of the new education than the author of the many educational papers included in Professor Larmor's volume. Although himself a splendid proof that a really powerful mind can survive the examination mill and come out of it with unimpaired originality, he well knew the numbing effects of "that horrible teaching for examinations." The short paper on "Universities and Research" should be read and known by all in the high places of education. FitzGerald's expressed intention of devoting himself even more entirely to educational questions cannot but be applauded, although certainly it had been deplored by less far-seeing men. The return on educational work is important and immediate. A very few years and the younger generation is acting in, and influencing, our times; to condemn or to reward us. Controversial letters on the educational questions agitating his own University are wisely omitted from the collection of his writings as being of passing and local interest only.

In the resurrection and collection of FitzGerald's important shorter letters published in various contemporary Journals, Professor Larmor confers a particular benefit. FitzGerald was so busy a man in discharging the duties towards his chair, towards societies and committees in his own city, and towards a wide circle of friends, that many valuable ideas were given to the world in such a form that from the ephemeral nature of their surroundings they were apt to be lost to those coming after.

The volume concludes with a contribution from the editor on the subject of the experiment suggested by FitzGerald shortly before his death as to whether convection through the æther can be detected electrically. Dr. Trouton's paper on this subject—reprinted from the Scientific Transactions of the Royal Dublin Society—is also given and will be read with interest. The editor in his introduction also discusses this subject, the interest of which is increased by the recent paper of Dr. Hicks's appearing in the Philosophical Magazine of last January. It is noteworthy that the idea of deriving energy from a relative motion of the Earth and the æther was in FitzGerald's mind when he penned his review of Professor Larmor's 'Æther and Matter' (p. 514) already referred to.

The editor takes occasion to acknowledge the able assistance he received from Professor W. E. Thrift—FitzGerald's successor to the Erasmus Smith Chair of Experimental Physics—more especially in the revision of the mathematical papers. A beautiful and prized addition to the volume is the portrait presented by Mr. J. W. Swan, F.R.S. Many who have enjoyed the friendship of the great original—and they *are* many—will be grateful for it. It is absolutely faithful. J. J.

A travers La Matière et L'Énergie. Par le Docteur F.-E. BLAISE. 68 photogravures dans le texte. Paris: Librairie Ch. Delagrave. Pp. 344.

THIS book is about the queerest medley of scrappy science and somewhat rash speculation which we have ever come across. The author attempts to develop a system of philosophy which—according to his own estimate—throws a flood of light on the many mysteries of human existence. In a footnote to p. 336, he informs us that for some twelve to fifteen years he lived a confirmed atheist and materialist; a perusal of the book would have led us to the conclusion that the mental history of its author must have been a very chequered one. We hardly think it necessary to enter into any detailed criticism. Some idea of the book may, however, be gathered from the headings of the chapters. One of these is "Magneto- and Dynamo-Electric Machines";

another, "Refutation of Darwinism"; a third, "Science and Religious Dogma." In this latter, the Doctrine of the Trinity is by the author found to be analogous to the three modes in which (according to him) energy is capable of manifesting itself. We may add in conclusion that the publishers of the book have very obligingly inserted into it a slip containing the sort of review of the book which they wish to appear; this, however, we have found it necessary to modify somewhat.

LVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 424.]

April 16th, 1902.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Carlisle Earthquakes of July 9th & 11th, 1901.' By Charles Davison, Sc.D., F.G.S.

The shocks were at least four in number, and there are single records of four other shocks. The isoseismal 5 of the first and principal shock is very nearly a circle 29 miles in diameter, with its centre 7 miles south-south-west of Carlisle, and is excentric with regard to the isoseismal 4. The continuity of the shock over a band extending from Carlisle to Coniston implies a corresponding continuity in the focus. The investigation of the earthquakes has led to the recognition of a deep-seated fault, the average direction of which is N. 5° E. and S. 5° W. and the hade throughout is to the east. In the surface-rocks there is no sign whatever of such a structure. The movements along the fault were somewhat peculiar. In the first shock the focus was of considerable length, and consisted of two principal portions, the centres of which were about 23 miles apart, connected by a region wherein the slipping was continuous throughout, and much less in amount. The northern part of the focus was smaller than the other, but was marked by a much stronger impulse. The third slip was complementary to the first, for it appears to have occupied the whole of the region between the two principal portions of the first focus, and to have been greatest near the centre of that region and to have gradually diminished towards both ends.

2. 'The Inverness Earthquake of September 18th, 1901, and its Accessory Shocks.' By Charles Davison, Sc.D., F.G.S.

Since the Comrie earthquake of 1839, which was followed by 330 tremors and earth-sounds within little more than two years, no British earthquake has been attended by so many accessory shocks as this one. The unusual intensity of the earthquake, its apparent connexion with the great northern boundary-fault of the Highlands, and the possibility of tracing oscillations in successive centres of disturbance along the fault-surface, combined in rendering a detailed investigation desirable. With a few exceptions, the earthquakes originated beneath the district lying between Inverness and the north-eastern end of Loch Ness. The mean direction of the fault, which follows the line of the Great Glen, is N. 35° E. and S. 35° W. and its hade is to the south-east. The isoseismal 8 contains 67 square miles, and its centre is about $1\frac{1}{2}$ miles east-north-east of Dochgarroch and $\frac{3}{4}$ mile south-east of the fault-line. The correspondence between the position of the great boundary-fault and of the fault inferred from the seismic evidence is so close, that there can be little doubt that the earthquake was due to a slip along this fault.

The nature of the shock, the sound-phenomena, time-relations, and after-shocks are described in detail, and some account is added of the earthquakes of 1890 and of sympathetic earthquakes in the valley of the Findhorn. There were two distinct slips in rapid succession, with continuous slight motion between them, the second being greater in amount and extending over an area which probably overlapped, even if it did not entirely include, that within which the first took place. The great slip reached nearly from Loch Ness to Inverness, and was greatest at a point about half-way between. The three chief after-slips resulted in an extension of this area in both directions along the fault-surface, the extension to the north-east being small, while that to the south-west amounted to 6 miles or more. In addition to this migration of the focus, there was also a continuous decrease in the depth of the focus. The earthquakes provide no evidence with regard to the direction of displacement along the boundary-fault. There can be little doubt, however, that Loch Ness is still growing; but it can hardly be determined whether the lake is now contracting in area, or whether it is gradually pushing its way outward to the sea.

3. 'The Wood's Point Dyke, Victoria (Australia).' By Frederic Philip Mennell, Esq., F.G.S.

This dyke is intrusive into a belt of Silurian (Upper Silurian) strata which strike in a direction somewhat west of north, and extend beyond Walhalla on the south. Wood's Point is about 75 miles east of Melbourne. It may be taken as typical of the intrusions associated with the Silurian rocks of the Victorian gold-fields. Brown, original, hornblende is the dominant constituent, but it is rarely idiomorphic; augite, three varieties of felspar, micropegmatite, and ilmenite are also present, in a microcrystalline or cryptocrystalline groundmass. The rock is called a hornblende-porphyrite. In certain varieties cordierite occurs, and is accounted for by derivation from the adjacent shales. The reefs in the Silurian and Ordovician rocks usually occur at or near the contact with intrusive rocks. At Wood's Point the reefs are nearly horizontal, traversing dykes and shales, the junction usually marking the occurrence of rich ore. The author notes the 'almost invariable association of gold in this class of deposit with rocks containing original hornblende.'

April 30th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read :—

1. 'The Origin and Associations of the Jaspers of South-eastern Anglesey.' By Edward Greenly, Esq., F.G.S.

Red jasper and jaspery phyllite are widely distributed in the southern and south-eastern parts of Anglesey, in the districts of Newborough, Pentraeth, and Beaumaris. They are associated with limestones, diabases, serpentines, and with grits and shales. They have been much modified by earth-movements, which have produced brecciated and schistose structures ; but where original structures have survived, the true relations of the rocks can often be seen. The diabases have the same characters as the pillowy and variolitic rocks so often associated with radiolarian cherts and jaspers in many parts of the world, and at several different geological horizons; and the relationships of the jaspers and igneous rocks resemble those seen in the radiolarian cherts of Southern Scotland. It is inferred that the jaspers are altered radiolarian cherts. The evidence for the age of the group is incomplete. There is not sufficient evidence to refer it to the Arenig Series, and it is possible that it belongs to an altogether different period. Its relation to the crystalline schists of the region is obscured by conflicting evidence : one chain of reasoning leads to the view that the group is older than the schists, and has been involved in their metamorphism ; while another gives strong reason for supposing that it is of later date.

2. 'The Mineralogical Constitution of the Finer Material of the Bunter Pebble-Bed in the West of England.' By Herbert Henry Thomas, Esq., B.A., F.G.S.

Specimens were collected at intervals, from Budleigh Salterton, in Devon, to Fitzhead near Milverton, in Somerset, and other sands, for comparison, were taken from the red rocks above and below. After treatment with acids, to remove iron-oxides, the sands were separated by heavy liquids into three parts :—

(*a*) Heavy residue : specific gravity exceeding 2·8.
(*b*) The bulk of the quartz.
(*c*) The lighter part, with most of the alkali-felspar.

The sands, on the whole, contain a very small percentage of minerals with a specific gravity of more than 2·8 ; while the proportion of material over, to that under, 2·58 is about 70 or 80 to 30 or 20 per cent. A list and description of twenty minerals found in the sands is given, with, in some instances, the chief characters by which they were identified. The compound grains include felsite, quartzite, chert, shimmer-aggregates, leucoxene, and other decomposition-products. The gradual decrease in the percentage of heavy minerals from Budleigh Salterton to Uffculm indicates the carriage of sediment by a southerly current, and this view is strengthened by the decrease in staurolite and a gradual diminution in the size of the tourmaline-grains. The increase in proportion of heavy grains from Uffculm to Milverton, and the further decline northward, together with the incoming of an assemblage of minerals markedly different from the normal southerly type, indicates an additional source of supply, perhaps a westerly current. The mass of material seems to have been furnished by a highly metamorphosed area, differing widely in its character from any now exposed in the South-west of England. The most probable source of much of the material is the Armorican massif of Triassic times.

3. 'Revision of the Phyllocarida from the Chemung and Waverly Groups of Pennsylvania.' By Prof. Charles Emerson Beecher, Ph.D., F.C.G.S.

May 14th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'On Pliocene Glacio-Fluviatile Conglomerates in Subalpine France and Switzerland.' By Charles S. Du Riche Preller, M.A., Ph.D., A.M.I.C.E., M.I.E.E., F.G.S.

In a paper read before the Society in 1896, the author described a variety of Deckenschotter deposits above, near, and below Zurich, which, occurring both on the hills and at low levels of the valleys of that district, tended to the conclusion that at the time of their formation, towards the end of the Pliocene Period, the principal valleys and lake-basins of Subalpine Switzerland were already eroded approximately to their present depth.

Further examination has, however, led him to recognize that the low-level deposits, although in manyrespects not unlike Deckenschotter, are the products of the younger or Pleistocene glaciation, and that only the deposits *in situ* on the ridge of the hills can be referred to the Pliocene glaciation of the Alps.

In the present paper, the author describes a number of further deposits of typical Deckenschotter conglomerate recently examined in the Aare and Rhine valleys, near the confluence of those rivers, and shows that these, in conjunction with the Deckenschotter deposits of the Zurich district, indicate the almost unbroken outline of a Subalpine Deckenschotter cone, which extended from the base of the Alps in a north-westerly direction over a distance of about 25 miles, and was formed by the waters of the retreating Rhine (Western) glacier and its affluents on a Molasse plateau, the upper and lower ends of which were at the contours of 900 metres and 500 metres respectively.

He further describes a series of Deckenschotter deposits examined in the Rhone Valley between Lausanne and Lyons, including the extensive plateau of the Dombes, east and north of Lyons, composed of marine marl overlain by the characteristic conglomérat ferrugineux, which some French geologists still regard as pre-Glacial and others as Quaternary, but which is typical Deckenschotter, and in the full acceptation of the term an alluvion des plateaux. The deposits thus described afford proof of the existence, in Upper Pliocene times, of an extensive alluvial cone about 100 miles in length, which reached from Lausanne (probably even from the base of the Alps) to Lyons, and was formed by the waters of the retreating Rhone and Arve glaciers on a Molasse-and-marl plateau, the altitude of which above sea-level was 800 metres near Lausanne, and 300 metres near Lyons.

From this concurrent evidence in Northern Switzerland and in the Rhone Valley, the author is led to conclude:

(1) That at the time of the deposition of those alluvial cones, the principal Subalpine valleys and lake-basins could not as yet have existed in their present form or depth, and must have been from 100 to 200 and 400 metres higher; and

(2) That the Subalpine valleys were eroded to their present depth in the course of the inter-Glacial Period—now recognized to have been of very long duration—between the Pliocene and the Middle Pleistocene (or maximum) glaciations, and that the Subalpine lake-basins were formed in the same period by the contemporaneous action of fluviatile erosion and of a zonal settling along the base of the Alps after these had been raised by horizontal pressure.

2. 'Overthrusts and other Disturbances in the Braysdown Colliery (Somerset), and the Bearing of these Phenomena upon the Effects of Overthrust-Faults in the Somerset Coalfield in general.' By Frederick Anthony Steart, Esq.

This coalfield, although covered by comparatively undisturbed Secondary rocks, is in part the most disturbed and contorted of those known and worked in the United Kingdom. It is seldom, in some parts of it, that one sees 200 yards of coal without a fault or other disturbance. The 'Radstock Seams' of the Upper Coal-Measures at Radstock are traversed by a huge 'overlap-fault, which thrusts them forward for a great distance; this runs nearly east and west, and has parallel to it two smaller overthrusts. In one of them the coal at first dips towards the thrust, then it thickens from 2 to 6 or 8 feet, next it becomes inverted, and eventually regains its former character. The continuity of the coal has been proved in the case of three of the coal-veins. As there is practically the same sequence of strata on both sides of the fault, it is concluded that the 'overthrusts' did not take place till all the coal-seams of the Radstock Series had been deposited. The areas of 'dead ground,' sometimes considered to be wash-outs, are probably also the result of movement. The areas occur near faults, frequently take a course parallel to overthrust-faults, and, at their margins, the coals are often reduplicated. 'Dead ground' is usually found only in those seams which lie on a floor of soft black shale, and sometimes, instead of dead ground, there are large areas with very thin coal. The flat roofs of coal-seams in the dead ground are invariably striated. The author's theory is that all these effects have been caused by the gradually increasing movement of the strata from the top seam or 'Great Vein' to the bottom seam or 'Bull Vein.' The coal-seams nearly always thin from their undersides upward, as though the floor had moved farther, or at a greater rate, than the roof.

THE
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PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

NOVEMBER 1902.

LIX. *On the Distillation of Binary Mixtures.*
By Lord RAYLEIGH, *O.M., F.R.S.*[*]

AT various times during the past twenty years I have turned my attention to the theory of distillation, and have made experiments upon a question, as to which information seemed to be almost entirely lacking, viz., the relation between the strengths of liquid and vapour which are in equilibrium with one another when a binary mixture is subjected to distillation. In order to be intelligible I must set forth a little in detail some matters which are now fairly well known and understood, although they were not so at the time when my notes were written.

Distillation of a Pure Liquid.

The temperature of the saturated vapour just over the liquid depends upon the pressure. If the end of the condenser-tube, *e. g.*, of the Liebig type, be open, the pressure is of necessity nearly atmospheric. Suppose that in this tube a piston, moving freely, separates pure vapour from pure air. Then the whole wall of the condenser on the vapour side is almost at boiling-point. If we imagine the piston removed, the air and vapour may mix, and it is now the total pressure which is atmospheric. Wherever the temperature is below boiling there must be admixture of air sufficient to bring up the pressure.

Two or more Liquids which press independently.

This is the case of liquids like water and bisulphide of carbon whose vapour-pressures are simply added. So long

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[*] Communicated by the Author.

as the number of ingredients remains unchanged, the composition of the vapour rising from the boiling mixture is a function of the temperature (or total pressure) only. Hence in simple distillation the composition of the distillate remains constant until perhaps one constituent of the liquid (not necessarily the most volatile) is exhausted. At this point the distillate, as well as the boiling-temperature, changes discontinuously and the altered values are preserved until a second constituent is exhausted, and so on. None of the separate distillates thus obtained would be altered by repetition of the process at the same pressure.

Liquids which form true Mixtures.

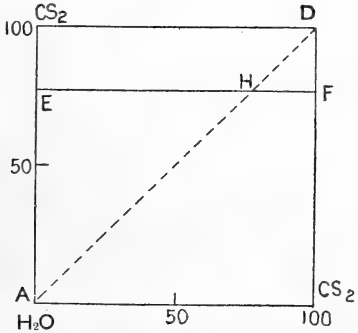
The above is as far as possible from what happens in the case of miscible liquids, *e. g.*, water and common alcohol. Here the composition of the vapour, as well as the boiling-point under given pressure, depends upon the composition of the liquid, and all three will in general change continuously as the distillation proceeds. But, so long as the total pressure is fixed, to a given composition of the liquid corresponds a definite composition of the vapour; and it is the function of experiment to determine the relation between the two. The results of such experiments may be exhibited graphically upon a square diagram (*e. g.* figs. 3 and 4, pp. 530 and 533) in the form of a curve stretching between opposite corners of the square, the abscissa of any point upon the curve representing the composition of the liquid and the ordinate representing the composition of the vapour in equilibrium with it. For the pure substances at the ends of the scale, represented by opposite corners of the square, the compositions of liquid and vapour are necessarily the same.

The character of the separation capable of being effected by distillation depends in great measure upon whether or not the curve meets the diagonal at any intermediate point, as well as at the extremities. If there be no such intersection, the curve lies entirely in the upper (or in the lower) triangular half of the square, so that for all mixtures the distillate is richer (or poorer) than the liquid. As the distillation of a limited quantity of mixed liquid proceeds, the composition of the residue moves always in one direction and must finally approach one or other condition of purity.

If on the other hand the curve crosses the diagonal, the point of intersection represents a state of things in which the liquid and vapour have the same composition, so that distillation ceases to produce any effect. This happens for example with a solution of hydrochloric acid at a strength of 20 per cent. (fig. 3) and with aqueous alcohol at a strength of 96 per cent. By no process of distillation can originally weak alcohol be strengthened beyond the point named, and if (Le Bel) we start with still stronger alcohol (prepared by chemical desiccation) the effect of distillation is reversed. The vapour being now weaker (in alcohol) than the liquid, the residue in the retort *strengthens* until it reaches purity.

In the case of substances which have no tendency to mix, *e.g.*, water and bisulphide of carbon, the composition of the vapour is, as we have seen, always the same. The representative curve, reducing to a straight line parallel to the axis of abscissæ, or rather to the broken line A E F D (fig. 1), necessarily crosses the diagonal. The point of intersection (H) represents a condition of things in which the compositions of the liquid and vapour are the same. As distillation proceeds, the residue retains its composition, and both ingredients are exhausted together.

Fig. 1.



If we commence with a liquid containing CS_2 in excess of the above proportion, the excess gradually increases until nothing but CS_2 remains behind. In the same way, if the water be originally in excess, the excess accentuates itself until the (finite) residue is pure water. The critical condition is thus in a sense unstable, and can only be realized by adjustment beforehand.

The conclusions drawn above may be generalized. Whatever may be the ingredients of a binary mixture, in the upper triangular half of the square the vapour is stronger (we will say) than the liquid, in the lower half weaker. Hence, as the liquid distills away, progress from a point in the upper half is towards diminishing abscissæ, and in the lower half towards increasing abscissæ. When, as in fig. 1, the curve in its course from A to D crosses AD from left to right, the condition represented by the point of intersection H is unstable. When, as in the case of hydrochloric acid (fig. 3), the crossing takes place from right to left, *i. e.* from the lower half to the upper half of the square, the progress from points in the neighbourhood is always *towards* the point of intersection, so that the state represented thereby is *stable.* We may sum up by saying that if, as the liquid strengthens, the vapour having been weaker than the liquid becomes the stronger, the point of transition, representing constant distillation, is stable; but if the vapour having been at first the stronger becomes the weaker, then the point of transition is unstable.

The question presents itself, whether as the liquid strengthens (in a particular ingredient) the vapour necessarily strengthens with it. Does the curve on our diagram slope everywhere upwards on its course from A to D? Although a formal proof may be lacking, it would seem probable that this must be so when the ingredients mix in all proportions. A limiting case is when two ingredients do not mix at all, *e. g.*, water and bisulphide of carbon, or when the mixture divides itself into two parts of constant composition as when ether and water are associated in certain proportions. In these cases the composition of the vapour is constant for the whole or for a part of the range (Konowalow), and the representative curve is without slope.

Konowalow's Theorem.

An important connexion has been formulated by Konowalow* between the vapour-pressure, regarded as a function of the composition of the liquid with which it is in equilibrium, and the existence of a point of constant distillation. "The pressure of the vapour from a fluid consisting of two different substances is in general a function of the composition of the mixture... Let such a mixture, confined in a closed space, be maintained at a constant temperature. We may conceive this space bounded by fixed walls and by a movable piston. The conditions of stable equilibrium are then (1) that the external pressure operative upon the piston should be equal to the pressure of the saturated vapour at the given temperature; (2) that by increase, or diminution, of the vapour space the pressure should become respectively not greater, or not less, than the external pressure. In expansion the vapour-pressure can thus either remain constant, or become smaller. On the basis of this law we can establish a relation between the composition of the liquid and that of the vapour."

Before proceeding further I must remark that the principle, as stated, appears to need elucidation. Why should the

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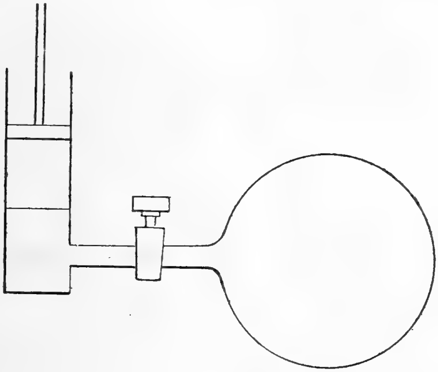
* Wied. *Ann.* xiv. p. 48 (1881).

equilibrium of the piston under a constant load be stable? There must of course be some position of stable equilibrium for a given load and temperature; but this might, for all that appears, correspond to complete evaporation of the liquid or to complete condensation of the vapour.

The following argument, however, suffices to show that Konowalow's principle is a necessary consequence of the second law of Thermodynamics. Suppose that the cylinder in which are contained the given liquid and vapour communicates by a lateral channel (fig. 2) with a large reservoir filled with liquid of similar composition, and that all are maintained at the prescribed temperature. As a first operation close the tap between the vessels, and then let the piston rise a little. The motion is supposed to be so slow that equilibrium prevails throughout. The result of the expansion may be that the compositions of the liquid and of the vapour undergo a change. Now open the tap, and allow diffusion to take place, if necessary, until equilibrium is again established. On account of the large quantity of liquid in the reservoir the pressure is sensibly restored to its original value and remains undisturbed as the piston is slowly pushed back to its first position. During this cycle of operations work cannot be gained; and thus is excluded the possibility of a rise of pressure during the expansion. It follows that a fall of pressure cannot accompany compression.

Fig. 2.



Upon the basis of this principle Konowalow proceeds as follows:—Suppose that at a particular composition-ratio the pressure of vapour increases as the liquid becomes richer in a specified component. In this case the expansion of the mass cannot enrich the liquid; for if this result occurred the pressure would rise, which we have proved it cannot do.

During the expansion fresh vapour is formed; and if the composition of the vapour were poorer than that of the liquid, the latter would inevitably be enriched by the operation. We conclude that at the point in question the vapour cannot be poorer than the liquid. In like manner if the vapour-pressure falls with increasing richness of liquid, compression of a given mass cannot enrich the liquid, and this requires that the vapour be not richer than the corresponding liquid. If we suppose the vapour-pressure to be plotted as a function of richness of corresponding liquid, we may express these results by saying that rising parts of the pressure-curve can have no representation in the lower triangle of our former diagrams (where vapour is poorer than liquid), and that falling parts cannot be represented in the upper triangle.

It is now evident that the passage from a rising to a falling part of the pressure-curve can only occur when the vapour is neither richer nor poorer than the liquid, and we arrive at Konowalow's important theorem that *any mixture, which corresponds to a maximum or minimum of vapour-pressure, has (at the temperature in question) the same composition as its vapour.*

The particular case in which one ingredient is wholly involatile is worth a moment's notice. The vapour over a solution of salt in water can never have the same composition as the liquid; and from this we may conclude that the vapour-pressure has no maximum or minimum, or rather that there is no transition anywhere between rising and falling.

The converse of Konowalow's theorem is also not without importance. Consider two mixtures of slightly differing composition, one of which is richer than its vapour and the other poorer. Expansion of the first entails an enrichment of the liquid, and during the operation the pressure cannot rise. Expansion of the second impoverishes the liquid, and again the pressure cannot rise. The curve exhibiting pressure as a function of composition (of liquid), if it slopes at all at the two points, must slope in opposite directions. Hence by approaching nearer and nearer to the point where the compositions of vapour and liquid are the same, we see that the vapour-pressure must there be stationary in value.

An example of the use of the converse theorem is afforded by the consideration of mixtures of water and common alcohol. The question of the existence of a mixture having the same composition as its vapour is not easily settled directly, but the recent observations of Noyes and Warfel* show conclusively that the mixture containing 96 per cent.

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* Am. Chem. Soc. xxiii. p. 463 (1901).

of alcohol by weight has a minimum boiling-point, and accordingly distils without change. It may be noted that the curve given by Konowalow himself would point to the contrary conclusion.

In the practical conduct of distillation it is the pressure that is constant rather than the temperature. Inasmuch, however, as pressure always rises with temperature, a maximum or minimum pressure when temperature is given necessarily corresponds with a minimum or maximum temperature when pressure is given. In the case of a solution of hydrochloric acid, for example, the thermometer marks a maximum temperature at the point where the solution distills without change.

Calculation of Residue.

Before proceeding to the experimental part of this paper it may be well to explain further the significance of the curves exhibiting the relative compositions of liquid and vapour. If w represent the whole quantity (weight) of liquid, say alcohol and water, remaining in the retort at any time, y the quantity of one ingredient (alcohol), the abscissa ξ of the curve is y/w. As the distillation proceeds for a short time w becomes $w+dw$, and y becomes $y+dy$*; and the composition of the vapour, that is the ordinate η of the diagram, is dy/dw. Thus

$$\xi=y/w, \qquad \eta=dy/dw,$$

while the functional relation between ξ and η is given by the curve, and may be analytically expressed by $\eta=f(\xi)$. Thus

$$\frac{d(w\xi)}{dw}=f(\xi),$$

whence

$$\log\frac{w}{w_0}=\int_{\xi_0}^{\xi}\frac{d\xi}{f(\xi)-\xi},$$

w_0, ξ_0 being corresponding values of w and ξ.

When ξ is small the curve is often approximately straight. If we set $f(\xi)=\kappa\xi$ we find

$$\xi/\xi_0=(w/w_0)^{\kappa-1}.$$

For example, in the case of alcohol and water, we have for very weak mixtures $\eta=12\,\xi$ approximately, so that $\kappa=12$. As the distillation proceeds, w diminishes and ξ soon becomes exceedingly small. The halving of w implies a diminution

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* dw and dy being negative.

of ξ in the ratio of $2^{11} : 1$. The residue in the retort thus approximates rapidly to pure water.

On the other hand, in the case of acetic acid and water κ is about $\frac{3}{4}$. When weak acetic acid is distilled the residue *strengthens*, but the earlier stages of the process are covered by the formula given, which now assumes the form

$$\xi / \xi_0 = (w_0 / w)^{\frac{1}{4}}.$$

In order to double the strength of the liquid remaining in the retort, 15/16 of it would have to be distilled away, or again, in order to increase the strength in the ratio of 3 : 2, the distillation must proceed until the liquid is reduced in the ratio of 16 : 81, or nearly of 1 : 5. An experiment of this sort upon acetic acid is recorded below.

Observations.

The experimental results about to be given were obtained by simple distillation of mixtures of known composition. In order to avoid too rapid a change of composition, somewhat large quantities were charged into a retort and were kept in vigorous ebullition. By special jacketing arrangements security was taken that the upper part of the retort should be maintained at a distinctly higher temperature than the liquid, so that there could be no premature condensation which would vitiate the result. *All* the vapour rising from the liquid must be condensed in the specially provided Liebig condenser and be collected as distillate. Subject to this condition, and in view of the rapid stirring effected by the rising vapour, it would seem safe to assume that the distillate really represents the vapour which is in equilibrium with the liquid at the time in question. The compositions of the liquid and vapour are of course continually changing as the distillation proceeds.

The distillates (including the first drop) were collected in 50 c.c. measuring flasks. It will save circumlocution to speak of a particular case, and I will take that of alcohol and water, for which the analyses were made by specific gravity. The successive collections of 50 c.c. show an increasing specific gravity corresponding to a diminishing strength. The specific gravity of each gives the total weight, and the strength, deduced from tables, allows us to calculate the alcohol and water in each collection. The total alcohol and water originally present in the retort being known in the same way, we are able to deduce by subtraction the quantities remaining in the retort at each stage, and thus to compare the strengths of corresponding liquid and vapour. In the reduction any particular distillate is considered to correspond with the mean condition of the liquid before and after its separation therefrom.

If the process above sketched could be absolutely relied on, it would be possible, starting with a strong spirit in the retort, to obtain from one distillation data relating to a great variety of strengths. But this method is not to be recommended, as the errors would tend to accumulate. The first 50 c.c., condensed under somewhat abnormal conditions, was not used directly, but only to allow for the change going on in the retort. The 2nd, 3rd, and 4th collections were usually calculated so as to show the strengths of these distillates in comparison with that of the liquid, but they were regarded rather as checks upon one another than as independent results relating to an altered state of affairs.

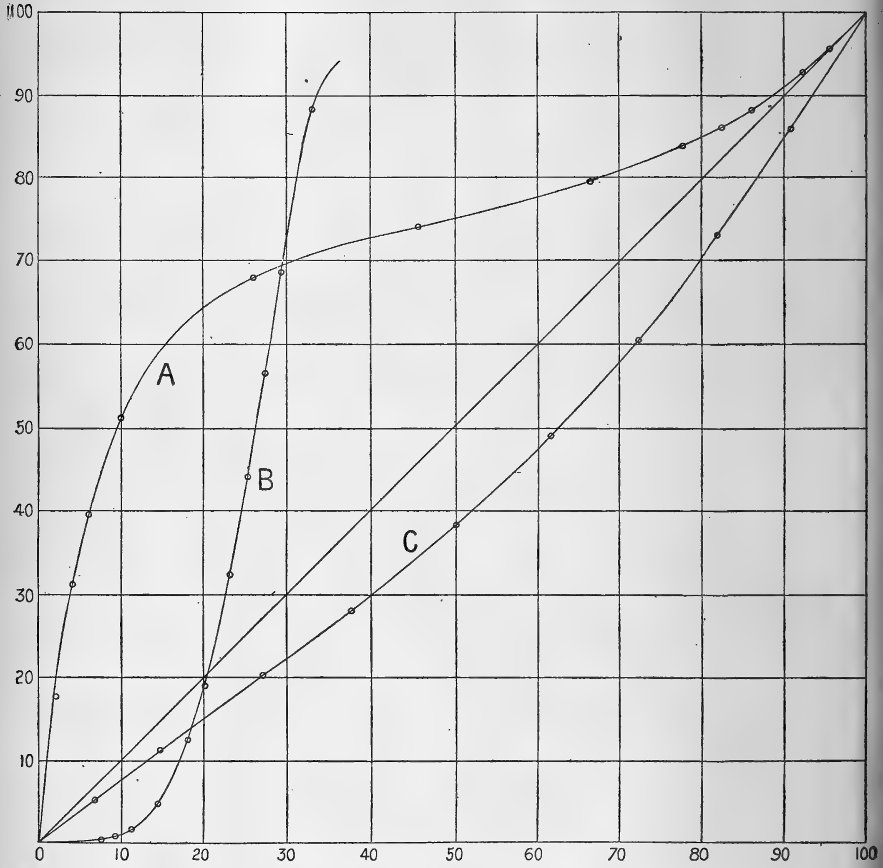
Alcohol and Water.

Observations upon mixtures of water and ethyl alcohol, sufficient to give a nearly complete curve, were made in 1891 and again in 1898 with good general agreement. The specific gravities were found in the balance with a bottle of 20 c.c. capacity, and the calculations of strength were by Mendeleef's tables with appropriate temperature correction. The results of the second series are given in the accompanying table and are exhibited as a curve, A, in fig. 3. The strengths are throughout reckoned by weight.

Date 1898.	Strength of Liquid.	Strength of Vapour.
May 4	·01970	·1750
„ 3	·03982	·3159
„ 5	·0601	·3979
„ 9	·0988	·5145
„ 10	·2586	·6803
„ 13	·4562	·7412
„ 16	·6606	·7976
„ 17	·7739	·8414
„ 20	·8221	·8622
„ 23	·8594	·8849
„ 24	·9241	·9284
„ 25	·9555	·9545

The observation of May 4 thus signifies that to a liquid containing by weight 1·97 per cent. of alcohol there corresponds a vapour containing by weight 17·5 per cent. of alcohol. From the results of May 24 we see that when the liquid reaches 92 per cent. the vapour is but little the stronger, and the difference practically disappears at 95 per cent. Indeed according to May 25 the vapour is a little the

Fig. 3.



A. Alcohol and Water. B. Hydrochloric Acid and Water. C. Acetic Acid and Water.

weaker at this point. The difference, however, is not to be trusted, since the difficulties of manipulation, depending partly upon the attraction of strong alcohol for aqueous vapour, are much increased at this stage. It was these difficulties and the uncertainty as to what exactly happened with spirit stronger than 95 per cent. that retarded the publication of the work. I had intended to make further experiments upon this point, but the matter was postponed from time to time. The observations of Noyes and Warfel (*l. c.*)

seem now to remove all doubt. The existence of a minimum boiling-temperature for a strength of 96 per cent. shows that the curve there crosses the diagonal. Between this point and 100 per cent. the vapour is the weaker, and the curve lies in the lower triangular half of the square. But the deviation from the diagonal in this region is probably extremely small.

The following from Noyes and Warfel's table may be useful:—

Strength.	Boiling-point.	Strength.	Boiling-point.
100	78°·300	85	78°·645
99	78·243	80	79·050
98	78·205	75	79·505
97	78·181	65	80·438
96	78·174	55	81·77
95	78·177	48	82·43
94	78·195	35	83·87
93	78·227	26	85·41
92	78·259	20	87·32
91	78·270	10	91·80
90	78·323	0	100·00

Hydrochloric Acid and Water.

One of the ingredients of the mixture being gaseous under ordinary conditions, the observations are limited to that portion of the curve for which the strength of the liquid does not exceed 35 per cent., unless freezing appliances are called into play. No attempt was made in the present experiments to pass the above limit, the object being merely to determine with moderate accuracy that part of the curve with which we are usually concerned in the laboratory. It was known from the experiments of Roscoe and others that the curve would cross the diagonal at the strength of about 20 per cent.

The general plan of the work was the same as in the case of alcohol and water, but the strengths were usually determined chemically. In the case of the stronger acids it was not possible to condense the vapour at atmospheric temperature; and I contented myself with a calculation in which the strength of the vapour was inferred from observations of the quantity and strength of the liquid in the retort before and after the operation. Results obtained in this way are doubtless of minor accuracy.

It may be worth while to reproduce in tabular form the data relating to the weakest acid.

Distillation of Hydrochloric Acid.—Sept. 13, 1898.

No.	Volume in c.c.	Specific gravity.	Total weight.	Percentage of HCl.	Weight of HCl.	Weight of H_2O.	HCl remaining in retort.	H_2O remaining in retort.	Total remaining.	Percentage of HCl remaining.
0	1800	1·031	1855·8	6·0	111·4	1744·4	...	...	...	6·0
1	250	1·0013	250·32	0·26	0·65	249·7	110·7	1494·7	1605·4	6·9
2	250	1·0023	250·58	0·45	1·12	249·4	109·6	1245·3	1354·9	8·1
3	250	1·0038	250·95	0·76	1·90	249·0	107·7	996·3	1103·9	9·8
4	250	1·0076	251·90	1·53	3·86	248·0	104·0	748·3	852·3	12·2

The first column contains the numbers of the successive distillates from 1 to 4, the entry 0 referring to the mixture with which the retort was originally charged. The volume of this mixture was 1800 c.c. of specific gravity 1·031 and of 6·0 per cent. strength. Of the total weight 1855·8 gms., 111·4 gms. is hydrochloric acid and 1744·4 gms. water. In like manner the volume of the first distillate is 250 c.c., the specific gravity 1·0013, the total weight 250·32 gms., of which 0·65 gms. is HCl and 249·7 gms. H_2O. The residue in the retort after the first 250 c.c. has been distilled over is accordingly composed of 111·4 − 0·65 or 110·7 gms. HCl and 1744·4 − 249·7 or 1494·7 gms. H_2O, making 1605·4 gms. in all. At this stage the percentage strength of the liquid remaining in the retort is 6·9. The strengths of the liquid in the retort after the 1st, 2nd, . . . 4th distillates have been removed are found in this way to be 6·9, 8·1, 9·8, and 12·2 per cent. The first distillate, whose strength is 0·26 per cent., thus corrresponds with a liquid whose strength varied from 6·0 to 6·9 per cent, on an average 6·45 per cent. We thus obtain the following corresponding strengths:—

Percentage Strengths.

Liquid.	Vapour.
6·45	0·26
7·50	0·45
8·95	0·76
11·00	1·53

It is hardly worth while to record all the separate results. In addition to the above the following will suffice for the construction of the curve. In the three last the strengths of the distillates were not directly observed, but were calculated from the condition of the liquid before and after as already mentioned.

Percentage Strengths.

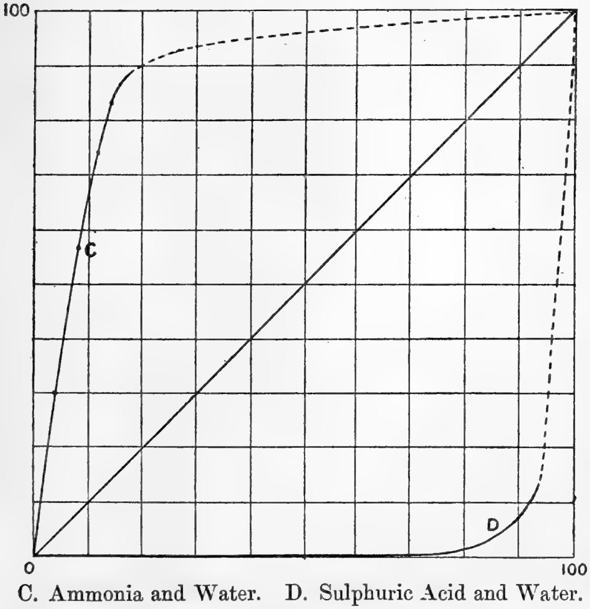
Date (1898).	Liquid.	Vapour.
Sept. 21 …………	14·5	4·46
„ 28 …………	18·0	12·8
Oct. 10 …………	20·3	18·9
„ 12 …………	23·3	32·4
„ 14 …………	25·2	44·2
„ 15 …………	27·4	56·6
„ 18 …………	29·0	68·8
„ 19 …………	32·8	88·3

The results are plotted in Curve B, fig. 3.

Ammonia and Water.

In this case the analysis was by specific gravity and the results were somewhat rough, the intention being merely to obtain an approximation to the form of the curve. On this account they are plotted upon a smaller scale C, fig. 4, the dotted portion of the curve being conjecturally added to indicate the progress towards the corner of the square.

Fig. 4.



C. Ammonia and Water. D. Sulphuric Acid and Water.

Sulphuric Acid and Water.

The distillates were here determined chemically. From acid in the retort of less strength than 60 per cent. the distillate failed to redden litmus. From 75 per cent. acid the distillate contained about one-thousandth part of H_2SO_4. From 81 per cent. the distillate contained 1·6 per cent.; from 90 per cent. the distillate contained 7·1 per cent.; and from 93 per cent. liquid the distillate contained 12·8 per cent. of acid. The curve is given in D, fig. 4, the dotted portion for strengths of liquid greater than 93 per cent. being conjectural.

Acetic Acid and Water.

This case was examined as likely to exemplify a very different behaviour from any of the others, since it was known that these substances are not easily separated by distillation. The retort was charged with 1000 c.c. of mixture and two distillates were collected of 150 c.c. each. The analyses were conducted chemically and the results calculated as already explained. Thus the first distillate was considered to correspond with the mean strength in the retort before and after its separation. The following were the results obtained:—

Acetic Acid and Water.

Date 1902.	Strength of Liquid.	Strength of Vapour.
Aug. 18	·0677	·0510
Aug. 11	·1458	·1136
Aug. 6	·2682	·2035
Aug. 18	·3746	·2810
Aug. 5	·4998	·3849
Aug. 23	·6156	·4907
Aug. 22	·7227	·6045
Aug. 21	·8166	·7306
Aug. 20	·9070	·8622

It appears that the vapour is always weaker than the liquid, but that the difference is never great. A plot of the corresponding strengths is given in C (fig. 3, p. 530).

In illustration of the preceding theory an experiment was tried in which three-quarters of the original volume of liquid was distilled over. The original liquid consisted of 1000 c. c. of acid of density 1·010, and of strength (as determined chemically) ·0757, representing as usual the proportion of the weight of acetic acid to the whole weight. The residue measuring 250 c. c. was of density 1·016 and of strength ·1100. From these data we find

$$\log(\xi/\xi_0) = \cdot 1624, \qquad \log(w_0/w) = \cdot 5995,$$

whence

$$1-\kappa = \cdot 27, \qquad \kappa = \cdot 73.$$

The number denoted by κ represents the ratio of strengths of vapour and liquid when weak mixtures are distilled.

A new Apparatus with uniform Régime.

In the theory and experiments so far considered the distillation has always been supposed to be simple, that is, the vapour rising from the boiling liquid is supposed to be removed and to be condensed as a whole, so that the distillate has the same composition as the vapour leaving the boiling liquid. In practice, as is well known, this condition is often and advantageously violated. A preliminary partial condensation of the vapour in the still-head frees it from some of the less volatile ingredient; and, when the residue is condensed and collected, the more volatile ingredient is obtained in a nearer approach to purity. Prof. S. Young has shown that the principle is more effectively carried out if the still-head be maintained at a suitable temperature.

Even with a preliminary partial condensation in the still-head, the "fractionation" of a mixture is usually regarded as a very tedious operation. The stock of mixture in the retort is constantly changing its composition as the distillation and partial condensation proceed, and no uniform *régime* can be established. Although theoretical simplicity and practical convenience are not always conjoined, a uniform *régime* seems very desirable, and it excludes the usual arrangement in which the whole supply of mixture is charged into the retort. The return into the retort of the liquid first condensed from the original vapour is also objectionable.

The problem of distillation may be stated to be the separation from a binary mixture of the whole of the two components in, as nearly as may be, a state of purity. There is no theoretical reason why this should not be effected at one operation; but for this purpose the mixture must be fed in continuously and not at the place of highest or lowest temperature. A description of the procedure followed in some illustrative experiments will make the nature of the process plain.

The mixtures actually employed were of water and common alcohol. The choice was perhaps not a happy one, as in consequence of the peculiar properties of strong alcohol it was unlikely that a distillate could be obtained stronger than about 90 per cent. As regards apparatus, the retort and still-head are replaced by a long length (12 metres) of copper tubing, 15 mm. in diameter. This is divided into two parts, arranged in spirals, like the worms of common condensers, and mounted in separate iron pails. The lower and longer spiral was surrounded with water which was kept boiling. The water surrounding the upper spiral was maintained at a suitable temperature, usually 77° C. The copper tubes forming the two spirals were connected by a straight length of glass, or brass, tubing of somewhat greater bore, and provided with a lateral junction through which the material could be supplied. The connecting piece and the spirals were so arranged that the entire length was on a slight and nearly uniform gradient, rising from near the bottom of the lower pail to the top of the upper pail. On leaving the latter the tube turned downwards and was connected with an ordinary Liebig's condenser capable of condensing the whole of the vapour which entered it. At the lower end of the system of tubing the watery constituent is collected. In strictness the receiver should be connected air-tight and be maintained at 100°. In distilling the stronger mixtures (60 or 75 per cent. alcohol) this precaution was found advisable or necessary; but in the case of the weaker ones the water could be allowed to discharge itself through a short length of pipe whose end was either exposed to the atmosphere or slightly sealed by the liquid in the receiver.

The feed of the mixture was arranged as a visible and rather rapid succession of drops, and was maintained at a uniform rate. In the case of the stronger mixtures the evaporating power of the lower coil was hardly sufficient, and was assisted by applying heat to the feed, so that a good proportion was evaporated before reaching the main tube. The weaker mixtures on the other hand could be fed in without any preliminary heating. The uniform *régime* should be maintained long enough to ensure that the liquids collected at the two ends shall be fairly representative and not complicated by anything special that may happen before the uniform *régime* is established.

During the operation every part of the tube (not too near the ends) is occupied by a double stream—an ascending stream of vapour and a descending stream of liquid. Between these streams an exchange of material is constantly taking place, the liquid, as it descends, becoming more aqueous and the vapour, as it rises, becoming more alcoholic. In view of the slowness of the feed and the length of the tube, we may regard the liquid and the vapour as being everywhere in approximate equilibrium. At the lower end, since the pressure is atmospheric and the temperature scarcely below 100°, there can be little alcohol; for similar reasons at the upper end there cannot be much water, although the exclusion is here less complete on account of the peculiar character of the curve representing the relation of compositions at this extreme.

Experiments were tried with four different strengths of mixture—20, 40, 60, and 75 per cent. of alcohol. In all cases the water was collected nearly pure, never containing more than ½ per cent. of alcohol. The alcoholic part condensed from the upper end varied but little. The weakest (from the 20 per cent. mixture) was of 89 per cent., and the strongest was of 90·3 per cent. All strengths are given by *weight*, and were calculated by Mendeleef's tables from the observed specific gravities with suitable temperature correction. The watery constituent which, not having been evaporated, sometimes looked a little dirty, was usually redistilled so as to obviate any risk of its purity being overestimated. In some cases it could not be distinguished from pure water.

The apparatus illustrates very well the principles of ideal distillation, and its performance may be regarded as satisfactory. When once the conditions, as to preliminary heating (if necessary) and as to rate of feed, have been found for a particular mixture, the continued working is almost self-acting, or at any rate could be made so without much difficulty; and it is probable that separations, otherwise very troublesome, could be easily effected by use of it.

LX. *Change of the Modulus of Rigidity of Ferromagnetic Substances by Magnetization.*

By K. HONDA, *Rigakushi*, S. SHIMIZU, *Rigakushi, and* S. KUSAKABE, *Rigakushi*[*].

1. WE have already seen that the change of elasticity by magnetization is not so small as generally admitted. The present experiments deal with the change of rigidity by magnetization. The investigation is especially important inasmuch as the change of rigidity is reciprocally related to that of magnetization by torsion.

In the course of his experiments on the mutual relations between torsion and magnetization, G. Wiedemann[†] observed

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[*] Communicated by Prof. Nagaoka.

[†] Wiedemann's *Electricität*, iii. p. 796.

that the torsion of an iron wire was diminished by magnetization. C. Barus* hung two identical iron wires in the same vertical line, separated by a rigid piece of brass which carried the index mirror; to the lower end of the wire a weight was attached. The wire was twisted, and then either the upper or the lower end of the system fastened. If both ends were twisted equally in opposite directions, the direction of the mirror remained unchanged. A magnetizing coil was placed coaxially with the upper wire. If the rigidity of the wire be changed by magnetization, the mirror would rotate in either direction when magnetized. Barus found that for soft iron and steel the increase of rigidity was 0·24 and 0·08 per cent. respectively. In his later experiments he observed an increase amounting to 1 per cent. for soft iron. With a similar arrangement H. D. Day† investigated the same subject in iron. He found that the change of rigidity increased with field and that it became generally less as the initial torsion was increased. The maximum value obtained was 0·8 per cent. The experiments of J. S. Stevens‡ for iron and steel rods gave an increase of rigidity. The change amounted to 2·3 per cent. for soft iron and 0·4 per cent. for steel in a field of 138 C.G.S. units. In his experiments the magnetizing coil was much less than the length of the rod, so that the magnetization was far from being uniform.

2. Our method of twisting the ferromagnetic rod was the same as that of Prof. Nagaoka§, used for studying the elastic constants of rocks; but the sensibility of the apparatus for measuring the angle of torsion was 106 times greater.

The front and side views of our apparatus are given in the accompanying figure (fig. 1).

AA is the lateral view of a stout wooden frame rectangular in shape. BB are the projections protruding from the frame; to the one, a brass rod, to which a ferromagnetic rod is soldered, is clamped by means of a screw H, and to the other a screw G is clamped, which carries an agate cup in one of its extremities. F is a double pulley whose axis is a thick brass cylinder; a point made of non-magnetic nickel steel is firmly fixed to one of its extremities, while the ferromagnetic rod is soldered to the other, as shown in fig. 2. The inner pulley serves to twist the specimen to be tested, and the outer to increase the sensibility of the apparatus.

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* Amer. Journ. of Sci. xxxiv. p. 175 (1887); Phys. Rev. xiii. p. 257 (1901).

† Day, 'Electrician,' xxxix. p. 480 (1897).

‡ J. S. Stevens, Phys. Rev. (3) x. p. 161 (1900).

§ H. Nagaoka, Phil. Mag. l. p. 53 (1900).

C is a magnetizing coil and E a block of wood, to which a rotating cylinder is fixed, as in the case of the former experiments. A fine copper wire, well annealed by passing an electric current, is attached to a point on the outer circumference of the pulley and goes vertically upward around it. The wire after passing round the cylinder is stretched by a weak spring D in the usual way. The deflexion of the mirror attached to the rotating cylinder is observed by means of a scale and telescope. The details of the apparatus can be readily understood from the above figures.

Fig. 1.

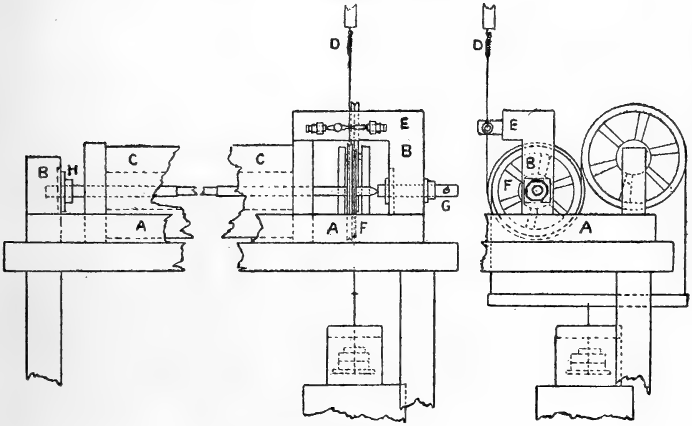
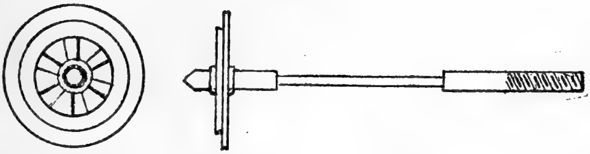


Fig. 2.



The dimensions of each part of our arrangement are as follows:—

Length of the coil	=30·0 cms.
Its internal diameter	= 3·0 cms.
$4\pi n$	=379·7
Large radius (R) of the pulley ...	=8·93 cms.
Small radius of the pulley	=7·15 cms.
Radii (r) of the rotating cylinders	=0·0802 cm. =0·1400 cm.
Radius of the copper wire	=0·004 cm.
Scale distance	=230·8 cms.

It is evident that if the ferromagnetic rod is twisted through a small angle ϕ, the rotating cylinder is turned through an angle $\frac{R\phi}{r}$; hence the angle of torsion is magnified in the ratio R : r. In the actual case we corrected for the thickness of the thin copper wire; the ratio was 106 : 1 in our case. With the arrangement we were able to measure a change of angle amounting only to $1''\cdot 92 \times 10^{-3}$ per cm. of the ferromagnetic rod.

3. The measurement was conducted in the following order:—The specimen to be tested was fixed in the axial line of the magnetizing coil so as to lie nearly in a uniform field. If the steel pivot on one end of the bar carrying the specimen was left free, and a magnetizing current passed through the coil, a deflexion of the mirror was observed, though there was no twisting couple. The deflexion is evidently not due to the twisting of the rod, but to its bending by magnetization. The case corresponds to the experiment of Guillemin described in the preceding paper *. The nature of the deflexion and its amount coincided with the change of elasticity by magnetization, which we have already studied. The steel pivot was then brought slightly in contact with the agate cup; if the contact was made in a suitable degree the deflexion due to magnetization, when acted on by no twisting couple, could be made negligibly small. In cases when the deflexion could not be sufficiently reduced, it was always corrected for. The contact being so adjusted a couple was applied by a suspended weight. The tension of the fine copper wire was then adjusted and the working of the apparatus tested by adding successively weights of 1, 10, 50 grams to the pan. If the deflexions of the mirror were proportional the adjustment was considered to be correct.

To begin with, the ferromagnetic rod was demagnetized by reversals, and then a current passed through the coil, taking the deflexion as soon as possible. These processes were repeated with successively increasing currents. In order to get rid of the minute oscillations of the mirror the thin copper wire and the mirror should be protected from air-currents.

The resistance of the magnetizing coil was only 0·6 Ω, so that the heating of the core due to current was negligibly small up to the strongest current used in the present experiment, and the creeping of the image of the scale was not at all observed; but we were careful to read the deflexion as quickly as possible.

Since the couples corresponding to 1, 10, 50 grams

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* *Suprà*, p. 459.

produced torsions proportional to their respective weights, the friction at the pivot does not seem to disturb our results.

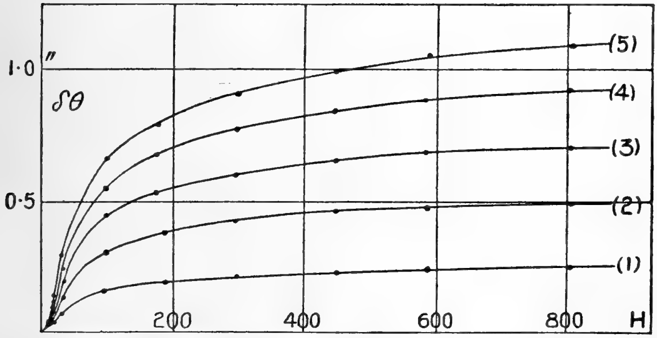
The examples tested were the same as used in the preceding experiment, except the nickel rod. In the present experiments the length of each rod was reduced to 22 cms., and the diameter of the cobalt bar also to 1·082 cm. The nickel rod used in the last experiment was not sufficiently thick for the torsion experiment, so that another nickel bar, whose diameter was 1·117 cm., was substituted for it.

Our apparatus was not suited for the absolute measurement of the modulus of rigidity, and therefore its determination was carried out in the usual manner with Prof. Nagaoka's apparatus above referred to. The results were:—

Metals ...	Soft iron.	Steel.	Wolfram steel.	Nickel.	Cobalt.
Rigidity	$7·92\times10^{11}$	$7·89\times10^{11}$	$8·57\times10^{11}$	$7·41\times10^{11}$	$6·04\times10^{11}$

4. *Soft Iron.*—The results of observation are given in fig. 3.

Fig. 3.



Here ordinates represent the change of twist due to magnetization given in seconds of arc, taken positive when the change indicates an increase of rigidity and taken negative when it indicates a decrease; abscissæ represent the effective field. N is the moment of force expressed in C.G.S. units.

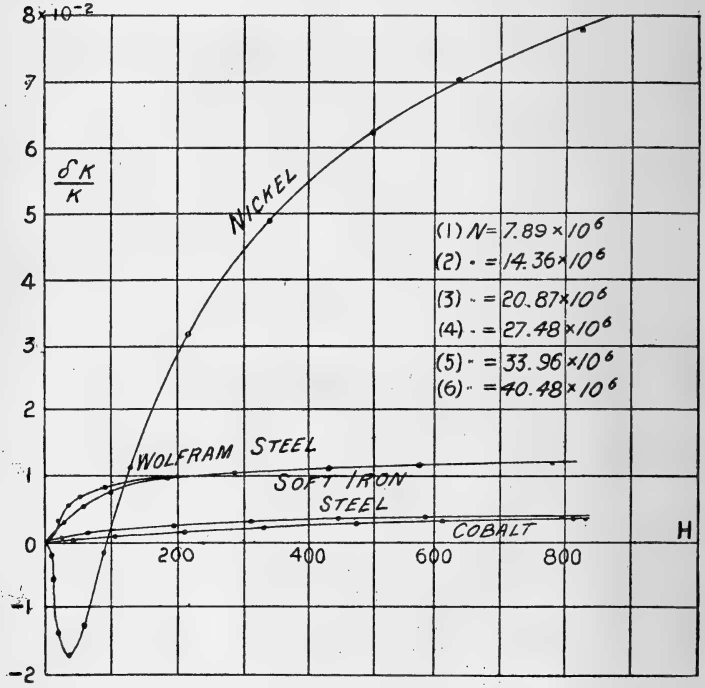
From the figure we see that the untwisting of the rod always increases with magnetizing force, its amount increasing in the same way as the intensity of magnetization with increasing magnetizing force. As the moment of force increases the amount of untwisting increases proportionally, so that the change of rigidity is fairly independent of the twisting couple for all magnetizing fields. The form of the curves is similar to that of the curves of depression in the former experiment, except in very weak fields. In the present case the initial minute depression of the curves was not observed.

The angle of torsion, as calculated from the applied couple and the rigidity, and the observed change of twist due to magnetization, gives the ratio of the change (δK) to the rigidity (K) itself.

H.........	20.	60.	100.	200.	400.	600.	800.
$\frac{\delta K}{K} \times 10^2$..	0·19	0·58	0·76	0·96	1·10	1·18	1·22

These numbers are also plotted against magnetizing force in fig. 4; the course of the curve resembles that of magnetization, having one inflexion point and approaching to an asymptotic value as the field is increased.

Fig. 4.

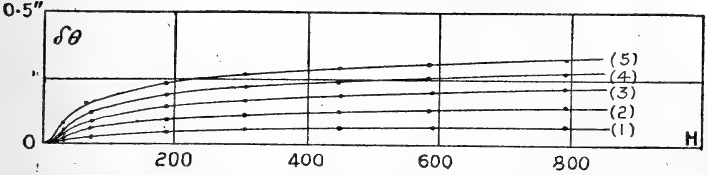


That there is untwisting by magnetization forms a reciprocal relation to the well-known fact that the magnetization of iron decreases by twisting.

The above results for soft iron agree in quality with those of previous experimenters, and the amount of the change nearly coincides with some of Barus's results. In the experiment of Day the change of rigidity was a little smaller than in the present case, and greatly affected by the amount of twisting couple, in contradiction to our results. Stevens's experiment gave much greater change of rigidity.

5. *Steel.*—We have seen that in steel the change of elasticity due to magnetization is much smaller than in soft iron. So, in the case of rigidity, we also observed comparatively little increase. The results are given in fig. 5. We see that the form of the curves is similar to that of magnetization in steel.

Fig. 5.



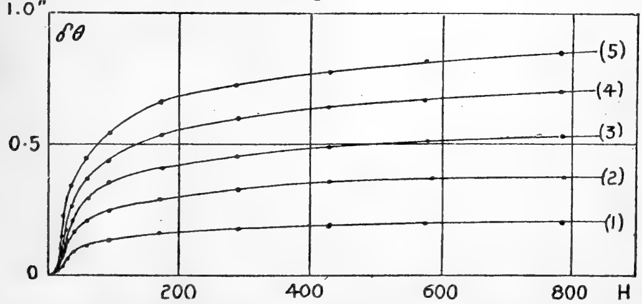
Here again, the change of rigidity is independent of the twisting couple for all magnetizing fields; the values of $\frac{\delta K}{K}$ for different fields are given in the following table and in fig. 4:—

H	60.	200.	400.	600.	800.
$\frac{\delta K}{K}\times 10^2$ ..	0·13	0·22	0·29	0·32	0·35

The results of previous experimenters fairly agree with those of the present case. The reciprocal relation between torsion and magnetization also holds for steel.

6. *Wolfram Steel.*—The change of elasticity in Wolfram steel due to magnetization is nearly the same as that of soft iron both in quality as well as in quantity. This remark also applies to the present case, so that what we have said about the change of rigidity in soft iron equally applies to the case of Wolfram steel, as will be seen from figs. 6 and 4, and the following table:—

Fig. 6.



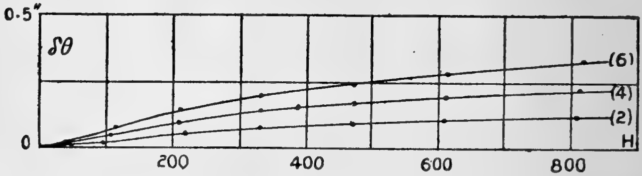
H	20.	60.	100.	200.	400.	600.	800.
$\frac{\delta K}{K}\times 10^2$ ..	0·15	0·73	0·85	0·98	1·10	1·16	1·22

These numbers are very close to the corresponding ones in soft iron, except in weak fields.

7. *Cobalt.*—As in the case of steel, the effect of magnetization on the rigidity of a cobalt bar is very small. The rigidity always increases by magnetization, as shown in figs. 7 and 4, and the following table:—

H	100.	200.	400.	600.	800.
$\frac{\delta K}{K} \times 10^2$..	0·05	0·12	0·21	0·28	0·31

Fig. 7.



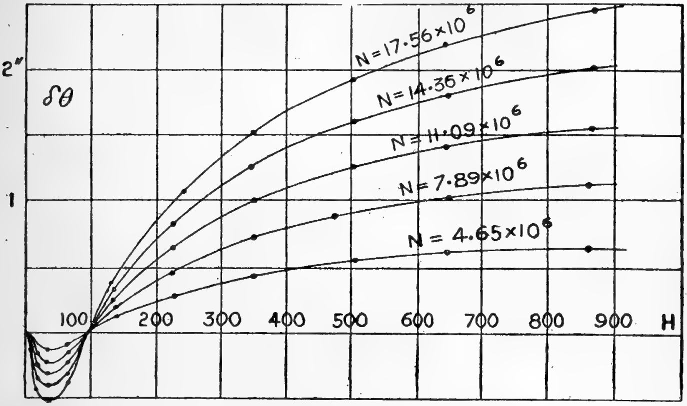
Thus the course of the curves is less steep in cobalt than in iron or steel; the inflexion point is not so marked in the former metal as in the latter. The change of rigidity is also independent of the applied couple.

So far as we are aware the effect of torsion on the magnetization of cobalt has not yet been studied; but if the reciprocal relation holds in the case of cobalt the above results show that the effect of torsion on the magnetization of cobalt is the same as in iron. We have seen from the experiment of Prof. Nagaoka and one of us that the behaviour of the cast cobalt as regards magnetostriction is remarkably different from that of annealed cobalt. The present specimen was well annealed, so that the above inference is to be restricted to an annealed cobalt.

8. *Nickel.*—The change of rigidity of a nickel bar is so large that it was necessary to reduce the sensibility of the apparatus by using a rotating cylinder of thicker diameter. As in the case of the change of elasticity, we again observe in the metal a singular phenomenon that the change of torsion by magnetization alters its sign as the magnetizing force is increased. The results are graphically drawn in fig. 8. In weak fields the deflexion shows a further twisting of nickel, that is a decrease of rigidity. This decrease reaches a maximum as the field becomes stronger; it then begins to decrease, and in a field of about 100 C.G.S. units the rigidity returns to its original value. When the field is further increased the rigidity rapidly increases, and then its rate of increase becomes gradually less. Thus the character of the change is quite analogous to that of the change of elasticity.

In a given field the change of rigidity is independent of the twisting couple. It is also a proof of the same fact that the curves corresponding to different couples pass through a point on the axis of the field. The ratio of the change to the modulus itself for different fields is given in the following table and in fig. 4.

Fig. 8.



H	20.	40.	80.	100.	200.	400.	600.	800.
$\frac{\delta K}{K} \times 10^2$ ..	−0·96	−1·68	−0·67	0·12	2·63	5·32	6·67	7·48

Thus in nickel the change of rigidity is considerably larger compared with other ferromagnetics. The nickel rod used in the preceding experiment was turned into a square rod from a plate, and the mechanical process, which the specimen underwent, hardened it in magnetic quality. If we study the change of elasticity with the present sample the proportionally large change would be observed.

According to Profs. Nagaoka* and Zehnder† the magnetization of nickel increases by twisting in weak fields; in strong fields, however, it diminishes by twisting. These results are reciprocally related to ours.

The change of twist so far described for iron, steel, nickel, and cobalt is independent of the direction of the magnetizing field.

9. In comparing the change of rigidity by magnetization with that of elasticity, we observe one marked difference that the former is independent of the applied stress while the latter is largely affected by it, especially with small stress.

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* Nagaoka, Journ. Coll. Sci. Tokyo, ii. p. 304 (1888); iii. p. 189 (1889).

† Zehnder, Wied. *Ann.* xli. p. 210 (1890).

It may also be noted that the reciprocal relations between torsion and magnetization, as found by the actual experiments, will be found to be of paramount importance in the theory of magnetostriction. We may conveniently place the results of our experiment with those of previous investigators under the following parallel statements :—

Magnetization to Twist.	*Twist to Magnetization.*
(*a*) The magnetization of iron decreases by twisting for all magnetizing fields.	(*a*′) The torsion of iron decreases in all magnetizing fields.
(*b*) The magnetization of nickel increases by twisting in weak fields.	(*b*′) The torsion of nickel increases in weak fields.
(*c*) The magnetization of nickel decreases by twisting in strong fields.	(*c*′) The torsion of nickel decreases in strong fields.

A similar reciprocal relation would probably exist in the case of cobalt. The actual verification of the relation will be undertaken in the near future.

In conclusion we have to express our best thanks to Prof. H. Nagaoka and also to Prof. A. Tanakadate for many valuable suggestions.

LXI. *A new Method of determining the Vapour-Density of Metallic Vapours, and an Experimental Application to the Cases of Sodium and Mercury.* By Frank B. Jewett *.

IN all investigations on the composition and distribution of light in the spectral lines it is of prime importance that the lines themselves be as narrow and sharply defined as possible ; this is especially true in those cases where the analysis is carried on by means of interference phenomena, for here the difference of path over which interference takes place decreases as the width of the line increases.

There are in general two causes which may affect the breadth of the lines : (*a*) motion of the light-producing molecules in the line of sight, and (*b*) change in the period of the source caused by frequent collisions of the molecules †. To these might be added a third cause, suggested by Lommel ‡, in which an inhomogeneity is produced in the source by forced changes in the period of ionic vibration, thus putting an upper limit on the power to produce interference-fringes ; this latter supposition is, however, yet to be verified, and from the present experimental data it seems probable that any

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* Communicated by the Author.

† Michelson, Phil. Mag. (5) xxxiv. p. 293.

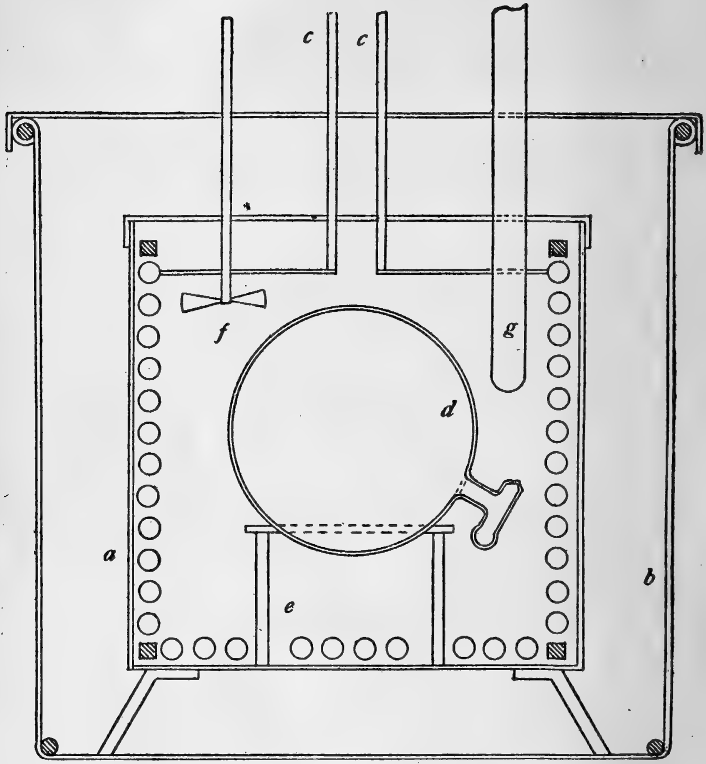
‡ Lommel, Wied. *Ann.* iii. p. 251 ; Drude, *Lehrbuch der Optik*, p. 498.

effect due to it must be almost if not wholly negligible in comparison with that of (*a*) and (*b*). This being the case, the determination of the relative importance of the two factors, pressure and temperature, is the question which at once presents itself for solution. In his very exhaustive article on "The Application of Interference Methods to Spectroscopic Measurements" Professor Michelson has taken up this problem in considerable detail. He finds that in the cases where the density of the vapour is very low the effect of changing pressure on the width of the spectral lines is almost wholly negligible; for hydrogen this is true even in the case where the pressure is as high as 2 or 3 mm.; in fact, when the relation between the breadth of the lines and 1/P (pressure) is plotted the influence of P is seen to become vanishingly small at about 5 mm. In summing up, Professor Michelson states as follows:—"It thus appears that in the case of hydrogen—and probably in all other cases—the width of the spectral line diminishes toward a limit as the pressure diminishes, which limit depends upon the substance and its temperature; and that the excess of width over this limit is simply proportional to the pressure."

As mercury and sodium are both readily usable in vacuum-tubes, the foregoing facts would suggest them at once as the ideal substances for an experiment on the effect of pressure and temperature on the broadening of the spectral lines. As a preliminary to such an experiment a knowledge of the densities of the saturated vapours at various temperatures is of course necessary. In addition to making a determination of the densities for such a purpose as the above, there is still another and even more urgent reason, viz., the evident dependence of the change in the lines in the Zeeman effect, and also in some cases the reversal of the same, upon the density of the light-producing vapour. It was particularly with a view to the solution of this latter problem that the following experiment was proposed and undertaken.

Apparatus.—The method employed was one suggested by Prof. Michelson, in which the amount of vapour filling a known volume is determined by finding the amount of condensed metal in the observing flask when the latter is cooled off. The apparatus consisted of three essential parts—the heating-bath, the gas-bulb, and the thermometer. The bath finally found most satisfactory is shown in section in fig. 1 (p. 548); *a* and *b* are two sheet-iron boxes lined inside and out with heavy sheet-asbestos, and having a 3-inch air-space between them; the inner box (*a*) is about 14 inches on a side; around the inside and on the bottom of *a* are a number of iron resistance-coils carried on an asbestos-covered iron frame, and ending in two heavy terminal wires *cc*, which pass out through the covers of both boxes; the bulb *d* is supported on a metal frame *e*, and constant circulation is maintained by an electrically-driven fan *f*; *g* represents the stem of a platinum thermometer. With this arrangement, and with suitable regulation for the current, the temperature may easily be kept constant at any desired point to within one or two degrees *.

Fig. 1.



The gas-bulb or reservoir (fig. 2) was of hard glass of known cubical content, and had a capacity of about 2000 c.c.; proceeding from the bulb were two tubes, one a heavy capillary and the other with an internal diameter of about 1 cm.

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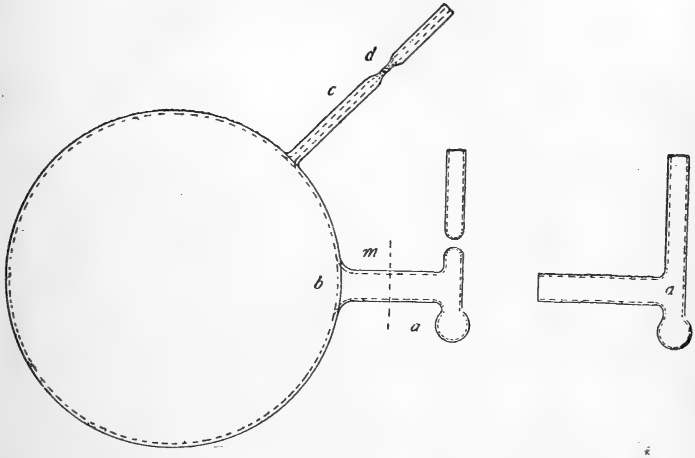
* In one instance where the bath was used for calibrating a Beckmann thermometer the temperature was held constant to 0°·1 for fifteen minutes.

The thermometer was of the Callendar platinum-resistance type *, with auxiliary compensating-leads and direct reading

Fig. 2.



Wheatstone bridge, and was capable of reading to 0°·005; this particular instrument was one of those calibrated at the Kew Observatory.

In order to make an observation a tube (*a*, fig. 2) was sealed to the larger tube (*b*), and the capillary-tube (*c*) drawn down at (*d*); this being done, and both tubes and bulb thoroughly dried, a small piece (0·5–0·7 gm.) of C.P. metallic sodium was introduced into (*a*), and the latter quickly sealed off at (*e*), as shown; (*c*) was now connected to a Geissler-pump, and the air drawn out to a residual pressure of 0·1–0·2 mm., after which the bulb was filled with some inert gas (H or N) and again pumped out and the capillary-tube sealed off at (*d*). The bulb thus prepared was now introduced into the bath and the temperature raised to any required point; the apparatus was kept at the desired temperature for fifteen or twenty minutes, thermometer-readings being taken every two minutes; the cooling had to be done very slowly, as the capsule containing the molten sodium was very liable to crack, and the inrushing air carried the metal into the bulb. Upon removing the latter from the bath, the whole inner surface showed a bright metallic coating of condensed sodium vapour, varying in thickness with the temperature to which the bulb had been subjected. To determine the amount of

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* E. H. Griffiths, 'Nature,' Nov. 14, 1895.

sodium in this coating, and consequently the amount of saturated vapour that had filled the bulb, the tube (*b*) was cracked off at some point (*m*), thus getting rid of the metal remaining in (*a*); the bulb was then thoroughly washed out with hot water until the washings failed to show an alkaline reaction with phenolphthaline, and the amount of Na present as NaOH in the washings determined by differential titration with standardized N/10 · NaOH and N/10 · H_2SO_4 solutions; this amount, together with the corrected volume of the bulb, furnished the requisite data for finding the vapour-density. As this process had to be repeated for every determination, the making of a large number of observations was an exceedingly tedious matter.

The above-described method was the one finally chosen for sodium; a number of methods depending upon the gravimetric determination of the amount of metal volatilized, while giving good results for those metals which do not oxidize easily at low temperatures, *e. g.* Cd, proved absolutely useless in the case of sodium on account of the rapid oxidization of the latter when in contact with the air.

A difficulty which it was at first feared might render the determination impossible at the higher temperatures, viz., the action of sodium on glass, was not encountered except when the residual atmosphere contained O or water-vapour, the solvent action being apparently exhibited only for the oxide or hydroxide; aside from this fact the results obtained in the presence of air were so extremely erratic that all the final determinations were made either in the presence of oxygen or nitrogen. (The majority of the tests were made with hydrogen, and as they gave consistent results the accuracy of the process was not questioned at the time, especially as the hydride, Na_4H_2, was not supposed to form at pressures so reduced as those employed *. Owing, however, to a peculiar brown metallic appearance of the deposit in some instances, doubt was cast on the validity of this assumption, so that while the great mass of chemical data seems to weigh against the formation of the hydride, there still remains the possibility that the density of the vapour, calculated on the assumption that it consisted of free Na, gave too low a result. This question can be easily settled, however, by the employment of N, since the nitride, NaN_3, is not formed by the direct combination of Na and N †.)

Some of the results are given in Table I., and the curve,

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* Roscoe & Schorlemmer, 'Treatise on Chemistry,' vol. ii. pt. i. p. 107.

† *Berichte*, xxv. p. 2084 (1892); *Zeit. f. anorg. Ch.* vi. p. 38 (1894).

with temperatures as ordinates and densities as abscissæ, is shown in fig. 3 (p. 552); the dotted curve shown is that for Hg at temperatures where the density of the vapour corresponds to that of Na; the temperatures for this latter curve are indicated on the curve.

TABLE I.

Temp.	Density.
368°	0·00000009
373	0·0000002
376	0·00000035
380	0·00000043
385	0·00000103
387	0·00000135
390	0·00000160
395	0·00000270
400	0·00000350
406	0·00000480
408	0·00000543
412	0·00000590
418	0·00000714
420	0·00000750

While the densities were not obtained much below 365°, it will be noticed that at this temperature—which cannot be far from that commonly employed in vacuum-tube work *—the density of the Na vapour increases at about the same rate as that of Hg at 85°, while at points slightly above this the Na curve increases much the more rapidly. This fact, taken together with its low atomic weight, might well account for the peculiarities observed by Professor Michelson.

As was stated above, the experiment was undertaken solely to determine the densities within the range between 350° and 450°, and indeed the use of a glass bulb precludes the possibility of anything being done above 500°; with a porcelain bulb it would be comparatively easy to attain any desired temperature below 1700°.

The ease with which the temperature of the electric bath could be regulated at once suggested the desirability of making a series of determinations on the vapour-density of Hg, and with the slight alteration in the form of the bulb

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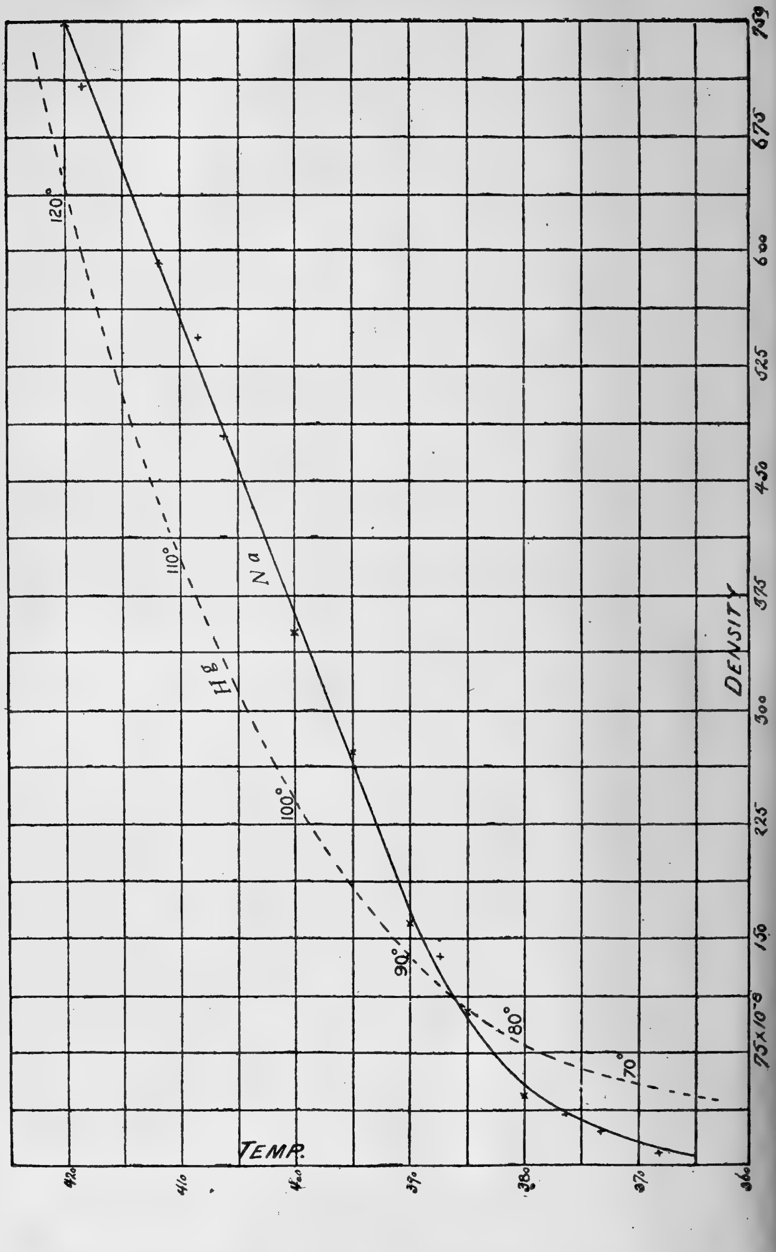
* Professor Michelson assumes that the temperature of the heating-box, 350°, is that of the vapour also. There appears to be some doubt as to the legitimacy of this assumption, owing to the very considerable heating produced by the discharge itself.

Fig. 3.


739
675
600
525
450
375
300
225
150
75×10⁻⁸
DENSITY
TEMP.
420
410
400
390
380
370
360
120°
110°
100°
90°
80°
70°
Hg
Na

shown in fig. 4, a set of continuous readings 5° apart was obtained. The mercury-reservoir (*a*, fig. 4) is a long narrow tube of hard glass of known coefficient of expansion, and having a carefully calibrated bore. In making a determination the reservoir is charged with a known weight of mercury, and the bulb exhausted and sealed off as in the case of sodium ; it is then introduced into the bath and supported in such a position that (*a*) is vertical ; the height of the mercury column is observed through glass windows in the

Fig. 4.

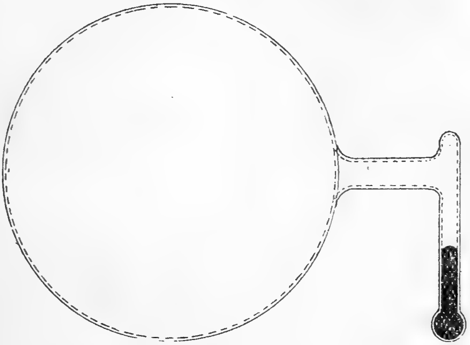


TABLE II.

Temp.	Density.	Regnault & Hertz.	Ramsay & Young.
40°	0·00000007	0·00000007	0·00000009
60	0·0000003	0·0000003	0·0000003
70	0·00000045	0·0000005	0·0000005
80	0·0000007	0·0000008	0·0000008
90	0·0000012	6·0000014	0·0000014
100	0·0000021	0·0000024	0·0000023
110	0·0000040	0·0000039	......
120	0·0000060	0·0000064	0·0000059
140	0·0000138	0·0000147	0·0000137
160	0·0000302	0·0000323	0·0000297
180	0·0000624	0·0000649	0·0000603
200	0·0001580	0·0001236	0·0001152
220	0·0002020	0·0002271	0·0002077
240	0·0003754	0·0003673	......
260	0·0005830	0·0005817	......
270	0·0006528	0·0007257	0·0007310
280	0·0008645	0·0008994	0·0009113
300	0·0013466	0·0013547	0·0013796
305	0·0013882	......	......
310	0·0016447	0·0016472	0·0016734
320	0·0019879	0·0019921	0·0020180
325	0·0019960	......	......

sides of the bath by means of a cathetometer. The readings thus obtained, together with the known coefficients of expansion of glass and mercury, furnish the requisite data for determining the amount of metal volatilized. A partial series of the results obtained is given in Table II., together with the results calculated from the observed tensions of mercury-vapour as given by Regnault and Hertz; a more complete set of readings will be published later.

In conclusion I desire to express my thanks to Professor Michelson for the encouragement and helpful criticism given throughout the work, and also to Dr. Gale for the assistance so kindly rendered in the work on the density of mercury-vapour.

Ryerson Physical Laboratory,
March 25, 1902.

LXII. *On the Electrical Resistance of Bismuth to Alternating Currents in a Magnetic Field.* *By* George C. Simpson, *B.Sc., Fellow of the Victoria University*[*].

In a previous paper (Phil. Mag. 1901, ii. p. 300) I described experiments which showed that the anomalous effect produced in a bismuth wire carrying an alternating current placed perpendicular to a strong magnetic field can be conveniently represented by an E.M.F. (called the "bismuth E.M.F.") set up in the bismuth itself. It was then found that this bismuth E.M.F. varies in phase and magnitude with different frequencies of alternating current used—the phase being 100° 13′ behind the applied E.M.F. with a frequency of 3 per second, the lag increasing to 126° 31′ with a frequency of 60 per sec.; the magnitude being a linear function of the frequency and increasing with it.

This investigation having given the variations of the bismuth E.M.F. with frequency, the field being kept constant, experiments have since been made to find how the bismuth E.M.F. varies with the field-strength for a given frequency. The investigation again consisted of two parts—determinations of the changes in the angle of lag and in the magnitude.

I. The determination of *the variation of the angle of lag with different field-strengths, the frequency being constant*, was made by the same method as that already used and described in the previous paper. The experiments were now more difficult owing to the diminution of the whole effect due to decreasing

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[*] Communicated by the Author.

the field-strength, the maximum field at my disposal having been employed in the previous experiments.

Three sets of experiments were made having frequencies of 30, 20, and 13·3 per sec., and in each set three different field-strengths were used. The results of these experiments plotted according to the theory given in the previous paper are shown in figs. 1, 2, and 3. In these figs. the points where the straight lines cut the abscissa give the cotangents of the angles of lag. In each of the figs. the straight lines for the different field-strengths cut the abscissa in the same point; hence the experiments show that the angle of lag is

Fig. 1.

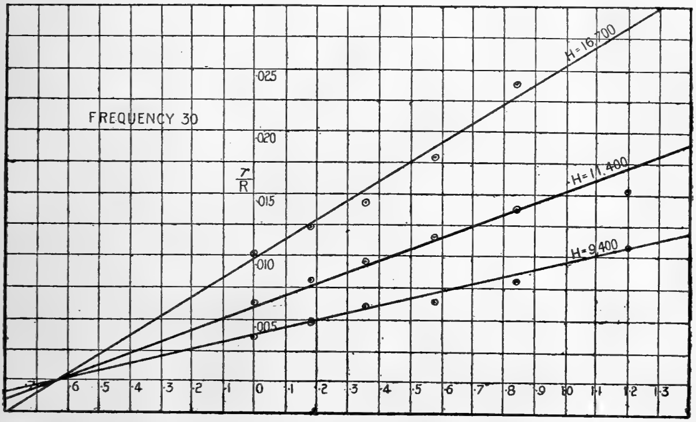
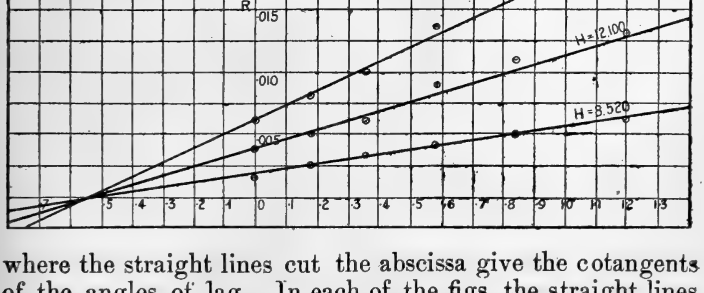
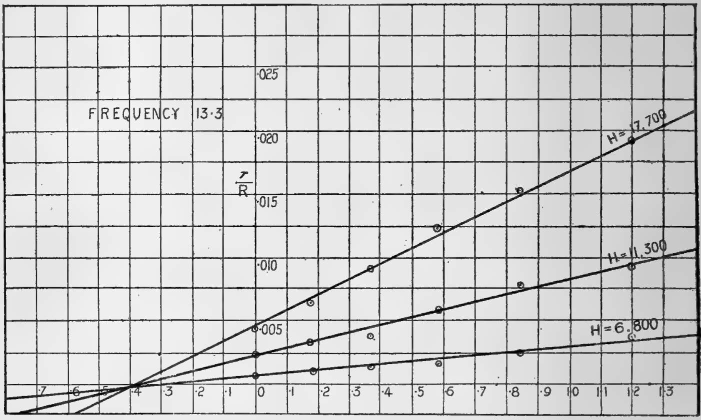


Fig. 2.



independent of field-strength. Thus the curve already given connecting angle of lag with frequency holds for all field-strengths.

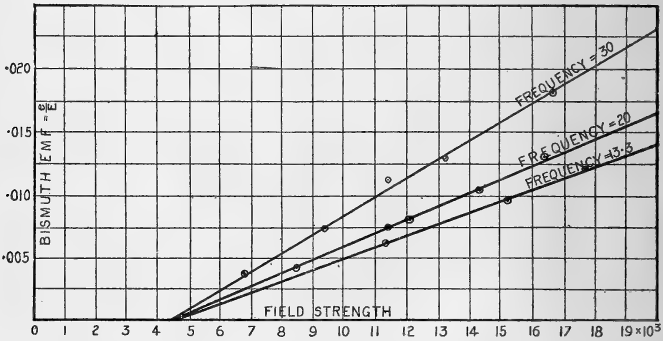
Fig. 3.



II. *The variation of the magnitude of the bismuth E.M.F. with different field-strengths, frequency constant*, was calculated from the results obtained in the above determination.

These results, with a few more from separate experiments,

Fig. 4.



are plotted in fig. 4, in which the value of the bismuth E.M.F. $\frac{e}{E}$, is plotted against field-strength. The conclusions to be drawn from this fig. are very interesting, showing as they do: 1st, that the magnitude of the bismuth E.M.F. is a linear function of the field-strength; 2nd, that the bismuth E.M.F. is zero at the same field-strength for all frequencies; and

3rd, that this field-strength is considerable—4500 lines per sq. cm. This latter result is also interesting from the fact that Lenard and others, using very high frequencies, have found a negative effect in no field; with the low frequencies used in my experiments the negative effect can just be detected, but could not be satisfactorily measured.

Temperature Variations.

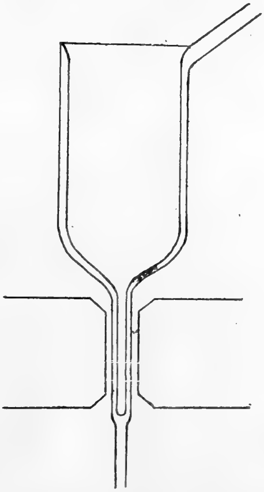
Experiments were next undertaken to find the effect of temperature variations on the bismuth E.M.F.

In all the previous experiments a Hartmann & Braun bismuth spiral, designed for field-testing, had been used, but this became useless when experiments were made at other than atmospheric temperatures, so it was replaced by a wire ·3 mm. in diameter and about 10 cm. long, bent into the form of a flat grid and soldered to two thick copper wires (fig. 5). These grids were very easily broken, and a number were used during the experiments; the bismuth wire was supplied by Messrs. Hartmann & Braun.

Fig. 5.

For temperatures above atmospheric a grid was placed in a glass vessel (fig. 6) consisting of an inner vessel having a flat tube joined on at the bottom, into which the bismuth wire projected, surrounded by a similar slightly larger vessel.

Fig. 6.



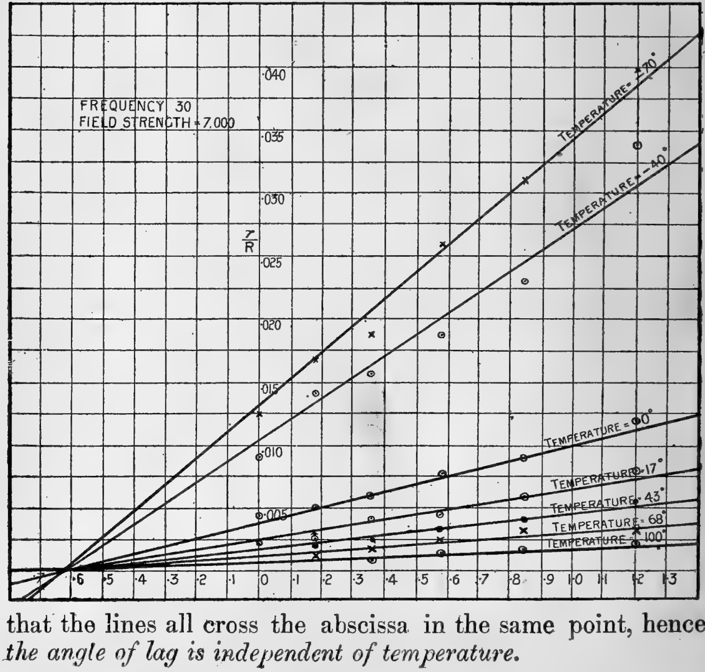
In the space between the two, water from a thermostat circulated, so keeping the bismuth (placed in oil) at the required temperature.

For temperatures below atmospheric a similar vessel was used, except that the space between the two walls was evacuated, and different freezing-mixtures placed in the inner vessel.

Low temperatures were obtained as follows:—Liquid air gave a constant temperature of −185°, a mixture of solid CO_2 and acetone gave −70°, while −95° was obtained by bubbling air through this mixture; solid CO_2 in alcohol produced −40°.

The bismuth wire having a very low resistance (about 2 ohms at 17°) and the field being comparatively weak, owing to the large separation of the pole-pieces necessitated by the glass vessel, the whole effect to be measured was extremely small, so that it was found convenient to work only with the strongest field to be obtained under the conditions (about 7000 lines) and with a frequency of 30 per sec. With this field and frequency complete experiments were made at −185°, −70°, −40°, 0°, 17°, 43°, 68°, and 100°, the results of which are given in fig. 7. In this figure it will be seen that the lines all cross the abscissa in the same point, hence *the angle of lag is independent of temperature.*

Fig. 7.

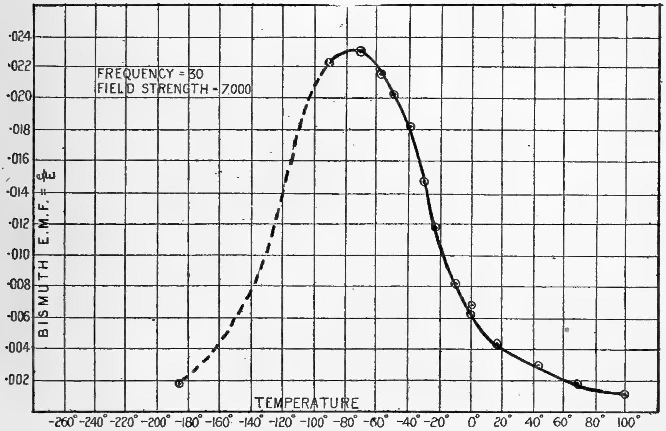


As the angle of lag has already been found to be independent of field-strength, it may now be safely said that the angle of lag is a function of the frequency only.

To find the *relation between the magnitude of the bismuth E.M.F. and temperature*, the results given in fig. 7 were used; but besides these it was found possible to get a measurement of the magnitude only, every 10° between −90° and 0°, by making use of the fact, just found, that the angle of lag is independent of temperature.

Fig. 8 gives the results of these experiments, and shows that the effect, which is small at −180° and 100°, becomes comparatively large between, reaching a maximum at −70°, where with the small field of 7000 lines and a frequency of 30 per sec. the bismuth E.M.F. is 2·2 per cent. of the E.M.F. applied to the bismuth, being five times greater than its value at ordinary temperatures.

Fig. 8.



This variation of the bismuth E.M.F. with temperature is most important, because it shows that the effect, if not due to the Hall effect, has a close connexion with it, for a very similar variation of the Hall effect with temperature has been demonstrated by Dr. A. Lebret (‘The Electrician,’ vol. xxxvi. 1896, p. 785).

In conclusion the results of the whole investigation may be briefly stated :—

I. The *magnitude* of the bismuth E.M.F.
  (*a*) is proportional to the current in the bismuth;
  (*b*) is a linear function of the field-strength;
  (*c*) increases with the frequency;
  (*d*) varies with temperature, having a maximum value about −70°, decreasing rapidly on either side.

At ordinary temperatures its value is given by

$$\frac{e}{\mathrm{E}} = (35 + 3{\cdot}9\,n)(\mathrm{H} - 4500)10^{-8},$$

where n = frequency, and H = field-strength.

II. The *angle of lag* of the bismuth E.M.F. behind the current in the bismuth

(*a*) varies with frequency;
(*b*) is independent of temperature and field-strength.

Owens College, Manchester.

LXIII. *On Radiation of Heat and Light from Heated Solid Bodies.* *By* J. T. Bottomley, *D.Sc., F.R.S.**

[Plates V. & VI.]

THE following paper describes a further instalment of experiments on radiation of heat and light from heated solid bodies, a subject to which I have given attention for a considerable number of years. It is a difficult subject, and it has only been at times that I have been able to make progress in the prosecution of the inquiry. I have treated it from first to last in a purely experimental way. I do not feel that there exists at present sufficient experimental information to admit of anything like a complete theory. Indeed the information which we possess is of the scantiest character.

My aim has been to determine directly the quantity of heat lost from a given surface under given conditions; and the method by which I have carried out my experiments has been to put the radiating body into a vacuum as complete as I can obtain, and then to measure the energy lost from it in a given time, noting the circumstances. By adopting this plan I avoid determinations of the value of heat-receptors, such as sooted bolometers or sooted thermojunctions; and I obtain results in absolute measure.

In a paper published in the Transactions of the Royal Society as far back as 1887 I showed that it is possible to obtain with the Sprengel-pump a vacuum so good that the effect of convection on loss of heat from a hot body, in so far as that loss is caused by non-condensable gases, ceases to be of importance in comparison with loss due to pure radiation; in fact, that increasing the vacuum, *as*

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* Communicated by Lord Kelvin.

indicated by the McLeod gauge, beyond a certain point makes no difference to the amount of heat lost.

It is not certain that the results would be quite the same could all the mercury vapour, which must undoubtedly exist in the vacuum-chamber, be removed; and this is a question which still requires investigation. Other condensable gases, such as vapour of phosphorus (given off from the drying apparatus) also need consideration. The last mentioned gas I have, however, recently done away with, I hope completely, by using phosphorus pentoxide which I have specially prepared for the purpose.

I only desire at present to call attention to one particular part of the general investigation.

In 1887, together with Mr. Mortimer Evans, I pointed out the marked difference in emissivity between a polished metallic-like surface and a dull sooted surface. I think it is now generally admitted* that such a difference does really exist, but at the time my conclusions were controverted. For example, in his book on 'Practical Electrical Measurement,' Mr. Swinburne has the following passage:—

> "Mr. Bottomley read a paper at the British Association in 1887 giving an account of some experiments as to colour and temperature. His conclusions are opposed to those generally accepted by physicists, and before they can be accepted a great deal more evidence must be given. Mr. Bottomley, apparently, regards his paper as a mere first notice, and intends to continue his important experiments. At present it may be suggested that his arguments as to Mr. Evans's experiments are open to criticism. The resistance of a lamp-carbon varies with the temperature in accordance with no evident law, and the colour of the light and radiation depend on the surface temperature of the whole carbon. A carbon of high emissivity would need a higher internal temperature to preserve a given surface temperature than one of low emissivity. The same reasoning applies to two platinum wires, one of which is blackened. Besides, Mr. Bottomley does not state whether the lampblacked wire was heated to incandescence before the tube was sealed off the pump†; and if it were not, it would be coated with hydrocarbons,

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* [*Note added July* 31*st*, 1902.] In the discussion which followed this paper at the meeting of the British Association, September 1901, one of the speakers expressed the view that incandescent-lamp makers do not find any difference between flashed and unflashed filaments. I venture to think, however, that this is incorrect. Incandescent-lamp makers are naturally reticent as to their experience, but I believe that all first-class makers are now fully alive to a difference in economy between a brightly flashed filament and a dull unflashed filament.

† The tube is never sealed off the pump. The pump is kept working the whole time to remove occluded gases given off from the platinum.

which would spoil the vacuum in that tube. It is, no doubt, unlikely that one so careful as Mr. Bottomley would make such mistakes; but, on the other hand, his results are so opposed to those of others that they may be disregarded for the present, and the law that efficiency is a test of surface-temperature, and colour is a test of both, may be taken as true."

I have always desired to examine further the question here referred to, and to come to definite conclusions on the subject, but it is only recently that I have been able to arrange for a set of perfectly conclusive experiments.

The apparatus which I use is shown in Pl. V., which will serve to explain the details.

The radiating body which I have used recently has been a thin platinum strip heated by an electric current. The strip was rolled for the purpose by Messrs. Johnson and Matthey, to whom I beg to express my thanks for the great trouble they have taken in order to provide me with perfectly uniform material. The way in which it is mounted is shown in the figures. The strip AB is held stretched between two spiral springs in a glass tube: the outer ends of the spiral springs terminate in loops, and two pieces of copper rod are passed into the tubes CC and C′C′ so that the springs pull on these rods. These rods pass down through long narrow side tubes into mercury cups, and by means of these the electric current which heats the platinum strip is passed into it.

At the points EE (see elevation) of the platinum strip fine platinum wires are attached by welding, and they are brought out through the sides of the glass envelope. These serve as potential electrodes; and it is to keep the platinum strip AB in the middle of the tube, and to avoid pulling unduly on the potential electrodes that the two spiral springs, one at each end of the tube, are introduced.

Two exactly similar tubes are employed, as shown in Pl. V. (plan). They are connected together at each end, as shown; and by means of a branch tube, attached to one of the two end tubes and connected to a Sprengel-pump, the air is withdrawn from both tubes at the same time. By this arrangement it is provided that the vacuum in the two experimental tubes shall be at all times precisely the same.

In one of the tubes the platinum strip is brightly polished and perfectly smooth, just as it came from the makers' hands. The other tube contains a platinum strip of exactly the same length between the points EE, and cut from the same hank, but with the surface covered with an exceedingly fine coating of lampblack.

The arrangements for drying the vacuum consist in (1) a flask of phosphorus pentoxide attached to the pump by a wide side tube, and so arranged that it does not choke the connexion between the pump and the apparatus; (2) four pockets, two on each experimenting tube, as shown in sketch, each one containing phosphorus pentoxide. These pockets are short side tubes of the same diameter as the main tubes, and they allow free access for diffusion of the water-vapour into the drying material.

This method of arranging the drying-tubes seems to me to be far better than the usual plan of putting a good long column of drying material between a pump and the apparatus to be exhausted. The effect of the latter is only to dry the gas that is pumped away, not to dry the gas remaining in the experimental apparatus, except by diffusion. Moreover, such an arrangement must very seriously retard the process of exhaustion at very low pressures, by choking the tube.

The vacuum is measured by a modification of the McLeod gauge attached to the second of the end tubes mentioned above (see Pl. V.), so that the experimenting tubes are between the pump and the gauge. By this arrangement it may be safely assumed that the vacuum in the experimenting tubes is at least as good as the vacuum in the gauge, especially as the gauge was so made as to allow a wide tube connexion with the apparatus, in order to assist diffusion and prevent its readings from lagging behind what they should be.

The electrical connexions, by means of which the currents of electricity, which heat the strips, are passed into them and are measured, will be easily understood from the figures (Pl. V.). The current is supplied by a storage-battery of ten cells. There are two separate circuits, one for each strip. The current sent into each is regulated partly by the number of cells, and partly by a rheostat in circuit; and an amperemeter in each circuit measures the current passing.

A voltmeter can be applied to the working part of either strip by means of the potential electrodes, EE, E′E′, and the double-pole change-over switch indicated in the figure.

It will be seen from the elevation on Pl. V. that the electrodes, EE, are attached at some distance from the ends of the strip AB. This is to avoid disturbance from the cooling effect of the end attachments. It is the portion EE which I call the working part of the strip.

In a very interesting paper by W. H. Weber, published in the *Annalen der Physik und Chemie,* vol. xxxii. p. 256, a paper which I think has scarcely received the attention which it deserves, the author traces from the very commencement the production of light by a heated solid body. He shows that a solid body first becomes luminous at a very much lower temperature than 535° C., which was given by Draper as the temperature of the lowest visible red heat. Weber found traces of luminosity at a temperature as low as 391° C. for platinum, and about 378° C. for iron.

He also describes very carefully, and in an extremely interesting manner, the dawn of a dusky gray light at these temperatures, and its transformation at higher temperatures into the light of low red heat, and subsequently into bright red light and white light.

Following Weber I have commenced by bringing up the platinum strips to the very lowest temperatures at which luminescence could be perceived, and I then measured the electrical power required to maintain the temperature of each strip, one of them polished and the other covered with lampblack. This being done, I passed on to very dull red, then to dull red, and subsequently to cherry-red, and to a white heat; and in each case I made similar measurements with the voltmeter and amperemeters, to ascertain the power in watts required in each case. The two strips were matched as to light-giving quality as closely as possible.

After some practice my assistant, Mr. W. T. Evans, whose accuracy I cannot sufficiently praise, attained great skill in matching the pairs of strips. The results of our experiments are shown in the following table (p. 565) and in the corresponding curves 1, 2, and 3, Plate VI.

Column 2 of the table describes the condition of the strips. The specification gray light, dull red, &c. is purely arbitrary, and mainly indicates the opinion of the experimenters, Mr. Evans and myself, as to the light-giving condition of the surface. The gray light referred to in experiments 1 and 2 is the colourless light of Weber; though in our experiments, at the lowest point of temperature at which he observed the beginnings of light, we could not see anything *. The nearly white light of experiment 13 is not nearly so white as the light produced from an incandescent electric lamp. It has been explained that the two strips were matched in appearance in our experiments, and Column 9 shows approximately the temperature of each strip, inferred from the resistance of the strip which is given in Column 6. The resistance is easily obtained as the ratio of the potential-difference to the current. The current in amperes passing through each strip is shown in Column 4, and the potential-difference in volts between the points EE, in each strip, is shown in Column 5.

By multiplying together the amperes and the volts and dividing by JS, the product of Joule's equivalent J, and S

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* Doubtless through want of practice.

the surface, in square centimetres, of the strip between the potential leads EE, the absolute amount of energy lost by the strip per square centimetre per second is found. This is equal to AV/4·2S, and is shown for all the experiments in Column 10. The figures in Column 10 represent the number of gramme-water-degree-centigrade-units of radiant energy lost per second from each square centimetre of surface of the strips.

Table of Results.

No. of Expt.	Condition.	Strip.	Amps.	Volts.	Ohms.	Watts.	Watt-ratio.	Temp.	AV/JS.
1.	Gray light.	Bright. Black.	1·9 5·35	1·01 2·81	0·532 0·525	1·922 15·09	7·85	435° 452	0·0417 0·327
2.	"	Bright. Black.	2·13 5·9	1·175 3·23	0·552 0·547	2·5 19·05	7·62	465 487	0·0543 0·414
3.	Very dull red.	Bright. Black.	2·31 6·2	1·32 3·45	0·572 0·557	3·05 21·4	7·02	495 503	0·0662 0·465
4.	"	Bright. Black.	2·34 6·25	1·43 3·7	0·611 0·592	3·31 23·1	6·98	550 560	0·0727 0·501
5.	Dull red.	Bright. Black.	2·8 7·2	1·74 4·32	0·622 0·600	4·87 31·1	6·53	573 573	0·106 0·676
6.	"	Bright. Black.	3·04 7·7	1·975 4·77	0·650 0·620	6·0 36·8	6·13	613 607	0·1302 0·799
7.	"	Bright. Black.	3·2 8·0	2·1 5·05	0·656 0·632	6·72 40·4	6·02	623 625	0·146 0·877
8.	Fair red.	Bright. Black.	3·5 8·5	2·37 5·47	0·677 0·644	8·3 46·5	5·6	655 643	0·180 1·01
9.	Good red.	Bright. Black.	4·0 9·45	2·79 6·32	0·697 0·670	11·15 59·7	5·36	685 685	0·242 1·296
10.	Bright red.	Bright. Black.	4·62 10·4	3·35 7·24	0·724 0·696	15·45 75·2	4·87	727 727	0·335 1·632
11.	Very bright red.	Bright. Black.	5·3 11·6	4·1 8·52	0·773 0·735	21·7 98·9	4·56	800 793	0·472 2·147
12.	"	Bright. Black.	5·99 12·75	4·8 9·85	0·801 0·772	28·7 125·6	4·38	843 848	0·623 2·73
13.	Nearly white.	Bright. Black.	6·4 13·2	5·35 10·5	0·836 0·796	34·2 138·7	4·06	898 891	0·742 3·01

Column 7 gives the power in watts supplied to each strip, *i. e.* the product of the current into the P.D. between the points EE. Column 8 gives the ratio of the watts used by the dull strip to the watts used by the bright one, both being matched in appearance, and both being practically at the same temperature, as is shown by the numbered experimental points on No. 1 curve lying so nearly on the same ordinates as the corresponding points on No. 2 curve.

Curves No. 1 and No. 2 were plotted from the results of measurements of resistance and temperature made on the two strips when dismounted after the radiation experiments. The resistance numbers of Column 6 were then marked on these curves, and the corresponding abscissæ gave at once the temperatures shown in Column 9.

It will be seen by the divergence of Curves 1 and 2 that the increase of resistance with temperature in the dull strip is very slightly lower than that in the bright strip. This is probably due to the conducting power of the thin filament of lampblack which covered the strip. The lampblack would have a slight effect in reducing the resistance of the strip, and it would also have an effect, of minor order, in reducing the rate of increase with temperature of resistance of the coated strip.

Curve 3 of the figure shows the watt-ratio for the two strips at the mean of the temperatures given in Column 9.

It appears from the table and the curves that the blackened strip consumes energy at a greater rate than the bright strip when the two are at the same temperature, and that at each point when the strips are giving off an equal amount of light the blackened strip is using much more energy per second than the polished strip.

It seems also that the ratio between the power used by the two strips is much higher at the commencement of luminescence than at a brighter heat; and it may be that a point would be reached at a very high temperature where this ratio might become constant, or else that at an extremely high temperature the power required to supply the blackened and the bright strips might not be very different in amount.

The platinum strips were used in order to give a better comparison by eye than can be got from thin wires of the same electric carrying capacity, but it has been very difficult to obtain platinum strips which would not break at a very moderate temperature. I have tried commercial platinum strip, and also strip of perfectly pure platinum; latterly I tried strip containing 10 per cent. of iridium in order to harden it, but none has been as successful as I hoped. It has been very disappointing that in every case one or other of the strips broke, and my experiments have been stopped before I could reach a really very high temperature. The breaking of the strips is not to be attributed to an over great tension in the spiral springs. The amount of pull in the spiral springs was only so great as to take up the slack due to the expansion of the platinum with heat. I have a very strong feeling, though I am not quite able to prove the assertion, that the platinum wires become excessively brittle, or as it is sometimes called with respect to brass wire, "rotten," during the long process of heating and pumping which is necessary, as a preliminary to the experiments, in order to remove from the platinum the gases occluded in it*.

In a paper which I published in 1900 along with Prof. J. C. Beattie (Royal Society Proceedings, March 1900)†, the radiation from polished and blackened platinum wires was determined in a somewhat different way. The apparatus used was practically the same as that which I have just now described, but instead of comparing the energy lost by the wires when they presented the same appearance to the eye as to light-giving quality, the comparison was made between pairs of wires at the same temperature, the temperature being known by the resistance of the wires. Three pairs of wires having different diameters were used in these experiments, and it was shown that the thermal energy lost by the sooted wire was from four to five times as great as that lost by the polished wire, the two being, as I have said, at the same temperature.

In one respect the determinations, an account of which is given in the present paper, and in the paper by Dr. Beattie and myself, are not perfectly satisfactory. We have not been able to take account in a proper way of the temperature of the enclosing envelope. In order to be able to see the condition of the wires, and in particular to observe their appearance when they became luminous, glass envelopes were used in these experiments; and owing to the nature of the arrangements and the method of experimenting it was not found possible to immerse the glass envelopes in a cooling bath. Consequently, the glass became more or less heated during the experiment, and the heating was unequal in the cases of the bright wire and the sooted wire. It has already been pointed out (Phil. Trans. A, 1887, p. 450) that the

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* [*Footnote added Oct 18th,* 1902.] In a paper by Dr. Hartley (Phil. Mag. July 1902) it is mentioned that the presence of carbon and phosphorus render platinum brittle. It is quite possible that some traces of phosphorus vapour may still find their way into my tubes, although I have made the greatest effort, by preparing the phosphorus pentoxide which I use with every care and every precaution I can think of, to avoid this contamination, of which I have always had a fear. My phosphorus pentoxide, the best I could buy, was most carefully redistilled, by myself, in a current of oxygen. The distillation was carried on in special tubes of hard glass, constructed by Mr. Evans, following the method of Shenstone.

† Phil. Mag. June 1900, pp. 543–559.

proportions in which the radiation of longer period and shorter period are present in the total radiation depends on the radiating surface, other things being the same. In the case of the sooted wire, the quantity of long-period radiation is, in proportion, far in excess of that proceeding from a bright metallic polished surface. Consequently, with the *same* total electric energy supplied to both wires, the glass tube containing the sooted wire becomes *very much* hotter than the tube containing the bright wire.

It has also been pointed out that with a substance like glass, conducting badly and somewhat diathermanous, it is impossible to tell how much heat is returned to the radiating wire from the interior skin of the tube, which no doubt rises to a high temperature during the experiment. To a certain extent, therefore, the results which we have recently obtained must be considered as not strictly comparable with those formerly obtained, in which a metallic envelope cooled with water was used.

The absolute value of the radiation observed ought to be somewhat lower in amount than would have been found had the enclosing envelope been of metal properly kept cool, and the disturbance from this cause must have been relatively greater in the case of the dull than in the case of the bright wire.

I cannot conclude without expressing my warmest thanks to my assistant, Mr. Evans, whose aid has been invaluable. Without the help which he has given me the experiments could not have been carried out at all. The investigation is still in progress, indeed, the present paper must be regarded as a description of preliminary trials; I hope before long, however, to obtain further results in the same direction of considerable interest. The temperatures shown on the curves and in the tables have been obtained partly by direct experiment and partly by using the results of other experimenters who have given comparisons between platinum resistances and temperatures. They must only be regarded as approximations, and may possibly require to be corrected. The amount of the correction cannot, however, alter the general conclusion that the polished surface is much more economical for the production of light than the sooted surface; and that as far as our experiments have gone, the polished platinum surface and the sooted surface are practically at the same temperature when they present a similar appearance to the eye.

LXIV. *The Cause and Nature of Radioactivity.*—Part II.

By E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, and* F. Soddy, *B.A. (Oxon.), Demonstrator in Chemistry, McGill University, Montreal*[*].

Contents.

I. Introduction.
II. Method of Measuring Emanating Power.
III. The De-emanation of Thoria and the Regeneration of the Emanating Power.
IV. The Effect of Conditions upon Emanating Power.
V. The Cause of the Emanating Power of Thorium.
VI. The Chemical Nature of the Emanation.
VII. The Nature of Emanating Power.
VIII. The Excited Radioactivity from Thorium.
IX. Further Theoretical Considerations.

I. *Introduction.*

The investigation of the radioactivity of thorium, detailed in the first part of this communication[†], arose out of an examination of the power possessed by thorium compounds of giving out a radioactive emanation. The nature of this property and its relation to the radioactivity of thorium remain to be considered.

A short résumé of what was known at the commencement of the work may be of interest. Thorium radioactivity was discovered by Schmidt and Curie independently in 1898, and Owens in the following year investigated its nature in detail (Phil. Mag. 1899, p. 360). He observed the inconstancy of the radiation and the effect of air currents in reducing its value. The discovery of the thorium emanation which explained these results, and its power of exciting activity on surrounding matter, followed shortly after (Rutherford, Phil. Mag. 1900, pp. 1 & 161).

It was shown that the radiation from the emanation decays rapidly, but at a perfectly defined rate, falling to about one-half the original value at the end of one minute. The emanation passes unchanged through cotton-wool, weak and strong sulphuric acid, and aluminium and other metals in the form of foil, but not through an extremely thin sheet of mica. The emanating power of thoria is independent of the surrounding atmosphere, but is destroyed to a large extent by intense ignition, and does not return when the substance is kept.

There is a very close connexion between the excited radioactivity produced by thorium compounds and the emanation.

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[*] Communicated by the Authors.

[†] For Part I. see Phil. Mag. Sept. 1902.

It was shown that the amount of the former produced under various conditions was proportional to the amount of the latter, and if the emanating power of thoria be destroyed by ignition, its power to excite radioactivity correspondingly disappears. Simultaneously with the appearance of the papers referred to, Curie showed that radium also possessed the power of exciting activity on surrounding objects. Later, Dorn (*Abk. der Naturforsch. Ges. für Halle-a.-S.*, 1900) repeated the work quoted for thoria, and extended it to include two preparations of radioactive barium compounds (radium) prepared by P. de Haen, and a preparation of radioactive bismuth (polonium). He found that radium, but not polonium, gave an emanation, especially on warming, and this possessed the power of exciting activity on surrounding objects. Radium and thorium are in this respect completely analogous and different from other radioactive substances, but the phenomena in the two cases are quite different. The emanation from radium retains its activity for many weeks, while the excited radioactivity it produces, on the other hand, decays much more rapidly than that from thorium.

One of the most interesting advances in this connexion was made during the progress of the work by Elster and Geitel (*Phys. Zeit.* 1901, ii. p. 590), who found that it is possible to produce excited radioactivity from the atmosphere, without further agency, by simply exposing a wire highly charged to a negative potential in the air for many hours, and that this also possesses the property of being dissolved off by acids, and of being left behind unchanged on the evaporation of the latter. But here again the rate of decay is different from that of the excited radioactivity produced by thorium.

At the commencement of the work the presumption seemed to be in favour of considering emanating power as a separate phenomenon not directly connected with the ordinary radioactivity of thorium. The former could be destroyed in thorium oxide by ignition without reducing the latter. Later many external conditions were found to affect the value of emanating power without influencing the radioactivity. The nature of the phenomenon had been fully examined from this point of view with very puzzling results, but the conclusion was arrived at that emanating power is probably the manifestation of a change of the nature of a chemical reaction.

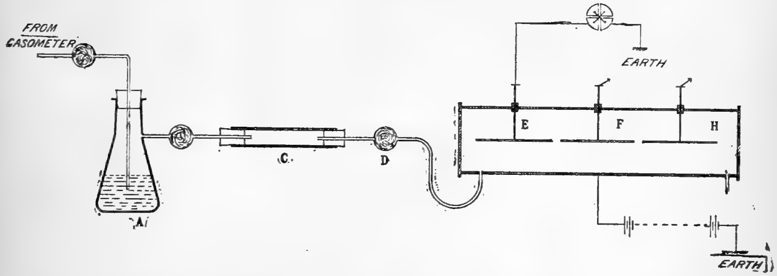
The discovery of ThX and its continuous production, however, revealed the true interpretation of the results, and enables a fairly complete explanation of the phenomenon to be given.

II. *Method of Measuring Emanating Power.*

The emanation from thorium (and from radium) behaves in all respects like a temporarily radioactive gas, and diffuses rapidly through porous substances, as, for example, thick cardboard, which are completely opaque to the straight line radiation. Each particle of the emanation behaves as if it were a radiating centre, producing charged carriers throughout the gas in its neighbourhood. The emanation passes through plugs of cotton-wool and can be bubbled through liquids without appreciable loss of radioactivity, whereas the charged carriers, produced by the emanation in common with the straight line radiation from radioactive substances, on the contrary, completely disappear on passing through a plug of cotton- or glass-wool, or by bubbling through liquids. The means of eliminating the effects of the straight line radiation and of measuring the amount of the emanation alone thus suggest themselves. Air passed over uranium or other non-emanating radioactive substance will no longer conduct a current after passage through cotton-wool. The conductivity in the case of thorium, however, will persist, and afford a measure of the amount of emanation present.

Fig. 1 shows the experimental arrangement for comparing the emanating power of substances. These are placed in the form of fine powder in a shallow lead vessel inside the glass cylinder, C, 17 cm. in length and 3·25 cm. in diameter, provided with indiarubber corks. A current of air from a large gas-bag, after passing through a tube containing cotton-wool to remove dust particles, bubbled through sulphuric acid in the vessel A. It then passed through a bulb containing tightly packed cotton-wool to prevent any spray being carried over. The emanation mixed with air was carried from the vessel C through a plug of cotton-wool, D, which completely removed all the charged carriers carried with the emanation. The latter then passed into a long brass cylinder 75 cm. in

Fig. 1.



length and 6 cm. in diameter. The cylinder insulated on paraffin blocks was connected to one pole of a battery of small lead accumulators, the other pole of which was connected to earth. Three electrodes E, F, H, of equal length were placed along the axis of the cylinder. The current through the gas was measured by means of a Kelvin electrometer of the White pattern. The electrometer and connexions were suitably screened by means of wire gauze connected to earth. An insulating key was arranged so that either of the electrodes E, F, H, or all of them together, could be rapidly connected to one pair of quadrants of the electrometer, the other two being always connected to earth. The measurements were carried out in the usual way by observing the rate of movement of the electrometer-needle after the one pair of quadrants were connected with the electrodes. On placing the emanating substance in C and continuing the air current for several minutes at a constant rate, the current through the gas due to the emanation attains a steady state. The number of divisions of the scale passed over per second may be taken as a measure of the current.

With this apparatus the emanation from 10 grams of ordinary thorium oxide produces a current of $3{\cdot}3 \times 10^{-11}$ amperes between the three electrodes connected together and the cylinder. With the electrometer working at an average sensitiveness, this corresponded to a deflexion of 100 divisions of the scale in 12 seconds, so that one-hundredth part of this current could be readily measured—that is, the emanation produced by one-tenth of a gram of thorium oxide. The electrometer one hundred times more sensitive than this failed to detect the presence of an emanation or radioactivity in the oxides of tin, zirconium, and titanium, the other elements of the same group in the periodic table.

Rate of Decay of the Radiation from the Emanation.—The three electrodes E, F, H, were used to compare the "rates of decay" of the radiations from the emanations of different substances. In the previous papers quoted, it has been shown that the radiating power of the thoria emanation falls to half its value in about a minute. In consequence of this, the current observed for the electrode E is greater than for the electrode H. Knowing the velocity of the current of air along the cylinder and the respective currents to the electrodes E, F, H, the rate of decay of the radiation can be readily deduced. If, however, we merely require to compare the rate of decay of one emanation with another, it is only necessary to compare the ratio of the currents to the electrodes E, F, H in each case, keeping the current of air constant. If the ratio of the currents is the same we may conclude that the radiating power of each diminishes at the same rate. The comparison of the emanation is thus rendered qualitative as well as quantitative. In most of the experiments the current to the electrode E was about twice that to the electrode H; the velocity of the current of air along the cylinder was thus about 0·8 cm. a second.

Comparison of Emanating Power.—The experiments in all cases on the amount of emanation from different substances are comparative. The standard of comparison was usually a sample of 10 grams of thoria as obtained from the maker, which gave out a conveniently measurable quantity of emanation. Preliminary experiments were made to find the connexion between the weight of thoria and the amount of emanation as tested in the cylinder. The following numbers show that the amount of emanation is within the limits of accuracy desired directly proportional to the weight of substance:—

Weight of thoria.	Divisions of scale per second.
2 grams.	1·41
4 ,,	2·43
10 ,,	6·33
20 ,,	13·2

Correction for Natural Leakage.—Even with no emanating material in C the electrometer generally indicates a slight movement on separating the quadrants. This is caused by a small current, chiefly made up of leakage due to conduction over the ebonite, as well as the current produced by the excited radioactivity which has collected on the negative electrode during the course of the day's experiments. It varies from day to day, and is as a rule negligible; but in case of bodies possessing very low emanating power it is necessary to correct for it. The number of divisions of the scale per second indicated by the electrometer-needle when no emanating material is present, is subtracted from the number obtained with the specimen being tested. The corrected number indicates the current due to the emanation alone.

Alternative Method of Comparing Emanating Power.—The apparatus (fig. 1) described in the first paper (Phil. Mag. Sept. 1902) for the comparison of radiations, can also be quite well employed for a comparison of emanating power. In this case, a thick layer of thoria (several grams) is spread over the plate and covered with two thicknesses of ordinary paper.

This has been found almost completely to stop the straight line radiation, whilst allowing the emanation to pass through unimpeded. The current is now measured when a steady state has been reached, due to the accumulation of the emanation. This takes some time, and draughts of air must be guarded against. For this reason, it is less convenient than that first described, but the results obtained by the two methods are almost exactly the same. Thus a sample of "de-emanated" thoria, which gave 12 per cent. of the emanating power of the comparison sample by the first method, gave 13 per cent. by the second method, whilst a sample of oxide prepared from thorium oxalate gave 37 per cent. and 39 per cent. by the two methods respectively. This close agreement in the values by methods so completely different in character is a proof that the indications of the methods are worthy of a great degree of confidence.

III. *The De-emanation of Thoria and the Regeneration of the Emanating Power.*

The emanating power of thoria, as has been stated, is destroyed to a large extent by intense ignition. A closer study of this is the first step in the investigation of the phenomenon. Previous experiments had not succeeded in completely de-emanating thoria, although a reduction to about 15 per cent. of its original value had been accomplished. A sample of this preparation which had been kept for two years had not altered from this value. An experiment was performed in which thoria was heated for one hour by means of a powerful gasoline furnace to the highest temperature which could be safely employed with platinum vessels. The temperature was such that the fireclay walls fused, and the pipeclay of a triangle showed signs of having been softened. It was found that the sample retained about 8 per cent. of its original emanating power. In another experiment, a small platinum crucible filled with thoria was heated for half-an-hour in a small furnace by a large blowpipe and powerful pair of bellows. Some asbestos-wool had completely fused on the outside of the crucible, and the temperature was probably but little lower than in the previous experiment. This sample also retained about 8 per cent. of its emanating power. No further attempt has yet been made to completely destroy the emanating power.

A small quantity of thoria heated in a platinum crucible in the open over an ordinary-sized blowpipe and bellows for five minutes retained about 45 per cent. of its emanating power. The effect of time as well as of temperature was studied by heating about equal quantities in a platinum crucible over an ordinary Bunsen burner for different periods.

Heated 10 minutes. Emanating power = 61 per cent.
„ 1 hour. „ „ = 59 „
„ 24 hours. „ „ = 42 „

It thus appears that there is a large and practically sudden decrease of emanating power for each temperature above a red heat, followed by a very gradual decrease with time when the temperature is maintained; thus, five minutes on the blowpipe, whilst much more effective than the same time at the temperature of the Bunsen burner, produced rather less effect than 24 hours at the latter temperature.

Effect of Moisture.—The next point to be examined was whether the loss of emanating power could be attributed to the loss of water and desiccation of the thoria by ignition. A sample of de-emanated thoria (retaining about 14 per cent.) was placed in the middle of a Jena glass tube, one end of which was closed and contained water, the other end being drawn out to a jet. This was supported in a powerful tube-furnace in a sloping position, and the part containing the thoria heated to the highest possible temperature, while a slow current of steam from the water at the end was passed over it, escaping by the jet. When all the water was evaporated, the jet was drawn off and the tube allowed to cool in an atmosphere of steam free from air. The thoria, on testing, was found to have been lowered in emanating power to about 7 per cent. The further heating had thus reduced the emanating power without the steam having at all regenerated it.

In the next experiment, the reverse was tried. Two exactly parallel processes were carried out for ordinary thoria possessing the normal amount of emanating power. In the first, it was heated in a porcelain tube in the tube-furnace for three hours, while about 500 c.c. of water were distilled over it from a retort. In the second, another quantity of thoria was heated in exactly the same way for the same time, only a current of well-dried air was substituted for the steam. The result was conclusive: each sample had had its emanating power reduced to exactly the same amount, that is, about 50 per cent. of the original.

These experiments prove that water-vapour exerts no influence either in de-emanating thoria or in effecting a recovery of its lost emanating power.

The Regeneration of the Emanating Power by Chemical Processes.—The task of subjecting de-emanated thoria to a series of chemical changes to see if it would recover its lost emanating power was then undertaken.

It may first be mentioned that thoria which has been subjected to ignition has changed very materially in chemical and physical properties. The pure white colour changes at temperatures corresponding to the first stages of de-emanation to a light brown, and after subjection to the very highest temperature to a pure pink. At the same time the solubility of the substance in sulphuric acid is greatly diminished. A part always obstinately refuses to dissolve, even after long and repeated boiling with the concentrated acid, although this part is diminished on each successive treatment, and appears to be in no way different from the rest of the substance. No difference, however, occurs in the readiness with which chlorine attacks it when intimately mixed with carbon. The formation of the chloride by this method is the easiest way of dissolving ignited thoria.

Preliminary experiments went to show that emanating power is a quantity which varies, not only with the nature of the chemical compound but also for the same compound very materially with its previous history. Thus the oxide from the oxalate does not possess as a rule so great an emanating power as that used for comparison. The following two exactly parallel experiments were therefore made, the one with the ordinary, and the other with de-emanated thoria possessing 9 to 10 per cent. of the emanating power of the first. Each was converted to chloride in the ordinary way, by mixing with sugar solution, carbonising, and igniting the mixture of oxide and carbon so obtained in a current of dry chlorine. Each sample was then treated with water, the thorium precipitated as hydroxide with ammonia, and the hydroxides washed and dried at 110°. The result was conclusive, for each sample showed the same emanating power. For the first few days after preparation this value increased rapidly, but after having been kept a fortnight both specimens showed about 260 per cent. of the emanating power of the thoria used as a comparison sample.

Thus the process of de-emanating thoria by ignition does not irretrievably destroy the emanating power, for after solution and reprecipitation no difference whatever exists in the emanating power between ordinary and de-emanated thoria. A fair conclusion from these experiments is that the cause of the emanating power is not removed by ignition, but only rendered for the time being inoperative.

IV. *Effect of Conditions upon Emanating Power.*

The experiments just described brought out two new points. Thorium hydroxide possessed an emanating power which increased with time since preparation, and when it attained its maximum it was much greater than that of the oxide. Before any further work was undertaken, it was necessary to make a close study of the influence of conditions upon the emanating power of thorium compounds.

Effect of Temperature.—The effect of increase of temperature on the emanating power of thoria has already been fully investigated by one of us (*Phys. Zeit.* ii. p. 429, 1901). The results, stated briefly, show that an increase in temperature up to a certain limit, in the neighbourhood of a red heat, correspondingly increases the emanating power. At the maximum this is between three and four times that at the ordinary temperature, and is maintained at this increased value for several hours without any sign of diminution with time. When the thoria is allowed to cool, the emanating power then returns to the neighbourhood of the normal value. If, however, the limit of temperature given is exceeded, de-emanation sets in, and even while the high temperature is maintained, the emanating power falls rapidly to a fraction of its former value. On cooling, the substance is found to be more or less de-emanated. It is of interest that no increase of emanating power is observed when de-emanation commences.

These experiments were extended to include the effects of cooling. The platinum tube which contained the thoria was surrounded with a felt jacket containing a mixture of solid carbon dioxide and ether. The emanating power immediately fell to 10 per cent. of its former value. On removing the cooling agent it again rose quickly to nearly the normal.

In another experiment some thoria was surrounded in a platinum crucible with a mixture of solid carbon dioxide and ether, and kept in a vacuum for several hours. On removing it, and allowing its temperature to rise, it possessed much the same value as an ordinary sample, and after standing some time in the air it was again tested, and no difference could be detected between the two.

Thus changes in temperature produce very marked simultaneous changes in emanating power, but between the limits of $-110°$ and an incipient red heat no permanent alteration in the value occurs.

Effect of Moisture.—Dorn (*loc. cit.*) had noticed that moisture produced a moderate increase in the power of thoria of giving an emanation, and of exciting radioactivity on surrounding surfaces. We have confirmed and extended his results by the following experiments.

Two similar samples of thoria left sealed up for a week, the one in a desiccated atmosphere, the other in air saturated with water-vapour, showed an increase and decrease in emanating power respectively. The moist sample possessed nearly twice as much emanating power as the dry. More complete desiccation, by sealing-up the specimens *in vacuo* with phosphorus pentoxide for a month, did not further reduce the emanating power. Some thoria mixed with concentrated sulphuric acid gave about one half of the usual amount of emanation when vigorously shaken. These experiments show that the presence of water, although producing a marked increase, is not essential for the production of the phenomenon.

Other experiments were made on the effect of light and air on emanating power. The most useful result obtained is that thoria does not change in emanating power when kept in closed vessels under different conditions, but when exposed to the air the emanating power varies within comparatively narrow limits.

Thorium Hydroxide.—This compound, like the oxide, has its emanating power increased by water-vapour. A similar experiment to that described for the oxide gave as the result an emanating power of 400 per cent. of that of thoria for the moist sample and 300 per cent. for the dry. Exposure to the air for a short time again equalized the two values. Carbon dioxide, which thorium hydroxide absorbs from the air to the extent of 2 per cent. of its weight, is without influence on the emanating power.

Effects of Molecular Condition and State of Aggregation of Thorium on the Emanating Power.—Unlike the radioactivity, the emanating power of thorium compounds is by no means mainly controlled by the proportion of thorium present. The effect of temperature in de-emanating thoria and the high value of the emanating power of thorium hydroxide illustrate this. Thorium sulphate, oxalate, and nitrate possess but low emanating power, while thorium carbonate has been obtained with a value five times as great as that of thoria. In general a dense crystalline compound in not very fine powder possesses a much higher emanating power than a light floury compound in a much finer state of division.

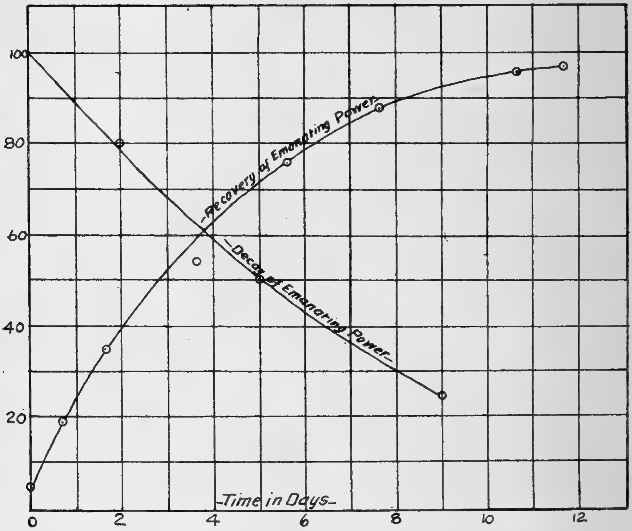
Solution, however, has been found generally to greatly increase the emanating power of soluble thorium salts. In a careful determination, using 20 grams of finely-powdered thorium nitrate, this worked out to be only 1·8 per cent. of the emanating power of thoria. Dissolved in water, however, and tested for emanation by bubbling a current of air through the solution, it gives about three times as much emanation as thorium oxide. That is, solution in water increases the emanating power of thorium nitrate nearly 200 times. The emanating power, as in the case of solids, is proportional to the weight of substance present, and within the limits tried is not much affected by dilution, for a solution of 10 grams made up to 25 c.c. in volume possessed a similar value when diluted four times.

V. *The Cause of the Emanating Power of Thorium.*

The separation from thorium of ThX, detailed in the first part of this communication, showed that not only the radioactivity but also the emanating power of thorium is connected with the presence of a non-thorium type of matter, ThX. The solutions from which thorium hydroxide had been precipitated by ammonia possessed, when concentrated, about as much emanating power as the solutions from which they were prepared, while the precipitated hydroxide was more or less completely de-emanated. On allowing these preparations to stand, the emanating power of the filtrates gradually disappeared, while that of the hydroxide in most cases rose steadily with time, till at the end of a fortnight they had attained a maximum between three and four times that of ordinary thoria. This recovery of the emanating power in the case of the hydroxide was noticed long before the similar change of its radioactivity was observed, but the two phenomena admit of a similar explanation. If, in the precipitation by ammonia, care is taken to remove the ThX completely, the thorium hydroxide is at first almost devoid of emanating power. The small fraction that remains—only a few per cent. of the maximum—can be accounted for by the reproduction of ThX during the time taken to dry the precipitate.

The Rate of Recovery and Decay of Emanating Power.—The rate of decay of the emanating power of ThX, and the recovery of this property by the thorium from which it had been separated, were then investigated in parallel with the similar experiments on radioactivity already described. One quarter of the concentrated filtrate used for the latter purpose was taken, and the decrease of its emanating power with time measured. The increase of emanating power of the thorium hydroxide from which it had been prepared was also measured. Fig. 2 expresses the results. The decay-curve is merely approximate, for it is not easy to accurately take the emanating power of a liquid without special arrangements to assure the constancy of the air-current and the shaking of the solution.

Fig. 2.



The experiments, although only of a preliminary character, bear out the conclusion that emanating power decays and recovers according to the same law and at the same rate as the radioactivity of ThX, and that it is therefore one of the properties of the latter and not of thorium. The decay-curve given, so far as it can be relied upon, shows that the emanating power of ThX at any instant is proportional to its radioactivity.

VI. *The Chemical Nature of the Emanation.*

The following work has reference to the emanation itself, and not to the material producing it, and was designed to see whether the emanation possesses chemical properties which would identify it with any known kind of matter. It had been noticed at the time of its discovery that it passed unchanged through concentrated sulphuric acid. The same holds true of every reagent that has been investigated.

The effect of temperature was first tried. The air containing the emanation, obtained in the usual way by passage over thoria, was led through the platinum tube heated electrically to the highest attainable temperature, and also through the tube cooled by solid carbon dioxide and ether. The tube was then filled with platinum-black, and the emanation passed through it in the cold, and with gradually increasing temperatures, until the limit was reached. The effect of the intense heat was to convert the platinum-black completely into platinum-sponge. In another experiment the emanation was passed through a layer of red hot lead-chromate in a glass tube. The current of air was replaced by a current of hydrogen, and the emanation sent through red hot magnesium-powder and red hot palladium-black, and, by using a current of carbon dioxide, through red hot zinc-dust. In every case the emanation passed without sensible change in the amount. If anything, a slight increase occurred, owing to the time taken for the gas-current to pass through the tubes when hot being slightly less than when cold, the decay *en route* being consequently less. It will be noticed that the only known gases capable of passing in unchanged amount through all the reagents employed are the recently-discovered members of the argon family.

But another interpretation may be put upon the results. If the emanation were the manifestation of excited radioactivity on the surrounding atmosphere, then since from the nature of the experiments it was necessary to employ in each case, as the atmosphere, a gas not acted on by the reagent employed, the result obtained might be explained. Red hot magnesium would not retain an emanation consisting of radioactive hydrogen, or red hot zinc-dust an emanation consisting of radioactive carbon dioxide. The correctness of this explanation was tested in the following way. Carbon dioxide was passed over thoria, then through a T-tube, where a current of air met and mixed with it, both passing on to the testing-cylinder. But between this and the T-tube a large soda-lime tube was introduced, and the current of gas thus freed from its admixed carbon dioxide before being tested in the cylinder for emanation. The amount of emanation found was quite unchanged, whether carbon dioxide was sent over thoria in the manner described, or whether an equally rapid current of air was substituted for it, keeping the other arrangements as before. The theory that the emanation is an effect of the excited activity on the surrounding medium is thus excluded. It is *a priori* improbable on account of the very different rates of decay of the activity in the two cases. The interpretation of the above experiments must therefore be that the emanation is a chemically inert gas analogous in nature to the members of the argon family.

In light of these results, and the view that has already been put forward of the nature of radioactivity, the speculation naturally arises whether the presence of helium in minerals and its invariable association with uranium and thorium may not be connected with their radioactivity.

VII. *The Nature of Emanating Power.*

The foregoing results therefore find their simplest expression on the view that, just as a chemical change is proceeding in thorium whereby a non-thorium material is produced, so the latter undergoes a further reaction, giving rise to a gaseous product which in the radioactive state constitutes the emanation.

It will be seen at once that this secondary change is of a different kind from the primary, for it is affected apparently by the conditions in a very marked manner. It was shown that moisture, the state of aggregation, and temperature influenced the value of the emanating power. From $-80°$ to a red heat the latter regularly increases in the ratio of $1:40$ in the case of thorium oxide, while the ratios between the values for thorium nitrate in the solid state and in solution is as $1:200$. The secondary reaction appears therefore at first sight much more nearly allied to ordinary chemical reaction than the primary. It must not be forgotten, however, that the laws controlling the manifestation of the two phenomena—radioactivity and emanating power—are of necessity very different. In the former we deal with the intensity of radiations emitted by a solid, in the latter with the rate of escape of a gas into the surrounding air from either a solid or a liquid. Since this gas is detected by its radioactivity, and this decays extremely rapidly with time, a very slight delay in the rate of its escape will enormously affect the experimental value obtained for emanating power.

On the other hand, it is now well established by experiment that sometimes thorium compounds de-emanated chemically by removal of ThX do not recover their normal emanating power with time, but remain constant at a lower value. On one occasion a carbonate was prepared which possessed hardly any emanating power until it was again dissolved and precipitated. In another experiment two samples of hydroxide prepared from different nitrates were tested together for rise of emanating power. That of the one rose normally to its maximum (as in fig. 2), which was twenty times the minimum. The other started from the same minimum, but rose to a maximum only one-fourth as great. When the experiment was repeated under the same conditions, using the same sample of nitrate, the compound behaved normally. It thus appears that the emanation can be almost entirely prevented from escaping in the radioactive state in some cases, and partially prevented in others, where no visible peculiarity of physical condition exists, and where other preparations similarly prepared behave normally.

These are outstanding points in the theory which remain to be explained. It is not possible at present to decide whether these variations of emanating power are caused by an alteration in the velocity of the reaction which produces the emanation, or by an alteration in the time taken for the latter to escape. The experiments detailed in the first paper on the augmentation of the proportion of excited activity in compounds de-emanated by ignition appear to favour the view that the change still proceeds, but the emanation does not succeed in escaping. The experiment on the regular variation of emanating power with temperature might be explained quite well by either hypothesis.

VIII. *The Excited Radioactivity from Thorium.*

Since the emanation gives rise to the phenomenon of excited radioactivity, and the latter appears to be caused by an intensely active invisible deposit of matter, it must be supposed that a tertiary change is taking place. The emanation, a gaseous product of the secondary reaction, is again changing and giving rise to a third reaction-product causing the excited activity. The fact that it is manifested entirely on the negative electrode in an electric field, points to the positive ion being the means by which it is transported. Without, in the present paper, going further into the consideration of excited radioactivity, it may be mentioned that the successive changes occurring in the thorium atom are not yet ended at this stage. The fact that the excited radiation consists in part of cathode-rays may be recalled here. Further, the intensity of excited activity at first *increases* from the time of its formation, exactly as in the case of ThX newly separated from thorium, the increase reversing the effect of the normal decay. The radium excited activity behaves in a somewhat analogous manner. The matter in this case causing excited activity does not appear to be homogeneous, but behaves in its action towards acids, &c. as if consisting of two different kinds (compare Rutherford, *Phys. Zeit.* p. 254, 1902).

IX. *Further Theoretical Considerations.*

Enough has been brought forward to make it clear that in the radioactivity of thorium, and, by analogy, of radium, we are witnessing the effect of a most complex series of changes, each of which is accompanied by the continuous production of a special kind of active matter. The complexity of the phenomenon gives rise to an important question concerning the fundamental relation between the changes which occur and radioactivity. So far it has been assumed, as the simplest explanation, that the radioactivity is *preceded* by chemical change, the products of the latter possessing a certain amount of available energy dissipated in the course of time. A slightly different view is at least open to consideration, and is in some ways preferable. Radioactivity may be an *accompaniment* of the change, the amount of the former at any instant being proportional to the amount of the latter. On this view the non-separable radioactivities of thorium and uranium would be caused by the primary change in which ThX and UrX are produced. The activity of ThX would be caused by the secondary change producing the emanation, the activity of the emanation by a tertiary change in which the matter causing the excited activity is produced, the activity of the latter being derived from still further changes. The law of the decay of the activity with time (equation 1 first part) in all cases but the primary then appears as the expression of the simple law of chemical change, in which one substance only alters at a rate proportional to the amount remaining. In the primary change the amount remaining is infinitely great compared with the amount that alters in short time, and therefore the velocity of reaction is constant. This view certainly affords an explanation of why the emanating power of ThX is proportional to the radioactivity. So long as the latter is considered a consequence of what has occurred there is no reason why this should be so. But if it is considered the accompaniment of the change in which the emanation is formed the result follows naturally. Further and more exact determinations of the rate of rise and decay of emanating power are therefore called for.

In the case of uranium the changes so far as they can be followed by the radioactivity appear to be at an end with that which causes the activity of UrX. It is of interest that this substance gives only cathode-rays, and that it continues to do so for many weeks after its separation from uranium. This gives rise to the question whether any connexion can be established between the nature of the radiation and the kind of change producing it.

The only consideration which is opposed to this view is the existence of polonium. The radiations of this body resemble closely the non-separable radioactivity of uranium, both in penetrating power and the absence of deviable rays. But all attempts (Soddy, *loc. cit.*) have so far failed to separate polonium from uranium, and until this is done its existence does not of itself affect the present question.

It seems as if a more satisfactory explanation of the residual activities common to both uranium and thorium, and of the connexion between the emanating power and radioactivity of ThX, is obtained on the modified view. But further work, both on this latter point and on the nature of polonium, must be awaited before the connexion between radioactivity and chemical change can be considered exactly determined.

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LXV. *On the Conditions necessary for Equipartition of Energy.* *By* J. H. Jeans, *B.A., Isaac Newton Student and Fellow of Trinity College, Cambridge* *.

Introduction.

§ 1. THE object of the present paper is, firstly, to give a proof of Boltzmann's Theorem on the Equipartition of Energy from a somewhat new point of view; and, secondly, to examine what are the precise conditions under which equipartition will take place, and whether these conditions are such as will occur in an actual gas.

At the outset it must be explained that the equations leading to the law of distribution admit of a simple hydrodynamical interpretation in generalized space of n-dimensions. I have made use of the hydrodynamical analogy for two reasons. In the first place it is easier to think in terms of generalized space than in terms of multiple integrals; and in the second place the terminology and results of hydrodynamics being ready to hand, a great deal of obscurity and repetition may be saved by starting at once from the hydrodynamical standpoint. So long as we only use hydrodynamical results and conceptions which have a mathematical (as opposed to a physical) basis, there will be no danger of a faulty "argument by analogy."

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* Communicated by the Author.

The General Dynamical Theorem.

§ 2. Let us begin by considering the motion of a very great number of exactly similar dynamical systems, the systems being supposed for the present not to influence the motion of one another. We shall ultimately take such a system to be a molecule of a gas.

Let us suppose the configuration of this system determined by n coordinates

$$q_1, q_2, \dots q_n, \qquad (1)$$

and let the corresponding momentoids be

$$p_1, p_2, \dots p_n. \qquad (2)$$

Now imagine a space of $2n$ dimensions, these dimensions corresponding to all possible values of the $2n$ independent variables

$$q_1, q_2, \dots q_n, p_1, p_2, \dots p_n. \qquad (3)$$

Then the configuration and rate of change of configuration of any system can be represented completely and uniquely in this generalized space by a single representative point *.

Instead of saying that a system is *in the phase* $(q_1, q_2, \dots p_1, p_2, \dots)$, we shall say that it is at the point $(q_1, q_2, \dots p_1, p_2, \dots)$, of our generalized space. Let us suppose that the number of systems of which the coordinates of the representative points lie between

$$q_1, q_2 \dots p_1, p_2 \dots$$

and $q_1+dq_1, q_2+dq_2 \dots p_1+dp_1, p_2+dp_2 \dots$

is $f(q_1, q_2, \dots p_1, p_2 \dots)\, dq_1, dq_2, \dots dp_1, dp_2 \dots$

This is the number of representative points which occupy the element of volume $dq_1\, dq_2 \dots dp_1\, dp_2 \dots$ of our generalized space. We may, therefore, speak of $f(q_1\, q_2 \dots p_1\, p_2 \dots)$ as the *density* at the point $q_1\, q_2 \dots$, and shall, for the sake of convenience, denote it by ρ.

§ 3. If we are given the values of the $2n$ coordinates of scheme (3) at any instant we shall be able, from a knowledge of the energy-function of the system, to calculate the values

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* It will tend to clearness of thought to imagine infinite space, so that all the coordinates can range from $+\infty$ to $-\infty$. If the coordinates are not uniquely defined from the configuration (*e.g.* if q_1 is an angle so that for a given configuration q_1 may have any of the values ϕ_0, $2\pi+\phi_0$, $4\pi+\phi_0 \dots$ &c.) we may either suppose just sufficient of the space taken to give only one possible value of each coordinate inside the space, or we may suppose one representative point for every possible system of values of the coordinates, so that the arrangement of points in our generalized space is periodic.

of these coordinates at any subsequent instant, so long as the system is not acted upon by any forces which are not included in the energy-function. In this way we find a "path" in the generalized space which is described by the system in question. In this way we may map out the whole of our generalized space into "stream-lines." It is obvious that there will be one, and only one, stream-line through every point of this space, and that stream-lines which are adjacent at one point remain adjacent throughout their whole course. The motion of the representative points may, therefore, be replaced by a hydrodynamical motion, this motion being continuous as regards both space and time.

Let us denote differentiation with respect to a fixed point in this space by d/dt, that with respect to a moving element by $\mathrm{D}/\mathrm{D}t$.

The velocity at any point is, under all circumstances, a function of the coordinates only. The *necessary and sufficient* condition for a steady state is therefore

$$\frac{d\rho}{dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From the hydrodynamical equation of continuity,

$$\frac{d\rho}{dt}=\frac{\mathrm{D}\rho}{\mathrm{D}t}-\sum_{(2n)}\frac{\partial\rho}{\partial\xi}\frac{\partial\xi}{\partial t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where ξ is any one of the $2n$ coordinates of scheme (3), and the summation extends to all.

Now the molecules which at any given instant occupy the element of volume $dq_1\,dq_2\ldots$ will be precisely those which at some subsequent instant will occupy some other element $dq_1'\,dq_2'\ldots$, and, by a known theorem,

$$dq_1\,dq_2\ldots=dq_1'\,dq_2'\ldots \quad . \quad . \quad . \quad (6)$$

In terms of our present notation equation (6) may be expressed concisely in the form

$$\frac{\mathrm{D}\rho}{\mathrm{D}t}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence from equation (5) the condition for a steady state is seen to be

$$\sum_{(2n)}\frac{\partial\rho}{\partial\xi}\frac{\partial\xi}{\partial t}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

§ 4. Let the total energy of the system, supposed expressed in the Hamiltonian form, be denoted by E. The energy includes the potential and kinetic energies of the system. It may include the potential energy of the system in a permanent field of force, if such exists, and it may include electrostatic or electrodynamic energies, or any other energies which are such that the equations of motion may be derived from the function E in the Hamiltonian manner. The equations of the system are $2n$ in number, being of the forms

$$\left.\begin{aligned} \frac{\partial q_r}{\partial t} &= \frac{\partial E}{\partial p_r} \ldots (r=1, 2, \ldots n) \\ \frac{\partial p_r}{\partial t} &= -\frac{\partial E}{\partial q_r} \ldots (r=1, 2, \ldots n) \end{aligned}\right\} \ldots \quad (9)$$

The elimination of t from these equations will give the equations of the stream-lines which determine the paths of the representative points in our generalized space. These equations will be $2n-1$ in number, and will be capable of expression in the forms

$$\psi_s = \text{constant}\,(s=1, 2, \ldots 2n-1), \quad \ldots \quad (10)$$

where ψ_s is a definite function of the $2n$ coordinates*.

There is one further equation which can be derived from equations (9), and this may be expressed in the form

$$\psi_{2n} = \text{constant} + f(t), \quad \ldots \quad (11)$$

where ψ_{2n} is a function of the $2n$ coordinates. This last equation determines the motion of the particles along the stream-lines. The $2n$ equations (10) and (11) are the exact equivalents of the $2n$ equations (9).

Now let us transform coordinates in our generalized space, from the coordinates of scheme (3) to the generalized coordinates

$$\psi_1, \psi_2, \ldots \psi_{2n-1}, \psi_{2n}. \quad \ldots \quad (12)$$

Transformed into these coordinates equation (8) becomes

$$\sum_{s=1}^{s=2n} \frac{\partial \rho}{\partial \psi_s} \frac{\partial \psi_s}{\partial t} = 0. \quad \ldots \quad (13)$$

For the first $(2n-1)$ values of s $(s=1, 2, \ldots 2n-1)$ we have

$$\frac{\partial \psi_s}{\partial t} = 0.$$

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* From another point of view equations (10) may be regarded as first integrals of the equations of motion. The whole question turns on the fact that the equations are $2n-1$ in number. That this is so is evident from the fact that the path of every point must be definitely and uniquely determined by them.

If we exclude (as we legitimately may) the case of systems which remain permanently at rest in an equilibrium configuration, it follows that we must have $\frac{\partial\psi_{2n}}{\partial t}$ different from zero. Hence equation (13) assumes the form

$$\frac{\partial\rho}{\partial\psi_{2n}}=0,$$

and the most general solution is

$$\rho=\phi(\psi_1, \psi_2, \dots \psi_{2n-1}) \quad \dots \quad (14)$$

in which ϕ is the most general function of the $(2n-1)$ variables.

§ 5. If the systems are not subject to external disturbance there is little more to be said. Of the $2n-1$ quantities $\psi_1, \psi_2, \dots \psi_{2n-1}$, one (say ψ_1) may, without loss of generality, be taken to be identical with E; the remaining $(2n-2)$ ψ's are necessarily functions of quantities other than E. Thus it appears that although

$$\rho=\phi(\mathrm{E}),$$

(the solution leading to equipartition of energy), is a particular solution of the general equations, it is by no means the only solution. In other words, equipartition, although possible, is not necessary. This is as it should be, for Maxwell's condition of continuity of path is not satisfied.

§ 6. Maxwell and Rayleigh now suppose that the system is subject to certain external agencies, and postulate that these agencies shall be such that by them each system is made to pass through all phases which are consistent with the conservation of energy. From the point of view of this paper, they postulate that the elements of fluid are moved out of their stream-lines, and this in such a way that every element is made to pass over the whole of the particular surface

$$\mathrm{E}=\text{constant}$$

to which it initially belongs. If this postulate is granted their proof is unassailable, but they do not prove that the postulate is true in the case of any single system, and it seems to the present writer that for a large class of natural systems the postulate cannot possibly be true.

Consider, for instance, the case of a particle moving upon a horizontal plane, in which the disturbing influence is supplied by a system of rigid barriers. As a preliminary, suppose these barriers replaced by a continuous field of force, such that the potential becomes infinite over certain lines $a, b, c, \dots$ in the plane. If this potential is included in the energy-function E of § 4 the analysis of § 4 must hold, and the system moves only over a single stream-line, not over a complete energy surface. Now suppose the field of force to continuously change so that ultimately the potential is infinite over the lines a, b, c . . ., and is zero over the rest of the plane. This ultimate state is an exact mathematical representation of the case in which the motion is disturbed by rigid boundaries placed over the lines a, b, c . . . However near the field of force may be to this ultimate state the argument of § 4 must be admitted to be valid. Hence *unless we assume the whole argument in some way to become invalid, when we finally pass to the limit*, it would seem that the theorem cannot possibly be true for the case in question. I cannot, for myself, see any reason for treating this limit as an exceptional case, and Lord Kelvin's recent experiments* seem to bear out this view.

§ 7. The same argument will, I think, apply to any case in which the motion is determined for all time by the state of the system at a given instant. For example, it applies if we try to replace our typical system by a mass of gas whether inclosed within rigid boundaries or not. When, however, the subsequent career of the system is in some way fortuitous the objection does not hold, and this class of exceptions includes the important case in which the systems are molecules of a gas, in which the disturbance of the path arises from fortuitous collisions with other molecules.

Application to Molecules of a Gas.

§ 8. Let us now suppose the exactly similar dynamical systems of § 2 to be the molecules of a gas.

Suppose that each molecule is surrounded by an imaginary sphere, and let it be supposed that these spheres are of such a radius that two molecules exert no action upon one another except when their spheres intersect. When two such spheres intersect an "encounter" is said to take place, lasting until the spheres again become clear of one another.

Binary Encounters.

§ 9. We shall begin by considering binary encounters only; that is to say, we assume that the event of a sphere being simultaneously intersected by two other spheres is so rare that it may be neglected.

We treat this case as follows:—As soon as an encounter

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* Kelvin, Phil. Mag. [6] ii. p. 1.

begins between two molecules their existence as single molecules is supposed to be abruptly terminated, and their representative points are removed from our generalized space of $2n$ dimensions. During the progress of the encounter the two molecules together will be supposed to form a new dynamical system—a double molecule. This system will be specified by $4n$ independent coordinates, $2n$ for each constituent molecule. Hence any such system can be represented by a point in a space of $4n$ dimensions, one dimension corresponding to each coordinate. We shall not, however, require the whole of this $4n$-dimensional space. If x, y, z, x', y', z' are the coordinates of the centres of the two molecules, the condition that an encounter is beginning or ending is

$$(x-x')^2+(y-y')^2+(z-z')^2=4R^2. \quad . \quad . \quad (15)$$

In the $4n$-dimensional space this equation will be the equation of a certain "surface" S (of dimensions $4n-1$), and the representative points of all double molecules will be inside S. We shall find it convenient to denote each double molecule by *two* representative points, since the rôles of first and second molecule can be alloted in two different ways.

Let σ be the density in this new space, then the necessary and sufficient conditions for a steady state are

$$\frac{d\sigma}{dt}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\frac{d\rho}{dt}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in the latter of which the change in ρ includes that caused by the formation and dissolution of double molecules.

§ 10. Before determining the relation between ρ and σ we must make Boltzmann's assumption that the gas is in a "molekular-ungeordnet" state. Having made this assumption we proceed to calculate the number of encounters of a given kind which occur in an interval dt. Equating this to the number of representative points which cross the corresponding element of the surface S during the same interval we arrive at the equation

$$\sigma=\rho\rho', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

in which σ is the density at any point on S, and ρ, ρ' the densities at the two points of $2n$-dimensional space which are determined by the coordinates of the two encountering molecules.

The analysis of § 4 applies (with obvious modifications) to the new space. Hence equation (16) may be replaced by the condition that σ shall be constant along a stream-line.

Let ρ, ρ' be the densities at points occupied by the representative points of the two component molecules, at the formation of a double molecule, and let $\overline{\rho}$, $\overline{\rho}'$ be the densities at the points representative of the same two molecules at the dissolution of the double molecule. Then $\rho\rho'$ and $\overline{\rho\rho'}$ are the two values of σ at the two ends of a single stream-line in the $4n$-dimensional space, and, therefore, by equation (18),

$$\rho\rho' = \overline{\rho\rho'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

the same result as is obtained by Boltzmann's well-known H-theorem.

Since the motion is dynamically reversible we may take $\overline{\rho}$, $\overline{\rho}'$ to be the densities at formation, then ρ, ρ' will be the densities at dissolution, and the same result holds.

From this it follows that in equation (17) the decrease in ρ caused by the formation of double molecules of any specified kind is exactly counterbalanced by the increase caused by the dissolution of double molecules of the same kind. Hence in equation (17) $d\rho/dt$ may be taken to be the change in ρ caused solely by the continuous motion of the fluid, and may be treated as in § 4.

§ 11. To sum up, we have found that the equations of steady motion, on the hypothesis of binary encounters, may be expressed as follows:—

(α) Throughout the $2n$-dimensional space, ρ must be constant along every stream-line.

(β) Throughout the $4n$-dimensional space σ must be constant along every stream-line.

(γ) At every point on the boundary of the $4n$-dimensional space we must have

$$\sigma = \rho\rho'.$$

To these may be added a fourth condition—

(δ) At every point on the boundary of the $2n$-dimensional space (*i. e.* at infinity) the flow across the boundary must be nil, or what is the same thing, we must have

$$\rho = 0.$$

These conditions are necessary and sufficient for steady motion.

Ternary and Higher Encounters.

§ 12. By a simple extension of the method already explained the possibility of encounters of ternary and higher orders may be considered. For instance, to take ternary encounters into account we imagine systems of triple molecules, these being represented in a space of $6n$-dimensions. The density in this space being τ we have as conditions additional to those given in § 11—

(ϵ) Throughout the $6n$-dimensional space τ must be constant along every stream-line.

(ζ) At every point on the boundary of the $6n$-dimensional space we must have

$$\tau = \rho\sigma.$$

§ 13. Encounters of higher orders may be similarly treated. If ρ_k is used to denote the density in the space of $2kn$-dimensions, in which k-ple molecules are represented, the complete system of conditions for steady motion is

(i.) Along every stream-line in the $2kn$-dimensional space,

$$\rho_k = \text{constant.} \qquad (20)$$

(ii.) At every point on the boundary of the $2kn$-dimensional space

$$\rho_k = \rho_a \rho_b, \qquad (21)$$

in which ρ_a, ρ_b refer to the two systems of molecules of orders a, b, of which the encounter results in the particular system of order k which is represented at the point in question (we therefore have always $a+b=k$).

If encounters of all orders are to be taken into account these conditions must be satisfied for all values of k from $k=1$ to $k=\infty$. In the case of $k=1$, equation (21) must be interpreted so as to become identical with the condition (δ) of § 11.

It will be noticed that if these conditions are satisfied for all values up to $k=\infty$, no hypothesis need be made as to the smallness of the radius of molecular action in comparison with the free path. The only assumption now made is that the gas is in a "molekular-ungeordnet" state.

Solution of Equations.

§ 14. Let χ be a quantity, a function of the coordinates of a molecule or system of molecules, such that throughout the undisturbed motion of the molecule or system χ maintains a constant value, and such that when two molecules or systems combine to form a new system the χ of the new system is equal to the sum of the χ's of the component systems. Speaking loosely we may say that χ is defined as being capable of exchange between molecules at a collision but is indestructible.

Then a solution of our equations (20) and (21) will be seen to be

$$\log \rho_k = \chi (k = 1, 2 \ldots \infty). \quad . \quad . \quad . \quad (22)$$

Further, the difference between this value for $\log \rho_k$ and the most general solution for $\log \rho_k$ which is such as to satisfy equations (20) and (21) must be a quantity satisfying the conditions satisfied by χ. In other words, the most general solution of our equations consists of the superposition of solutions of the type of (22). Let $\chi_1, \chi_2, \chi_3, \ldots \chi_s$ be independent quantities, each satisfying the conditions already postulated for χ, and let it be supposed that there are no other such quantities, then the most general solution of the equations of steady motion will be

$$\log \rho_k = A_1 \chi_1 + A_2 \chi_2 + \ . \ . \ . \ + A_s \chi_s,$$

in which $A_1 A_2 \ldots A_s$ are independent and, so far, arbitrary constants.

§ 15. The quantities $A_1 A_2 \ldots A_s$ can be uniquely determined from a knowledge of the values of $\Sigma\chi_1, \Sigma\chi_2, \ldots$ the summation extending throughout the gas, and the various sums accordingly each remaining constant throughout the motion of the gas. Hence for a given mass of gas (the values of $\Sigma\chi_1, \Sigma\chi_2 \ldots$ being given) there is a unique solution for a steady state, provided that a steady state is possible.

§ 16. Let us next examine what quantities satisfy the conditions assumed for χ. Firstly, if we take $\chi_1 = 1$ for a single molecule, $\chi_1 = 2$ for a double molecule, &c., we see that χ_1 satisfies the requisite conditions, and $\Sigma\chi$ is proportional to the total mass of gas. Again, if we take $\chi_2 = 2E$, where E is the total energy of the molecule or system of molecules (including, if necessary, the potential energy in an external field of force), we see that χ_2 satisfies these conditions. As other obvious instances we may suppose χ to represent the amounts of translational or rotational momentum. As a final instance we may consider imaginary molecules which are capable of carrying a charge of electricity, and we notice that the amount of this charge would be a possible value for χ.

For instance, if we have a number of electrically charged spheres each of mass m and capacity C, inclosed in a vessel of which the velocity is (u_0, v_0, w_0), the solution will be found to be

$$\rho = Ae^{-h\left[m\left((u-u_0)^2+(v-v_0)^2+(w-w_0)^2\right)+\frac{1}{C}(Q-Q_0)^2\right]},$$

in which Q_0 is the mean value of Q, the electric charge.

§ 17. The ideal gas of the kinetic theory may be supposed to be devoid of mass-velocity, both translational and rotational, and to be fully defined, in its steady state, by its density and temperature. For such a gas the only χ's which can occur are the χ_1 and χ_2 of the last section, so that the solution is

$$\log \rho = A_1\chi_1 + A_2\chi_2.$$

Changing the constants this becomes

$$\rho = Ae^{-2hE}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

in which A, h are determined *uniquely* by the values of the density and temperature.

For such a gas we have, therefore, proved that there is only one steady state, subject to the hypothesis that the gas is "molekular-ungeordnet," and this steady state is that given by the well-known Boltzmann law.

To arrive at this result we have found it necessary to suppose that there are only two invariable quantities—the mass and energy of the gas (corresponding to the two variables density and temperature). The result may break down for either of two reasons:

(i.) It may be that there is some third invariable quantity connected with the coordinates of the gas. If this is so, two samples of a gas having the same temperature and density will not in general possess the same physical properties. The uniformity of the experimental results obtained from different samples of gas, seems to supply an argument of overwhelming strength against supposing this to be the case.

(ii.) It may be that the two quantities ($\Sigma\chi_1$ and $\Sigma\chi_2$) which have been supposed to be invariable are not really so. This is certainly the case with the gases of nature, in which the aggregate energy of the molecules is subject to dissipation into the æther.

If we admit this latter objection it is at once obvious, on physical grounds, that no steady state is possible. Mathematically we are left with a solution in which ρ is proportional to χ_1, and is therefore constant in the $2n$-dimensional space. This solution fails because it does not give $\rho=0$ at infinity.

Conclusion.

§ 18. To sum up, we have seen that for a gas of which the molecules are of any kind whatever, the solution for the steady state is unique when a steady state is possible. We have found out how to determine this steady state when the structure of the molecules is completely known. For an ideal gas, defined as one in which the aggregate mass and aggregate energy of the molecules remain constant throughout any possible natural motion, and which is such that the physical state of the gas is fully defined by its density and temperature, this steady state is given by the well-known Boltzmann law. These results depend upon the "molekular-ungeordnet" assumption, but are not limited by the hypothesis of binary encounters.

If the Boltzmann law does not give the steady state there must be some other variables besides the density and temperature, a knowledge of which is necessary to determine the physical properties of a sample of gas.

A gas in nature can never attain a steady state on account of the interaction between matter and æther. I have tried to follow out some of the consequences of this in former papers [*].

In a future paper I hope to apply the methods of the present paper to some problems of dissociation and ionization.

LXVI. *The Electrical Conductivity of Metals and their Vapours. By the* Hon. R. J. STRUTT, *Fellow of Trinity College, Cambridge* [†].

§ 1. *Introduction.*

IT is known that mercury vapour, even at very high temperatures, is a good insulator; a better one in fact than air under similar conditions [‡]. Liquid mercury, on the other hand, is of course a good conductor, like other metals. Let us try to form some idea of what the difference in conductivity between the liquid and the saturated vapour amounts to.

It is stated in the paper referred to that mercury vapour at atmospheric pressure, even at a yellow heat, allowed a much smaller current to pass than air under similar conditions. With air, contained in a tube 7 × 1 inches, into which the electrodes dipped, a current was observed which was measured by ten scale-divisions on a sensitive galvanometer, when an E.M.F. of 156 volts was applied. We may suppose that one scale-division represented a current of not more than 10^{-9} amperes, and that the mercury vapour gave only $\frac{1}{5}$ the current observed with air. Thus the current would be 2×10^{-9} amp.

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[*] "The Distribution of Molecular Energy," Phil. Trans. cxcvi. p. 397; "The Mechanism of Radiation," Phil. Mag. [6] ii. p. 421; "The Theoretical Evolution of γ," Phil. Mag. [6] ii. p. 638.

[†] Communicated by the Author.

[‡] J. J. Thomson, Phil. Mag. [5] xxix. p. 364.

If the electrodes were each 10 × 1 cms. in dimensions, and 1 cm. apart, the specific resistance would then be no less than $\frac{157}{2\times 10^{-10}}=8\times 10^{11}$ ohms, roughly. On the other hand, the specific resistance of liquid mercury at ordinary temperatures is about 10^{-4} ohms. At a yellow heat, it would not at the most be more than 5 times this amount, according to the experiments which have been made on the variation of its resistance with temperature; this would make the liquid resistance 2×10^{-3} ohms. But in all probability it is not more than half as much. Thus, at a yellow heat, so far as can be judged from existing data, the resistance of the vapour, at atmospheric pressure, should be

$$\frac{8\times 10^{11}}{2\times 10^{-3}}=4\times 10^{14}$$

that of the liquid.

This stupendous difference of properties is very remarkable. And the question presents itself, what changes do the resistance of the liquid and of the vapour respectively undergo, as the critical temperature and pressure are approached? It must be supposed that, since above that temperature the liquid and the saturated vapour are indistinguishable, they have the same electrical resistance, whether that resistance be high or low. In what manner does this wonderful change of electrical properties set in? Is it gradual or is it abrupt, like the change in the magnetic permeability of iron at high temperatures?

I have not succeeded in going far towards an answer to this question, but have thought it desirable to record such small progress as I have been able to make.

§ 2. *On the Probable Values of the Critical Temperatures of Metals.*

There are various methods by which some estimate of the critical temperatures of ordinary liquids may be made in the absence of direct observations. These, however, lead to hopelessly discrepant results when it is attempted to apply them to mercury. One of these methods depends on the temperature coefficient of the surface-tension of the liquid. Since the surface-tension of a liquid is a linear function of the temperature*, it is easy to find by extrapolation the temperature at which the surface-tension would vanish.

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* There is reason to think that this surface-tension should be multiplied by the (specific volume)$^{\frac{2}{3}}$ for the linear relation to hold strictly. But this hardly affects the result in the case of mercury.

This gives an approximation to the critical temperature. In the case of mercury the surface-tension for different temperatures is given by Frankenheim[*]. His results point to a critical temperature of about 750°.

Again, in the large majority of cases, the absolute critical temperature bears a fairly constant ratio, about 1·6, to the absolute boiling-point. This holds fairly well through a great range of boiling-points, from liquid hydrogen upwards. This would make the critical temperature about 724°, in fair agreement with the estimate from surface-tension.

If these estimates were anywhere near the mark, there would be no great difficulty in determining the electrical resistance up to the critical temperature. But other methods of estimating this critical temperature unfortunately lead to a very different conclusion. Thorpe and Rücker[†] have found that in many cases the absolute critical temperature (θ) can be calculated from the formula

$$\theta = \frac{(t+273)V_t - 273}{1{\cdot}995(V_t - 1)}$$

where V_t is the volume at some temperature t, the volume at 0° being taken as unity. If this be applied to mercury, taking t as 100° C., the critical temperature indicated is no less than 2700° C.

Let us now consider the matter from the standpoint of density.

It is usually found that the critical density of a substance is about one-third the density of the liquid at low temperatures, also that it is about 4·4 times the density which the same substance would have at that temperature and pressure if it behaved like a perfect gas[‡]. (This may be alluded to as the theoretical gas density.)

Combining these two generalizations, we see that the theoretical gas density under the critical conditions would be about $\frac{1}{13{\cdot}2}$ of the liquid density at low temperature. This latter for mercury is about 13·6. Thus the theoretical gas density for this substance under critical conditions should be very nearly unity. This does not of course in itself determine the value of the other critical data. But if a value be assumed for one of them, the corresponding value for the other can be found. The following are approximate values:—

Assumed critical temperature (°C.)	273	546	819	1092	1365	1638	1911
Corresponding critical pressure in atmospheres…………	222	333	444	555	666	777	886

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[*] Pogg. *Ann.* lxxv. p. 229 (1848).

[†] Chem. Soc. Journ. vol. xlv. p. 135 (1884).

[‡] Young, Phil. Mag. Feb. 1892, p. 185.

We have, then:—

Critical Temperature of Mercury.

From temperature coefficient of surface-tension	750°
From the boiling-point...	724°
From the thermal expansion at moderate temperature	2700°

It is evident from this table that the methods which are successful in estimating the critical temperatures of ordinary liquids entirely fail when it is attempted to apply them to a metal.

The fundamental difference between mercury and other liquids, so far as critical phenomena are concerned, probably lies in the very great density of the former. Few of the ordinary liquids which have been investigated are so much as 1·5 times the density of water. Mercury has 14 times that density. Thus the vapour-density has to increase enormously before it can compare with that of the liquid.

It is, however, difficult to understand the entire failure of the argument from increase of surface-tension. Probably a careful investigation of the surface-tension of mercury up to the highest temperatures practicable would yield interesting results.

I have attempted, but without success, to observe the critical phenomena of mercury. The experiment was carried out as follows:—

A tube of quartz was built up according to the directions given by Shenstone *. Its length was about 3 cms., internal diameter 1 mm., external diameter about 7 mms. It was provided with a handle of quartz rod, fused on at one end. About two-thirds of the length were filled with mercury, and the end was hermetically sealed, taking care to make the sealed end as strong as the rest. The tube was then heated in a bunsen-burner, and the appearance of the mercury watched from behind a thick plate-glass screen. The liquid mercury attained a full red heat, but nothing could be seen in the part of the tube occupied by the vapour. The temperature was further increased by means of a Herapath blowpipe, and subsequently by placing the tube inside a Fletcher's injector-furnace. At the highest temperatures attained (probably above the melting-point of silver) the vapour in the space above the mercury showed a pale steely-blue tint, which, so far as could be judged, was due to absorption. This tint is probably analogous to the green colour of gold-leaf as seen by transmitted light. The liquid mercury, on the other hand,

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* 'Methods of Glass-blowing.'

presented the ordinary appearance of a metal at a yellow, or nearly yellow, heat. When this stage was reached, the tube, which was the strongest I was able to make, burst with a loud explosion. Some of the fragments were examined, and they showed a "conchoidal" fracture, along a diametral plane of the tube. The quartz had ruptured abruptly under the internal pressure. There was no sign of viscous yielding.

Of those elements which behave electrically as undoubted metals, mercury is the most volatile. The next is arsenic, and it was thought desirable to try to observe its critical phenomena. Some powdered arsenic was hermetically sealed up in a strong quartz tube, and the tube heated as before. At a dull red heat the arsenic melted to a silvery liquid. As is well known, it will not melt at ordinary pressures, but passes from the solid to the gaseous condition.

The vapour began at once to show a strong yellow absorption tint. I satisfied myself that the colour was due to absorption, and not to radiation, by observing it against a background of bright sky. The vapour of arsenic begins to show (selective) absorption of light at a very much lower temperature than does mercury. So that it sooner approaches the opaque quality of the liquid metal. There seemed, therefore, to be a chance that its critical temperature might be reached. This hope was disappointed. The tube containing arsenic was heated (all over) in a large blowpipe-flame, and the temperature raised by enriching the air-blast with gradually increasing proportions of oxygen. The liquid and vapour began to look somewhat alike, but with close observation could easily be distinguished. Finally, the quartz began to yield, viscously in this case, and the experiment could be carried no further.

§ 3. *Observations on the Electrical Resistance of Hot Mercury and its Vapour.*

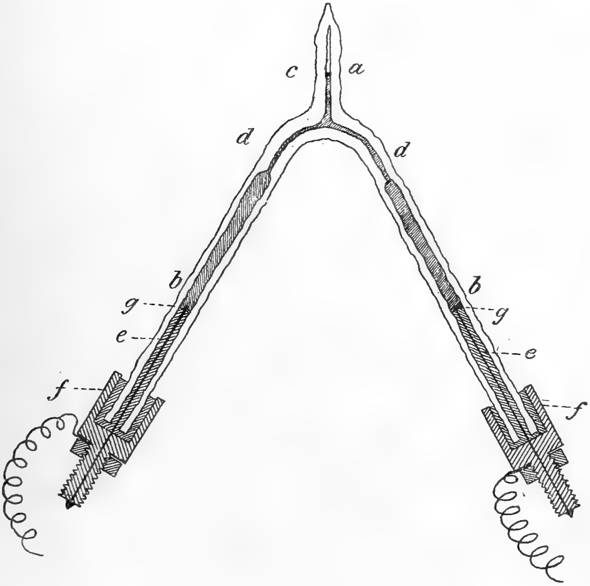
Although the above experiments made it unlikely that the critical temperature of mercury could be reached in quartz tubes, it remained possible that some indication of the changes which the electrical resistance would undergo at that temperature might be got by observations at lower temperatures.

To make a tight joint whereby a conducting wire can be led into a quartz tube containing mercury, red hot, and at an enormous pressure, seems at first sight a somewhat formidable mechanical problem, the more so since it is not possible to fuse platinum air-tight into quartz.

Success was attained as follows :—

The quartz tube took the form of an inverted Y (*a b b*, fig. 1). It was constricted to a very small diameter at the parts *dd*, for a length of about 1 cm. on either side of the joint. The lower parts of the limbs *bb* were of much larger diameter. The tube was filled with mercury up to the level *c*, the current being led in and out by iron wires *ee*, which projected some distance up inside the arms *bb*.

Fig. 1.



The iron wires terminated in brass cups *ff*, carrying appropriate binding screws. These cups were filled with sealing-wax, which cemented them to the quartz tube. This sealing-wax had been sucked up the limbs while hot for a considerable distance, up to the points *gg*, so as to fill the space between the iron wires *ee* and the lower parts of the quartz tube. The tops of the iron wires projected out through the sealing-wax, making contact with the mercury. It may be well to explain that the mercury was introduced through the open end of *a* by making a vacuum in the apparatus beforehand. *a* was then strongly sealed. The resistance between the electrodes *ff* lay mainly in the narrow portion *dd*, and this alone, with the branch *a*, was kept hot. The limbs *bb* were immersed in tanks of water to keep them cold, so as to avoid melting the sealing-wax.

It is evident that if the parts *dd* had alone been heated, the mercury in them would simply have distilled into the branch *a*. To avoid this, *a* was kept somewhat hotter, so that the vapour-pressure of the mercury in it effectually prevented the thread of mercury in the parts *dd* from separating. The resistance between the electrodes *ff* was about ½ ohm. It was determined by means of a slide-bridge and 1 ohm coil. Though the greater part of the resistance was in the narrow parts *dd*, the limbs *bb*, which were not heated, contributed something. The amount to be allowed could only roughly be guessed, since the temperature of the limbs was uncertain, varying from point to point. In fact the experiments made no pretension to accuracy, since the temperature was only estimated without measurement. It was merely attempted to ascertain whether or not the resistance increased enormously.

Thus, in an experiment, the bridge balanced at 52·4, when the mercury was cold, and at 64·7 when it was heated as hot as a bunsen-burner would make it. This makes the resistance 1·7 times as much when hot as when cold. If we make allowance for the fact that the limbs of the tube were not heated, the resistance was probably twice as great at the red heat as at ordinary temperatures. This is something like what might be anticipated from the known temperature coefficient at lower temperatures.

The experiments had to be somewhat hastily carried out, since the heat soon travelled down the limbs of the tube by conduction, and made the cement slightly viscous. It then soon yielded to the enormous pressure, and the mercury forced its way out, leaving the top of the tube empty. For this reason it was not possible to go beyond the full red heat attainable in the bunsen flame. The same tube was used to obtain a measurement of the conductivity of saturated mercury vapour at the same temperature. This was easily done. The top branch *a* of the tube was no longer kept hot. The mercury from the narrow parts *dd* distilled into it, leaving these parts filled with vapour. The tube was joined up in series with a battery-cell (E.M.F. 1·5 volts) and a high-resistance D'Arsonval galvanometer. A deflexion of about forty scale-divisions was observed, indicating about 4×10^{-7} amperes. The resistance was thus about

$\frac{1 \cdot 5}{4 \times 10^{-7}} = 4 \times 10^6$ ohms. It cannot be considered certain that the current really passed altogether through the vapour. Quartz conducts appreciably at such temperatures, especially if it contains the slightest trace of alkali.

A special experiment was made in which a current was sent through the hot quartz by means of wires passed up the limbs of the tube, in the absence of mercury. This experiment showed that the conduction through the quartz was comparatively insignificant.

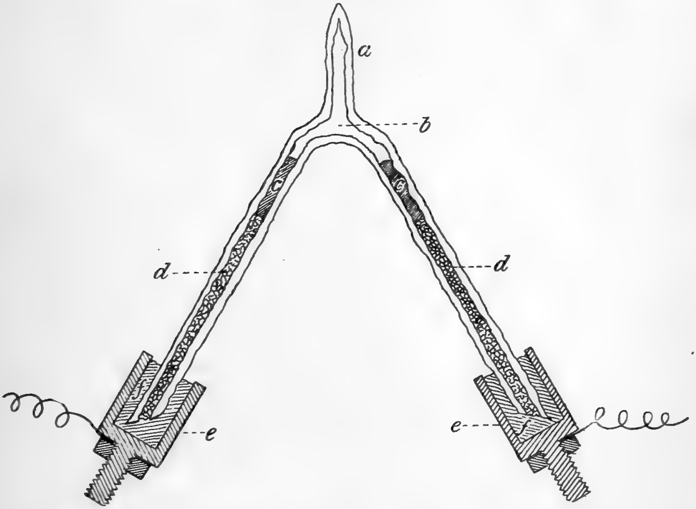
We have, then, as the resistance of the liquid, in the tube, about ·25 ohm, and for that of the vapour, not less than 4×10^6 ohms.

The liquid resistance is therefore, at a full red heat, still 10^7 times that of the saturated vapour.

A few experiments were made on arsenic vapour. The procedure was very similar to that adopted in the case of mercury. The inverted **Y**-tube had, however, to be filled in a special manner; this was as follows.

The two branches were sealed at the ends. The finely powdered arsenic was introduced through *a* (fig. 2) and

Fig. 2.



shaken down till it filled the side limbs. *a* was then sealed also. The whole tube was heated so as to melt the arsenic, under pressure. On cooling, the metal solidified in an aggregate of crystals, which were electrically continuous*. To make contacts with the ends, the sealed extremities of the limbs were ground off obliquely on a grindstone. They were then plunged into a fusible metallic alloy *ff*, contained in the brass caps *cc* shown in the figure. This alloy is the same as that introduced by Mr. E. H. Griffiths. It contracted firmly round the quartz on solidifying, and made good contact with the arsenic.

On heating the top of the tube the arsenic melted in the parts *cc*, and liquid portion rested on the solid *dd*, which acted as a conducting cement. The top part *b* contained arsenic vapour.

This method of leading the current in and out proved quite satisfactory ; the joints remained tight as long as was desired.

In an experiment the tube was joined up with the battery-cell and galvanometer previously mentioned. A deflexion of 60 mms. was observed at a bright red heat, the highest temperature attainable in a Herapath blowpipe.

The length of the vapour-column was about 3 cms., and its cross-section about 1 mm. square. Thus the specific resistance of the saturated vapour at a bright red heat is about 10^4 ohms.

The specific resistance of solid arsenic at 0° is about $3{\cdot}5 \times 10^{-5}$ ohms. There are no data for exactly predicting the resistance of the liquid above the melting point, but it must be of the order of 10^{-5} ohms at 1000° C.

Thus the resistance of the vapour is 10^9 times that of the liquid at this temperature.

It was thought interesting to determine whether or not the vapour of arsenic obeyed Ohm's law. For this purpose an E.M.F. of 400 volts was applied to the tube, and the galvanometer shunted in a known manner so as to make the deflexion suitable. The temperature was kept at a bright red heat as before. It was not possible to keep the temperature very steady, but within the limits of accuracy of the experiment the current observed was 200 times as much as before when the E.M.F. was increased two hundred fold.

§ 4. *Conclusion.*

The results of the preeeding reasoning and experiments may be summarized as follows :—

(1) Mercury vapour is an insulator, while liquid mercury

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* Finely powdered arsenic appears to insulate perfectly, so far as can be observed by ordinary experiments with a galvanometer.

is a conductor. Since the liquid and saturated vapour are indistinguishable above the critical temperature, one or both of these must undergo a remarkable change of electrical properties as that temperature is approached.

(2) Attempts to predict the critical temperature of mercury seem to lead to results altogether inconsistent with one another.

(3) Attempts to observe the critical phenomena of mercury and arsenic in quartz tubes have failed. In both cases experiment proves that the critical temperature lies above a dull yellow heat.

(4) Up to a full red heat the conductivity of saturated mercury vapour remains of quite a different order of magnitude from that of the liquid, the latter being 10 million (10^7) times as great as the former. But, on the other hand, the conductivity of the saturated vapour is immensely greater than that of the vapour at atmospheric pressure. For the former was found to have a resistance 10^7 times that of the liquid, the latter more than 4×10^{14} that of the liquid.

Thus the vapour at atmospheric pressure has a resistance about 4×10^7 times that of the saturated vapour, both at a full red heat. It need scarcely be said that this ratio is of quite a different order from the ratio of the densities of these vapours.

It seems likely that as the critical temperature is approached the vapour begins to conduct freely, while the liquid changes its electrical character to a much less extent.

(5) The conductivity of saturated arsenic vapour at a bright red heat is of the same order as that of mercury, and obeys Ohm's law, at all events up to an electromotive intensity of more than 100 volts per cm.

I do not think it is likely that the critical phenomena of metals will ever be observed. It would, however, be worth while to make more elaborate observations on the resistance of mercury as the temperature rises. This could perhaps be best done by heating the mercury electrically, the necessary pressure being applied by means of hydraulic testing machinery. I propose to attempt this as soon as I have command of the necessary appliances.

Terling Place, Witham, Sept. 1902.

LXVII. *The Clayden Effect and Reversal of Spectrum Lines.*
By Prof. R. W. Wood *.

IN the July number of the Philosophical Magazine Professor Trowbridge publishes a series of photographs of the spectra obtained by passing single powerful discharges through Plücker tubes containing hydrogen. Some of the lines of the spectra appear reversed, which the author explains by supposing a selective reversibility of the silver salts for certain wave-lengths, expressing the opinion that the phenomenon is of great significance in the application of photography to astrophysics.

"One immediately thinks," he says, "of the phenomenon of dark lightning or the Clayden effect."

Strong reversals were found at wave-lengths 4227, 3930, and 3965. These are undoubtedly the calcium lines, which almost always appear in the spectra of heavy discharges.

It appears to me that the whole matter can be very easily referred to the Clayden effect; and I cannot see how the phenomena have any bearing on the interpretation of astrophysical photographic records.

It will be remembered that Clayden showed that if the image of a lightning flash or spark was thrown on a photographic plate, which was subsequently illuminated with diffused light, the spark-images were reversed. That this was not ordinary reversal due to extreme brilliancy he proved by reversing the order of the two exposures, in which case there was no reversal.

He was unable to obtain the effect with any other source of light than the electric spark, and referred the phenomenon to some peculiarity of the light originating in an electrical disturbance.

In repeating and extending the work of Clayden I showed (Nature, Nov. 30, 1899; Science, Nov. 17, 1899) that the reversing power extended throughout the entire spectrum; in other words, that it WAS NOT SELECTIVE, and that it could be obtained with the light from the crater of an arc-lamp, and from the incandescent lime of the oxy-hydrogen light. It was also shown in the same paper that the time element was the all-important factor, flashes of light of a duration of $\frac{1}{10,000}$ of a second or longer not reversing under any circumstances.

The effect of a "light-shock" of a very brief duration, say less than $\frac{1}{20,000}$ sec., is to diminish the sensibility of the

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* Communicated by the Author.

plate, so that a subsequent exposure does not produce so intense an image as it otherwise would.

The two things necessary for a Clayden reversal are, first, a light-shock of great intensity and exceedingly brief duration; and, secondly, a subsequent illumination by a feebler light of longer duration. It is not difficult, it seems to me, to see how both of these conditions could have been fulfilled in Professor Trowbridge's experiments. The heavy discharge produced a bright-line spectrum of sufficient intensity and sufficiently brief duration to give the necessary light-shock to those portions of the plate on which the images of the bright lines fell.

The heat of the discharge raised the inner wall of the tube to incandescence, superposing a continuous spectrum of much longer duration on the bright-line spectrum already impressed. The bright lines would then come out reversed exactly as they did in the experiment which I described in 'Nature.'

Professor Trowbridge showed me some of the tubes used in the experiments, and the badly corroded inner surface indicates that it must have been raised to an exceedingly high temperature. A brief phosphorescence of the gas following the discharge may have helped in the production of the continuous spectrum, though I am inclined to refer it chiefly to the incandescence of the glass surface.

I feel confident that a photograph of one of these discharges with a revolving mirror or moving plate would reveal the dual nature of the illumination.

One other point requires mention. Professor Trowbridge states that the strongest bright lines are not reversed, and that there is therefore a selective reversibility. That the strongest lines should not appear reversed is precisely what we should expect; for, as I showed in the experiments referred to, if the initial illumination is TOO intense reversal does not take place, *i. e.* the light-shock must not be too heavy.

By taking a series of photographs of very bright sparks, with different stops in the lens I found that only the images obtained with the small and medium stops came out reversed. It seems probable that the calcium lines in Professor Trowbridge's experiments had the requisite intensity for reversal, while the other lines were too bright. If this explanation of these pseudo-reversals be accepted, it does not seem to me that they can have any bearing on stellar photographs, for it is difficult to imagine how the dual illumination could be produced.

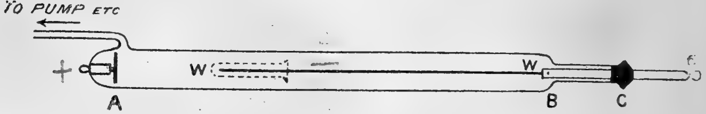
LXVIII. *The Current-Density at the Cathode in the Electric Discharge in Air.* *By* HAROLD A. WILSON, *B.A., D.Sc. (Lond.), Clerk-Maxwell Student, Fellow of Trinity College, Cambridge*[*].

THE experiments described in this paper were undertaken with the object of measuring the current per square centimetre on the cathode, in the electric discharge in air at low pressures. It is well known that the negative glow at pressures of about one millimetre is confined to a definite area on the cathode, and that this area covered by the glow increases with the current through the tube. Wehnelt (*Ann. der Physik*, No. 2, 1902) has shown that the discharge from the cathode is confined to the area covered by the glow and that the current-density is uniform throughout this area. So long as the cathode is not entirely covered by the glow the fall of potential between the glow and the cathode remains independent of the current, but when the cathode is entirely covered the "cathode drop" increases with the current. This fact leads one to expect the area covered by the glow to be proportional to the current through the tube, and the experiments now to be described show that this is the case.

The method employed was very simple; the cathode used consisted of a straight wire fixed along the axis of the discharge-tube and the length of the wire covered by the glow was measured and also the current through the tube.

The discharge-tube used is shown in the figure. It consisted of a glass tube, AB, about 3 cms. in diameter and 30 cms. long, having an aluminium disk electrode A sealed in at one end, and a narrow tube BC joined on at the other. This narrow tube served to support a glass tube E which carried the cathode WW. The glass tube E was fastened in with sealing-wax at C, so that it could be easily taken out when it was desired to try a new cathode.

Fig. 1.



The discharge-tube was connected to a Toepler pump and McLeod gauge and to bulbs containing phosphorus pentoxide.

The discharge was passed from the disk A to the cathode wire, and it was found that the glow appeared on the end of

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[*] Communicated by Prof. J. J. Thomson.

the wire nearest to A and formed a uniform coating over the wire, covering a definite length of it. This length was measured by means of a millimetre-scale placed along the tube and backed by a mirror, so that errors due to parallax could be avoided. The shape of the glow is indicated by the dotted line. It resembled a test-tube. The discharge was produced by means of a battery of small secondary cells, and an adjustable resistance and telephone were included in the circuit.

The Crookes's dark space between the glow and the cathode of course increased in thickness when the pressure was reduced, and ultimately the glow extended to the walls of the tube. When the pressure was so low that this occurred the length of wire covered by the glow was not proportional to the current, and the glow appeared to tend to concentrate itself at the end of the cathode, showing that the walls of the tube impeded it from spreading out uniformly. Measurements were therefore only made when the glow did not reach the walls of the discharge-tube.

Table I. gives the results obtained with a platinum wire

TABLE I.—Platinum wire 1·42 mm. in diameter.

p.	*l*.	C.	$\frac{C}{lp}$.
5·1	5·35	7·36	0·27
„	5·1	·38	0·28
„	1·6	·54	0·31
2·53	8·1	5·16	0·25
„	3·0	·79	0·24
2·04	5·1	2·63	0·25
„	7·55	3·72	0·24
1·40	8·5	2·51	0·21
„	7·6	2·26	0·21
„	4·5	1·32	0·21
0·96	5·55	1·20	0·23
„	9·2	1·69	0·19
„	3·4	0·70	0·21
0·67	4·5	0·69	0·23
„	8·9	1·31	0·22
„	9·1	1·33	0·22
„	3·8	0·61	0·24
		Mean	0·236

1·42 mm. in diameter as cathode. p is the pressure in mms. of mercury, l the length of the glow in cms., and C the current in milliamperes.

The quantity $\frac{C}{lp}$ is approximately independent of the current at any one pressure, which shows that the current per unit-length of cathode covered by the glow is a constant.

$\frac{C}{lp}$ is also nearly independent of the pressure, so that the current per unit-length of the cathode is proportional to the pressure.

Tables II. III. and IV. contain the results obtained with other wires as cathodes. In every case $\frac{C}{lp}$ is approximately independent of l and p.

TABLE II.—Platinum wire, 0·19 mm. in diameter.

p.	l.	C.	$\frac{C}{lp}$.
2·93	4·4	1·07	0·083
"	12·8	3·66	0·098
"	13·4	3·76	0·096
"	3·4	0·875	0·088
2·18	7·5	1·56	0·095
"	4·4	0·67	0·070
1·475	12·5	1·62	0·088
"	11·25	1·21	0·073
1·36	8·6	0·794	0·068
"	4·8	0·513	0·079
"	4·2	0·47	0·082
"	12·4	1·39	0·082
0·93	7·27	0·622	0·092
"	5·4	0·454	0·090
"	8·95	0·75	0·090
0·65	10·1	0·745	0·110
"	6·9	0·496	0·110
		Mean	0·088

If $\frac{C}{lp}$ is divided by πd (d being the diameter of the wire) we get the current-density at the surface of the cathode.

TABLE III.—Aluminium wire, 2·08 mms. in diameter.

p.	l.	C.	$\frac{C}{lp}$.
6·7	1·5	5·8	0·58
3·64	5·3	7·49	0·39
"	1·3	2·16	0·46
3·13	6·3	6·96	0·35
2·37	8·13	5·78	0·30
"	2·6	2·26	0·37
"	2·2	1·97	0·38
"	13·05	11·95	0·39
2·07	7·4	5·96	0·39
"	3·3	2·49	0·37
"	10·8	9·7	0·43
1·46	12·25	5·46	0·31
1·16	7·5	2·30	0·27
"	12·25	4·09	0·29
1·13	7·95	2·35	0·26
0·975	11·4	3·23	0·29
"	4·8	1·18	0·25
0·78	3·1	0·60	0·25
"	8·8	1·63	0·24
"	12·3	2·43	0·25
0·68	12·9	2·35	0·27
0·53	6·1	0·68	0·21
"	12·2	1·75	0·27
0·45	9·2	1·13	0·27
"	13·0	1·79	0·31
"	5·7	0·63	0·25
0·23	5·2	0·54	0·45
		Mean	0·323

Table V. contains the values of $\frac{C}{lp\pi d}$ for each of the wires used.

The current-density for the two thickest wires is nearly the same, but for the smaller wires it is much greater. This suggests that the effective diameters of the wires are really greater than their actual diameters, so that if, in calculating the current-density, a small constant quantity was added to the diameter of each wire, then the current-density would be the same in every case. It was found by trial that if 0·5 mm. is added to the diameters the calculated current-

TABLE IV.—Aluminium wire, diameter 0·61 mm.

p.	*l*.	C.	$\frac{C}{lp}$.
8·5	6·6	8·83	0·16
4·07	13·1	6·92	0·13
2·87	5·3	2·30	0·15
„	5·55	2·36	0·15
„	2·85	1·18	0·14
„	10·45	5·36	0·18
2·43	6·65	2·52	0·16
„	5·8	1·93	0·14
1·94	10·9	3·29	0·16
„	5·1	1·35	0·14
„	3·0	0·81	0·14
1·38	4·75	0·67	0·10
„	6·15	0·97	0·11
„	5·85	0·98	0·12
„	10·85	2·14	0·14
„	11·95	2·40	0·15
0·94	7·4	0·80	0·12
„	9·9	1·01	0·11
0·48	13·9	0·885	0·13
„	9·4	0·57	0·13
		Mean	0·139

TABLE V.

Diameter.	$\frac{C}{lp}$.	$\frac{C}{lp\pi d}$.	$\frac{C}{lp\pi(d+0\cdot05)}$.
0·208 cm.	0·323	0·50	0·403
0·142 „	0·236	0·53	0·394
0·061 „	0·139	0·72	0·397
0·019 „	0·088	1·47	0·406

density is the same for all four wires. The results of this calculation are given in the last column of Table V.

It appears, therefore, that the effective area of a cathode is that of a layer 0·25 mm. thick covering it. At the surface of this layer the current-density is given by the formula $\iota=0\cdot4\,p$. The above results also show that the current-density is the same for cathodes of platinum as for cathodes of aluminium.

If we suppose that the current at the cathode is entirely carried by negative ions produced close to its surface, it is easy to calculate what proportion of the air-molecules which strike the cathode must be ionized to give a current-density of $0{\cdot}4\,p$ milliamperes per sq. cm.

If e is the charge carried by one ion, and n the number of molecules striking the surface of the cathode per sq. cm., then if every molecule striking the surface were ionized there the current would be ne. Now $n=\frac{1}{6}\mathrm{NG}$ where N is the number of molecules in a cubic centimetre of the gas, and G the square root of the mean square of their velocities. For air at the ordinary temperature $\mathrm{G}=5\times 10^4 \frac{\text{cms}}{\text{sec.}}$. Also for a gas at 760 mms. pressure $2\mathrm{N}e=\frac{1}{0{\cdot}115}$ coulombs.

Hence

$$ne=\frac{p\times 5\times 10^4}{760\times 6\times 2\times 0{\cdot}115}$$

$$=47{\cdot}7\,p \text{ amperes per sq. cm.}$$

The actual current observed is $0{\cdot}4\,p$ milliamperes per sq. cm. so that the fraction of the molecules striking the cathode which would have to be ionized to carry the current is

$$\frac{0{\cdot}40}{47{\cdot}7\times 1000}=\frac{1}{120{,}000}.$$

It is therefore clear that the amount of gas present in the tube is amply sufficient to account for the observed current-density at the cathode. J. Stark (*Physikalische Zeitschrift*, 2 Jahrgang, No. 5) has given a formula which represents the variation of the cathode fall of potential with the current-density. This formula is $\mathrm{K}=\mathrm{K}_n+\frac{k}{pf^{\frac{1}{2}}}(\mathrm{C}-xpf)^{\frac{1}{2}}$ where K is the cathode drop, K_n the "normal" drop when the cathode is only partly covered by the glow, p the gas pressure, f the area of the cathode, C the current, and k and x constants. When the cathode is only partly covered, as in the present experiments, $\mathrm{K}=\mathrm{K}_n$, so that Stark's formula becomes $\mathrm{C}=xpf$. This equation becomes identical with that which my experiments have led to, viz., $\iota=0{\cdot}4p$ on putting $\frac{\mathrm{C}}{f}=\iota$. Stark does not give the value of his constant x and his experiments do not appear to be well adapted for its determination since he was mainly concerned with the variation of the cathode drop with the current-density when the cathode is entirely covered by the glow.

Skinner (Phil. Mag. Dec. 1901) has also given a formula for the variation of K with C. It is $K=K_n+\frac{b}{p}(C-a)$ where b and a are constants. This gives $C=a$ when $K=K_n$ and is therefore evidently incorrect, for a should certainly depend on p.

That Skinner's formula will not do has been pointed out by Stark (*Physikalische Zeitschrift*, 3 Jahrgang, No. 13). The results described in this paper therefore confirm Stark's formula in so far as it applies to the current-density when the cathode is only partially covered by the glow.

The fact that the glow only covers a definite area on the cathode is evidently a consequence of the existence of a minimum value for the cathode drop. As the current-density falls the drop falls until it reaches the minimum value. Any further diminution of the current-density would then involve an increase in the drop, so instead of the current-density diminishing, the area of the glow diminishes.

In conclusion I wish to say that my best thanks are due to Prof. J. J. Thomson for his kindly interest and advice during the carrying out of these experiments in the Cavendish laboratory.

LXIX. *Notices respecting New Books.*

VECTOR ANALYSIS, *a Text-book for the use of Students of Mathematics and Physics, founded upon the Lectures of* Professor J. WILLARD GIBBS. *By* DR. EDWIN BIDWELL WILSON. (New York, Scribner's; London, Arnold, 1901.)

THIS is one of the Yale Bicentennial Publications, and is in some respects a very remarkable treatise. It is essentially an expansion of a short pamphlet circulated privately by Professor Gibbs some twenty years ago, and forms a goodly volume of fully 400 pages. As in that pamphlet, so in this book, the feature which distinguishes the vector methods elaborated by Professor Gibbs from the vector methods associated with the names of Hamilton, O'Brien, and Grassmann (to name only the *originators* of distinct methods) is the treatment of the linear vector function in terms of the so-called "dyad." It is this which gives significance to the notation adopted for the scalar and vector parts of vector products. So far as these important quantities are concerned, the substitution of $\alpha . \beta$ for $-S\alpha\beta$ and of $\alpha \times \beta$ for $V\alpha\beta$ is a trifle, for which there could be absolutely no excuse unless the dot-cross notation is based upon some fundamental principle more important than anything which occurs in quaternion vector analysis. If then we leave the "dyad" out of account, there seems to be no sufficient reason why the pictorial notation of Hamilton should be discarded in favour of a purely artificial notation, which is simply a commutation of that used by Hamilton's brilliant contemporary, O'Brien. On the other hand, if we find that Gibbs's conception of the "indeterminate product" known as the "dyad" is fundamentally more important than Hamilton's conception of the quaternion, and that this general indeterminate product is analytically more effective than the quaternion, then we cannot but recognise the value of the notation used by Professor Gibbs. When we have occasion to discuss them we shall speak of these rival notations as the dyadic and quaternion notations respectively.

There is a widespread feeling that vector analysis is a growing necessity for physical investigation; and yet some of the most strenuous supporters of this view have protested that the vector analysis developed with great fullness and logical rigour in Hamilton's quaternions is not what is wanted. These criticisms find a faint echo in the preface to the present volume. It is said that "Heaviside has set forth the claims of vector analysis as against quaternions, and others have expressed similar views." And again, "As yet, however, no system of vector analysis which makes any claim to completeness has been published." Now in the first place there is no antagonism between quaternions and vector analysis, since the most completely developed system of the latter is to be found in the former. In the second place, although till now no general treatise called "vector analysis" has been in existence, it is simply against the facts to state that no system which makes any claim to completeness has ever been published. On the contrary it is a fact which it is pure sophistry to deny that in Hamilton's two great works there is contained a complete system of vector analysis in a highly developed state.

The main objection urged against the quaternionic system by Professor Gibbs (see 'Nature' vol. 43, pp. 511–12) is that neither the quaternionic product nor the quaternionic quotient of two vectors can claim a prominent or fundamental place among such fundamental geometrical conceptions as the sum of vectors, the vector product of two vectors, or the scalar product of two vectors. This is perhaps largely a matter of opinion; and yet after a student has formed a clear conception of the vector as a directed quantity is it not reasonable and natural for him to ask, What is involved in the conception of the quotient α/β as the operator which changes β into α? This is Hamilton's method, and leads at once to the conception of the quaternion, and the whole system of vector analysis unfolds itself naturally and consistently.

Professor Gibbs's method is very different. He first defines as independent and fundamental conceptions the "direct" and "skew" products of two vectors, the direct product being Hamilton's scalar of the product of two vectors with the sign changed, and the skew product being the vector of the same quaternion product.

Now these well-known quantities are not *factorisable* products. They may be taken to be, as the quaternion nomenclature clearly shows, parts of a real product which can be factorised, in the sense that if $AB=C$, then $A=C/B$. But Professor Gibbs takes no account of the possibility of the existence of such a factorisable product. In a footnote on page 67 the student is promised (if he persevere) the definition of the product of two vectors where neither dot nor cross occurs. This is at last given on page 271, where we read that "the symbolic product formed by the juxtaposition of the two vectors **a b** without the intervention of a dot or a cross is called the indeterminate product." Six pages previous we are told that "an expression **a b** formed by the juxtaposition of two vectors without the intervention of a dot or a cross is called a dyad." The dyad and indeterminate product are thus by definition one and the same thing. It is called indeterminate because it is neither a scalar nor a vector*. Since each vector involves three numbers the most general conceivable product should involve six. The dyad, however, involves only five, since the assumption is made that the product of the tensors of the constituent vectors only is involved. Given the dyad, the directions of both vectors are fully determined, so that equality between two dyads means that the constituent vectors are, in regard to direction, the same in both. It is difficult to see what service such a restricted product is to be in any system of vector algebra, nor do we gain any enlightenment from subsequent parts of the book. In fact this product with its five disposable numbers is indeterminate, does not appear to be factorisable, and has no attachable meaning until it *ceases to be itself by being defined anew* as an operator in combination with other vectors. The quaternion involves four numbers, and having therefore what might be called from analogy two degrees of freedom is fitted to play an important rôle in vector combinations. It has pleased Professor Gibbs to introduce the one condition that scalar multiplication in vector products is to be associative. Thereby he gets a purely symbolic indeterminate and uninterpreted product. It pleased Hamilton to introduce the condition that vector multiplication in products of three or more vectors was to be associative. Thereby he obtained a real determinate and fully interpreted product called the quaternion. It is very difficult to understand the argument that the real quaternion should be disallowed in a vector analysis, but the dyad as a symbolic indeterminate product welcomed with open arms. There are hints throughout the book regarding higher indeterminate products of vectors called triads, tetrads, etc.; but the theory of these is not given, there being, we are told, no real need for them in physical applications. As a matter of strict logic, there is no real theory given of the dyad *as an indeterminate product.*

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* Dr. Heaviside demands that vectors be treated "vectorially," and that a vector analysis be purged of products which are non-vectorial. This is his reason for condemning the quaternion. It is curious that he has expressed intense admiration of the dyad or indeterminate product, which its inventor tells us explicitly is no vector but purely symbolic, and acquires a determinate physical meaning only when used as an operator. Could anything so hopelessly "unvectorial" be said of the quaternion?

What then is the use of this indeterminate product? By the simple insertion of a dot or a cross we get the scalar or vector product; and these are stated to be functions of the indeterminate product in the sense that when it is assigned the others are determined. But how can an indeterminate purely symbolic product be assigned in any true and real sense? And what is the functional relationship connecting the indeterminate product with the "dot and cross" products? We know that the quantity $\alpha\times\beta-\alpha\,.\,\beta$ which is Hamilton's $V\alpha\beta+S\alpha\beta$ is a quantity which is associative in products and which has a definite geometric meaning. It is in fact the quaternion $\alpha\beta$. Gibbs's dyad, written in exactly the same way, has no such useful properties. Out of it the scalar and vector parts of the quaternion product are obtained by the artificial introduction of a dot and a cross; there is no indication that the properties of the scalar and vector parts are in any way connected with the properties of the dyad, *viewed as a product complete in itself.*

There is, however, another use of the dyad, a use which connects it in a very ingenious manner with the linear vector function. The artifice consists in adding to either side of the dyad a vector with a dot between. We thus get the quantities $\alpha\beta.\rho$, $\rho.\alpha\beta$ which are in quaternion notation $-\alpha S\beta\rho$, $-\beta S\alpha\rho$. If we take the sum of several of these operating dyads we get what is called a dyadic, which then becomes a symbol for Hamilton's linear vector function. Thus

$$(\alpha_1\beta_1+\alpha_2\beta_2+\alpha_3\beta_3).\rho=-\Sigma\alpha S\beta\rho=-\phi\rho.$$

This is undoubtedly a very neat way of representing the trinomial form of the linear vector function, and it has its merits. For example, by merely shifting the operand vector from the one side to the other we pass to the conjugate function. That in itself is, however, of passing moment and seems to have no analytical significance, for writing the dyadic trinomial in the concise form ϕ Professor Gibbs falls back upon Hamilton's time-honoured expression and gets *absolutely nothing more.* The dyadic method leads of course to a special discussion of the properties of the linear vector function, and the usual cubic is deduced. It is then stated on page 321 that "this equation may be called the Hamilton-Cayley equation. Hamilton showed that a quaternion (*sic*) satisfied an equation analogous to this one and Cayley gave the generalization to matrices ..... The analogy between the theory of dyadics and the theory of matrices is very close. In fact a dyadic may be regarded as a matrix of the third order, and conversely a matrix of the third order may be looked upon as a dyadic." This sentence contains a mis-statement, and to the ignorant reader would convey a very inadequate idea of the great services rendered by Hamilton. The truth is that Hamilton's linear vector function *is* the matrix of the third order, and the cubic equation first established by him, five years at least before

Cayley, is the equation satisfied by the matrix of the third order and by the dyadic viewed as a functional operator. There is in fact identity—no mere analogy. There is, on the other hand, no evidence that the "indeterminate product" with its five involved numbers, or the dyadic trinomial with its fifteen numbers, satisfies an equation of this kind at all. As soon as the dyadic is regarded as an operator of the kind defined, it becomes Hamilton's linear vector function, and of course satisfies the same cubic equation. In fact if, as seems to be the case practically throughout the book, the dyadic exists only as an operator, then the dyad should strictly speaking be written $\alpha\beta.$ or $.\alpha\beta$, just as in working in quaternions we may put the linear vector function in the symbolic form $\alpha_1 S\beta_1. + \alpha_2 S\beta_2. + \alpha_3 S\beta_3.$, meaning that the operand is to follow.

Professor Gibbs also defines the "skew" products of a dyad into a vector. They are

$$(\alpha\beta)\times\gamma = \alpha(\beta\times\gamma),\ \alpha\times(\beta\gamma) = (\alpha\times\beta)\gamma$$

That is, the original indeterminate product is split up, and one of the members is joined with the new operand to form a new vector, which with the other member forms a new indeterminate product. This is then to be used as a dyad operator. To find what the relation of this new dyad is to the original dyad, we must let it act upon a vector. Extending to dyadics we find the quaternion equivalents to be as follows :—

$$\begin{aligned}
(\alpha_1\beta_1+\alpha_2\beta_2+\ldots)\times\rho.\sigma &= -\phi V\rho\sigma,\\
\sigma.(\alpha_1\beta_1+\alpha_2\beta_2+\ldots)\times\rho &= \quad V\rho\phi'\sigma,\\
\rho\times(\alpha_1\beta_1+\ldots\ldots).\sigma &= -V\rho\phi\sigma,\\
\sigma.\rho\times(\alpha_1\beta_1+\ldots\ldots) &= \phi' V\rho\sigma,
\end{aligned}$$

where ϕ is $\Sigma\alpha S\beta.$, and ϕ' is the conjugate $\Sigma\beta S\alpha$. Hence these "skew" products are equivalent to the quaternion operators $\phi V\rho.$, $V\rho\phi.$, which in the quaternionic treatment come naturally to the front when needed without the necessity for new definitions. This constant appeal at every turn to new definitions is certainly not a pleasing feature of Professor Gibbs's method.

The section on Double Multiplication starts as usual from arbitrary definitions, and seems to us to make serious demands upon the memorizing power of the student. Its value is not very apparent; for its chief if not only use in the treatise seems to be to arrive at the inversion of the linear vector function. Passing it over meanwhile, we shall confine our remaining remarks to a description of the dyadic treatment of what corresponds to Hamilton's beautiful operator ∇. In quaternion vector analysis, ∇ is a differential vector operator of the form $id_1+jd_2+kd_3$ where $d_1\ d_2\ d_3$ are differentiations in the directions of the mutually perpendicular unit vectors $i\ j\ k$. From this single definition (or from any other equivalent to it) the properties of ∇ evolve themselves naturally along the lines of the calculus.

It is far otherwise with the dyadic treatment. Professor Gibbs virtually starts with the definitions of what are to him *four distinct* operators, ∇ operating on a scalar, $\alpha.\nabla$ operating on a vector, $\nabla.$ operating on a vector, and $\nabla\times$ operating on a vector. It is noted, however, that "for practical purposes and for remembering formulæ it seems by all means advisable to regard

$$\nabla = i\frac{d}{dx} + j\frac{d}{dy} + k\frac{d}{dz}$$

as a symbolic vector differentiator." Remembering formulæ! Here again it is difficult to imagine a mind finding rest in such an arbitrarily constructed calculus, when already in Hamilton's and Tait's works there lay to hand an effective vector analysis in which ∇ was a *real* vector differentiator. The collocation $\nabla\alpha$ is defined in chapter vii. as meaning a dyad, and then we read: "The operators $\nabla.$ and $\nabla\times$ which were applied to a vector function now become superfluous from a purely analytical standpoint. For they* are nothing more or less than the scalar and vector of the dyadic $\nabla\mathbf{w}$. The analytical advantages of the introduction of the variable dyadic $\nabla\mathbf{w}$ are therefore these. In the first place the operator may be applied to a vector function just as to a scalar function. In the second place the two operators $\nabla.$ and $\nabla\times$ are reduced to positions as functions of the dyadic. On the other hand, from the standpoint of physics nothing is to be gained and indeed much is lost if the important interpretations of $\nabla.\mathbf{w}$ and $\nabla\times\mathbf{w}$ as the divergence and curl of $\mathbf{w}$ be forgotten and their places taken by the analytic idea of the scalar and vector of $\nabla\mathbf{w}$." With this last statement we are quite in accord if by $\nabla\mathbf{w}$ we understand the purely symbolic indeterminate and uninterpreted product. But it is otherwise with the quaternion quantity $\nabla\mathbf{w}$, to which a real meaning can be assigned. ∇ is then a vector operator and the scalar and vector parts of the result of its operation on a vector have *analytically and geometrically* just those very meanings which make them all-important in physical investigations. To a worker in quaternions these meanings are always in evidence. "Curl" and "Div" are useful descriptively, but they are not analytical working symbols like $S\nabla.$ and $V\nabla.$. When the quaternion method is adopted and the true ∇ *associative with itself in product combinations* is used, everything develops in a perfectly natural manner, and there is no need for the complicated tabulations of the different types of the second order combinations of the dyadic ∇, so characteristic of the pages of Professor Gibbs's 'Vector Analysis.'

We have not space to discuss the integral functions Pot, New, Lap, and Max †, which are analytically inverse functions of the true ∇,

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* This is loose language. $\nabla.$ and $\nabla\times$ are not the scalar and vector of $\nabla\mathbf{w}$.

† They are discussed at some length in a paper on *Recent Innovations in Vector Theory* (Proc. R. S. E., xix. pp. 212–237, 1893).

and the necessity for which seems to arise mainly from the neglect of the associative principle in product combinations of ∇. This particular section, however, is very instructive reading, quite apart from the dyadic system of vector analysis.

The collocation $\nabla\phi$ is called a *triadic,* but its properties (if there be any) are not discussed. The dyadic $\nabla\times\phi$ and the *quantity* $\nabla.\phi$ are, however, defined. The former is the quaternion operator $V\nabla\phi.$; hence when realized it means not the more general quantity $V.\nabla\phi\varpi$, but the particular case $V.\nabla_1\phi_1\varpi$, where the suffixes mean that ∇ acts on the constituents of ϕ and not on ϖ. In this respect the dyadic notation is not so general as the quaternion. The quantity $\nabla.\phi$ corresponds to what McAulay writes in the form $\phi_1\nabla_1$, meaning

$$\frac{d}{dx}\phi i+\frac{d}{dy}\phi j+\frac{d}{dz}\phi k,$$

$i\,j\,k$ being the usual rectangular system and the constituents of ϕ varying with position. If ϕ is written in the form

$$\phi\varpi=\alpha Si\varpi+\beta Sj\varpi+\gamma Sk\varpi$$

then
$$\phi_1\nabla_1=-\frac{d\alpha}{dx}-\frac{d\beta}{dy}-\frac{d\gamma}{dz}.$$

So far there does not seem to be the least advantage in the "dyadic" over the "quaternion." It leads to nothing more, gives no greater generality, and is occasionally indeed less general.

Passing over various examples which a quaternionist would not need to tabulate as they are perfectly simple transformations in quaternions, we come to the equations among line, surface, and volume integrals. Tait has practically given these; but we owe to McAulay the completely general form which includes all. He shows that if Q be *any* linear function of a vector

$$\int Qd\rho=\iint Q(Vda\nabla),\ \ \iint Qda=\iiint Q\nabla dv$$

where da represents the vector area element of the surface, bounded in the first case by the curve (ρ), and bounding in the second case the volume v, and where it is understood that ∇ acts on all the varying factors in the expression.

Professor Gibbs gives four relations connecting line and surface integrals, namely,

$$\iint da\times\nabla u=\int d\rho u,\quad \iint da\times\nabla\varpi=\int d\rho.\varpi,$$

$$\iint da.\nabla\times\varpi=\int d\rho.\varpi,\ \ \iint da.\nabla\times\phi=\int d\rho.\phi,$$

where u is a scalar function, ϖ a vector, and ϕ a linear vector function.

In quaternions, the first is $\int u d\rho = \iint \mathrm{V} d\alpha \nabla u$.

The second, if regarded from a quaternion standpoint, would be

$$\int d\rho \varpi = \iint \mathrm{V} d\alpha \nabla . \varpi.$$

But to find its meaning in dyadics, we must realize the expressions by adding $.\sigma$ or prefixing σ. We then get (1) $\int d\rho \mathrm{S} \varpi \sigma = \iint \mathrm{V} d\alpha \nabla \mathrm{S} \varpi \sigma$ which is simply a repetition of the first case, or (2)

$$\int \mathrm{S} \sigma d\rho . \varpi = \iint \mathrm{S} \sigma d\alpha \nabla . \varpi,$$

an equation which is true if σ is constant, or if $\mathrm{V} \nabla \sigma$ vanishes. But generally $\int \mathrm{S} d\rho \sigma . \varpi = \iint \varpi \mathrm{S} d\alpha \nabla \sigma + \iint \mathrm{S} \sigma d\alpha \nabla . \varpi$.

The third relation given is $\iint d\alpha . \nabla \times \varpi = \int d\rho . \varpi$. This in quaternion notation is $\int \mathrm{S} d\rho \varpi = \iint \mathrm{S} d\alpha \nabla \varpi$.

The fourth relation again deals with dyadics. If we consider the dyadic as representing the linear vector function we find the quaternion relation to be

$$\int \mathrm{S} d\rho \phi \sigma = \iint \mathrm{S} d\alpha \nabla \phi \sigma$$

where ∇ acts both on ϕ and σ. In the dyadic notation, however, $\nabla \times \phi . \sigma$ means $\mathrm{V} . \nabla_1 \varphi_1 \sigma$, so that the relation given by Professor Gibbs is

$$\int \mathrm{S} d\rho \phi \sigma = \iint \mathrm{S} d\alpha \nabla_1 \phi_1 \sigma$$

and is true only when σ is constant or when $\mathrm{S} d\alpha \nabla_1 \phi \sigma_1$ vanishes.

The six relations connecting volume and surface integrals, given on page 400, may be discussed in a similar way, and will be found in no respect more general than the quaternion equivalents, and in some cases less general. One example will suffice, namely,

$$\iiint dv \nabla \times \phi = \iint d\alpha \times \phi.$$

By definition $d\alpha \times \phi$ means in quaternion notation $-\mathrm{V} d\alpha \phi.$ if the operand vector follows, and $\phi' \mathrm{V} d\alpha.$ if the operand vector precedes. Thus in quaternions

$$\iint \mathrm{V} d\alpha \phi \sigma = \iiint dv \mathrm{V} \nabla \phi \sigma,$$

and $$\iint \phi' \mathrm{V} d\alpha \sigma = \iiint dv \phi' \mathrm{V} \nabla \sigma,$$

where ∇ acts on σ and on the constituents of the linear vector function. But in the dyadic notation $\nabla \times \phi . \sigma = V \nabla_1 \phi_1 \sigma$. Hence the dyadic formula is true only if σ is constant or if $V . \nabla_1 \phi \sigma_1$ vanishes.

Because of the great importance of the subject, we have given a fairly full description of the essential parts of Professor Gibbs's dyadic theory. It certainly gives us nothing more in the way of a practical working vector analysis than we already possess in the Hamiltonian system. The so-called indeterminate product as such is useless. Cayley has said that "a product which is not associative has no meaning until the grouping of the factors is determined." To such a category evidently belong the triads and tetrads hinted at; and the dyad regarded as a product is so far like unto them. Not till it is used as an operator does the dyad take on a determinate meaning; and then it is found to be nothing more than a bit of the linear vector function, one of the most beautiful of Hamilton's discoveries. The Gibbsian dyad is in fact a kind of lay figure for decorating with notations.

There is, of course, no fundamental reason why vectors should obey the associative law in products; but we have only to try to master the meanings of Professor Gibbs's combinations of dots and crosses with the vector operator ∇, to be convinced that the neglect of the associative principle leads to an increased complexity with absolutely no advantage whatever. The one excuse, it seems to us, for elaborating a vector analysis in rivalry to that developed by Hamilton is that a greatly superior thing is being presented. In the dyadic system of vector analysis we find no evidence of superiority. On the contrary, it is demonstrably more arbitrary, more complicated, and less flexible than the quaternion system. Had the quaternion system been unknown, the other would have been, as a kind of shorthand notation at any rate, a welcome aid in physical research; but when we bear in mind that Professor Gibbs deliberately set out to construct a system free from the fancied blemish of the quaternion and yet did not scruple to introduce in its stead an indeterminate product which is without any geometric significance whatever, and when we find on careful comparison that *practically* the dyadic system is simply a modification of quaternion methods, in large measure a mere difference of notation, we can find no satisfactory reason for a man of Professor Gibbs's great powers leaving quaternionic paths to invent new notations, new names for old things, and an indeterminate purely symbolic product to take the place of the determinate real quaternion.

Whatever views, however, may be formed as to the merits or demerits of the system, there can be only one opinion as to the zeal, ability, and self-abnegation with which Dr. Wilson has fulfilled his task. Professor Gibbs is indeed to be congratulated in having a pupil so capable of producing in systematic book-form the subject matter of his lectures. C. G. K.

The Electric Arc. *By* HERTHA AYRTON, *Member of the Institution of Electrical Engineers.* London: "The Electrician" Printing and Publishing Company, Limited, 1902. Pp. xxvi+479.

THE Electric Arc is one of those physical phenomena which, although generally known for well-nigh a century, have defied the efforts of the experimenter, and resisted most of the attempts to lift the veil of mystery surrounding them. It is only within recent years that our notions regarding the processes which take place in the electric arc have begun to clear; and this result is in no small measure due to the distinguished writer of the book before us, who by a series of experiments requiring an amount of care and patience that few could command, has succeeded not only in establishing definite laws regarding the phenomenon of the arc, but has also thrown a flood of light on the labours of previous experimenters, and put forward a hypothesis regarding the mechanism of the arc which is in striking agreement with the experimental knowledge of the present day.

Notwithstanding the striking nature of the phenomenon, and the fascination which it seems at all times to have exerted upon the experimenter, the origin of its discovery seems to be hidden in obscurity. Davy is generally credited with the discovery of the electric arc, but, as Mrs. Ayrton clearly points out in the interesting chapter on the History of the Arc, his claims are by no means as substantial as is generally assumed to be the case. The difference between an ordinary electric spark and an arc does not appear to have been realized in the early days of the arc, this latter being regarded simply as a species of spark.

It will be useful here to give a brief outline of the contents of Mrs. Ayrton's book. Chapter I. contains a very clear description, illustrated by numerous fine diagrams and sketches, of the appearance of the arc, and the effects produced by changes in the current and length of arc, and by coring the carbons. In Chapter II. we have a brief history of the arc, which includes a most useful summary of the researches of Continental physicists. This chapter must have involved an immense amount of labour, and English readers will feel grateful to Mrs. Ayrton for having brought within their reach much information which has up to the present remained inaccessible. Chapters IV., V. and VI. deal with the relations connecting P.D., current, and length of arc. The distribution of potential in the arc, and the drop of potential in passing from the arc to either carbon, are considered in Chapter VII. The next two Chapters, VIII. and IX., deal with the steadying resistance included in the arc circuit, and the power efficiency of the arc. Chapter X. contains an account of Mrs. Ayrton's highly interesting experiments on hissing arcs, and her theory regarding the cause of hissing. Chapters XI. and XII. are concerned with the luminous efficiency of the arc, and include an account of Mrs. Ayrton's theory regarding the mechanism of the arc, such questions as the existence of a back-E.M.F., and the effect of superposing a small alternating current on the continuous current of the arc, being also considered in this connexion.

An Appendix which is mainly concerned with the mathematical aspect of photometry, and which also contains a list of the most recent papers on the electric arc, forms the concluding section of the work. A very copious index is also appended.

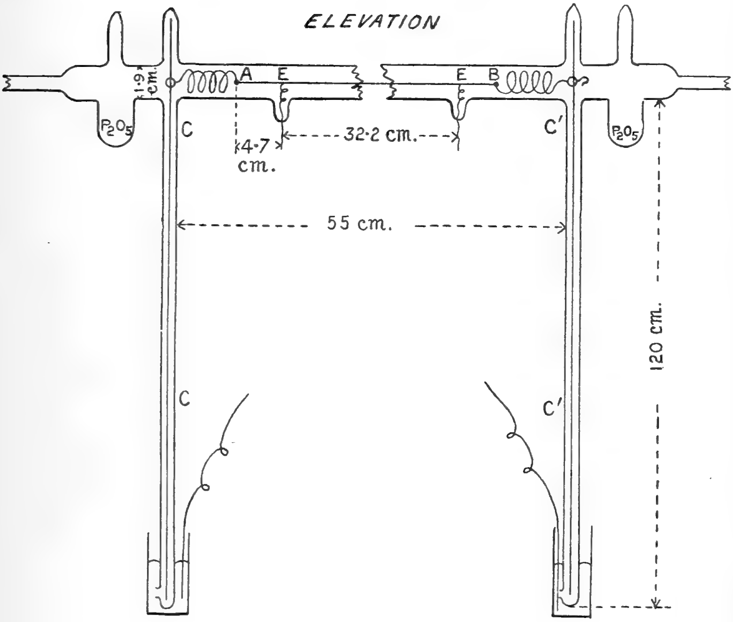
There is little that we have to find fault with in the book, but it may be pointed out that the chapter on the luminous efficiency of the arc emphasizes the need for a thorough revision of our system of photometric units, which at the present time are in a somewhat chaotic condition. Thus, although the useful term "luminous flux" is employed by Mrs. Ayrton, it is used in the same sense as "quantity of light." It would seem preferable to restrict this latter term, in accordance with Blondel's recommendation, to the time-integral of the luminous flux—a quantity which is of importance in photography, and for which "quantity of light" certainly seems to be the right term. The time seems ripe for the appointment of a Committee of Scientific Experts to deal with the question of nomenclature in photometry.

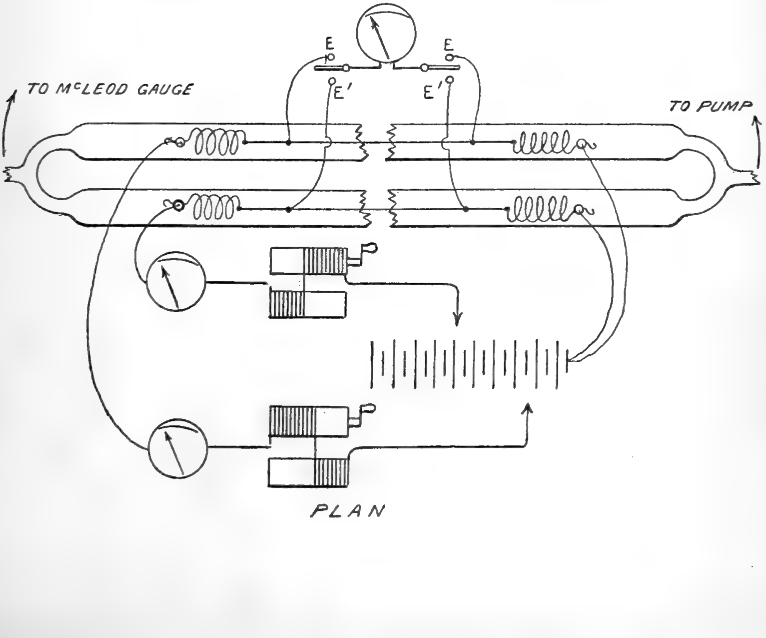
Le Phénomène de Kerr et les Phénomènes Électro-Optiques. Par EUGÈNE NÉCULCÉA. Paris: C. Naud, 1902. ("Scientia" Series, No. 16.) Pp. x+92.

THE title of this monograph, which forms one of the most recent additions to the excellent "Scientia" series now being brought out by Messrs. C. Naud, is somewhat ambiguous, if not misleading. By "Kerr's phenomenon" we generally mean the rotation of the plane of polarization due to the reflexion of polarized light from the pole of a magnet. This, however, is not the effect which forms the subject of the present memoir. The author studies another electro-optic effect, also discovered by Kerr—the double refraction produced by electric polarization of the medium. The very existence of this effect has been doubted by some physicists, who attributed the results obtained by Kerr to purely secondary causes, and not to electric polarization of the medium. In the light of more recent experiments, however, there seems to be no room for any further doubt, and the excellent *résumé* of both the experimental and theoretical investigations bearing on this subject contained in the present volume will be found most useful by physicists. The author gives an exhaustive bibliography of the subject, and references to various physical text-books in which it is dealt with. The book itself is divided into three parts: Part I. deals with experiments; Part II. with theory; and Part III. is devoted to theoretical considerations regarding the possible existence of a phenomenon analogous to the Zeeman effect in a magnetic field.

Phil. Mag. Ser. 6, Vol. 4, Pl. V.

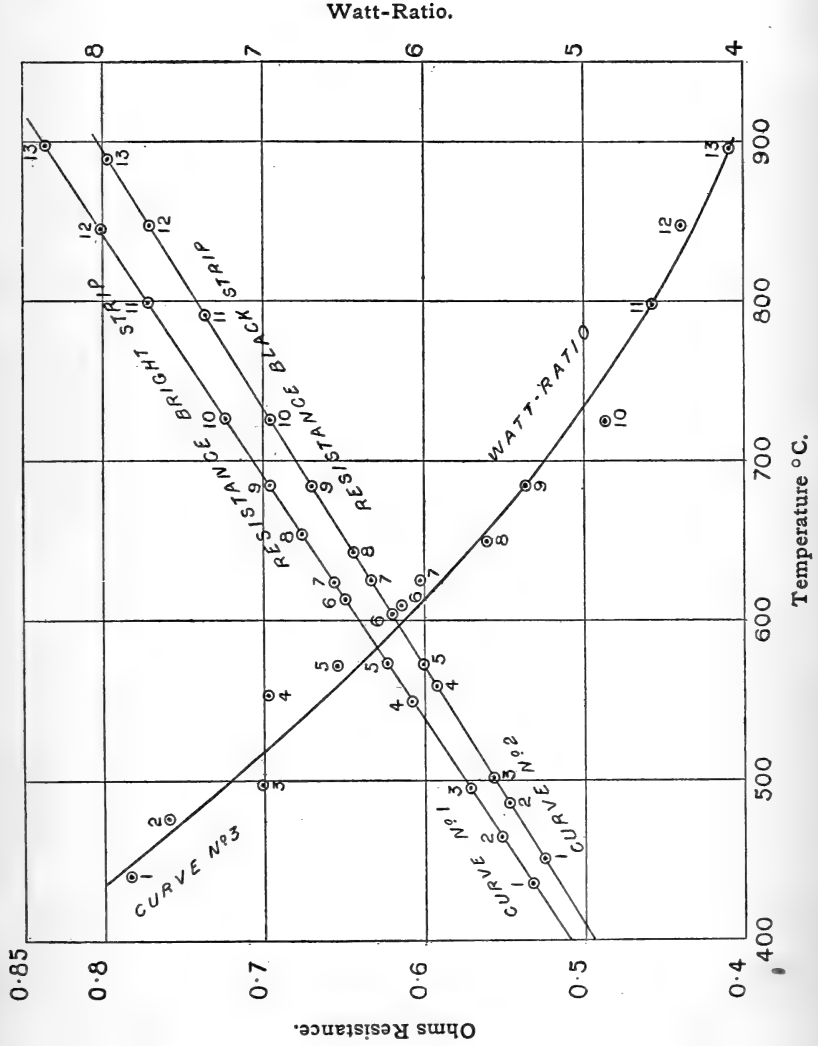
ELEVATION





PLAN

Phil. Mag. Ser. 6, Vol. 4, Pl. VI.



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LXX. *The Electric Origin of Molecular Attraction.*

By WILLIAM SUTHERLAND[*].

Introduction.

BY molecular attraction we understand intermolecular forces whose effects are not appreciable at distances of a larger order than molecular, thus excluding ordinary gravitation and ordinary electric and magnetic force. But the law of molecular attraction which I have discussed (Phil. Mag. [5] xxxv., xxxix., and other volumes), namely, that of the inverse fourth power, can be most readily accounted for by tracing it to the electric polarity which the electron theory of chemical valency necessarily ascribes to molecules, because the theory of magnetism familiarizes us with an inverse fourth power force between magnets at distances great compared with their lengths. In applying this known magnetic result to account for molecular attraction we are at the outset confronted with the difficulty that in the case of magnets the force is as often repulsive as attractive, the nature of the force depending on the relative direction of polarities in the magnets, whereas the molecular forces required to account for cohesion must be preponderatingly attractive.

We have to investigate how, if the electric axes of molecules are distributed at random, and repulsive forces would therefore seem to be as common as attractive, it is possible for the attractive so to prevail over the repulsive as to leave a final balance of attraction, as if on the average all the forces were

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[*] Communicated by the Author.

attractive. There is this fundamental distinction in the effects of attractive and repulsive forces whose strength decreases with increasing distance, that the attractive forces by their own operation tend to increase themselves, while the repulsive tend to decrease themselves. Consider, for example, a diatomic gas in which each molecule contains a single electric doublet formed by the opposite electrons holding its two atoms together. If two neighbouring molecules are approaching one another with their electric axes similarly directed in the straight line of relative motion, then the attractive force acts with strength increasing to the maximum possible value at the instant of collision. If their electric axes were oppositely directed in the line of motion the forces would be repulsive, and could reverse the motion before their maximum possible strength had been attained. In general there is the same tendency for attractive forces to increase their strength and for repulsive to diminish. This causes attraction to preponderate. The idea that molecular polarity might account for the inverse fourth power law of molecular attraction encouraged me when first investigating that law, though I failed to see how the attractive forces due to polarity could on the average be of more importance than the repulsive. It therefore seemed better at that time to work inductively at the accumulating mass of experimental material on molecular force, than to follow out a deductive theory of molecular attraction founded on molecular polarity, of which until recently we have had little convincing evidence. But with recent developments of the electron theory, which forces on our consideration electric doublets as a prominent feature in molecular structure, it becomes imperative to follow the deductive path. For if with Helmholtz we regard every chemical bond as consisting of a ♯ and a ♭ electron (Phil. Mag. [6] iii. Feb. 1902), we see that every junction of atom to atom involves the existence of an electric doublet ♯♭, analogous to a magnet and exercising on every other such doublet a force of attraction or repulsion varying inversely as the fourth power of the distance between them. The electron theory supplies us therefore with a true cause of molecular attraction on a very simple basis, namely, the inverse square law of electric force and the existence of the two sorts of electrons in equal numbers. The results to be interpreted in the light of the electron theory are contained in the following communications in the Phil. Mag.: series [5] "A Kinetic Theory of Solids," vol. xxxii., "The Laws of Molecular Force," xxxv., "The Viscosity of Gases and Molecular Force," xxxvi., "The Attraction of Unlike Molecules," xxxviii., "Further Studies on Molecular Force," xxxix., "The Fundamental Atomic

Laws of Thermochemistry," xl., "Molecular Force and the Surface-Tension of Solutions," xl., "The Molecular Constitution of Water," l.; and series [6] "Ionization, Ionic Velocities, and Atomic Sizes," iii. The scope of the present paper is outlined in the following Table of Contents :—

1. Statement of the theory, consideration of difficulties, and a short digression on the Maxwell-Faraday stresses in the æther and cohesion of the æther.

1*a*. The range of molecular force.

2. Comparison of results with known laws of molecular attraction.

3. Relation to Helmholtz's theory of chemical valence.

4. Period of rotation of an electric doublet.

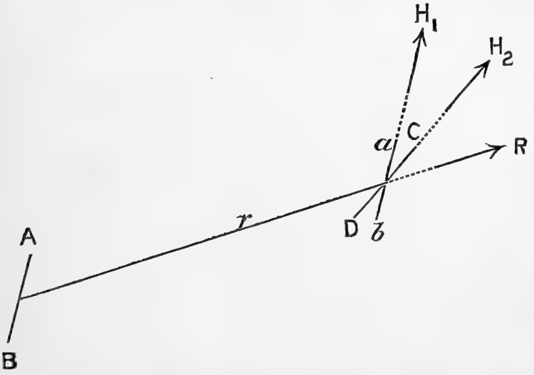
5. Electric doublets in different classes of chemical substances.

6. Molecular couples and gyrostats.

1. *Statement of the Theory.*

Briefly it is this :—That the electric doublets in molecules exercise mutual directive actions as do magnets, so that the nearer two neighbours approach the more do their electric axes tend to take the same direction, and therefore on this account they exercise a stronger attraction on one another; and also because attracting forces varying inversely as the fourth power of the distance produce motion which increases their strength, there are two causes which make the attractive forces amongst a number of moving doublets of more dynamical importance than the repulsive. To fix ideas we must look more closely into the system of forces between two magnets.

In Maxwell's 'Electricity and Magnetism' (2nd edit.) art. 387, we have Tait's results for the forces of magnets on magnets translated from quaternion into ordinary expressions. Let A B and C D be two magnets of moments m_1 and m_2 in



different planes with their centres at distance r apart. Through the centre of C D draw $a\,b$ parallel to A B, and let μ_{12} be the cosine of the angle between C D and $a\,b$, and λ_1, λ_2 the cosines of the angles made by A B and C D with r, then the action of A B on C D consists of forces R, H_1, and H_2 given by the equations

$$R=(\mu_{12}-5\lambda_1\lambda_2)3m_1m_2/r^4,$$
$$H_1=\lambda_2 3m_1m_2/r^4, \qquad H_2=\lambda_1 3m_1m_2/r^4;$$

and also of two couples one of which acts in the plane of $a\,b$ and C D with a moment $\sin(H_1H_2)m_1m_2/r^3$, where (H_1H_2) is the angle between H_1 and H_2 which the couple tends to increase, while the second couple acts in the plane of R and H_2 and tends to diminish the angle between these directions with a moment $\cos(RH_1)\sin(RH_2)3m_1m_2/r^3$.

The more important standard case for our present purpose is that in which the two magnetic axes are in the same plane with the join of the middle points of the magnets. This can be further simplified for the discussion of a typical case by assuming the two magnetic axes to be parallel with one another and making an angle θ with the join. Then the forces reduce to a central repulsion

$$-(2\cos^2\theta-\sin^2\theta)3m_1m_2/r^4, \quad . \quad . \quad . \quad . \quad (1)$$

and a component $2\sin\theta\cos\theta\,.\,3m_1m_2/r^4$ acting at right angles to the join. These latter rotational forces and the couples equilibrate one another if the two magnets are part of a rigid system. We shall neglect them for the present, and confine our attention to the central force. When $\theta=0$ this becomes $-6m_1m_2/r^4$, the minus sign denoting that it is an attraction; and when $\theta=\pi/2$ the force is repulsive of amount $3m_1m_2/r^4$. This well-known case of the attraction in one standard position being double the repulsion in another might lead to an erroneous conception of how attractive force might preponderate over repulsive. For example, we might determine the average force acting between two magnets as one moves in a quarter circle of radius r from $\theta=0$ to $\theta=\pi/2$, namely,

$$-\frac{2}{\pi}\int_0^{\frac{\pi}{2}}\frac{3m_1m_2}{r^4}(2\cos^2\theta-\sin^2\theta)d\theta=-\frac{3m_1m_2}{r^4}\cdot\frac{1}{2};$$

and imagine that, if a number of magnets or electric doublets direct their axes to parallelism, they will exert forces on one another which are preponderatingly attractive. It is important to expose the fallacy of this incomplete reasoning, because in doing so we can touch upon a matter germane to the present inquiry.

If the electric properties of matter are to be explained in terms of electrons, so also must the electric and magnetic properties of the æther. I have proposed to call the molecule of electricity formed in the æther by the union of the atoms ♯ and ♭ of electricity the neutron, and to denote it by ♮. In an electrostatic field we must suppose the electric axes of the neutrons so turned in the direction of the field that each has a positive component of electric moment in that direction. This acquisition of a common direction by the axes of the neutrons constitutes what is called the polarization of the æther regarded as a dielectric. The amount of the component electric moment is proportional to what Maxwell calls the electric displacement, which we can thus realize as a veritable displacement to be specified by an actual distance, namely, the component of the vector joining the centres of the two electrons in a neutron in the direction of the electric field. We thus come into contact with an important point in the dynamics of the æther bearing also on the subject in hand. We shall therefore glance at the problem: What is the virial of the forcive of a set of doublets uniformly distributed with parallel axes through any space?

Take a spherical shell of radius r and thickness dr, and take the ring cut out by cones whose axis passes through the centre parallel to the axes of the doublets, and whose semivertical angles are θ and $\theta+d\theta$; then if there are n doublets per unit volume, and if R denotes the central force between a doublet at the centre and any doublet in the shell, we have for the part of $\frac{1}{2}\Sigma\mathrm{R}r$ due to the doublets in the ring and at the centre, using the value of R given by (1), the expression

$$\frac{n}{2}\cdot\frac{3m_1m_2}{r^3}(2\cos^2\theta-\sin^2\theta)2\pi r^2\sin\theta\,d\theta\,dr=f(\theta)\,d\theta,\ \text{say};$$

and for the whole shell

$$2\int_0^{\frac{\pi}{2}}f(\theta)\,d\theta=0.$$

Thus the tendency is for the virial $\frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma\mathrm{R}r$ for all the doublets in a large space to vanish. Neither attractive nor repulsive forces predominate in the virial; and thus we see how it would not be correct to argue from elementary considerations that in parallel doublets uniformly distributed attractive forces could be assumed to preponderate.

Moreover, we see that if to the neutrons of the æther we apply Clausius's equation of the virial, as in the kinetic theory of matter, the production of an electrostatic field does not cause any variation of the virial of the internal forces. Now the Maxwellian specification of the Faraday stress in the æther, when acting as an electrostatic field of intensity F, is a tension $F^2/8\pi$ along the lines of force, and a pressure of equal amount in every direction at right angles. Thus the change of the external virial for a volume v occupied by neutrons is $-vF^2/16\pi$ on account of the tension, and $2vF^2/16\pi$ on account of pressure. But by Clausius's equation, if there are no other forces this must represent the change of the kinetic energy in volume v; so that we find half the energy $F^2/8\pi$, which Maxwell considers to be stored in each unit volume of the electrostatic field, is stored there as kinetic energy of the neutrons, if our simple conception of the action of the neutrons is correct. The other half of the energy must be that which has been put into the field in turning the electric axes of the neutrons so that they have all a positive component of moment in the direction of the field.

When the æther is not a field of force and the neutrons have their electric axes disposed at random, two cases will arise according as the neutrons have velocities of translation or not. If they have, then on account of the nearer approach of those attracting one another there will be a preponderance of attraction, which will give cohesion to the æther. If, on the other hand, the neutrons have no translatory velocities, but only rotate, then attractions and repulsions will act with the same strength, and there will be no cohesion in the æther on account of its neutrons. Having indicated how the principles of electric doublets must be applied to the æther as well as to matter, we had better now analyse some of the known laws of molecular force to test, before we proceed farther, whether they are compatible with an origin in the properties of electric doublets. But first to fix ideas we must interpose the following section.

1*a*. *The Range of Molecular Force.*

For the central force between two small magnets no range can be assigned, and similarly none can be specified for that between two electric doublets by themselves. But in considering a large number of such doublets we find conditions arise which practically fix the range of molecular attraction as a distance of the same order of magnitude as the average distance between two neighbour molecules. We have seen that there are two reasons for the preponderance of attractions over repulsions, namely, an effect analogous to induction by which two approaching doublets tend to pull one another's electric axes into the straight line joining their centres, and an effect due to the large departure from average conditions when a pair of neighbours collide. For example, two molecules A and B, separated by a large number of others, may have their axes so directed that they have the maximum mutual inductive effect and maximum attraction at that distance, but it will be possible to find near A a molecule C whose effect on B is nearly equal and opposite to that of A, and a molecule D near B which neutralizes the effect of B on A. But if A and B are on the point of collision it is not in general possible to find another pair C and D capable of neutralizing the mutual effects of A and B. For molecules whose distance apart is several times the mean molecular interval, the preponderance of the attractive over the repulsive forces diminishes rapidly with increasing distance. To take account of the average effect of this phenomenon we can replace the perpetually varying actual forces by a fictitious molecular attraction $f(r)/r^4$, in which $f(r)$ can be assigned a form which best represents the average facts, and introduces a fairly definite range beyond which molecular attraction is negligible. A speculation of van der Waals (*Ann. d. Ph. Beibl.* xviii. p. 734) suggests one form that $f(r)$ might conveniently have assigned to it provisionally. He assumes that molecules attract one another according to Newton's law of gravitation, but that the lines of force are absorbed by the medium in such a way that the potential energy of two molecules may be written $-fe^{-r/\lambda}/r$, where λ is a parameter characteristic of the substance and is equal to H/K, the ratio of Laplace's two capillary parameters. But we shall see immediately that molecular attraction has no direct connexion with gravitation. Moreover, the absorption of lines of force would be difficult to reconcile with the absence of any known gravitational property corresponding to the electric one of dielectric capacity. But van der Waals' factor $e^{-r/\lambda}$ becomes intelligible if taken as representing our $f(r)$. In the absence of knowledge as to the form of $f(r)$ perhaps the simplest way of taking account of it is to remove it and assume that the force $1/r^4$ acts from a distance $r=\nu$, where ν is of the order of the distance between contiguous molecules, up to a distance $r=\mathrm{L}$ and not beyond, L being so chosen that the effects due to distances greater than L are allowed for by exaggerating the effects up to distance L through treating the function $f(r)$ as 1. This simple method of treating the unknown $f(r)$ has the temporary advantage of agreeing with that which I have already adopted in investigating the law $1/r^4$ while providing a more definite meaning for L than that formerly suggested. In one place

I proposed that L might mark the linear dimensions of molecular swarms, but according to the present line of reasoning the idea of a molecular swarm gives place to that of a range limited to a small multiple of the average distance between two neighbours. Thus the range for an ordinary vapour would be different from that in its liquid. In steam over boiling water the average distance between neighbour molecules is about twelve times that in the water, but we cannot assert that because steam still shows measurable effects of molecular attraction therefore the range of molecular attraction in water extends to at least twelve times the distance between two neighbour molecules. The correct deduction according to the principles under discussion would be that in steam the range of molecular attraction must be taken to be about twelve times as large as in water. In the next section we shall introduce a great simplification by treating the range of molecular attraction as the average distance between two neighbour molecules, thereby expressing that attractions which eventuate in collisions are by far the most important of the forces we are now considering.

2. *Comparison of Results with known Laws of Molecular Attraction.*

It will now be shown that the laws of force so far discovered satisfy the conditions required by the electron theory. In the first place, although the force between two molecules was on the analogy of gravitation written by me in the form $3Am^2/r^4$, it soon appeared from its application to experimental data that $3Am^2$ ought to be regarded as a single parameter of molecular force $3a^2$ which had no direct dependence on the mass m of a molecule. This marks a strong contrast to the law of gravitation, and satisfies the first condition of the electron theory, namely, that molecular mass does not enter into the expression for molecular attraction. In the second place it has been proved (xxxviii.) that the force between two unlike molecules 1 and 2 is $3a_1a_2/r^4$, a_1 and a_2 being characteristic constants of 1 and 2. In the third place an almost direct proof of the electronic origin of molecular attraction is furnished by the law of the parameter a^2 for binary molecules of the type RS_n (Phil. Mag. [5] xxxix. pp. 25 & 45), namely,

$$a^2/n = (\rho/n + \sigma)^2, \quad \ldots\ldots \quad \text{(A)}$$

ρ and σ being parameters having definite values for each element R and each element S, because, to quote from the paper just referred to (p. 45), it "means that the mutual energy of two molecules of this type divided by the number of equivalents in each can be obtained by regarding each equivalent as a separate attracting entity." For if each pair of electrons forming a chemical bond attracts each other one, then in Clausius's equation of the virial if, neglecting for the present purpose external pressure, we write

$$\tfrac{1}{2}\mathrm{N}mv^2=\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma 3a^2r/r^4,$$

where the double summation $\Sigma\Sigma$ is to be effected for all the N molecules, we have really to sum for the electric doublets which produce the molecular attraction. In the first place, then, we have to evaluate $\Sigma 3a^2r/r^4$, where r represents the distance of any one definite molecule from any other, and the summation is to be effected for all molecules within a distance L. Now if there are n doublets in each molecule and α is the value of a appropriate to a doublet, this would take the form $n^2\Sigma\alpha^2r/r^4$, if each doublet were associated with a molecule entirely its own. But as there are n doublets in each molecule, it is clear that in general the parameter a cannot be equal to $n\alpha$. But there is an important exception to this, namely, when the axes of the doublets are all directed the same way, so that their moments are simply added together and then $a=n\alpha$. We shall see in section 5 that complex molecules show a tendency towards this state of identical direction in the doublets which they contain. But the case of the simpler types of binary compounds is one where considerations of symmetry do not favour the hypothesis of similarly directed doublets in the molecule. For example, the structure of $CaCl_2$ would be best represented by the formula ♭Cl♯Ca♯Cl♭, where the two doublets are oppositely directed. In the case of $SnCl_4$ we should expect the four doublets to be pointing from the centre to the corners of a regular tetrahedron. The collision of molecules carrying doublets directed in such ways as these can be regarded in the following manner. The circumstance chiefly directing the occurrence of attraction between two molecules is that the doublet in one which is nearest to a doublet in the other should have its axis in nearly the same direction as that of the latter. It is true that there are n^2 ways of arranging two molecules so that they may have a pair of doublets in the most favourable position for attraction. But out of every n chances which the n doublets give a molecule of being attracted by another only one eventuates in attraction, because it happens to be the strongest and ultimately leads to a collision. Thus on the average the attracting power of molecules containing n symmetrically arranged doublets each is only $n^2/n=n$ times that due to a single doublet. In this way the remarkable equation (A) may be explained. The attraction of such molecules depends on the number of equivalents in each in a way that points suggestively to the doublet origin of molecular attraction.

The most important point now is to determine the definite connexion between the electric properties of doublets and the experimental parameters of molecular attraction. If we write Clausius's equation of the Virial as adapted for the kinetic theory of N molecules in a volume v we have

$$3pv/2=\mathrm{N}mu^2/2+\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma \mathrm{R}r,$$

where the last term, which is the virial of the internal central forces R (different from Maxwell's R for magnets), includes the virial of the preponderating attractive force as well as that of the repulsive forces coming into play during molecular collisions. These latter give a virial proportional to the kinetic energy, so that the last equation may be cast in the form

$$pv=\mathrm{RT}vf(v)+v\phi(v), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $v\phi(v)$ represents two-thirds of the virial of the attractive forces, and R is now the usual gas constant. Now according to the law of attraction $3\mathrm{A}m^2/r^4$, or better $3a^2/r^4$, I have shown (xxxv.) that if the N molecules form a sphere of radius R (still another signification for R, but the context prevents confusion), and if b is a length of the order of the distance between neighbour molecules,

$$\begin{aligned}&\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma 3a^2/r^3\\ &\quad=6a\pi^2\frac{\rho^2}{m^2}\Big\{\tfrac{1}{3}(\mathrm{R}-b)^3\log\frac{2\mathrm{R}-b}{b}-\tfrac{2}{9}(\mathrm{R}-b)^3\\ &\qquad\qquad-\tfrac{2}{3}\mathrm{R}^2(\mathrm{R}-b)+\frac{\mathrm{R}^3}{3}\log\frac{2\mathrm{R}+b}{b}\Big\}, \quad . \quad (3)\end{aligned}$$

where ρ is the density of the substance formed by the N molecules.

But according to what we have stipulated about the origin of our preponderating attraction and the range of molecular force we can evaluate $\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma \mathrm{R}r$ in a far simpler manner. Let es_1 and es_2 be the electric moments of any two doublets, where e is the numerical value of the charge $\sharp$ or $\flat$ and s_1 and s_2 are the distances between $\sharp$ and $\flat$ in the doublets, then, if r denote the average distance apart of two neighbours which have their axes so directed as to attract one another with the maximum force at that distance, we may consider the total attraction in which these two take part at a given instant to be expressed on our magnetic analogy by $6e^2s_1s_2/r^4$, all other forces in which these two are involved cancelling one another. Thus, as in the theory of the viscosity of gases and molecular force (xxxvi.), we replace the almost intractable medley of nature by a simple representative pair of molecules. The part contributed to the first summation in the internal virial by this pair is $3e^2s_1s_2/2r^3$, which stands for $\frac{1}{2}\Sigma \mathrm{R}r$, and then

$$\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma \mathrm{R}r = 3\mathrm{N}e^2s_1s_2/2r^3.$$

In a homogeneous substance $s_1 = s_2 = s$, and we may write $r^3 = v/\mathrm{N}$, obtaining for the virial of the attractions $3\mathrm{N}^2e^2s^2/2v$.

The expression (3) may be written

$$6a^2\pi\,(\mathrm{N}^2/v^2)\,(4\pi \mathrm{R}^3/3)\,f\,(b/\mathrm{R}) = 6\pi f\,(b/\mathrm{R})\,a^2\mathrm{N}^2/v,$$

making it evident that a is proportional to es. The simplest way of comparing the results of the two methods of calculating the virial of the attractive forces, namely that which treats the attractions as operating between each molecule and all the rest within a sphere of radius R, and that which treats them as on the average acting only between immediate neighbours taken in pairs, is to calculate numerical values for $f(b/\mathrm{R})$ when $\mathrm{R}/b = 2$, 10, and 100, namely 0·60, 2·69, and 7·78, which give (3) the three values (0·94, 4·2, and 12·2) $a^2\mathrm{N}^2/v$. By increasing R from $2b$ to $100b$, that is by increasing the number of molecules included in the first summation of ΣΣ from 8 to 100,000, the value of the internal virial of the attractions is increased only 13-fold. This illustrates how the effect of molecular attraction depends mostly on the mutual actions of immediate neighbours, as we indicated in discussing the range of molecular force.

In the papers referred to, the internal virial term $v\phi(v)$ in (2) is proved for the element gases to take the form $-l/v$, while for compounds at small enough values of v it also takes the form $-l/2v$, passing at larger values of v through a very interesting transition to be discussed in section 5. In these communications values of l have been found for many substances, though mostly given indirectly by the tabulation of M^2l, where M is the molecular mass referred to that of the hydrogen atom as 1, and l is given for unit mass of the substance in terms of 10^{12} dynes as unit of force. Then, since l is $(2/3)\,6\pi f\,(b/\mathrm{R})\,\mathrm{N}^2a^2$ or $\mathrm{N}^2e^2s^2$, and if N refers to unit mass it is $1/m$ where m is the actual mass of a molecule, and so $N=1/Mh$ where h is the actual mass of an atom of hydrogen, the tabulated values of M^2l are really values of e^2s^2/h^2. But e/h is a standard electrolytic constant. Hence it follows that in investigating the laws of $(M^2l)^{\frac{1}{2}}$, as in some of the communications referred to, we were really studying the law of s the distance between $\sharp$ and $\flat$ in the doublets which form the chemical bonds. The electric theory of molecular attraction leads thus to the simplest possible physical interpretation of the parameters of molecular force, and invests their laws with a more immediate interest.

The best test to apply to the theory at this stage is to calculate the order of magnitude of s to see whether it is consistent with what we know of molecular sizes. The linear dimensions of molecules are of the order 10^{-8} cm., and of electrons (Phil. Mag. [5] xlvii.) of the order 10^{-14}, and these are limits for the size of s. Let us take the simplest type of binary molecule such as NaCl, for which the tabulated value of $(M^2l)^{\frac{1}{2}}$ (xxxix.) is 5·6, which is to be multiplied by 10^6 to give the value when the dyne is the unit of force. Now

$$es/h=(M^2l)^{\frac{1}{2}} \quad \text{and} \quad h/e=345\times10^{-17},$$

$$\therefore \quad \text{for NaCl } s=1{\cdot}93\times10^{-8}.$$

To determine the linear dimensions of the NaCl molecule we can proceed as for that of the Li atom in "Ionization &c." (Phil. Mag. [6] iii. p. 176) where the radius of the Li atom is found from its ionic velocity in water to be 2×10^{-9}. The volume of the Na atom is 7·4/2 times that of Li, and of Cl is 19/2 times (see Table III. of that paper), so that the mean radius of NaCl will be $(26{\cdot}4/2)^{\frac{1}{3}}\times2\times10^{-9}=7{\cdot}26\times10^{-9}$ cm. The diameter d of the NaCl molecule is thus found to be $1{\cdot}45\times10^{-8}$. The fact that we have found s a little larger than d indicates that we have overshot the mark in reducing molecular attraction so that it operates between only immediate neighbours at their average distance apart. But from the nature of the case we can expect to obtain only the order of magnitude of s, which is about equal to that of molecular diameters.

3. *Relation to Helmholtz's Electric Theory of Chemical Valence.*

It is of great importance in chemical dynamics that we should be able to find accurately the ratio of s to d in order to push farther with Helmholtz's theory that the chemical forces between atoms are identical with the forces between the electric charges constituting their valencies. Richarz

(Wied. *Ann.* lii.), to test this theory in the simplest concrete way, treats the dissociation of N_2O_4 into $2NO_2$ and of I_2 into $2I$ as the performance of work e^2/r against electric force for each molecule of N_2O_4 or I_2 dissociated, r being the distance apart of the charges ♯ and ♭ which hold the two parts of N_2O_4 or I_2 together. Richarz, assuming 10^{20} to be the number of molecules in a c.c. of gas at 0° C. and 1 atmo, and r to be 10^{-8}, finds for e a value agreeing with that derived from other sources. In order to make his results more definitely comparable with those of this paper, I will carry out his reckoning in the following manner:—Let μ be the mass of 1 c.c. of H_2 at 0° C. and 1 atmo, then the number of molecules in a c.c. of any gas under standard conditions is $\mu/2h$, and the work of dissociating such a c.c. of N_2O_4 is

$$W = \frac{\mu}{2h} \cdot \frac{e^2}{r} = \frac{\mu}{2}\left(\frac{e}{h}\right)^2 \frac{h}{r} = \frac{\mu}{2}\left(\frac{e}{h}\right)^2 \frac{1}{M} \cdot \frac{m}{r}.$$

But if ρ is the density of the molecule $m = 4\pi\rho r^3/3$, taking r to be its radius,

$$\therefore \quad W = \frac{\mu}{2}\left(\frac{e}{h}\right)^2 \frac{1}{M}\,\frac{4}{3}\pi\rho r^2,$$

$$W = 25 \times 10^6 \text{ ergs}, \qquad M = 92,$$
$$\rho = 92/49 \text{ (Phil. Mag. [5] xxxix. p. 7).}$$
$$\mu = {\cdot}0896 \times 10^{-3}, \qquad h/e = 345 \times 10^{-17}.$$
$$\therefore \quad r = 8{\cdot}8 \times 10^{-9} \text{ cm.}$$

We have followed the method of Richarz in identifying r, the distance apart of the charges, with the radius of N_2O_4. Strictly, according to our reasoning, the electrical work per molecule e^2/r ought to be written e^2/s, and the previous reasoning would give us an equation for r^3/s. But the important point at present is that the distance apart of the electric charges forming chemical valencies in molecules is found to be of the same order of magnitude as molecular diameters both from the electric theory of molecular attraction and from the simple cases to which Helmholtz's electric theory of chemical forces has been applied. Of course Richarz's simplifying assumptions require that when N_2O_4 is dissociated into $2NO_2$ the mass of gas should consist of a mixture of NO_2 ions, namely ♯NO_2 and ♭NO_2 evenly mixed and forming a conductor for any difference of potential. In the same way, when iodine is dissociated to the atomic state it ought to be a good conductor of electricity if Richarz's calculation applies to it. Now J. J. Thomson's experiments on the passage of electricity through hot gases (Phil. Mag. [5] xxix.) proved that the specific conductivity of gaseous iodine at about 1100° C. is about the same as that of glass at 300° C., and enormously less than that of ordinary electrolytic solutions. But the vapour-density measurements of Crafts and Meier show that at this temperature about a quarter of the I_2 is dissociated into 2I, and therefore if Richarz's simplifying hypothesis were true for iodine the conductivity ought to have been found enormously greater by J. J. Thomson than it was. Until this difficulty with I_2 and the corresponding one with N_2O_4 has been cleared up, we do not know what becomes of the electric charges which Richarz assumes to be separated, and are therefore not entitled to write e^2/r or e^2/s as the electrical work done in dissociating a molecule such as I_2 or N_2O_4. To account for the facts with iodine we shall have to assume a rearrangement of doublets rather than the splitting of them into separate electrons. Moreover, we have in Helmholtz's theory to take account of changes in the mutual potential energy of electrons and atoms in any change of relative positions caused by rearrangement of doublets. Therefore at present we must not attach too much importance to the agreement in order of magnitude between our s and Richarz's r as derived from Helmholtz's theory in a form which is the simplest possible and is apparently too simple for the facts of nature. There is obviously room for immediate further experimental and theoretical work in this interesting department.

4. *Period of Rotation of an Electric Doublet.*

If we carry out the Richarz simplification to one of its logical consequences we shall consider the two electrons of a molecule like NaCl, when giving the line spectrum of Na, to be revolving round one another with their relative path (perhaps entirely in the Na atom) a circle of such size that centrifugal force and electric attraction are in equilibrium. Let i be the inertia of an electron, then

$$\frac{iv^2}{s}=\frac{e^2}{s^2}\cdot\frac{1}{\mathrm{K}}=\frac{e^2}{s^2\mathrm{N}^2},$$

where K is dielectric constant and N index of refraction for NaCl (preferably perhaps for Na), and for the period of revolution we have

$$\frac{2\pi s}{v}=\frac{2\pi \mathrm{N} s^{3} i^{\frac{1}{2}}}{e},$$

with the values s of order 4×10^{-9}, $i/e=345\times10^{-17}\div500$ (J. J. Thomson), e of order 3×10^{-10}, and $\mathrm{N}=1{\cdot}5$, this gives a period 36×10^{-17}. It is worth noting that this period corresponds to a frequency 28×10^{14} which is about ten times as large as that of the visible part of the spectrum, and is nearly equal to the 33×10^{14} which in "The Cause of the Structure of Spectra" (Phil. Mag. [6] ii. p. 273) was found to be the value of a fundamental spectral constant denoted by $1/A=VB$, where V is the velocity of light in free æther and B the parameter in Balmer's formula, which Rydberg assumes to be a constant of nature in his modified form of it, namely $n=n_0-B/(m+\mu)^2$.

We shall now resume the study of the Laws of Molecular Force in the light of the electron theory.

5. *Electric Doublets in different classes of Chemical Substances.*

Before considering in some little detail the laws of $(M^2l)^{\frac{1}{2}}$, which are those of s, for different chemical types, we must discuss the remarkable contrast shown (xxxv.) between the characteristic equations of element and compound gases. For the element gases H_2, N_2, O_2 and also for the compound CH_4 the equation of van der Waals represents the experimental facts down to nearly two-thirds of the critical volume. It can be written

$$pv=RT+RT\frac{k}{2(v-k/2)}-\frac{l}{v}\cdot \quad \ldots\ldots \quad (4)$$

where the terms are respectively two thirds of the following, the virial of the pressure, the kinetic energy, the virial of the collisional forces, and the virial of the molecular attractions. For compound gases in general the type is

$$pv=RT+RT\frac{2k}{v+k}-\frac{l}{v+k}\cdot \quad \ldots\ldots \quad (5)$$

Ethylene was found to have an intermediate form of equation, and probably other substances could be investigated to show different stages of transition from (4) to (5). Evidently (5) could be made more general by replacing k in each of the three places where it occurs by a different parameter, but, as in xxxv., we will continue to use it in its more convenient simple form. When we contrast the collisional virial term for element gases $RTk/2(v-k/2)$ with $RT2k/(v+k)$ for compounds, we see that in the first case v is diminished by $k/2$, and in the second v is increased by k. Now, according to the kinetic theory, the $-k/2$ comes in because the molecular free path is shortened by an amount depending on the molecular radius on account of the mutual impenetrability of molecules. According to the kinetic theory $k/2$ stands for 4 times the volume of the molecules which occupy v. Then in compounds we must regard the $v+k$, which comes in instead of volume minus 4 times the actual volume of the molecules, to represent a lengthening of the mean free path, that is to say a diminution of the number of collisions. In the case of compounds then a collision is an event which, instead of shortening the interval between two successive ones from what it would be if the molecules could penetrate one another, actually prolongs it, so as not only to neutralize the term (-4 times volume of molecules) but to add on k. In ethylene we meet with a transition case where the negative term is only neutralized, and the collisional virial is RTk/v. In compounds in general then, a collision is an entanglement of the parts of the molecules which lasts long enough to produce an appreciable effect on the dynamics of the molecules, namely a diminution of the collisional virial below what it would be if the molecules collided like hard spheres.

But in the present connexion the contrast between the virials of the attractive forces in element and compound gases is most important. From $v=\infty$ to $v=k$ (nearly) in element gases it is $-l/v$, and in compounds $-l/(v+k)$. For volumes less than k the form for compounds is $-l/2v$. For compounds then we write the virial of the attractions

$$-\frac{l}{v+k}=-\frac{l}{v}+\frac{l}{v}\cdot\frac{k}{v+k},$$

and so see in it the general attractional virial $-l/v$ numerically reduced because a repulsional virial, which is a fraction $k/(v+k)$ of it, enters into the equation. When $v=k$ the fraction takes the value $\frac{1}{2}$, which it retains for smaller values of v, the virial then being $-l/v+l/2v=-l/2v$. Evidently then the entanglement during a collision of two compound molecules, which diminishes the virial of the collisional repulsive forces, introduces the virial $(l/v)\{k/(v+k)\}$ of repulsive forces of electrical origin.

We must briefly inquire into the probable cause of the contrast between the behaviour of element and compound gas-molecules during collision. In an element gas like H_2 we have ♯ attached to H, and also ♭ attached to H, whereas in a compound gas like HCl ♯ is associated only with H, and ♭ with Cl. We can imagine then that in H_2 or ♯H H♭ it is possible for ♯ and ♭ to change places so as to form ♭H H♯ without displacing the atoms, whereas in the case of ♯HCl♭

it is impossible to get the electrons to change places without the atoms doing so also. When NaCl is giving the spectrum of Na perhaps both ♯ and ♭ are in Na. In a compound molecule, then, an electric doublet has less freedom of motion than in the molecule of an element gas. On this account the collision of molecules of an element gas is a simpler event than that of compounds. Moreover, in all compounds but the simple binary ones there are several doublets in each molecule, and during a collision a variety of possible combinations of positions of the doublets will succeed one another, causing an alternation of attractions and repulsions, which leave a different average preponderance of attraction at close quarters than at a distance. Thus below volume k the preponderance of attraction is expressed by a virial $-l/2v$, and above k by a virial $-l/(v+k)$, which, when v is large, can be identified with the standard form $-l/v$. Now this contrast between the behaviour of compound and element gas-molecules at close quarters was verified in the Viscosity of Gases &c. (xxxvi.), where it was found that at close quarters the mutual potential energy of two compound molecules is only half of what it would be if they behaved as the molecules of element gases.

In this way I have sought to explain the most important difficulty in the way of the electric theory of molecular attraction, namely that the attractional virial for compounds appears in the form $-l/(v+k)$ instead of $-l/v$, which is required by the general theory. Previously (xxxv.) I suggested that this phenomenon in compounds might be due to the pairing of compound molecules. This explanation must be withdrawn to be replaced by that of molecular entanglement here suggested, an entanglement being only a temporary sort of pairing.

We proceed now with the investigation of the laws of s.

In the case of the haloid compounds of the alkali metals it was shown in "Further Studies" (xxxix.) that to $(M^2l)^{\frac{1}{2}}$, which is proportional to s, the metallic and halogen atoms contribute parts as follow :

Li.	Na.	K.	Rb.	Cs.	F.	Cl.	Br.	I.
2·4	3·5	4·6	6·0	7·3	0·9	2·1	2·7	3·6

For the Li family these can be written 1·2 (2, 3, 4, 5, 6), and for the F family 0·9 (1, 2, 3, 4). With the haloid compounds of the dyad metals of the Be family, we must remember that $(M^2l/2)^{\frac{1}{2}}$ now consists of a part F_s due to the halogen atom as given above, and a part $F_r/2$ due to the equivalent of metal, the latter having the values

Be.	Mg.	Ca.	Sr.	Ba.
2·1	2·7	3·2	3·7	4·2

which can be written 0·53 (4, 5, 6, 7, 8).

These simple laws for s lead to the following statement in regard to the Periodic Classification of the elements:—In successive columns the valency charges form the arithmetical progression e, $2e$, $3e$ and so on, while in the successive rows the values contributed by atoms to s, which is the other component factor of electric moment, form arithmetical progressions such as are exemplified above. In conjunction with these simple numerical relationships amongst the elements we must take the corresponding ones demonstrated in "A New Periodic Property of the Elements" and "The Cause of the Structure of Spectra" (Phil. Mag. [5] xxx. and [6] ii.). The volumes of the gramme-atom B of the alkali metals as given in "Further Studies" are subject to a simple numerical law, being given by

$$2+(n-1)n2{\cdot}7=2{\cdot}7\{(n-\tfrac{1}{2})^2+\tfrac{1}{2}\} \text{ nearly};$$

where n has the values 1, 2, 3 and so on, as the following comparison shows

	Li.	Na.	K.	Rb.	Cs.
B found ...	2·0	7·4	18·6	34·4	——
B calc. ...	2·0	7·4	18·2	34·4	56·0

The volumes of the gramme-atom of the halogens in compounds run as 1, 2, 3, 4. But in the Be family there is no such simple relation discoverable. But in "Further Studies" it was shown that the following relations hold approximately between F and B, namely in the Li family $F^2=0{\cdot}9B+4{\cdot}4$, and in the Be family $F^2/4=0{\cdot}9B+3{\cdot}0$. From formulæ just given we see that for the Li family a more accurate relation is

$$B=2+2{\cdot}7\,(F/1{\cdot}2-1)\,(F/1{\cdot}2-2).$$

For the uncombined metals the following results are established by Tables XXIX. and XXX. of "Further Studies." First that $(M/\rho)/M^2l$ or B/M^2l is the same for the members of one chemical family, and second that for families of different valency n the values of nB/M^2l are nearly 2·8, except in the case of the Be family, for which it is 2·0. Thus, then, for the metals we have the relation that e^2s^2 is proportional to the volume of the atom with which the doublet is associated. To assign a simple meaning to this formula let us assume a doublet in a metallic atom, and use for it the formula we used in calculating the period of rotation of ♯♭ in NaCl, namely,

$$\frac{iv^2}{s}=\frac{e^2}{s^2}\cdot\frac{1}{\mathrm{N}^2};$$

$$\therefore\quad e^2s^2=\mathrm{N}^2v^2is^3.$$

Now i is constant; and if Nv is constant for the metals, then $e^2s^2 \propto s^3$; and if s is equal or proportional to the linear dimension of the atom, the remarkable proportionality between e^2s^2 and volume of atom in the uncombined metals would be accounted for. It would seem as though the ♯ and ♭ in a metallic atom moved out till centrifugal force balanced electrical attraction, and so determined the linear dimensions of the atom. If we remember that N varies inversely as the velocity of light through the atom, the condition that Nv is to be constant makes the ratio of v the linear velocity of ♯ or ♭ to that of light through the atom constant, a result already made probable in the 7th section of "The Cause of the Structure of Spectra."

On passing from the simple cases of metals and binary compounds, where we are dealing with only a few regularly arranged doublets in each molecule, to typical organic compounds where the atoms are built up to molecules by means of elaborate ramifications of doublets, we must expect to pass through intermediate types, where the simplicity of the binary compounds is lost without being replaced by the other sort of simplicity which we may expect on account of the law of averages coming into play in the complex organic compounds. We had better then study the case of the typical complex organic molecule first. We must expect the doublets in such a molecule to exercise a mutual directive action on one another, so that the whole molecule may be considered to have an electric moment obtained in the following way. It is known that with a uniformly magnetized sphere the external field of force is the same as that of a small magnet at its centre with a magnetic moment equal to the intensity of magnetization multiplied by the volume of the sphere. Therefore for a number of magnetic spheres of different sizes uniformly magnetized with the same intensity the magnetic moment of each will be proportional to its volume. Now in a complex molecule we must on the average expect the doublets to arrange themselves so as to correspond as nearly as possible to the case of uniform magnetization. For the electric doublet I have already proposed the name neutron, so the proposal we are considering might be called that of an average uniform neutration in complex molecules or an approximation to it. The electric moment of such a molecule must then be proportional to its volume. But this is one of the main results obtained in "Further Studies," being expressed as follows at the end of section 1:—"As a subsidiary result, it has been shown that the attracting powers of the atoms of Cl, Br, I, O, S, N, and C (C unattached to H) are approximately proportional to their volumes in the combined state."

In the complex organic molecule the different atoms and radicals contribute to the limiting volume of the gramme-molecule parts which are, on the average, 10 times the part which they contribute to $(M^2l)^{\frac{1}{2}}$, l being the virial parameter expressed for a gramme of the substance with 10^{12} dynes as the unit of force. But the fundamental radical CH_2 has a limiting volume which is 19 times the part it contributes to $(M^2l)^{\frac{1}{2}}$. On the other hand, the two terminal hydrogen atoms of the paraffin molecule C_nH_{2n+2} seem to possess a ratio 4 instead of 10. For the great majority of gaseous compounds such as CO_2, SO_2, C_2N_2, and the simpler volatile liquids the ratio $B/(M^2l)^{\frac{1}{2}}$ is nearly 10. For a few such substances the ratio is small; thus for H_2O it is 6, for H_2S it is 7, and for NH_3 also 7. It is worth noticing that these are substances possessing remarkable powers of ionizing electrolytes. This power would thus seem to be due to a high intensity of neutration. In the case of electrolytes of the simplest binary type we have $B/(M^2l)^{\frac{1}{2}}$ ranging from 3·3 for LiF to 7·3 for RbI. On the other hand, the element gases H_2, O_2, N_2, and the compound CH_4 have values for this ratio near 19. Now when dissolved in water these are not electrolytes; and this fact would seem to be due to their small intensity of neutration. In these gases also the attractional virial is $-l/v$, molecular entanglement during collision is slight. Obviously then intensity of neutration and the related magnitude of electric moment of doublets are important physical properties of substances, requiring detailed study.

6. *Molecular Couples and Gyrostats.*

As to the couples which doublets like magnets exercise on one another, their chief action appears to be that of giving similarity of direction to the electric axes of neighbouring molecules. The question as to whether they may appear in a kinetic theory of solids will require special examination; but as molecular attraction in liquids is of the same order as in solids, and yet the rigidity of liquids is very small indeed, it would appear that molecular couples do not enter directly into the molecular theory of rigidity. But the existence of similarly directed electric axes in neighbouring molecules is suggestive of the existence of similarly directed axes of rotation in neighbouring molecules; and this would bring in gyrostatic properties of molecules as an element in rigidity. In "A Kinetic Theory of Solids" (Phil. Mag. [5] xxxii.) the ascription of independent kinetic energies in the directions of three rectangular axes amounts to the same thing as taking account of gyrostatic energy.

It is obvious that a logical deduction from the above principles must be the formulation of a dynamic theory of dielectric capacity in which electric doublets and molecular gyrostatic properties will play the most important part, and also the systematic development of an electrical theory of thermochemistry on Helmholtz's lines.

Melbourne, August 1902.

LXXI. *Note on the Vibration of Ferromagnetic Wires placed in a Varying Magnetizing Field. By* K. Honda *and* S. Shimizu[*].

It is well known that ferromagnetic bodies emit an audible sound at the moment of making and breaking the magnetizing current. Page[†] first heard the sound in the magnet, when an electric current passed through a copper spiral placed between the poles of a horse-shoe magnet. The sound was more intense at the break than at the make. A similar phenomenon was also observed by Delezenne[‡]. Marrian[§] placed iron and steel wires in a coil, and by making and breaking the magnetizing current, he heard a sound due to the longitudinal fundamental vibration of the wires. Matteucci[||] examined the effect of tension, and found that the pitch of the sound was independent of the tension, but that the intensity was decidedly increased. The investigation with iron bars of different lengths led Wertheim[¶] to the conclusion that each bar vibrated in its fundamental mode. By passing an intermittent current through the magnetizing coil, he heard a continuous sound, the pitch of which was the same as that

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[*] Communicated by the Authors.

[†] Page, Pogg. *Ann.* vol. xliii. p. 411 (1838); Wiedemann's *Electricität*, vol. iii. p. 838.

[‡] Delezenne, Pogg. *Ann.* vol. lxiii. p. 530 (1838).

[§] Marrian, Phil Mag. vol. xxv. p. 382 (1844).

[||] Matteucci, *Archives*, vol. v. p. 389 (1845).

[¶] Wertheim, Pogg. *Ann.* vol. lxxvii. p. 43 (1848).

of the make or break of the current. The thickness of the bar had no effect on the pitch of the sound. Non-magnetic bodies gave no sound under similar conditions. He then concluded that the vibration of the wire was produced by the magnetic change of length. Beatson* noticed a sound produced in a stretched iron or steel wire carrying an intermittent current. De la Rive † tried, not only bars of iron and steel, but also those of lead, zinc, bismuth, tin, antimony, platinum, gold, and silver. He placed these bars between the poles of an electromagnet and passed an intermittent current through them. They all sounded, the ferromagnetic metals producing sound with only the intermittent current through them, although there was no magnetizing field acting. The experiments with fine powders of several metals and powdered coke gave similar results. He ascribed the phenomenon to some molecular transposition. Ferguson ‡ and Ader § noticed similar phenomena with intermittent as well as alternate currents. Trowbridge ‖ found that nickel and cobalt also produced sound under similar conditions. In studying the effect of tension and compression on the intensity of sound produced in iron and nickel bars, Bachmetjew ¶ found that the effect was parallel to that of tension on the magnetic change of length. He thus concluded that the intensity of the sound is a function of the change of length by magnetization.

A short consideration of these results leads us to distinguish three kinds of the sound. The first is the combined effect of the magnetic force and the electric current. The sounds noticed by Page, Delezenne, and De la Rive belong to this category; they do not depend upon the magnetic property of the substance, but on the mechanical action produced by the magnetic force and the current.

The second kind of sounds accompanies the magnetization or demagnetization of a magnetic substance in making or breaking a magnetizing current. The sounds noticed by Marrian and others belong to this category. The cause of

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* Beatson, Electr. Mag. April 1846; *Arch. de Genève*, vol. ii. p. 113.

† De la Rive, Phil. Trans. i. p. 39 (1847); Pogg. *Ann.* vol. lxxvi. p. 270; *Arch. des Sc. phys. et nat.* vol. xxv. p. 311 (1866); Pogg. *Ann.* vol. cxxviii. p. 452; *Ann. de chim. et de phys.* [4] vol. viii. p. 305 (1866).

‡ Ferguson, Proc. Roy. Soc. Edinb. March 6, 1878; *Beibl.* vol. iii. p. 205.

§ Ader, *Compt. Rend.* vol. lxxxviii. p. 641 (1879); *Beibl.* vol. iii. p. 642.

‖ Trowbridge, *Beibl.* vol. iii. p. 289 (1879); Proc. Amer. Acad. vol. xi. p. 114 (Dec. 1878).

¶ Bachmetjew, Exner's *Rep.* vol. xxvi. p. 137 (1890); *Beibl.* vol. xiv. p. 537.

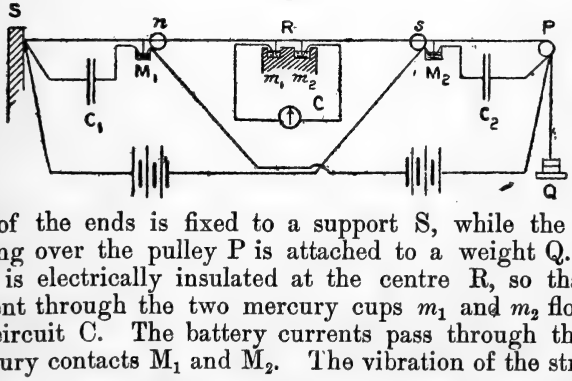
the sound is probably the change in length by magnetization. When a magnetic substance is suddenly magnetized or demagnetized it elongates or contracts, and attains its initial length, after several oscillatory changes in length have occurred in quick succession. This oscillation will produce a clinking note at the moment of magnetization or demagnetization. This view is favoured by the experiments of Marrian and Wertheim. But Matteucci found that the tension does not affect the pitch of the sound; if his result were true, the vibration would be of more complex nature.

The third kind of sounds is one accompanying magnetization by an intermittent or alternate current of a definite frequency, or one produced when the above-mentioned current is passed directly through the substance. The sound is probably caused by the continuous series of vibrations above referred to. The experiments of Beatson and others will agree with this view.

De la Rive and Wiedemann ascribe the phenomenon to the molecular effect, but Wertheim and Bachmetjew to the magnetic change in length. We also consider it highly probable that the change of length is the cause producing the sound belonging to the second and third categories. The present experiment was undertaken to get a clearer insight into the nature of the phenomenon.

In all previous experiments, the range of the frequency of an intermittent or alternate current was very limited; but in our case, a string alternator * was introduced for continuously varying the period of the current. The arrangement is shown in fig. 1. A copper wire is horizontally stretched; one of the ends is fixed to a support S, while the other passing over the pulley P is attached to a weight Q. The wire is electrically insulated at the centre R, so that the current through the two mercury cups m_1 and m_2 flows in the circuit C. The battery currents pass through the two mercury contacts M_1 and M_2. The vibration of the string is

Fig. 1.



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* K. Honda and S. Shimizu, Amer. Journ. Sci. vol. x. p. 64 (1900); *Phys. Zeitsch.* 2 Jahrgang, vol. xxv. p. 371 (1901).

maintained constantly oscillating by the electromagnet *n* and *s*. If the string is set in vibration with a single node at R, an alternate current is produced in the circuit C; if only one set of batteries is used, an intermittent current is produced in the same circuit. The frequency of alternation or of interruption can easily be varied by the change of length and of tension of the wire. C_1 and C_2 are two condensers with suitable capacity to diminish the sparks at the mercury contacts M_1 and M_2.

For the study of the longitudinal vibration of a ferromagnetic wire under a varying field, we used Professor Nagaoka's apparatus for the measurement of minute changes of length. In the present experiment, the glass fibre in the slit of the collimator was removed and the fine slit illuminated by a gas flame was used instead. The image of the slit, after reflexion by the revolving mirror and refraction through a converging lens, was formed in the field of a micrometer ocular. If the wire makes a rapid longitudinal vibration, its amplitude can be measured by observing the broadening of the image of the slit.

The wire to be tested was 21 cm. long and 0·150 cm. thick. The magnetizing coil was 30 cm. long and wound in 4 layers on a wooden frame, and gave a field of 19·82 C.G.S. units due to a current of one ampere. The coefficient of self-induction of the whole circuit was $5{\cdot}2 \times 10^6$ C.G.S. units and its resistance 12·9 Ω, so that the time of relaxation was 0·000403 second.

The results of experiments may be summarized as follows:—

(*a*) Wires of non-magnetic metals give no sound by an intermittent or alternate field of any frequency up to 200 per second.

(*b*) A ferromagnetic wire emits an audible sound in an intermittent or alternate field.

(*c*) The pitch of the sound is always the same as that of an intermittent or alternate current.

(*d*) The amplitude of vibration is in general far greater than the change of length produced by a steady field of such strength that it is equal to the maximum value of the intermittent or alternate field.

The pitch of the sound was determined by tuning a monochord to the period of the current and counting the number of beats. From the results above mentioned, we may safely conclude that the sound emitted by the ferromagnetics is due to the magnetic change in length of the wire. One make or break of the current forces the wire to accomplish a vibration, and a succession of such series constitutes a sound, the pitch of which is the same as that of the make and break. If this view be true, the pitch of the sound due to an alternate current must be double that of the sound due to an intermittent current for the same number of vibrations of the string alternator, because the magnetic change of length is independent of the direction of the field. By an actual experiment analogous to that of Lissajous, we found this inference to be verified. Our experiments also showed that the magnetic change of length occurs so quickly as to follow a rapid change of magnetization of as much as 150 reversals per second.

If the frequency be kept constant, the relation between the amplitude of vibration and the maximum field during one complete period of vibration is similar to the relation of the change in length to a steady field. The maximum field used in most of our experiments was 30·3 C.G.S. units. It is also to be observed that if an intermittent or alternate current is passed through a spiral of non-magnetic metals, an audible sound is produced. This is perhaps due to the periodic attraction of the currents flowing through the spiral in the same direction, and is of a quite different nature from the sound just mentioned.

Gradually varying the frequency of the intermittent or alternate current while the range of the field is kept constant, we observed the singular phenomenon that the amplitude of vibration passed through several maxima and minima. Two marked maxima and minima were observed in the case of a nickel wire. The phenomenon, which was principally due to the longitudinal vibration of the wire, was, to a certain extent, modified by the resonance of the system consisting of a reflecting mirror and two springs attached to it, and to the periodic vibration of the wire due to the magnetic change of length. The position of the maxima and minima were not, however, materially changed by the length of the wire or the tension of the springs. In the case of iron, the magnetic change of length for the same field strength was small, so that the phenomenon was not marked.

To study the phenomenon specially, we used another arrangement; the apparatus was the same as that used for the measurement of the magnetic change in length under constant tension. The wire to be tested was about 60 cm. long and 0·05 cm. thick; to the extremities of the wire, two copper wires of nearly the same thickness were soldered. It was hung vertically in the axial line of a magnetizing coil 80 cm. long, so as to lie nearly in a uniform field, and to its lower end was attached a weight. Near the same end, a thin rotating cylinder carrying a reflecting mirror was placed horizontally, and came in contact with the vertical wire at a suitable pressure. The working of the arrangement was the same as in the case above referred to.

The magnetizing coil was wound in 4 layers, and gave a field of 26·0 C.G.S. units due to a current of one ampere. The coefficient of self-induction of the whole circuit was $1{\cdot}66 \times 10^7$ C.G.S. units and its resistance 18·2 Ω, so that the time of relaxation was 0·00091 second.

With the above arrangement, we also found two marked maxima in the amplitude of vibration for iron as well as for nickel. The amplitude of vibration is plotted against the frequency of the current in figs. 2 and 3. In both cases, the maximum field during one complete period of vibration was 28·5 C.G.S. units, and the weight attached to the lower end of the wire was reduced to the tension per square millimetre.

Fig. 2.—Iron Wire. Length 59·6 cm.; Diam. 0·0405 cm.

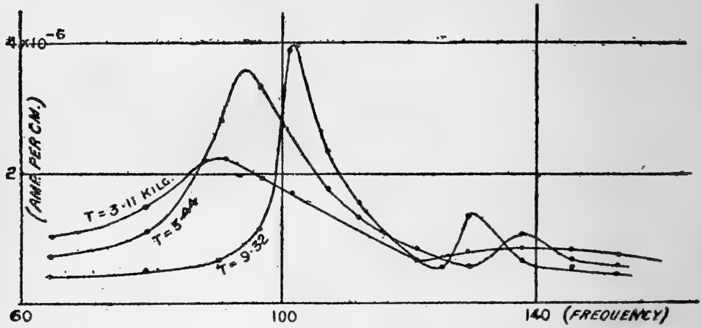
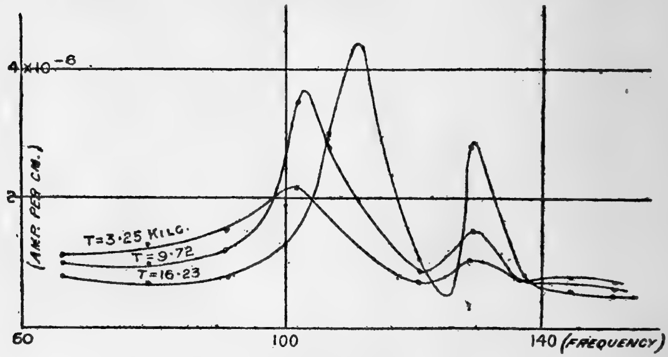


Fig. 3.—Nickel Wire. Length 60·3 cm.; Diam. 0·0396.



As will be seen from the figures, the amplitude of vibration and the frequency corresponding to the maximum amplitude increase with tension. By altering the length of the ferromagnetic wire, the positions of the maxima and minima are imperceptibly affected.

These positions of the maxima and minima do not coincide with those in the former experiment, the first maximum occurring at a little higher frequency, and the second at a considerably lower frequency. The first maximum is also of a frequency higher by at least 2·5 times than that calculated on the consideration that the phenomenon is due simply to the elastic vibration of the wire.

Instead of attaching a weight to the free end of the wire, the same end was stretched by means of a spiral spring fixed to the stand. Varying the frequency of the intermittent or alternate current, the maxima and minima of the amplitude of vibration were also observed, as shown in figs. 4 and 5.

Fig. 4.—Iron Wire.

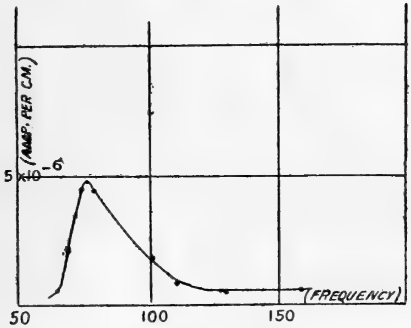
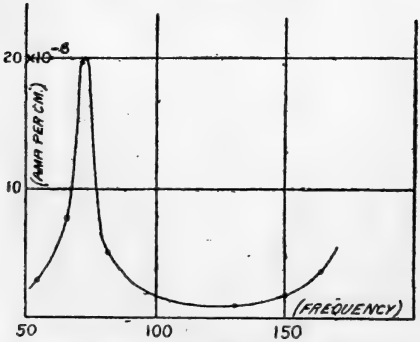


Fig. 5.—Nickel Wire.



In this case, the first maximum occurred at a frequency of about 75 per second for iron as well as for nickel, and the second at a frequency higher than 160 per second for these two metals. These positions of maxima and minima were almost independent of the tension and of the length of the spring.

Whether these complicated phenomena are capable of being explained simply by the elastic vibration and the magnetic change in length without taking account of the time lag, or whether they prove the existence of the time effect, requires further experimental and theoretical consideration.

Our best thanks are due to Professor Nagaoka and also to Professor A. Tanakadate for their kind guidance in carrying out the present experiment.

LXXII. *On the Electrical Properties of Thin Metal Films.*

By J. Patterson, *B.A., Professor of Physics, Muir Central College, Allahabad, India*; 1851 *Exhibition Science Scholar, Emmanuel College, Cambridge*[*].

Introduction.

THIS investigation was suggested by Longden's[†] experiments on the electrical resistance of thin films deposited *in vacuo* by the cathode discharge. From his experiments he arrived at the following conclusions:—

I. It was probable that the product of the resistance and the thickness of the film was not constant, but increased very rapidly with the decrease in thickness.

II. The temperature-coefficient of very thin platinum films was negative and within a certain range zero or negligible.

III. The effect of artificial ageing on the film was proportional to the magnitude of the temperature-coefficient.

Miss Stone[‡] had previously made some experiments on silver films deposited by the "Rochelle salt process," and had arrived at the conclusions: That the resistance of very thin films was much greater than the calculated resistance, and that heat decreased the resistance of the films, the rate of decrease being much greater for the thin films than thick ones.

Vincent[§] quite recently has made very careful experiments on the relation between resistance and thickness of silver films deposited from a silver solution. He found that the conductivity varied as the thickness down to 5×10^{-6} cm., and below this thickness the conductivity decreased very rapidly.

[*] Communicated by Prof. J. J. Thomson.

[†] Physical Review, vol. xi. p. 40 (1900).

[‡] Ibid. vol. vi. p. 1 (1898).

[§] *Annales de Chemie et de Physique*, [7] xix. p. 421 (1900).

Prof. Thomson[*] has shown that this variation of the resistance with the thickness may be explained by the corpuscular theory of electric conduction in metals. According to this theory the current is carried by negatively charged particles moving with a definite velocity under an applied E.M.F. These particles have the properties of a perfect gas, consequently they have a mean free path. When this mean free path becomes comparable with the thickness of the film it will be decreased, and consequently the resistance of the film will be increased. (This theory will be discussed more fully later.)

If, then, the point at which the resistance of the film becomes abnormal can be obtained, this thickness would be an approximate value for λ the mean free path.

The mean free path of the corpuscles in a number of metals has been determined by the author (Phil. Mag. June 1902) by measuring the change of resistance in the metal, produced by a transverse magnetic field.

It was hoped that the present investigation would furnish another and entirely different method of determining the mean free path.

Description of Apparatus.

The metallic films, which will be called simply films throughout the paper, were obtained by sputtering from a cathode *in vacuo* on glass strips. These strips were of ordinary glass about 1 mm. thick, 12 mm. wide, and from 4 to 7 cm. long. To ensure good contact between the electrodes and the film the ends of the strips were silvered for about 1 cm. with one of the ordinary silvering solutions. Owing to the surface-tension of the silvering solution the thickness of the silver deposit gradually increased from zero up to its full value. This ensured good contact between the silver and the film. The surface-tension also made the line of contact between the film and the silver curve at the edges, and thus made it difficult to measure the length accurately. This defect was overcome in the later experiments by cutting glass plates about 4 cm. wide and 20 cm. long. The sides were silvered as before, and then the plate was cut into strips of the desired width. Fig. 1 (p. 650) shows the plate with the sides silvered, and the dotted lines denote where it was cut. The two end pieces were rejected, and the others were all of a uniform length and the line of contact between film and silver was

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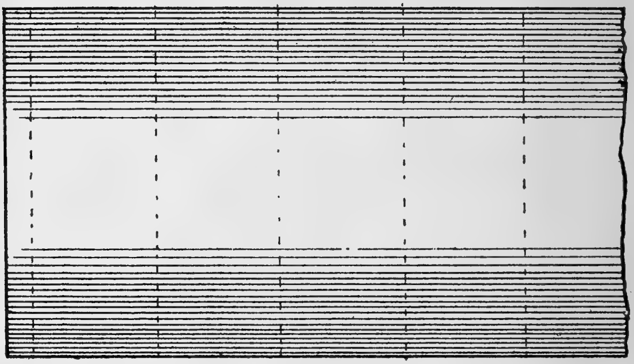
[*] Proc. Camb. Phil. Soc. vol. xi. pt 2, p. 119 (1901).

straight. Before the film was deposited on the glass the silvered ends were carefully polished.

Fig. 1.

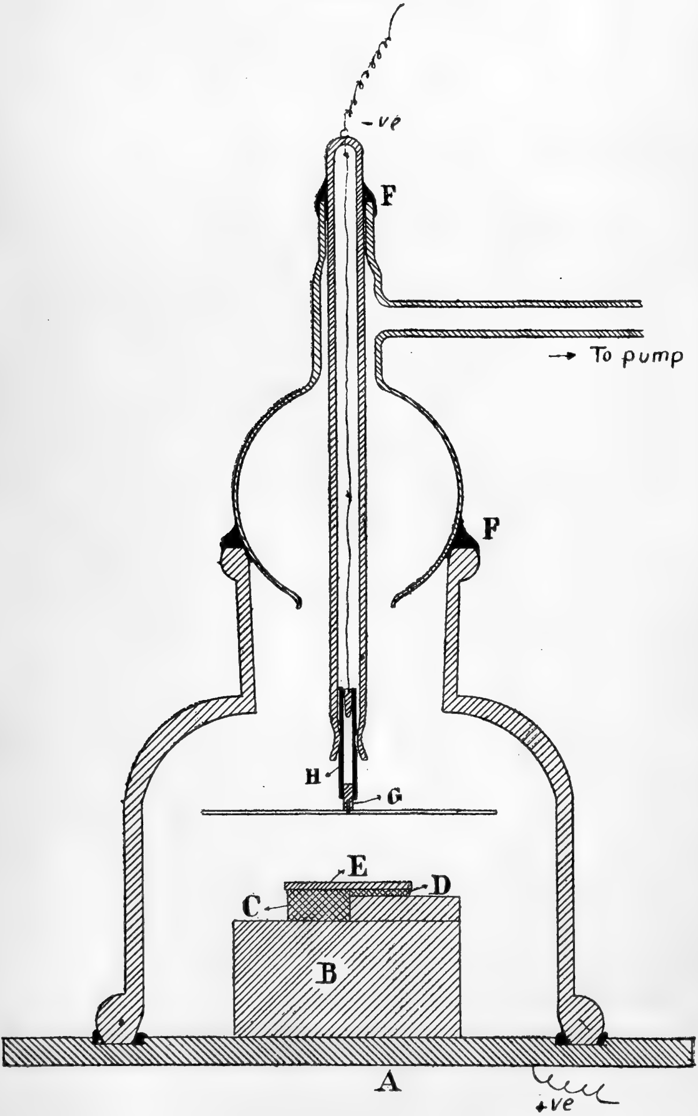


The apparatus used in depositing the films is shown in fig. 2. B consisted of a number of pieces of plate glass of such a height that the glass strip D, which rested on them, was at the proper distance from the cathode. C is a piece of optical glass so adjusted that its surface is in the same plane as that of D, while E is a cover-glass which could be shaken off when the proper conditions were obtained. The cathode was held in a horizontal position by means of the small rod G, which fitted tightly into the brass tube H. All the joints marked F were made air-tight with sealing-wax and were very satisfactory. The glass strips were put in and taken out by removing the base plate. The apparatus was connected to the pump and drying-bulb with compression tubing. This enabled the cover-glass E to be shaken off by tilting the jar.

The discharge was produced by an induction-coil with an Apps' interrupter. The jar was exhausted until the strip was in the negative glow and about 2 mm. from the Crookes's dark space. The discharge was then allowed to pass for some time and the exhaustion continued until the vacuum became constant. The cover-glass was then shaken off and the film deposited. It usually required from one to two hours to exhaust the bell-jar and deposit the film.

The distance of the glass strip from the cathode was usually about 15 or 20 mm. This seemed to be the most satisfactory distance, for if greater than this it was difficult to keep the vacuum constant long enough to deposit the film without a great loss of time in letting the discharge pass and exhausting until the vacuum became steady, and then no better results were obtained. If the distance was less than 15 mm. the vacuum was not carried far enough to produce the best results.

Fig. 2.



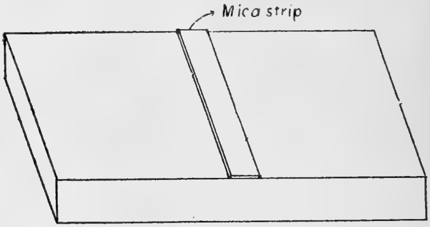
Method of Measuring the Thickness of the Film.

To determine the specific resistance of the films it was necessary to measure both their resistance and thickness as accurately as possible. As the films were too thin for their thickness to be determined by weighing, Wiener's * interference method was used. In determining the thickness by this method, the best optical glass had to be used to obtain any accuracy, and, moreover, in measuring the thickness the films had to be spoiled for measurements of resistance, besides, putting electrodes on the optical glass would spoil it, hence it was necessary to make two films at the same time, one on the optical glass C (fig. 2) for measuring the thickness, and the other on the glass strip D (fig. 2) for the resistance.

Since the cathode was at least 6 cm. in diameter, and as the glass strip and optical glass when placed side by side formed a square 25 mm. to a side, and were placed as nearly central as possible, it was assumed that the deposit was uniform over these surfaces. This was tested by depositing films on two pieces of glass and measuring their resistance. The results agreed closely enough to warrant the assumption.

The optical glass was about 25 mm. long and 12·5 mm. wide. A strip of very thin mica about 4 mm. wide was placed over the optical glass, as shown in fig. 3. This prevented the film from depositing on that portion of the glass.

Fig. 3.



When the films were deposited they were taken out of the bell-jar, and the optical glass was then replaced without the mica strip and another film deposited on it. By this means a metallic surface was obtained over the whole surface of the glass (fig. 4), and the part A was thicker than the part B by the thickness of the first film. The metallic surface also ensured that the change of phase of the reflected light would be the same at both parts A and B. A piece of optically plane parallel glass was placed over the metallic surface and

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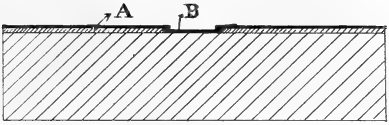
* Wied. *Ann.* xxxi. p. 629.

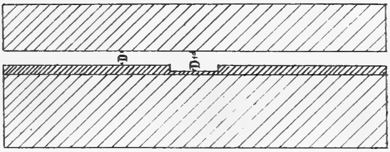
fastened with a little soft wax at the edges. When a beam of parallel white light was allowed to fall on this, interference-bands were produced by the thin air-film between the two plates.

Fig. 4.



As the air-film in one part was thicker than in the other by the thickness of the first film deposited, two sets of interference-bands were produced, one of which was displaced relatively to the other. By measuring the width of each band in the one set and the displacement of the corresponding band in the other set the thickness of the metallic film could be obtained. If D (fig. 5) is the thickness of the thinner air-film and $D+d$ the thickness of the other, and λ_n, λ_{n+1}, λ'_m, λ'_{m+1}, the wave-lengths extinguished by interference respectively in the thicker and thinner of the adjacent air-films, the indices of the λ's giving the order of the bands, then we have

Fig. 5.



$$2(D+d)=n\lambda_n=\overline{n+1}\,\lambda_{n+1}=\&c.$$
$$2D=m\lambda'_m=\overline{m+1}\,\lambda'_{m+1}=\&c.,$$

or from the three following equations which correspond to three interference-bands,

$$2(D+d)=n\lambda_n=\overline{n+1}\,\lambda_{n+1},$$
$$2D=n\lambda'_n,$$

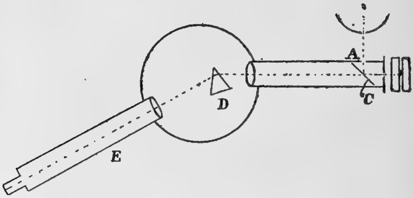
from which we have

$$d=\frac{\lambda_n-\lambda'_n}{\lambda_n-\lambda_{n+1}}\,\frac{\lambda_{n+1}}{2}=\alpha\,\frac{\lambda_{n+1}}{2}\quad.\quad.\quad.\quad.\quad.\quad(1)$$

That is, the number of band-widths λ_n is displaced towards the red end of the spectrum, gives a multiple of $\frac{\lambda_{n+1}}{2}$, which is the thickness required.

The displacement of one set of bands relatively to the other was measured with the spectrometer. The optical glass was placed in front of the slit of the collimator (fig. 6).

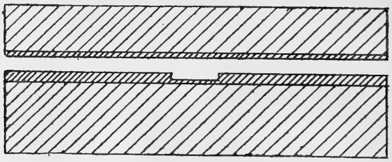
Fig. 6.



The line of junction of the two laminæ was placed so as to be perpendicular to the slit.

The light from a Welsbach entered the collimator through an opening A, and part of it was reflected by the glass mirror C through the collimator-slit, and fell at perpendicular incidence on the air-film. It was then reflected back through the collimator and glass prism D and viewed by the telescope E. Two sets of dark bands were thus obtained in the spectrum, one of which was displaced relatively to the other. By measuring the angular width of each band and the displacement of the corresponding band in the other set, the thickness of the metallic film was obtained from formula 1. The spectrometer was calibrated by means of known lines and a curve was drawn connecting wave-lengths and the angles of the graduated circle. From this curve the wave-length corresponding to any angle could be obtained.

Fig. 7.



The chief difficulty in measuring the thickness arose from the indefiniteness of the dark bands. By depositing a very thin film of metal on the cover-glass so that the interference-bands were obtained from the arrangement shown in fig. 7, the phase of the light was changed so that, instead of dark bands on a bright background, there were bright bands on a dark background. This gave greater distinctness to the spectrum, and enabled one to measure the thickness with greater accuracy. An example is given in Table I. of a set

TABLE I.—Determination of the Thickness of a Film.

Vernier readings.		Fraction of wave-length displaced.	Wave-length in μμ.	Thickness of film in cm.
First set of bands.	Displaced position.			
31° 53′	31° 48′			
31 17	31 12	5/72	4960	3·44 10^{-6}
30 48	30 44	5/58	5220	4·50
30 23	30 19	4/50	5490	4·39
29 57	29 54	4/52	5800	4·46
29 36	29 33	3/42	6090	4·35
29 12	......	3/48	6520	4·08
32 12	32 06			
31 38	31 32·5	6/68	4800	4·22
31 10	31 06	5·5/56	5020	4·93
30 44	30 40	4 52	5260	4·05
30 19	30 15·5	4 50	5540	4·43
29 56	29 53	3 5/46	5820	4·43
29 36·5		3/39	6080	4·67

Mean of 12 readings............4·33 10^{-6}.

of readings taken to determine the thickness of a film. Not all the measurements of the thickness of the films were as good as this. The greatest error occurred in the very thin films as the displacement was so small that it was exceedingly difficult to measure it. It was impossible to measure less than 2×10^{-6} cm. by this method.

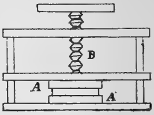
Measurement of Resistance.

The resistance was measured with a standard Wheatstone bridge. The resistance of the silvered ends was neglected as it was negligible compared with the resistance of the film itself. The length of the film between the silvered ends was measured with a cathetometer. Several methods of fastening electrodes to the silvered ends were tried. One method was to wind fine copper wire around the silvered end and then deposit copper electrolytically on the silver and copper wire to ensure good contact. This precaution was found to be unnecessary unless the films were to be heated or coated with paraffin. The electrodes represented in figs. 8 and 9 were also used.

Fig. 8.

Longitudinal Section.

Fig. 9.



End View.

Fig. 8 represents a longitudinal section through the electrodes, and fig. 9 an end view of one of them. A and A′ were copper plates with plane surfaces and carefully polished. The glass strip was tightly clamped between the plates by means of the screw B. These electrodes were very satisfactory, but they could not be used if the films had to be placed in oil or paraffin. Another form of electrode that could be used to advantage if the films were to be used as standards of resistance would be a rectangular metal cap, made so as to leave about a millimetre space around the glass strip, and fill this space with fusible metal. This form would ensure the best of contact, and, moreover, would be very strong.

Resistance of Bismuth Films.

The bismuth cathode from which the films were made was cast from the best commercial bismuth obtainable. The surface of the cathode was very carefully polished and scraped from time to time with a steel tool. A piece of mica was put on the back of the cathode. This seemed to make the film deposit faster, and also prevented the top of the jar and sides from getting covered with the deposit as quickly as they otherwise would.

The results obtained for a number of films are given in Table II. There appears to be an increase of specific resistance for the thicker films, but this was due to the surfaces losing their metallic lustre and becoming dull and powdery in appearance. On this account it was impossible to make bismuth films thicker than about 10^{-5} cm.

The resistance of the films gradually increased with the time, as is seen from the examples of three films (Table III.) whose resistances were measured every day for

Table II.—Resistance of Bismuth Films.

Number of film.	Time of deposit in min.	Dimensions of film in cm.			Resistance.	Resistance per cm. square.	Resistance per cm. cube × 10^6.
		Length.	Breadth.	Thickness.			
2	4	3·97	1·22	$3{\cdot}83 \times 10^{-6}$	666·5	204·8	784
3	5	4·23	1·25	4·76 ,,	579·7	171·3	815
5	8	3·90	1·17	6·70 ,,	468·7	140·6	942
13	8	3·95	1·25	7·46 ,,	416·2	131·7	983
6	10	3·9	1·15	9·94 ,,	435	128·3	1275
15	11	1·2	0·8	11·0 ,,	187·8	125·2	1375
14	15	1·2	0·6	15·6 ,,	196·4	98·2	1531
11	12	3·6	1·25	15·6 ,,	262·8	91·4	1423
10	16	4·05	1·3	17·1 ,,	220·4	70·74	1209

Table III.—Change of Resistance in Bismuth Films with Time.

Date.	Temperature. ° C.	Resistance of film.		
		A.	B.	C.
Mar. 16, 12 noon	......	390·00	345·5	
,, 18, 9.35 A.M. ...	12	405·1	359·7	545·2
,, 19, 12.10 P.M. ...	14	409·62	371·83	547·25
,, 20, 4.35 P.M. ...	13	411·30	373·33	552·47
,, 21, 3.40 P.M. ...	13	412·30	373·83	557·25
,, 26, 3.30 P.M. ...	13	418·40	378·65	571·80
Apr. 3, 3.00 P.M. ...	13	425·20	383·15	598·60
May 16	......	...	...	824·7

a short time. This was found to be typical of all the bismuth films. The rate of increase depended on the thickness of the film. The thinner the film the more rapid was the increase, and for very thin films it was hardly possible to measure their resistance on this account. In Table II. the resistances were all measured a short time after the films were deposited.

Longden * found that in the case of platinum the resistance decreased with the time, and that this decrease was more rapid if the films were heated, and with heating their resistance finally became constant.

Miss Stone † observed the same phenomenon for silver films deposited from solutions. It was hoped that by treating

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* Physical Review, vol. xi. p. 40 (1900).

† Ibid. vol. vi. p. 1 (1898).

the bismuth films in a similar manner their resistance would also be decreased. A number of films were heated in different oils and to temperatures from 40° C. to 70° C. The oil was carefully dried before the films were put in, but in every case they were destroyed.

A bismuth film was put into a glass tube having the electrodes sealed through the glass. The tube was exhausted as far as possible, dried, and then heated. The resistance of film before heating was 398·70 ohms. It was then heated for twenty-four hours to 70° C. and allowed to cool, the resistance was then 411·8. After heating for seven hours more to 110° C. its resistance was 439·7 ohms, and heating for four hours to 120° C. did not change its resistance, which was then 439·8 ohms. Its resistance was also measured while it was cooling, and the result indicated a negative temperature-coefficient. This was measured accurately and found to be −0 002.

This same film was kept sealed up in the tube and its resistance ten months afterwards was 438·4 ohms at the temperature of the room.

These results indicate that the gradual increase of the resistance of the films was due to the action of the air on them, and that when they were kept *in vacuo*, the resistance did not decrease with time or on being heated, but remained fairly constant.

Resistance of Platinum Films.

The cathode from which the films were deposited consisted of platinum foil fixed on a mica disk 5 cm. in diameter.

The resistances of the films were measured shortly after they were made. Longden* found that heating the films reduced their resistance, and if the heating was continued the resistance finally became constant. To test this two films were heated in a hot-air bath for several hours and their resistance measured before and after heating. This operation was repeated until the resistance became constant. The effect of heating on the resistances of the films is shown in Table IV.

From Table IV. it will be seen that the greatest fall in resistance occurs during the first heating, and that subsequent heatings have a comparatively small effect on the resistance of the films.

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* Physical Review, vol. xi. p. 40 (1900).

TABLE IV.—Effect of Heat on Platinum Films.

Time films were heated and temperature.	No. 20 Resistance.	No. 24 Resistance.
Initial resistance	14·84	51·90
Heated for 30 hours to 100° C. ...	10·52	33·30
,, 9 ,, more to 90° C.	10·322	32·115
,, 9 ,, ,, 100° C.	10·305	31·945
,, 60 ,, ,, 110° C.	10·05	28·66

Table V. gives the results obtained for a number of films. The resistances of the films were measured immediately after they were made. They were then heated for sixty hours in a hot-air bath to a temperature of 110° C. and their resistance again measured.

Duplicates on optical glass and glass strips were made in the cases marked with an asterisk. In some of the others two films were made at the same time on glass strips and the

TABLE V.—Resistance of Platinum Films.

o. of ilm.	Dimensions in cm. Length.	Breadth.	Thickness.	Time of deposit in min.	Resistance Before heating.	After heating 60 hrs. to 110° C.	per cm. square.	per cm. cube ×10⁶.	Res. pe cm. square × time of deposit.
19*	1·25	1·3	17·6×10−6	40	6·91	4·89	5·086	90	203
18*	1·15	1·25	10·4 ,,	25	7·94	6·84	7·43	77	186
20*	1·35	1·25	9·44 ,,	15	14·84	10·05	9·306	84	140
22*	1·1	1·25	5·49 ,,	13	14·37	11·50	13·06	72	170
23*	1·4	1·25	4·97 ,,	9	27·25	20·23	18·06	90	163
24*	1·2	1·25	3·02 ,,	6	51·90	28·66	29·85	90	179
30*	1·35	1·3	1·87 ,,	4½	71·17	54·50	52·48	98	236
31	1·25	1·25	1·66 ,,	4	76·87	58·46	58·46	97	234
38 A	1·1	1·3	1·41 ,,	3	102·05	49·73	58·77 }	81	176
38 B	1·15	1·3	1·41 ,,	3	101·80	49·61	56·08 }		178
40	1·2	1·35	1·17 ,,	2½	167·7	68·61	77·18	90	182
4 A	1·35	1·3	0·94 ,,	2	397	159·05	153·16 }	142	306
4 B	1·4	1·3	0·94 ,,	2	498	161·05	149·95 }		
1	1·05	1·05	0·7 ,,	1½	815·7	168·6	168·6	118	253
5 A	1·45	1·27	0·47 ,,	1	950·5	480·8	421·11 }	188	421
5 B	1·30	1·25	0·47 ,,	1	1082·5	393·4	378·34 }		378
6 A	1·15	1·3	0·36 ,,	45 sec.	1755	563·8	637·34 }	222	478
6 B	1·30	1·25	0·36 ,,	45 ,,	2150	623·0	599·04 }		449
7	1·15	1·25	0·23 ,,	30 ,,	32200	1341	1457·6 }	336	728
3	1·1	1·32	0·23 ,,	30 ,,	118500	1213	1461·1 }		730
9	1·25	1·30	0·16 ,,	20 ,,	...	3×10^6	$3·12\times10^6$	5×10^5	

resistance of both measured. These films are marked with the suffixes A and B. The greatest difference between the resistance of two films deposited at the same time occurs in 35 A and 35 B, where the difference amounts to 11 per cent. The least difference occurs in 34 A and 34 B, and amounts to 2 per cent. The films are, moreover, very thin, so that the agreement is fairly close.

If the specific resistance of the films is constant and the rate of deposition constant, then the resistance per cm. square multiplied by the time of deposit is a constant, and the thickness is directly proportional to the time of deposit. As will be seen from the last column in Table V. the product of the resistance per cm. square and the time of deposit varies very much for the thicker films. In the case of the thinner films or those deposited in a minute or less the product is too great to be accounted for by variations in the conditions, but it would seem to be due to a change in the specific resistance. There was no attempt to keep the conditions constant when depositing the film, so that the variation of the product of resistance multiplied by time of deposit for the thicker films was probably due to changes in the induction-coil, and, moreover, the films were not deposited in succession, so that this would also make a difference.

To obtain a rough approximation of the thickness of the films, which were too thin to be measured by Wiener's method, the average value of the rate of deposit per minute of the films whose thickness could be measured was taken, and the thickness of the others calculated from that and the time of deposit. The values of the thickness of all the films not marked with an asterisk were calculated on the above assumption.

The above results would indicate that the specific resistance is fairly constant for all thicknesses above 10^{-6} cm., and below this value the specific resistance changes very rapidly.

Another set of platinum films was made, and this time the conditions were kept as constant as possible. A new cathode 6 cm. in diameter of rolled platinum 1/10 mm. thick was used. The induction-coil, which gave a 6-inch spark, was adjusted to run very steadily. The films were deposited in succession, and the depositing apparatus was never taken off the pump for a longer period than was necessary to change the glass strips. It usually required about one hour to make a film. After the film was removed from the bell-jar in which it was made, it was put into a glass tube and protected from the air and dust. Four films thick enough to be measured by the interference method were made and their thicknesses measured.

After the films were all made they were put into a glass vessel. This vessel was exhausted as far as possible and dried ; it was then sealed off and heated for seventy-three hours to a temperature of 110° C. All the films were thus treated exactly alike.

The resistance of the films was not measured before ageing in order that they might be handled as little as possible. The values obtained for this set of films are given in Table VI.

Table VI.—Resistance of Platinum Films.

No. of film.	Dimensions of Film in cm.			Time of deposit in min.	Resistance			Res. per cm. sq. times time of deposit.
	Length.	Breadth.	Thickness.		After heating 73 hours to 110° C.	per cm. square.	per cm. cube $\times 10^6$.	
66 *	1·32	1·16	5·92 × 10^{-6}	10	16·58	14·57	86	146
75 *	1·32	1·18	4·92 ,,	7½	20·24	18·09	89	136
69 *	1·17	1·16	2·95 ,,	5	26·605	26·39	79	132
80 *	1·47	1·16	2·49 ,,	4	34·34	27·09	68	108
74	1·32	1·15	2·15 ,,	3½	39·69	34·59	74	121
64	1·50	1·15	1·85 ,,	3	55·19	42·31	78	127
76	1·34	1·20	1·69 ,,	2¾	50·71	45·41	77	125
68	1·18	1·16	1·53 ,,	2½	53·57	52·66	81	132
72	1·19	1·17	1·37 ,,	2¼	58·49	57·50	79	129
65	1·41	1·19	1·22 ,,	2	71·72	60·53	74	121
73	1·20	1·14	1·08 ,,	1¾	73·65	69·97	76	122
71	1·17	1·16	0·91 ,,	1½	88·85	88·08	80	132
78	1·46	1·11	0·77 ,,	1¼	128·5	97·69	75	122
67	1·38	1·12	0·62 ,,	1	102·2	82·94	51	83
77	1·51	1·14	0·46 ,,	¾	320·7	242·1	111	182
81	1·48	1·07	0·38 ,,	37½ sec.	564·8	408·3	155	255
70	1·18	1·18	0·31 ,,	30 ,,	579·3	579·3	179	290
82	1·18	1·05	0·26 ,,	25 ,,	1332·5	1185·6	308	494
79	1·43	1·09	0·21 ,,	20 ,,	3409	2598·4	546	866

The films are numbered in the order in which they were made. As far as possible a thick and a thin film were made alternately. The films whose thicknesses were measured directly are marked with an asterisk.

It will be seen from Table VI. that with the exception of the very thin films the resistance per sq. cm. multiplied by the time of deposit is fairly constant. No. 67, however, seems to be a very marked exception to the above, but as the time of deposit is the only means of knowing the thickness, it may be that the film was deposited in 1½ min. instead of

1 min., in which case the result would be in agreement with the others. It was impossible to make another film without making a complete set. The average rate of deposition of the four films whose thickness was measured directly is $0{\cdot}612 \times 10^{-6}$ cm. per min. The thickness of all the other films was obtained by multiplying $0{\cdot}612 \times 10^{-6}$ cm. by the time of deposit.

In fig. 10 time multiplied by resistance per cm. square is plotted against the time of deposit, and in fig. 11 the specific resistance for a given thickness against that thickness. These results confirm those previously obtained; that the specific resistance remains constant down to a thickness of less than 10^{-6} cm., and that the specific resistance becomes abnormal between 7·7 and $4{\cdot}6 \times 10^{-7}$ cm. Below this thickness the increase of resistance with decrease in thickness is very rapid.

Fig. 10.

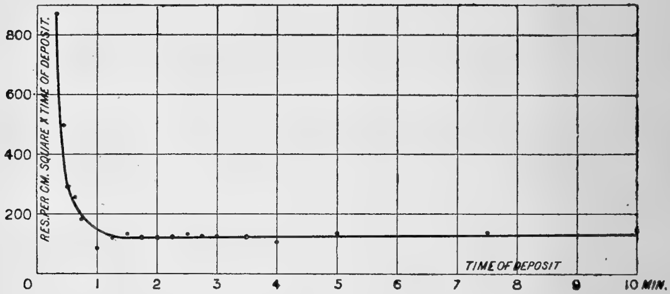
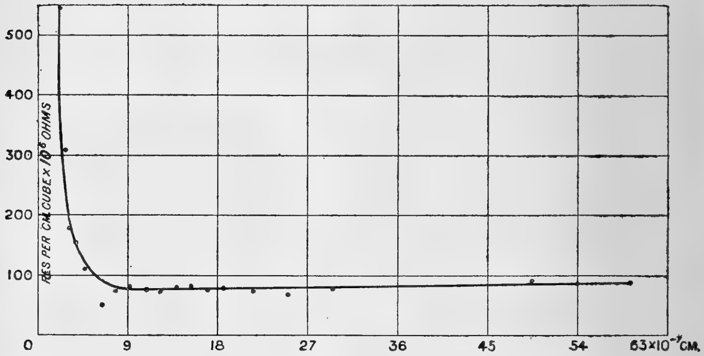


Fig. 11.



The effect of heating the films by an electric current was also tried. The current from an 8-volt cell was passed through a film $4{\cdot}38 \times 10^{-6}$ cm. thick, and having an initial resistance of 26·72 ohms per cm. square. After heating the film for some time by the above means the resistance was reduced to 12·06 ohms per cm. square. The resistance was not further reduced by heating with the current. Glass, however, would not stand the temperature to which the films were raised, so mica was used instead. The films deposited on mica were heated *in vacuo* by the electric current. They were found to stand a current-density from 1·0 to $2·0 \times 10^5$ amperes for a few minutes, and then only when the current was gradually increased. Putting the full current on at once destroyed the films instantly.

Two films were deposited on mica with resistances of 15·80 and 20·24 ohms respectively. They were heated *in vacuo* by the electric current, and the following results were obtained :—

1 ampere for 8 hours reduced resistance of 1st from 15·80 to 5·18 ohms.
1·2 amperes „ 20 „ more, resistance became 14·89 ohms.
0·4 ampere „ 8 „ reduced resistance of 2nd from 20·24 to 15·77 ohms.
0·6 „ „ 20 „ more, resistance became 8·88 ohms.
0·6 „ „ 24 „ „ „ „ 8·98 „

The first film had a resistance of 1·79 ohms per cm. square when it was least, and the second 2·62 ohms per cm. square. The thickness of these films was not measured, but the specific resistance would be about 30×10^{-6} ohms per cm. cube.

These results show that the final specific resistance of the films depends on the treatment that they receive. It was impossible to reduce the resistance of the films to that for ordinary platinum.

These results also show that heating the films with the electric current has a much greater effect than heating in an air-bath. This is most likely due to the higher temperature to which the films are raised in the former case.

The temperature-coefficient of a number of the films was also measured. They were heated in an air-bath to about 50° C. or cooled down to 0° C., the temperature of the room being about 15° C. The temperature-coefficients for a number of the films are recorded in Table VII.

Table VII.—Temperature-Coefficient of Platinum Films.

Number of film.	Thickness in cm.	Resistance per cm. square.	Temperature-coefficient.
66	$5·92 \times 10^{-6}$	14·57	0·00049
64	1·85 „	42·31	0·0005
77	0·46 „	242·1	0·00033
81	0·38 „	408·3	0·00024
82	0·26 „	1185·5	0·00027
79	0·21 „	2598·4	0·00011

Longden* found that films having a resistance of 53 ohms per cm. square had a temperature-coefficient of −0·0003. This is somewhat smaller than those obtained for films of about the same resistance. In the above table all the coefficients are positive and too large to be negligible. Longden found, however, that for resistances from about 670 to 14000 ohms per cm. square the temperature-coefficients were negligible or zero, and above this they were negative. Moreover, he found that the artificial ageing of the films depended very much on the temperature-coefficient, and that if the temperature-coefficient was negligible there was very little if any artificial ageing required. From Table V. it will be seen that in the experiments described in this paper, there was a very great decrease in the resistance of the films on heating, and that the greatest decrease occurred in those films which came within the limits of Longden's results, for no temperature-coefficient and no ageing. Longden used the Wehnelt interrupter on his induction-coil, and it may be that the rapidity with which the films are deposited has a very marked effect on the results. It is more probable, however, that the different results are due to different degrees of purity of the cathode. It is well known that a very small amount of impurity has a very marked effect on the resistance of platinum and the temperature-coefficient. Owing to the exceedingly small quantity of metal in the films a very small amount of impurity in it could cause all the difference. Besides, the rate at which the impurity is disintegrated from the cathode may be very much greater than for the platinum itself (Recent Researches), and consequently the amount of impurity in the film would be greater than that in the cathode.

Resistance of Silver Films.

The silver from which the films were deposited was not chemically pure although the amount of impurity in it was very small.

Silver deposits very rapidly in the cathode discharge so that it was very difficult to get a film. The films were often crystalline in appearance or powdery so that they rubbed off the glass ; this was especially true of the thicker films. By letting the induction-coil run very lightly so that the deposit was slow very good films were obtained. The depositing apparatus was exhausted until the dark space was about half way between the cathode and the glass strip. This degree of exhaustion was found to be better for the silver films than exhausting until the dark space just reached the glass strip.

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* Physical Review, vol. xi. p. 84 (1900).

A few films were made and their thickness and resistance measured. They were then heated *in vacuo* for ninety hours to a temperature of 90° C., and their resistance again measured. The results obtained are given in Table VIII.

TABLE VIII.—Resistance of Silver Films.

No. of film.	Dimensions of film in cm.			Resistance			
	Length.	Breadth.	Thickness.	Before heating.	After heating 90 hours to 90° C.	per cm. square.	per cm. cube $\times 10^6$.
85	1·38	1·07	5·72 10^{-6}	2·339	1·561	1·210	6·9
88	1·89	1·04	5·75 10^{-6}	3·080	2·538	1·397	7·9
86	1·45	1·06	8·92 10^{-6}	2·588	1·892	1·383	12·0
84	1·96	1·1	......	1·852	1·410	0·791	

The specific resistance of film No. 86 appears considerably greater than that for the other films, but this was most probably due to the crystalline structure of the film which was lacking in the others.

It will be seen from Table VIII. that heating has a considerable effect on the resistance of the films, although probably not so much as in the case of platinum. Film No. 85 was heated *in vacuo* by the electric current for 4½ hours with 0·5 ampere, and then for 2 hours with 0·75 ampere, when the resistance became 2·068 ohms. In this case the electric current increased the resistance instead of diminishing it. These results are sufficient to show that in silver, as well as in platinum and bismuth, the specific resistance is much greater than for silver in bulk, and consequently these experiments were not pursued further.

Some thick silver films were also made by depositing the silver from the solution known as Common's silvering solution *.

The films were thoroughly dried and their resistances measured. They were then heated, one *in vacuo* by the electric current, and the other in a hot-air bath, while the third was left exposed to the air. Table IX. (p. 670) exhibits the effect of heat on these films.

The resistances were measured at the temperature of the room, and a slight change in that would account for the small difference obtained in the second case. It would seem from

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* Proc. R. I. vol. xiii. (1890–92).

TABLE IX.—Resistance of Silver Films.

Treatment of film.	Resistance of film.	Resistance per cm. square.
Initial resistance of No. 1	0·3766	0·157
Heated *in vacuo* 30 hours to 85° C.	0·3875	
No. 2 initial resistance	0·2533	
After 4 days without being heated	0·2530	0·1163
No. 3 initial resistance	0·2828	0·1169
Heated *in vacuo* with electric current for 4½ hours with 0·5 ampere, and 2 hours with 0·7 ampere	0·3240	

the first two that heating had very little effect on the resistance except that it increased the resistance when heated by the electric current.

The thickness of these films was also measured roughly, and showed that their specific resistance would be the same as that obtained by Vincent*, namely, $2·4 \times 10^{-6}$ ohms per cm. cube. These experiments were not pursued further.

The Change of Resistance of the Films produced by a Magnetic Field.

The change of resistance produced by a magnetic field on a few films was also measured. The apparatus was the same as that used by the author † in the experiments on the change of the electrical resistance of metals when placed in a magnetic field. The method is briefly as follows:—Three other resistances nearly equal to the resistance of the film were made, and the four connected in the form of the Wheatstone-bridge. The bridge was balanced by placing one of the arms in multiple arc with a variable resistance. A very sensitive D'Arsonval galvanometer was used. The films of bismuth and platinum were made by sputtering from the cathode *in vacuo*, while the silver films were deposited chemically from Common's silvering solution.

The resistance of the silver films was increased by slotting them, as shown in fig. 12.

The platinum films were heated *in vacuo* until their resistance became constant. They were treated exactly like the films whose resistances were measured. Their thickness was not measured, but they were thick films. The results for the

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* *Annales de Chimie et de Physique* [7] tome xix. p. 494 (1900).

† Phil. Mag. June 1902.

bismuth films were given in a note communicated to the Cambridge Philosophical Society*, and are given here for completeness. The results are given in Table X.

Fig. 12.

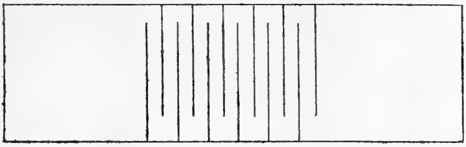

TABLE X.—Change of Resistance in Magnetic Field.

Film.	Thickness in cm.	Resistance.	Magnetic field.	$\frac{\partial\sigma}{\sigma} 10^4$.
Bismuth ...	1×10^{-5}	58·04	26200	27·0
			27300	31·0
	6×10^{-6}	103·05	26200	5·3
			27300	5·9
	4×10^{-6}	968·7	26200	1·0
Platinum ...	...	...	24400	0·35
Silver.........	...	...	24400	1·0

Comparing these results with those obtained by the author† for the change of resistance produced by the magnetic field, it will be seen that in platinum and silver the values are slightly greater for the metal than for the film, but they are of the same order in both cases. In bismuth films, however, the change is very small compared with the change in the metal, and the magnitude of the change decreases very rapidly with the decrease of thickness.

Contact-Difference of Potential.

The contact-difference of potential between the film and the cathode from which it was deposited was measured. The film and cathode were each connected to one pair of quadrants of a quadrant electrometer. All connecting wires were carefully screened with conductors connected to earth. The film and cathode were placed about 1 cm. apart, and the air between the plates ionized by Röntgen rays. The electrodes took up the potential-difference in a few seconds, but the rays were left on until the electrometer remained steady. Using the bismuth cathode and a film deposited from it, a contact-difference of potential of 0·034 volt was obtained, the film being

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* Proc. Camb. Phil. Soc. vol. xi. pt. 2, p. 117.

† Phil. Mag. June 1902.

positive to the cathode. In platinum, however, the results varied considerably. The cathode, after being used for some time, was tested against a freshly deposited film and gave a difference of 0·047 volt, the film being positive to the cathode. After carefully polishing the cathode and depositing some more films from it, these were tested against the cathode, and a difference of 0·15 volt was obtained, but this time the cathode was positive to the film. The cathode and film were next put in a weak solution of platinic chloride, and they then gave a difference of 0·09 volt, the cathode being positive to the film. The film, which was at first positive to the cathode, was again tested about a month afterwards with the freshly polished cathode, and this time it was negative to the cathode and gave a difference of 0·015 volt.

Photo-Electric Effect and Radiation from Hot Films.

Experiments were made to see whether there was any difference between the rate at which the cathode and the film deposited from it discharged electricity under the influence of ultra-violet light, but no difference was detected.

Experiments were also made to see whether it was possible to get negative radiation from hot platinum films *in vacuo*. The films were deposited on mica and electrodes clamped on the ends. The film was heated by a steady current from a number of accumulators which were insulated. The film was charged to a known potential. The leak was observed between the film and an insulated electrode which was placed above it. The electrode was connected to one pair of quadrants of a quadrant-electrometer, the other pair being earthed. It was not possible to heat the film hot enough to get the negative radiation, but the positive radiation was obtained. The positive leak increased very rapidly with the increase of current through the film, but did not reach a maximum when the film broke down. Table XI. shows the

TABLE XI.—Radiation from Hot Pt. Film.

Current in amperes through film.	Potential on film in volts.	Time of 200 div. on electrometer scale.
0·5	+40	no leak.
0·6	”	”
0·72	”	530 sec.
0·81	”	80 ”
0·93	”	9 ”
1·0	”	8½ ”
1·1	”	1¾ ”

connexion between the current through the film and the positive leak.

These experiments were not pursued further since they show that owing to the large radiating surface, the film would not stand temperatures high enough to give negative radiation.

Change of Phase of the Light Reflected from a Platinum Film.

Duplicates of the platinum films given in Table VI. were deposited on mica thin enough to give interference-bands in the spectroscope. One half of the mica was covered with another thin sheet so that no metal could be deposited on that half while it deposited on the other part. This mica was then placed before the slit in a collimator of a spectroscope with the metal side away from the aperture. Two sets of bands were thus obtained, one due to the reflexion from the mica-air surface, and the other from the mica-metal surface. The displacement of the bands due to the change of phase at the mica-metal surface was towards the red end of the spectrum.

With the very thin films the displacement was very small, but increased rapidly with the thickness up to its full value and then became fairly constant.

Theoretical Considerations.

The films of the three metals—platinum, silver, and bismuth—deposited *in vacuo* by the cathode discharge, all have their resistance considerably higher than the value calculated from the specific resistance of the metal. A number of films were examined under the microscope but no discontinuity could be observed. Reducing the width of the film did not affect its resistance per cm. square, and, moreover, the effect of the electric current on the platinum films would tend to increase rather than to diminish any discontinuity that might exist. The experiments would show that the thickness was fairly uniform, and would not vary by more than a small fraction of the average thickness.

Small quantities of many different gases are present in a vacuum-tube, hydrogen and mercury vapour being always present unless very special precautions are taken to get rid of them. Most metals absorb gases to a greater or less extent, platinum especially absorbs a good deal of hydrogen. It may be that from the manner in which the films are deposited a good deal of gas is absorbed by them, but the amount is so small that it would be impossible to detect it. Lord Kelvin[*] has shown that a platinum plate which has absorbed hydrogen is electro-positive to one that has not, while if it has been kept in oxygen for some time it is electro-negative to the standard. In the experiments on the contact-difference of potential the film was positive to the platinum cathode when the cathode was old, but negative when it was polished, so that these experiments would not indicate whether the gas was absorbed by the film or not. It is not known just what effect the gas in the depositing apparatus has on the disintegration of the cathode by the discharge, but that there is some effect is seen from the fact that aluminium which sputters very little in air does so very freely in helium and argon.

The condition of the surface of the cathode has also a considerable effect on the rate of deposition, at least, of the film. After the cathode had been used for a long time its surface became dull and spongy in appearance. In this state the rate of deposit was slower than when the surface was freshly polished.

It is most probable that part of the difference between the measured resistance and the calculated resistance is due to the manner in which the film is obtained. The film is formed by particles of the metal striking on the glass surface and adhering. These particles are more or less loosely connected, and by heating they settle down into a more and more compact mass, and consequently their resistance is decreased. This is also seen from the fact that the rate at which the films are deposited has a great effect on the condition of the film. If the deposit is too rapid the film is powdery and does not adhere to the glass. This phenomenon was very noticeable in depositing the silver films, and Longden (*loc. cit.*) has also noticed the same effect in platinum when using the Wehnelt interrupter. It was also noticed in the bismuth films, and that after a certain thickness was reached the surface lost its metallic lustre and became dull and powdery in appearance.

Another cause of the discrepancy would probably be the impurity in the cathode, as small amounts of impurity affect the resistance of the three metals very much.

From the corpuscular theory of electrical conduction in metals we have, if

n be the number of corpuscles per unit volume,
e the charge on a corpuscle and m its mass,
λ the mean free path,
c the initial velocity,

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[*] 'Nature,' vol. xxiii. p. 567.

then the conductivity is given by

$$\frac{1}{\sigma}=\frac{1}{2}\frac{ne^2}{m}\frac{\lambda}{c}.^{*}$$

This equation holds until the thickness of the film becomes comparable with λ.

When the thickness becomes comparable with λ there are three cases to be considered, namely :—

When t the thickness is

(i.) greater than 2 λ,
(ii.) between 2 λ and λ,
(iii.) less than λ.

Assuming that the corpuscles cannot leave the metal, Prof. Thomson has calculated that for (i.) λ becomes

$$\lambda\left(1-\frac{\lambda}{4t}\right),$$

and for (iii.) λ becomes

$$\frac{t}{2}\left(\log\frac{\lambda}{t}+\frac{3}{2}\right).^{\dagger}$$

On substituting these values of λ in the equation

$$\frac{1}{\sigma}=\frac{1}{2}\frac{ne^2}{m}\frac{\lambda}{c},$$

we get when

$$t=2\lambda$$

$$\frac{1}{\sigma}=\frac{1}{2}\frac{ne^2}{m}\frac{\lambda}{c}\frac{7}{8},$$

and when

$$t=\lambda$$

$$\frac{1}{\sigma}=\frac{1}{2}\frac{ne^2}{m}\frac{\lambda}{c}\frac{3}{4};$$

that is, that the resistance of the film has increased one-seventh in the first case and one-third in the last. Hence the resistance of the film does not change very much until it becomes equal to the mean free path of the corpuscle.

From the results obtained for platinum films it will be seen that the resistance began to change rapidly between 7·6 and 4×10^{-7} cm.

The value of λ calculated from the change of resistance of the film is 6×10^{-7} cm. These numbers agree very closely.

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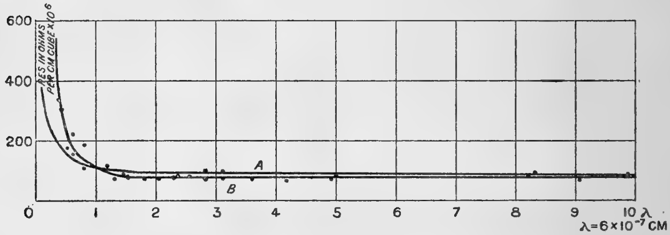
* J. J. Thomson, *Rapports présentés au Congrès International de Physique,* vol. iii. p. 138, Paris, 1900.

† Proc. Camb. Phil. Soc. vol. xi. pt. ii. p. 119 (1901).

The average resistance of all the films whose resistances are normal is 82 ohms for a thickness of 10^{-6} cm. and 1 cm. square. Using the value 6×10^{-7} for λ and 82 for σ the relation between specific resistance and thickness given by the above formulæ is plotted in fig. 14, curve A, where the ordinates represent specific resistance and abscissæ thickness. The experimental values are plotted in curve B.

Fig. 14.



From these two curves it will be seen that the experimental values agree very well with the calculated for films whose thickness is greater than 6×10^{-7} cm., and for those below that thickness the experimental values vary more rapidly.

Vincent*, from his experiments on silver films, concluded that at the surface of a metal there exists a thin layer which he called a transition-layer or the range of molecular action. The thickness of a thick film thus consisted of three parts, namely:—

A transition-layer from air to metal: an intermediate layer of constant specific resistance: a transition-layer from metal to glass. On this theory he obtained the following empirical formula for the conductivity

$$\frac{1}{\sigma}=-\mathrm{A}+ce,$$

where σ is the resistance, c the specific resistance which is constant, and e the thickness, A the correction to be applied for the two transition-layers. He found that this relationship held down to 5×10^{-6} cm. and below this the formula no longer held, and consequently the intermediate layer was absent. He concluded from this result that the upper limit for the range of molecular action was half this limiting value or $2{\cdot}5\times10^{-6}$ cm. Moreau † confirmed these results for silver. He also made nickel films by depositing nickel electrolytically on the silver films. He found that the range of molecular action was $2{\cdot}2\times10^{-6}$ cm. for nickel.

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* *Annales de Chimie et de Physique* [7] vol. xix. p. 421 (1900).

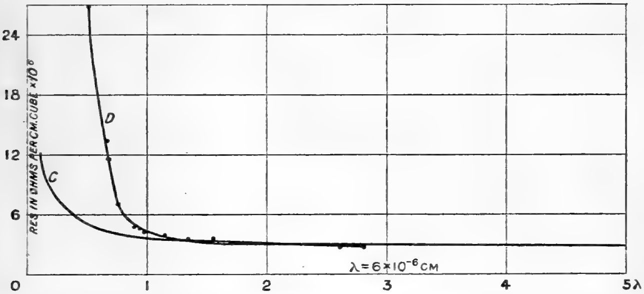
† *Journal de Physique* [3] x. p. 478 (1901).

This view in regard to the transition-layers existing at the surface of a metal is included in the corpuscular theory of electrical conduction in metal films. From the equation

$$\frac{1}{\sigma}=\frac{1}{2}\frac{ne^2}{m}\frac{1}{c}\frac{t}{2}\left(\log\frac{\lambda}{t}+\frac{3}{2}\right)$$

the specific resistance for a film of thickness λ is $\frac{4}{3}$ of the normal specific resistance. This would give a value for λ of about 6×10^{-6} cm. from Vincent's results. The value calculated from the change of resistance of pure silver in a transverse magnetic field is $1{\cdot}3\times10^{-6}$ cm.*, and from the silver film itself it is $1{\cdot}1\times10^{-6}$ cm. The numbers are all of the same order. The specific resistance for a given thickness is plotted against the thickness in curve C, fig. 15, where the upper limit 6×10^{-6} cm. is taken for λ and the normal specific resistance as $2{\cdot}65\times10^{-6}$ ohms per cm. cube, which would be the value given by Vincent's results from the above formula. The experimental values obtained by Vincent are given in curve D.

Fig. 15.



It will be seen from the above curves that the experimental values also vary more rapidly than the theoretical.

At the surface of the metal, in order that equilibrium may be maintained between the air and the metal, there exists a layer of negative corpuscles†. It is most probable that owing to this layer of negative corpuscles the number of corpuscles per unit volume is not constant throughout the surface-layer λ, but that it decreases towards the outside. This would make the resistance vary still more rapidly than the above theoretical equation would indicate.

Vincent and Moreau (*locc. citt.*) concluded from their observations that the transition-layer was the same thickness for all

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* Phil. Mag. June 1902, p. 655.

† J. J. Thomson, *Rapports présentés au Congrès International de Physique*, vol. iii. p. 138, Paris, 1900.

metals, namely, about $2{\cdot}5\times10^{-6}$ cm. for the upper limit. The experiments on platinum films, however, would indicate that for platinum films the thickness of the layer is much less. According to the corpuscular theory this transition-layer would be determined by λ, the mean free path of the corpuscles, and λ has about the same value for a number of the metals[*].

The thickness at which the specific resistance of the platinum film becomes abnormal cannot be taken as the value of λ in the metal itself, owing to the properties of the films being so very different from those of the metal.

Summary of Results.

(i.) The specific resistance of the films deposited *in vacuo* by the cathode discharge is several times greater than the specific resistance of the metal from which they are deposited.

(ii.) The specific resistance of platinum films which have been subjected to the same treatment remains constant above a thickness of about 7×10^{-7} cm. Below this thickness the increase of specific resistance with decrease in thickness is very rapid.

(iii.) Heat decreases the resistance of both silver and platinum films, and the thinner the film the greater the decrease. In platinum films the greatest decrease is produced by the electric current.

(iv.) The values obtained for λ, the mean free path of the corpuscle in the metal, are of the same order as those obtained from the change of resistance produced by a transverse magnetic field.

In conclusion my most sincere thanks are due to Professor Thomson for his valuable advice and kindly interest throughout the whole course of the investigation described in this paper.

Cavendish Laboratory,
May 12, 1902.

LXXIII. *Does Motion through the Æther cause Double Refraction?* *By* Lord Rayleigh, *O.M., F.R.S.*[†]

THE well-known negative result of the Michelson-Morley experiment in which interference takes place between two rays, one travelling to and fro in the direction of the earth's motion, and the other to and fro in a perpendicular direction, is most naturally interpreted as proving that the

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[*] Phil. Mag. June 1902, p. 655.

[†] Communicated by the Author. Read before Section A of the British Association at Belfast.

æther in the laboratory shares the earth's motion. But other phenomena, especially stellar aberration, favour the opposite theory of a stationary æther. The difficulty thus arising has been met by the at first sight startling hypothesis of FitzGerald and Lorentz that solid bodies, such as the stone platform of Michelson's apparatus, alter their relative dimensions, when rotated, in such a way as to compensate the optical change that might naturally be looked for. Larmor ('Æther and Matter,' Cambridge, 1900) has shown that a good case may be made out for this view.

It occurred to me that such a deformation of matter when moving through the æther might be accompanied by a sensible double refraction; and as the beginning of double refraction can be tested with extraordinary delicacy, I thought that even a small chance of arriving at a positive result justified a careful experiment. Whether the result were positive or negative, it might at least afford further guidance for speculation upon this important and delicate subject.

So far as liquids are concerned, the experiment is of no great difficulty, and the conclusion may be stated that there is no double refraction of the order to be expected, that is comparable with 10^{-8} of the single refraction [*]. But the question arises whether experiments upon liquids really settle the matter. Probably no complete answer can be given, unless in the light of some particular theory of these relations. But it may be remarked that the liquid condition is no obstacle to the development of double refraction under electric stress, as is shown in Dr. Kerr's experiments.

The apparatus was mounted upon the same revolving board as was employed for somewhat analogous experiments upon the rotation in quartz (Phil. Mag. vol. iv. p. 215, 1902). Light, at first from the electric arc but later and preferably from lime heated by an oxyhydrogen jet, after passing a spectacle-lens so held as to form an image of the source upon the analysing nicol, was polarized by the first nicol in a plane inclined to the horizontal at 45°. The liquid, held in a horizontal tube closed at the ends by plates of thin glass, was placed, of course, between the nicols. When at 12 o'clock the board stands north and south, the earth's motion is transverse and the situation is such as to exhibit any double refraction which may ensue. It might be supposed, for instance, that luminous vibrations parallel to the earth's motion, *i. e.* east and west, are propagated a little differently from those whose direction is transverse to the earth's motion, *i. e.* vertical. But if the

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[*] $10^{-8}=(10^{-4})^2$, where 10^{-4} is the ratio of the velocity of the earth in its orbit to the velocity of light.

board be turned through a right angle so as to point east and west, both directions of vibration for light passing the tube are transverse to the earth's motion, and therefore no double refraction could manifest itself. The question is whether turning the board from the north and south position to the east and west position makes any difference. In no case is any effect to be expected from a rotation through 180°, and such effect as a rotation through 90° may entail must be of the *second* order in the ratio which expresses the velocity of the earth relatively to that of light.

It should not be overlooked that according to the theory of a stationary æther, we have to do not only with the motion of the earth in its orbit, but also with that of the sun in space. The latter is supposed to be much the smaller, and to be directed towards the constellation Hercules. In the month of April, when successful experiments were first made, the two motions would approximately conspire.

If the suggested double refraction, due to the earth's motion, were large enough, it would suffice to set the analysing nicol to extinction in one position of the board, and to observe the revival of light consequent on a rotation of the latter through 90°. But a more delicate method is possible and necessary. Between the polarizing nicol and the liquid column we introduce a strip of glass whose length is horizontal and transverse to the board. This strip, being supported (at two points) near the middle of its length, and being somewhat loaded at its ends, is in a condition of strain, and causes a revival of light except in the neighbourhood of a horizontal band along the "neutral axis." Above and below this band the strained condition of the glass produces just such a double refraction as might be caused by the motion of the liquid through the æther, so that the existence of the latter would be evidenced by a displacement of the dark band upwards or downwards. In order the better to observe a displacement, two horizontal wires are disposed close to the bent glass so as just to inclose the band, and a small opera-glass focussed upon these is introduced beyond the analysing nicol. The slightest motion of the band is rendered evident by changes in the feeble illumination just inside the wires.

The board is mounted upon a point so as to revolve with the utmost freedom. The point is carried on the table and faces upwards. The bearing is a small depression in an iron strap, rigidly attached to the board, and raised sufficiently to give stability. The gas-leading tubes are connected in such a manner as to give rise to no forces which could appreciably vary as the board turns.

Observations were made upon bisulphide of carbon in a tube 76 cms. long, and upon water in a tube $73\frac{1}{2}$ cms. long. In neither case could the slightest shift of the band be seen on rotation of the board from the north-south position to the east-west position, whether at noon or at 6 P.M. The time required to pass from one observation to the other did not exceed 15 seconds, and the alternate observations were repeated until it was quite certain that nothing could be detected.

Of course the significance of this result depends entirely upon the delicacy of the apparatus, and it is worth little without an estimate of the smallest double refraction that would have been detected. It may even be objected that the investigation stands self-condemned. In consequence of the earth's magnetism there must be a rotation of the plane of polarization when the light traverses the bisulphide of carbon in the north and south position; and this effect, it may be argued, ought to manifest itself upon rotation of the board.

To take the objection first, it is easy to calculate the rotation of the plane of polarization. For one C.G.S. unit of magnetic potential the rotation in CS_2 at 18° is ·042 minute of angle*. In the present case the length is 76 cms. and the earth's horizontal force is ·18; so that the whole rotation to be expected† is

$$76 \times {}^{\cdot}18 \times {}^{\cdot}042 = {}^{\cdot}58'.$$

So small a rotation of the plane, which would show itself, if at all, by a *fading* and not by a *displacement* of the band, is below the limit of observation.

The delicacy of the apparatus for its purpose may, indeed, be inferred indirectly from the rotation of the nicol found necessary to engender a marked revival of light at the darkest part of the band. If θ be this angle, the revived light is $\sin^2\theta$, expressed as a fraction of the maximum obtainable with parallel nicols. In the actual observation the nicols remain accurately crossed, and the question is as to the effect of a double refraction causing *e.g.* a retardation of vertical vibrations relatively to horizontal ones. If this retardation amounted to $\frac{1}{2}\lambda$, λ being the wave-length, the effect would be the same as of a rotation of the nicol through 90°. In general, a retardation of phase ϵ, in place of π, gives a revival of light measured by $\sin^2(\frac{1}{2}\epsilon)$. If the revivals of light in the two cases be the same, we may equate

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* Phil. Trans. clxxvi. p. 343 (1885); Scientific Papers, vol. ii. p 377.

† The difference between astronomical and magnetic north is here neglected.

θ to $\frac{1}{2}\epsilon$. Hence if we find that rotation θ produces a sensible effect in lessening the darkness at the darkest place, we may infer that there is delicacy sufficient to detect a relative retardation of 2θ due to double refraction. This comparison would apply if the test for double refraction were made by simple observation of the revival of light. As actually carried out by location of the band, the test must be many times more delicate.

It was found that a marked fading of the band attended a rotation of the nicol through 4′. According to this ϵ would be $\frac{1}{450}$; or since a retardation of $\frac{1}{2}\lambda$ corresponds to $\epsilon=\pi$, a retardation amounting to $\frac{1}{1400} \times \frac{1}{2}\lambda$ should be perceptible many times over, regard being paid to the superior delicacy of the method in which a band is displaced relatively to fixed marks.

Another and perhaps more satisfactory method of determining the sensitiveness was by introducing a thin upright strip of glass which could be compressed in the direction of its length by small loads. These loads were applied symmetrically in such a manner as to cause no flexure. The double refraction due to the loads is of exactly the character to be tested for, and accordingly this method affords a very direct check. If the load be given, the effect is independent of the length of the strip and of its thickness along the line of vision, but is inversely as the width. The strip actually employed had a width of 15 mm.; and the application (or removal) of a total of 50 gms. caused a marked shifting of the band, while 25 gms. was just perceptible with certainty.

To interpret this we may employ some results of Wertheim (Mascart's *Traité d'Optique*, t. ii. p. 232), who found that it requires a load of 10 kilograms per millimetre of width to give a relative retardation of $\frac{1}{2}\lambda$, so that with the actual strip the load would need to be 150 kilograms. The retardation just perceptible is accordingly $\frac{1}{2}\lambda \div 6000$. This may be considered to agree well with what was expected from the effect of rotating the nicol.

We have now only to compare the relative retardation which would be detected with the whole retardation incurred in traversing the 76 cm. of bisulphide of carbon. In this length there are contained 1,200,000 wave-lengths of yellow light, or 2,400,000 half wave-lengths. The retardation due to the refraction may be reckoned at ·6 of this, or 1,440,000 half wave-lengths. Thus the double refraction that might be detected, estimated as a fraction of the whole refraction, is $1{\cdot}2 \times 10^{-10}$. The effect to be expected is of the order 10^{-8}, so that there is nearly 100 times to spare. The above relates to the bisulphide of carbon. With the water the delicacy of the test was somewhat less.

When it is attempted to replace the liquid by solid matter, the difficulties of experiment are greatly increased. The best results that I have been able to obtain were with built up thicknesses of plate-glass. A sufficient thickness in one piece is liable to exhibit too much double refraction from the effect of internal strains. A number of triangular pieces of plate-glass, no larger than necessary, and about 6 mm. thick, were put together in a trough to a total thickness of about 110 mm. The interstices between the faces being filled up with bisulphide of carbon, the internal reflexions were sufficiently reduced. One difficulty is to get quit of motes and threads which adhere to the glass and become extraordinarily conspicuous. Advantage was thought to be derived from shaking up the bisulphide of carbon with strong sulphuric acid. At the best the residual motes and specks in the glass interfere very seriously with the observation, and the loss of light due to imperfect transparency operates in the same direction. The least load upon the upright strip that could be detected with certainty was now 100 grms., so that as compared with the observations upon liquid there was a loss of delicacy of four times. In addition to this, the effect to be expected is reduced in the proportion of 7 : 1, that being the ratio of lengths traversed by the light. Thus in all we lose 28 times as compared with the liquid. In the latter case we calculated a margin of 100 times, so that here there would remain a margin of about 3 times.

A subsequent attempt was made to increase the total thickness of the combined glasses to about 220 mm., but no real advantage was gained. The loss of light and increase of disturbance from motes and residual double refraction prejudiced the delicacy in about the same proportion as the length of path was increased.

But although the results of the observations upon solids are very much less satisfactory than in the case of liquids, enough remains to justify us in concluding that even here there is no double refraction (of the order to be expected) due to motion through the æther.

Terling Place, Witham.

LXXIV. *The Discharge of Electricity through Gases and the Temperature of the Electrodes.* *By* J. A. CUNNINGHAM, *B.A.* (*R.U.I. & Camb.*), *A.R.C.Sc.I.*, 1851 *Exhibition Scholar, Cavendish Laboratory, Cambridge* [*].

Introduction.

THE conduction of electricity through hot gases and vapours has been the subject of investigations by Becquerel, Blondlot, Grove, Maxwell, and Hittorf. In 1890 Prof. Thomson [†] reinvestigated the whole subject, and showed that the heating of the electrodes was an essential part of the phenomenon. Recently Dr. H. A. Wilson [‡] has investigated the conductivity of air and salt vapours up to about 1300°. His electrodes were, of course, also hot, and from his previous experiments on flames he had concluded that the ionization of the air took place quite close to the hot electrodes.

It has long been known that hot bodies possessed the property of discharging electricity [§]. The experiments of Elster and Geitel [||] are fundamental, and the subject has been taken up at the Cavendish Laboratory by Prof. Thomson [¶], who showed that the carriers were charged particles, Prof. McClelland [**], Mr. O. W. Richardson [††], and Prof. Rutherford [‡‡]. The result of all these experiments is to show that a hot metal gives off positive ions at a red heat and negative ions at a white heat, and that this negative current increases very rapidly with further rise of temperature, the potential-difference being much less than is necessary to produce a discharge in the ordinary sense.

When we pass to the discharge in a vacuum-tube the phenomena become more complicated, and the results more difficult to interpret. Hittorf [§§] carried out a very extensive series of experiments on the temperature effects at various parts of the discharge. He found that the luminosity in the positive column was extinguished in the neighbourhood of a heated platinum spiral, or if the anode itself were made white hot. On heating up the cathode he found no marked diminution in the total potential-difference until a yellow heat

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[*] Communicated by Prof. J. J. Thomson, F.R.S.

[†] Phil. Mag. [5] xxix. pp. 358, 441.

[‡] Phil. Trans. cxcvii. p. 415 (1901).

[§] Guthrie, Phil. Mag. [4] xlvi. p. 257 (1873).

[||] Wied. *Ann.* xxxviii. p. 27 (1889).

[¶] Phil. Mag. [5] xliv. p. 203 (1897).

[**] Proc. Camb. Phil. Soc. x. p. 241 (1900), and xi. p. 296 (1901).

[††] Ibid. xi. p. 286 (1901).

[‡‡] Phys. Rev. xiii. p. 321 (1901).

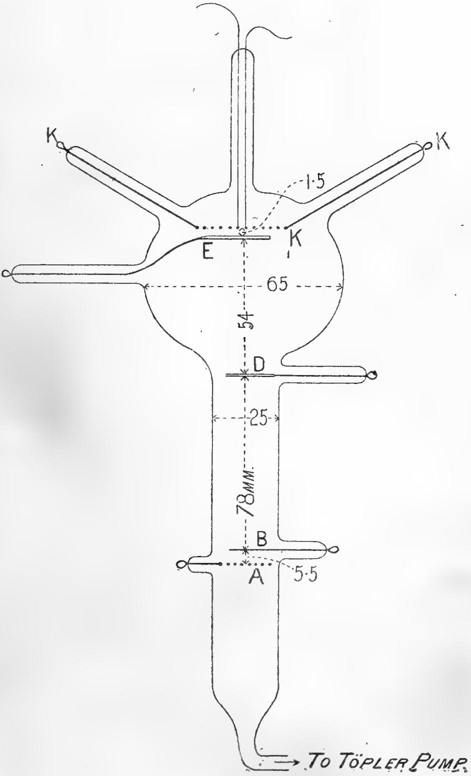
[§§] Wied. *Ann.* xxi. p. 90 (1884).

was attained, after which it began to diminish rapidly. The differences were more marked at reduced pressures. Hittorf also found that the potential gradient in the positive column was independent of the current, but diminished with the pressure. The "cathode fall" remained practically constant until the cathode was covered with the negative glow, after which it increased with increasing current. It also increased very rapidly with diminishing pressure.

Apparatus.

The form of vacuum-tube used in the present series of experiments is shown in the diagram (fig. 1). The electrode (KK) consisted of a platinum wire bent backwards and forwards on itself so as to form a plane grating. Four strands of wire of the same thickness fused into each of two side

Fig. 1.



tubes served to lead the heating current through the grating without undue heating of the blue-glass joint. The grating could thus be included in the circuit of a carefully insulated secondary wound on a ring transformer. The current for the primary was taken from the Cambridge town (alternating) supply, and was regulated by means of a rheostat.

The opposite electrode (A) was made of a similar grating, but could not be artificially heated. The three intermediate electrodes (E, D, & B) were made of fine platinum wires whose free ends inside the discharge-tube were hammered out flat, and the edges then trimmed off parallel, so that the width of the blade was only about double the diameter of the original wire. They were fused into side tubes perpendicular to the bars of the gratings, and so that the plane of the blade was parallel to the axis of the discharge-tube. Professor Thomson has pointed out that, especially when working at low pressures, an ordinary wire placed in front of the cathode would be subjected to a bombardment of negatively charged corpuscles, from which it would derive a negative charge and acquire a potential which might have nothing much to do with the potential of the surrounding gas. Prof. Thomson's scheme of using a transverse pencil of cathode particles whose deflexion would measure the electric intensity at the point was not easily applicable in the present case, since when the cathode was at a high temperature the illumination from it would render a phosphorescent spot practically invisible. It was thought that the flat-bladed electrodes here adopted would expose only a very thin edge to particles moving rapidly along the axis of the tube, and a maximum surface to the ionized gas whose potential it was desired to ascertain.

This tube was connected by means of a short glass tube with the Töpler-pump, P_2O_5 bulb, and McLeod gauge, so that the whole system rapidly came to one uniform pressure. A three-way tap served to admit fresh supplies of air, and by being closed at night prevented an excessive diffusion of mercury-vapour into the discharge-tube. The discharges below described always presented a rich red colour without any apparent traces of the blue due to mercury.

The current from a battery of 1000 small secondary cells, used for generating the discharge, passed through two variable liquid resistances, and was measured by means of a low resistance d'Arsonval galvanometer of the Ayrton and Mather type. A telephone in series served to check the steadiness of the discharge.

A German voltmeter of simple construction (with an aluminium needle suspended about a horizontal axis a little above its centre of gravity) served to measure the total potential-difference between the electrodes, and at very low pressures (Table XIV.) also for the cathode fall. Its scale was carefully calibrated by direct comparison with the Kelvin multicellular voltmeter, which was used for measuring potential-differences between the other electrodes ranging from 250 to 1000 volts. The German instrument was a little sluggish in its movements, and its indications were used mainly as a check on those of the other instruments, except when special precautions were taken to tap it before each reading. For potentials between 100 and 300 volts an Ayrton and Mather direct-reading voltmeter (with vertical cylindrical quadrants) was employed.

The temperature of the hot electrode (KK) was measured by means of a platinum platinum-rhodium thermo-couple. The wires (0·1 mm. in diameter) were attached to adjacent bars of the grating. They were fused through the end of a small glass tube at the top of the discharge-tube, and passed over into two glass tubes immersed alongside a mercury thermometer in a bottle of water. These glass tubes were partly filled with mercury, which served to make good contact with the copper wires leading to the galvanometer. This was also a d'Arsonval of the Ayrton and Mather type. To reduce the deflexions of the galvanometer to degrees centigrade use was made of Messrs. Heycock and Neville's determination of the melting-point of potassium sulphate*. The thermal junction was attached to a strip of platinum-foil which was heated up as in the course of the experiments. The deflexion of the spot of light on the scale was then read off just when the K_2SO_4 began to melt. The observation was repeated with very slow increments of current through the foil. From the final value thus obtained a curve of temperatures against deflexions was plotted in the manner described by Callendar †, and verified by a determination of the melting-point of sodium sulphate. The deflexions of the spot at all distances of the galvanometer from the scale were readily reduced to this standard distance.

There is a little doubt attaching to some of the highest temperatures recorded owing to a sagging of the wire-grating which left the portion to which the thermo-couple wires were attached slightly out of the plane of the grating, and so made them rather cooler than the rest.

With this apparatus, where there were only glass joints and there was therefore practically no leak until very high

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[*] Chem. Soc. Journal, lxvii. p. 160 (1895).

[†] Phil. Mag. [5] xlviii. p. 519 (1899).

temperatures were reached, it was often thought desirable to vary the temperature backwards and forwards so as to try and isolate the temperature effect as completely as possible. It was also possible to raise the temperature of the platinum grating by more gradual steps than would actually appear from the numbers recorded in the accompanying tables. Where in such cases a gradual change of temperature was accompanied by a gradual and continuous change in the distribution of potential, it was often thought sufficient to record the measurements of successive maxima and minima. And in nearly all cases plenty of time was allowed to elapse for the instruments to settle down to perfectly steady readings.

A few general remarks on some of the appearances observed may not, perhaps, be out of place here before proceeding to a detailed record of the actual measurements made.

The temperature of the cathode was observed to rise gradually by the action of the discharge. At moderately high pressures (0·5 to 2 mm.) and with small currents, on first starting the discharge the negative glow was seen to wander about in an unsteady manner over the surface of the cathode, accompanied by a noise in the telephone which only ceased after a very considerable lapse of time. This unsettledness was most marked on starting the discharge for the first time with a new wire.

When the cathode was now gradually heated up the negative glow was observed to move away from the central hottest portion of the grating and wander up into the side tubes, where the wire was cooler. On further heating the discharge would come back again and proceed from the hottest part of the cathode. This phenomenon is consistent with the measurements recorded below, which show a more or less well-marked maximum "cathode fall" at temperatures below a yellow heat varying with the pressure; and it seems natural to suppose that the discharge will pass where it can do so with the greatest ease.

It will be seen at a glance from all the tables where the cathode was taken through a cycle of temperature changes that a sort of *hysteresis* becomes apparent. This may be partly due to an error of observation. The cooling was nearly always more rapid than the heating up. The method of observation adopted was to keep an eye fixed on the voltmeter after each successive reduction of current in the primary of the transformer, and at successive readings of the voltmeter to look up quickly at the corresponding reading on the conveniently placed scale of the galvanometer connected with the thermo-couple. Particular attention was paid to recording maxima and minima on the voltmeter with their corresponding temperatures. As in all recorded cases, the potential indicated on the voltmeter was changing but slowly, and as the coil of the d'Arsonval galvanometer was inclosed in a silver cylinder and was very dead beat, it was thought that the error of observation could not really be very great. Some such lag is, after all, only to be expected.

Results.

In Tables I. to VIII. are shown the measurements of the fall of potential along the discharge at different pressures, the temperature of the cathode being kept constant.

TABLE I.

Temperature of Cathode.		Potential Difference, Volts.					Pressure, mm. of Mercury.
Deflexion.	° C.	K−A.	K−E.	E−A.	K−D.	K−B.	
0·90	35	815	300	(515)	...	665	1·18
0·90	35	780	240	(540)	...	520	0·88
0·90	35	720	214	(508)	...	500	0·66
0·90	35	650	228	(422)	...	396	0·51
0·95	38	600	259	(341)	...	345	0·38
0·90	35	538	320	218	340	(350)	0·29
0·90	35	522	352	170	...	...	0·221
0·90	35	519	370	149	...	...	0·168
0·65	27	558	395	163	...	...	0·105
0·90	35	580	418	162	...	...	0·104
0·90	35	654	478	176	...	...	0·079
0·95	38	705	503	202	...	...	0·050
0·95	38	1100	770	>310	...	...	0·031

TABLE II.

Temp. of Cathode.		Potential Difference.			Current.		Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−E.	E−A.	Defln.	Amp. × 10^5.	
32·8	820	1150	293	860	6·60	3·96	2·67
33·3	832	960	268	680	7·40	4·44	1·92
33·3	832	800	292	512	8·35	5·01	1·42
33·3	832	755	290	(465)	(8·6)	(5·16)	1·03
33·3	832	730	293	(437)	9·0	5·40	0·76
33·3	832	660	230 ?	(430)	9·15	5·49	0·563
33·3	832	625	290	(335)	...	...	0·507
33·3	832	580	387	181	9·25	5·55	0·294
33·3	832	625	430	190	9·65	5·79	0·210
33·3	832	650	465	192	8·45	5·07	0·155
33·3	832	710	537	197	7·95	4·77	0·108
33·3	832	690	482	212	7·85	4·71	0·079
33·3	832	730	520	255	7·40	4·44	0·058
		840	527	313	6·55	3·93	0·041
33·3	832	1070	540	(530)	...	...	0·029

TABLE III.

Temp. of Cathode.		Potential Difference.			Current.		Pressure, mm. of Hg.
Defln.	° C.	K–A.	K–E.	E–A.	Defln.	Amp. × 10^5.	
43·7	1040	1200	300	900	5·45	3·27	2·70
43·9	1043	955	272	682	6·70	4·02	1·95
43·9	1043	810	292	518	7·60	4·56	1·43
43·9	1043	780	300	490	7·70	4·62	1·35
43·9	1043	(725)?	(200)	(525)	...	...	1·00
43·9	1043	750	215	...	(7·4)	(4·5)	0·74
43·9	1043	690	260	430	(7·8)	...	0·53
43·9	1043	565	367	199	8·3	4·98	0·39
43·9	1043	565	377	184	8·15	4·89	0·280
40·4	986	630	440	201	7·7	4·62	0·196
42·7	1020	625	432	199	7·7	4·62	0·196
43·3	1030	(680)	(490)	207	(7·3)	...	0·143
43·1	1028	670	468	200	7·6	4·56	0·096
43·7	1040	710	487	226	(7·1)	...	0·068
43·9	1043	800	522	282	6·70	4·02	0·054
43·9	1043	865	502	(363)	6·05	3·63	0·042
43·9	1043	970	464	(506)	(5·5)	...	0·031
43·9	1043	1045	435	(610)	5·0	3·00	0·027
43·9	1043	1340	437	(900)	3·3	1·98	0·020

TABLE IV.

Temp. of Cathode.		Potential Difference.			Current.		Pressure, mm. of Hg.
Defln.	° C.	K–A.	K–E.	E–A.	Defln.	Amp. × 10^5.	
50·2	1163	960	275	661	5·9	3·54	1·90
50·3	1165	810	300	512	(6·6)	...	1·40
50·4	1167	730	(317)	413	7·1	4·26	1·05
50·4	1167	730	296	(430)	7·0	4·20	0·74
50·4	1167	685	285	(400)	7·2	4·32	0·55
50·4	1167	570	366	204	7·5	4·50	0·40
50·4	1167	570	372	195	7·45	4·47	0·30
50·2	1163	630	426	206	7·2	4·32	0·206
50·4	1167	680	482	204	(6·7)	...	0·151
50·4	1167	780	565	220	6·3	3·78	0·108
50·4	1167	770	560	210	6·1	3·66	0·079
50·4	1167	795	508	284	...	...	0·055
50·4	1167	900	500	(400)	5·4	3·24	0·039
50·4	1167	1080	690	(390)	4·2 ?	2·52 ?	0·037
50·4	1167	1450	950	(500)	...	...	0·025

TABLE V.

Temp. of Cathode.		Potential Difference.			Current.		Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−E.	E−A.	Defln.	Amp. × 10^5.	
55·4	1256	1010	277	720	(5·2)	...	2·15
55·4	1256	860	293	538	6·1	3·66	1·53
55·4	1256	790	(337)	453	6·4	3·84	1·10
55·5	1259	740	300	(440)	(6·6)	...	0·82
55·4	1256	660	220	(440)	...	...	0·60
55·4	1256	570	345	224	(7·2)	...	0·43
55·4	1256	570	350	214	...	...	0·314
55·4	1256	575	360	196	7·0	4·20	0·224
55·4	1256	640	390	241	(6·6)	...	0·171
55·4	1256	680	480	199	(6·3)	...	0·130
55·4	1256	750	558	196	...	...	0·106
55·4	1256	780	(566)	214	5·75	3·45	0·082
55·4	1256	780	521	259	(5·65)	3·39	0·066
55·4	1256	810	500	(310)	5·7	3·42	0·057
55·4	1256	880	545	(335)	5·1	3·06	0·050
55·4	1256	920	612	(310)	5·1	3·06	0·054
55·4	1256	1120	715	(405)	...	...	0·037
55·4	1256	1310	860	(450)	3·1	1·86	0·034
55·3	1254	1420	930	(490)	3·1	1·86	0·029

TABLE VI.

Temp. of Cathode K.		Potential Difference.				Current.		Pressure, mm.
Defln.	° C.	K−A.	K−E.	E−A.	K−D.	Defln.	Amps. × 10^5.	
59·8	1335	1160	(330)	830	...	(4·5)	...	2·10
60·3	1340	960	(360)	602	...	(5·4)	...	1·40
63·3	1394	790	(340)	450	...	(6·0)	...	1·02
60·3	1340	700	(343)	357	...	6·7	4·02	0·75
60·3	1340	665	(342)	323	...	6·8	4·08	0·55
60·4	1344	575	340	235	...	7·1	4·26	0·39
60·4	1344	565	350	215	...	7·0	4·20	0·29
60·4	1344	570	370	202	...	6·85	4·11	0·22
60·4	1344	640	425	215	...	6·6	3·96	0·174
60·4	1344	710	500	206	...	(6·2)	...	0·116
60·4	1344	770	573	196	...	...	...	0·088
60·4	1344	820	563	250	...	...	...	0·065
60·4	1344	840	580	258	700	(5·4)	...	0·058
60·4	1344	990	(590)	(400)	840	4·5	2·70	0·041
60·4	1344	1150	725	(425)	1020	...	...	0·035
60·4	1344	1220	800	(420)	...	...	...	0·032
60·4	1344	1200	775	(425)	...	3·55	2·13	0·033
60·46	1346	1300	860	(440)	...	...	...	0·032

TABLE VII.

Temp. of Cathode.		Potential Difference.					Current.		Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−E.	E−A.	E−D.	D−A.	Defln.	Amps. ×10⁵.	
65·5	1432	1350	360	990	280	720	...	(2·6)	2·13
65·5	1432	1020	328	692	190	500	5·1	3·06	1·53
65·3	1429	850	(280)	(570)	120	450	...	(3·2)	1·13
65·5	1432	770	300	470	100	380	5·9	3·54	1·07
65·5	1432	650	302	348	< 90	...	...	(3·8)	0·604
65·55	1434	587	328	259	...	...	...	(3·8)	0·431
65·5	1432	583	370	213	...	...	6·3	3·78	0·226
65·5	1432	680	470	210	...	...	...	(3·4)	0·122
65·5	1432	780	510	270	...	...	...	(3·2)	0·078
65·5	1432	1110	565	545	>310	90	3·9	2·35	0·035
65·3	1429	1480	430	1050	920	150	...	...	0·023
65·5	1432	2000	...	...	...	...	0	0	0·017

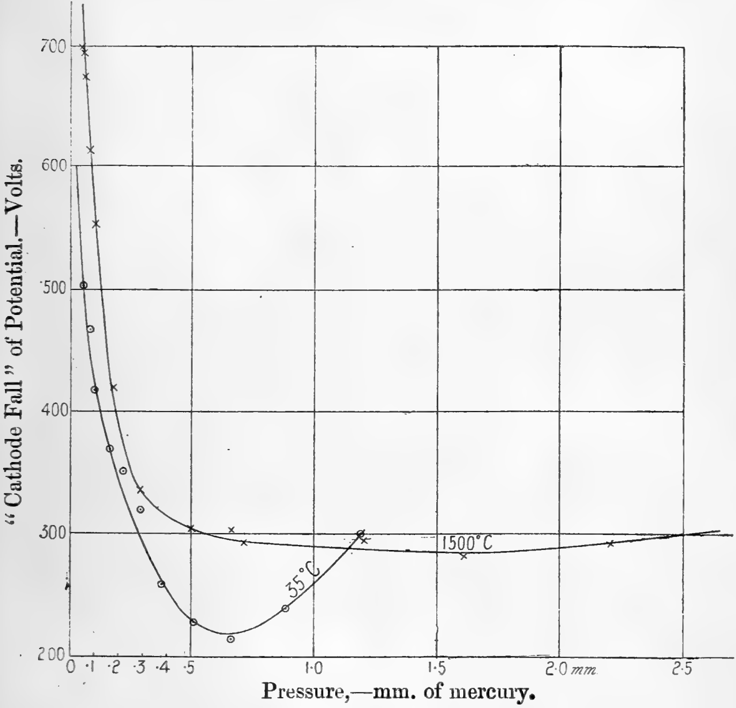
TABLE VIII.

Temp. of Cathode.		Potential Difference.					Current.	Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−E.	E−A.	K−D.	K−B.	Defln.	
69·4	1500	1650?	305	1190	(760)	...	6·09	2·95
69·4	1500	1220	293	930	340	930	10·54	2·20
69·5	1502	970	283	670	333	720	(16·4)	1·60
69·4	1500	800	295	490	...	610	(22·0)	1·20
69·4	1500	690	295	380	310	500	(28·0)	0·71
69·4	1500	635	304	326	305	435	27·7	0·66
69·5	1502	580	304	280	335	...	29·34	0·50
69·4	1500	575	(335)	240	352	472	32·44	0·29
69·4	1500	630	420	203	508	585	34·44	0·18
69·4	1500	750	554	194	640	700	34·04	0·103
69·4	1500	860	614	220	740	820	(31·8)	0·078
69·4	1500	960	674	262	850	905	30·54	0·058
69·4	1500	1030	695	335	900	980	30·00	0·056
69·4	1500	1050	700	350	920	1010	...	0·048

At low temperatures of the cathode the "cathode fall" (K−E) shows a well-marked minimum at a pressure of about 0·65 mm. of mercury. At higher temperatures this minimum tends to become less marked, and to occur at a greater pressure. In fact the cathode fall becomes almost independent of pressure above 0·5 mm. The cathode fall at the highest (1500° C.) and at the lowest (35° C.) are plotted in fig. 2.

The potential-differences between the fixed electrodes A, B, D, E, and K when the cathode is at a temperature of

Fig. 2.



about 1500° C. are shown in fig. 3 (p. 694) and Table VIII. The fall of potential close to the anode (B—A) decreases steadily with diminishing pressure. The potential-gradient in the positive column (D—B) is approximately proportional to the pressure above 0·5 mm. The gradient at the negative end of the positive column, and including the Faraday dark space (E—D), is very much less than anywhere else in the discharge, and seems almost to vanish at a pressure of about 0·65 mm.

In Tables IX. to XIV. we pass on to the results obtained by pumping down to any required exhaustion and then gradually heating up the cathode, the actual pressure being measured and recorded at intervals. As the volume of the discharge-tube bore but a small ratio to that of the pump cylinder, McLeod gauge, and P_2O_5 bulb, the heating of the cathode only produced trifling changes of pressure, and it has been shown already that the cathode fall is hardly affected by slight changes of pressure except at very high exhaustion. At very high temperatures and low pressures the slight leak did, however, produce quite appreciable effects, as is well illustrated by the latter part of Table XIV.

Fig. 3.—(Temperature=1500° C.)

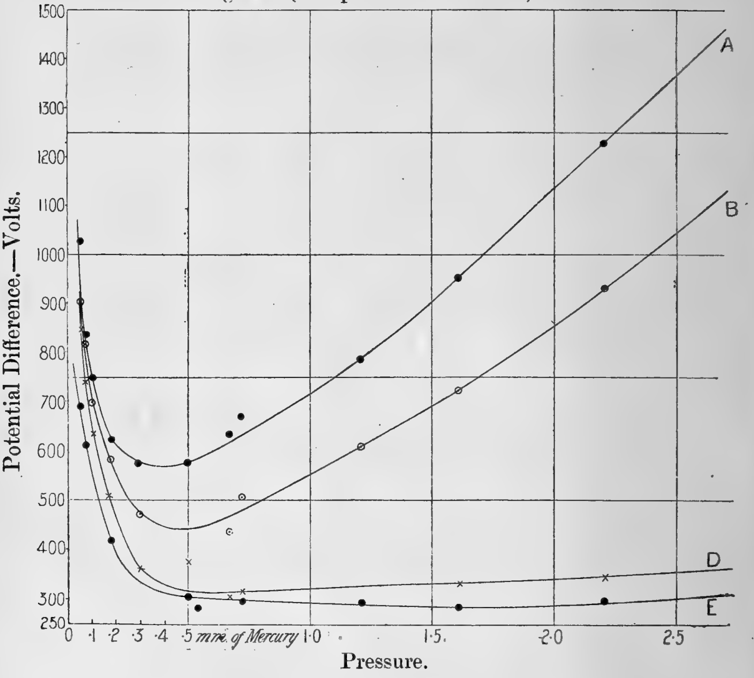


TABLE IX.

Temperature of Cathode K.		Potential Difference.			Current.		Pressure, mm. of Mercury.
Defln.	° C.	K−A.	K−E.	E−A. (calculated)	Defln. of Galvanr.	Amps. $\times 10^4$.	
16·8	468	793	336	457	25·2	8·4	1·8
5·8	195	...	320				
2·7	102	804	324	480	25·2	8·4	
7·8	248	...	318				
16·3	455	804	330	474			
19·7	532	...	340				
20·2	545	...	337	...	...	...	
46·3	1112	...	306	...	26·9	8·97	
55·3	1255	747	302	445			
59·3	1325	752	300	452			
67·3	1463	793	296	497			
70·3	1514	798	294	504	26·5	8·83	

TABLE X.

Temperature of Cathode.		Potential Difference.			Current.		Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−D.	D−A.	Defln.	Amps. ×10⁴.	
80·3	1681	787	350	437	...	...	1·9
78·6	1653	798	358	440			
73·4	1566	793	362	431			
53·3	1220	770	366	404			
52·3	1202	770	360	410			
24·8	650	782	373	409			
19·8	535	...	390				
19·3	524	804	400	404	24·9	8·30	
10	305	815	455	360			
7	227	...	420				
5	173	...	410				
4	142	...	420				
2·8	105	...	450	...	24·1	8·03	

TABLE XI.

Temp. of Cathode.		Potential Difference.					Current.		Pressure, mm. of Hg.
Defln.	° C.	K−A.	K−D.	D−A.	D−B.	B−A.	Defln.	Amp. ×10⁴.	
3·7	133	720	410	(310)	262	(48)	20·4	6·80	1·07
17·4	480	710	398	(312)	259	(53)	20·9	6·97	
18·0	495	700	390	(310)	258	(52)	21·9	7·30	
37·7	920	665	368	(297)	250	(47)	19·9	6·63	1·14
37·7	920	665	358	(307)	253	(54)	23·0	7·67	
44·9	1063	665	365	(300)	252	(48)	19·85	6·62	
52·0	1196	665	365	(300)	252	(48)	19·65	6·55	
53·8	1230	663	352	(311)	262	(49)	19·90	6·63	1·14
56·1	1270	660	351	(309)	265	(44)	19·80	6·60	
60·9	1352	660	353	(307)	271	(36)	19·3	6·43	
67·9	1475	665	357	(308)	277	(31)	18·5	6·17	1·16
71·4	1533	673	362	(311)	282	(29)	18·6	6·20	1·17
72·4	1550	675	360	(315)	284	(31)	19·0	6·33	
73·5	1570	680	359	(321)	287	(34)	17·5	5·87	
62·5	1380	675	356	(319)	275	(44)			
24·1	635	700	402	(298)	273	(25)	12·4	4·13	1·12
23·4?	610?	...	412						
22·4	597	740	445	(295)	278	(17)			
21·4	575	742	453	(289)	279	(10)			
20·1	542	735	434	(301)	275	(26)	15·7	5·23	
18·7	510	742	450	(288)	278	(10)	15·0	5·00	1·14
2·9	108	...	...	...	285				
2·4	90	...	525	...	290	...	11·0	3·67	

TABLE XII.

Temp. of Cathode.		Potential Difference.				Current.		Pressure, mm.
Defln.	° C.	K – A.	K – D.	D – A.	D – B.	Defln.	Amp. × 10⁴.	
1·9	75	525	370	148	...	22·8	7·60	0·376
1·95	76	...	376	...	119			
9·0	280	...	382					
16·2	451	...	388	...	121			
19·2	520	535	392	152	122	20·4	6·80	
21·7	580	535	394	152	...	19·7	6·57	
24·7	648	535	393	152	...	19·7	6·57	
28·0	720	545	395	153	...	19·2	6·40	
40·7	980	(555)	400	155	...	18·8	6·27	
41·2	990	(548)	393	155	...	18·8	6·27	
61·7	1367	(545)	390	155	...	18·6	6·20	
66·4	1450	545	392	154	...	18·5	6·17	
71·4	1533	(553)	392	161	...	18·3	6·10	0·406
71·0	1525	550	392	160	128			
74·2	1580	555	394	158				
77·4	1634	(545)	388	157	...	17·8	5 93	
79·0	1660	(528)	375	153	...	18·0	6·00	
81·2	1696	...	240					
77·7	1638	(523)	372	151				
85·0	1750	320	190	151	...	...	...	0·392
78·0	1642	470	343	148	...	17·2	5·73	
76·4	1617	525	389	150				
75·1	1594	560	407	150				
72·2	1547	570	415	150	...	17·0	5·67	
		565	420	150				
53·0	1213	565	412	150				
34·2	850	580	426	152	...	16·8	5·60	
24·2	637	(575)	423	152				
8·0	250	(542)	390	152	...	16·8	5·6	
3·7	133	560	400	151	...	19·2	6·4	0·374
3·6	130	565	404					

The results of Tables IX. and X. are plotted in fig. 4, curves E and D respectively. The one was obtained while the cathode was being warmed up, while the other was a cooling curve, which may account for the shifting of the initial minimum and maximum along the axis of temperature. The curve D shows the potential-difference between the cathode and a point in the top of the positive column (K – D).

The results obtained at a rather lower pressure (about 1·1 mm.) are given in Table XI. and plotted in fig. 5, where the cathode (K) is supposed to lie along the line of zero-potential below the diagram, and the P.D. between it and each of the electrodes A, B, and D is measured by the ordinate drawn to the respective curve at any given temperature. Here the initial variations (at a temperature below 600° C.)

Fig. 4.

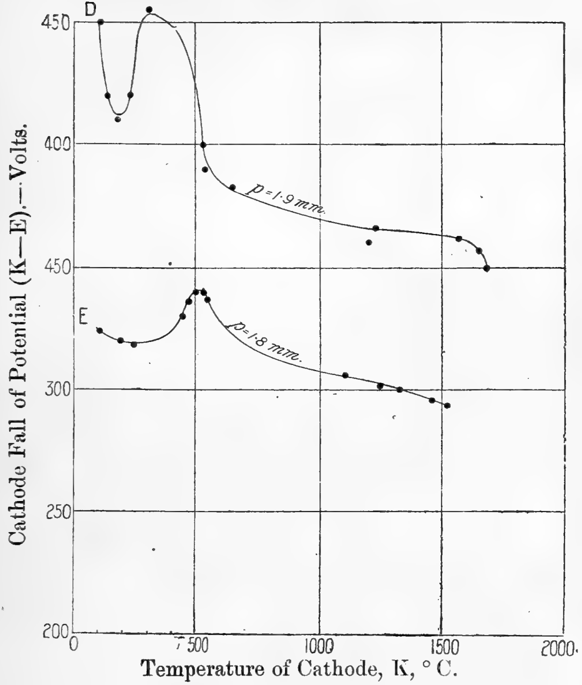
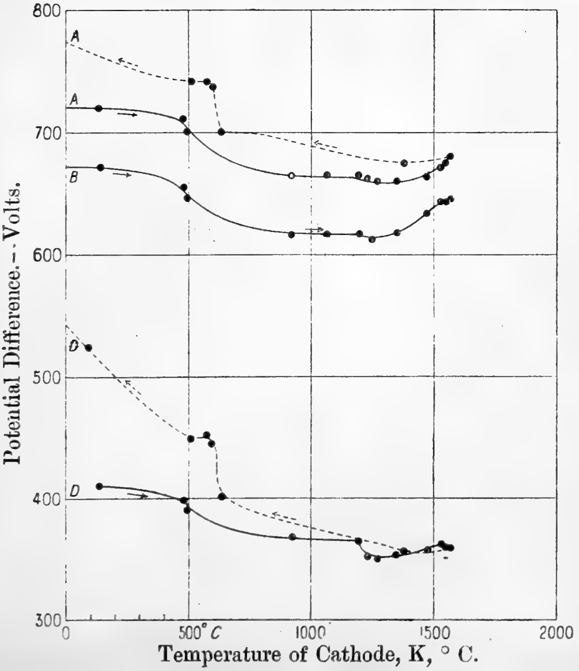


Fig. 5.—(Pressure=1·1 mm.)



have become less marked though still apparent. The difference of potential between the cathode and the top of the positive column (K—D) shows a distinct tendency to a maximum above 1500° C. The potential-gradient in the positive column (D—B) is pretty nearly constant with a slight minimum about 920°, after which it increases uniformly up to the highest temperature attained. The curves for heating up and cooling down are indicated by the arrows, cooling curves being dotted.

In Table XII. and fig. 6 the pressure is still further reduced to 0·4 mm. The initial minimum and maximum of potential-difference at the negative end of the discharge have broadened out, so to speak, along the axis of temperature, and contracted parallel to the axis of potential. There is a gentle maximum about 800° C., and a second above 1500° C. before the final very rapid diminution.

Table XIII. and fig. 7:—In this series of experiments, made soon after admitting a fresh supply of air, so far from the apparatus showing any tendency to leak, the pressure steadily diminished during the course of the experiments. This could only be accounted for as being due to the constant

TABLE XIII.

Temp. of Cathode.		Potential Difference.					Current.		Pressure, mm. of Hg.
Defln.	° C.	K – A.	K – E.	E – A.	K – D.	K – B.	Defln.	Amp. $\times 10^5$.	
1·9	74	540	355	187	430	510	29·0	17·40	0·172
20·5	550	580	410	185	490	560	32·1	19·22	0·173
28·6	732	600	429	178	510	587	33·2	19·92	0·171
33·5	837	615	453	177	530	602	35·6	21·36	0·167
49·7	1153	640	474	172	552	623	...	...	0·167
60·9	1350	670	515	169	586	654	41·1	24·66	0·156
69·5	1500	710	542	169					
70·5	1518	705	(530)	173	620	...	42·7	25·62	
71·6	1536	710	(546)	164	640				
72·6	1552	710	(549)	161	641				
73·3	1566	710	(549)	161	630	...	45·0	27·00	
73·8	1574	705	(550)	155	615				
74·2	1580	700	(546)	154	598	...	...	...	0·150
		665	(515)	150	560				
		655	(502)	153	565				
71·0	1526	740	(583)	157	660				
75·0	1593	700	(546)	154	624				
76·1	1612	680	(528)	152	600				
76·7	1620	670	(520)	150	590				
74·5	1585	740	(585)	155	655				
72·0	1540	760	605	155	670				
67·5	1468	...	...	...	670				
57·2	1290	755	598	157	660				
		740	583	157	655				
38·5	937	720	562	158	637				
5·5	188	670	514	156	573	...	57·6	34·56	0·140

Fig. 6.—(Pressure 0·4 mm.)

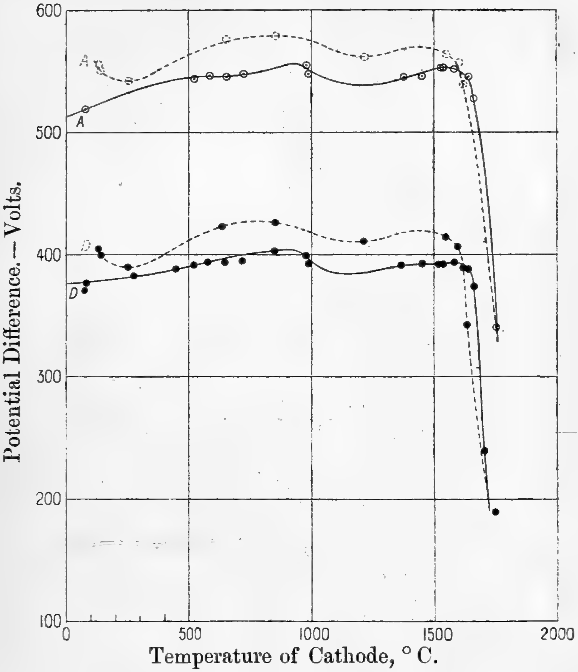
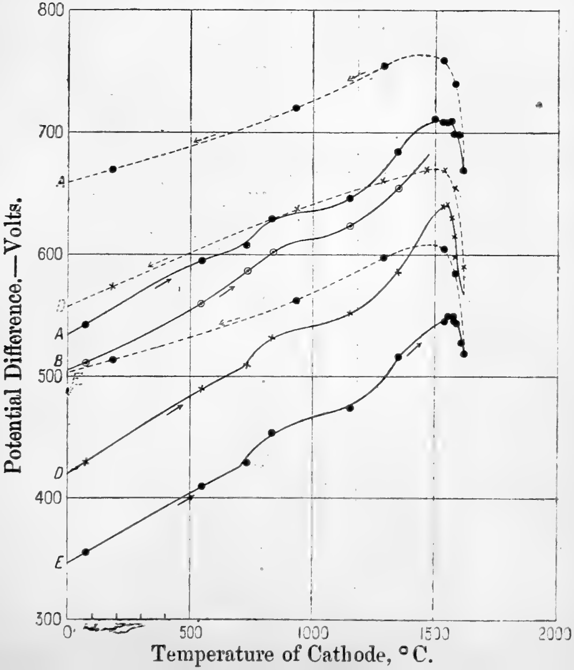


Fig. 7.—(Pressure 0·15 mm.)



raising and lowering of the mercury in the McLeod gauge causing a movement of the heated and ionized air to and fro between the discharge-tube and the P_2O_5 bulb, and so bringing about a more perfect drying which would, perhaps, also partly explain the cathode-fall being so much greater after the cathode had cooled down than it was before heating. We have, however, already noticed a progressive increase of this "lag" as the pressure was diminished. At this low pressure (0·15 mm.) the whole curve is, as it were, tilted up and there is only one real maximum value of the cathode-fall a little below 1600° C. The previous maximum is here only represented by a change of curvature. Above 1600° the diminution of cathode-fall becomes very rapid.

The potential-gradient in the rest of the tube (E—A) remains practically unchanged with temperature.

TABLE XIV.

Temp. of Cathode.		Potential Difference.				Current.		Pressure, mm. of Hg.
Defln.	° C.	K—A.	K—D.	D—A.	D—B.	Defln.	Amps. × 10^4.	
2·7	103	...	1460	< 90	...	10·4	3·47	0·030
2·8	105	...	1420	,,	...	8·6	2·87	
15·2	430	...	1490	,,				
20·2	545	...	1490	,,				
26·2	682	...	1460	,,				
26·8	693	...	1420	,,				
49·9	1158	...	1400	,,				
64·2	1410	...	1470	,,				
65·2	1428	...	1490	,,	...	10·6	3·53	
73·8	1573	...	1560	,,				
79·7	1670	...	1490	,,	...	10·6	3·53	
79·7	1670	...	1500	,,	...	10·0	3·33	
79·9	1675	...	1510	,,				
80·4	1683	...	1510	,,				
80·7	1688	...	1500	100	...	...	...	0·040
80·0	1676	...	1420	145				
80·8	1690	...	1410	185				
80·4	1683	...	1380	240				
80·4	1683	...	1385	> 310	> 310	6·6	2·20	
80·2	1680	...	1250	90	...	17·8	5·93	0·052
74·7	1589	...	1200	,,	...	19·1	6·37	
66·9	1458	...	1140	,,	...	20·6	6·87	
57·2	1290	...	1100	,,	...	21·5	7·17	
34·2	850	...	1080	,,	...	22·2	7·40	
32·2	809	...	1030	,,				
13·7	395	...	970	,,				
11·2	335	...	960	,,				
10·6	320	1030	940	,,	...	24·5	8·17	0·061
3·9	140	925	830	,,	...	11·6	3·87	
3·1	115	890	790	,,	...	10·5	3·50	
2·8	105	870	770	,,	...	9·8	3·27	
			725	220	...	5·1	1·70	
2·2	85	1030	720	> 310	...	0·8	0·27	0·076

On reducing the pressure to 0·04 mm. (Table XIV.) the potential-gradient becomes so steep that only the German voltmeter was available for measuring the cathode-fall, and even it was working at a very unsensitive part of its scale. The electrode D was right in the middle of the negative glow, and the whole of the rest of the tube was practically dark. But as soon as the cathode became white-hot the pressure began to rise so much that the measurements on cooling down were not strictly comparable.

The most interesting part, however, of this table is that which shows the effect of variations of current on the potential-gradient in different parts of the discharge. For all values of the current greater than about $2·5 \times 10^{-4}$ amperes the potential-difference across the whole 83·5 mm. (D−A) at the positive end of the discharge remained too small to be measured by any of the available instruments; and, as has

Table XV.

A=Cathode; K=Anode.

Temp. of Anode.		Potential Difference.					Current.		Pressure, mm. of Hg.
Defln.	° C.	A−K.	A−B.	B−D.	A−D. (calc.)	D−K. (calc.)	Defln.	Amps. $\times 10^4$.	
1·8	70	875	352	255	607	268	24·2	8·07	
1·8	70	850	366	214	580	270	24·5	8·17	
		...	370	210	580	...	24·9	8·30	
		850	366	231	597	253	24·3	8·10	
15·5	438	780	367	194	561	229	24·2	8·07	1·83
17·4	482	775	368	194	562	213			
18·1	498	775	368	198	566	209	24·1	8·03	
17·9	492	775	370	192	562	213	24·0	8·00	
44·8	1060	770	370	202	572	198	23·9	7·97	
50·4	1167	770	369	208	577	193	23·6	7·87	
60·3	1340	768	367	213	580	188			
71·4	1533	765	365	220	585	180	22·6	7·53	
71·4	1533	768	358	230	588	180	23·6	7·80	
71·4	1533	765	362	217	579	186	24·1	8·03	
77·5	1635	765	362	225	587	178	23·95	7·98	
82·4	1716	770	370	232	602	168	23·2	7·73	
			370	224	594	...	24·5	8·17	
83	1725	...	375	220	595	...	25·1	8·37	
63·4	1397	793	380	208	588	205	24·9	8·30	
51·4	1185	793	383	198	581	212	24·9	8·30	
19·4	525	793	383	190	573	220	24·6	8·20	
17·6	485	800	383	187	570	230	24·5	8·17	
2·4	91	...	383	220	603	...	23·5	7·83	
2·4	91	845	383	207	590	255	24·8	8·27	
2·3	89	810	385	166	551	259	34·5	11·50	
		810	383	160	543	267	41·7	13·90	1·82

TABLE XVI.

A = Cathode ; K = Anode.

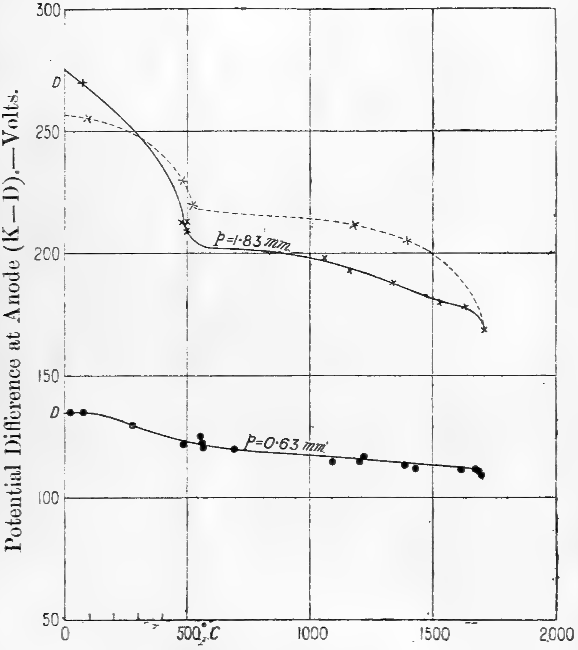
Temp. of Anode.		Potential Difference.					Current.		Pressure, mm. of Mercury.
Defln.	° C.	A − K.	A − B.	B − D. (calc. *obs.)	A − D. (calc. *obs.)	D − K.	Defln.	Amps. ×10⁴.	
0·55	20	632	407	90*	497	135	25·1	8·37	0·602
0·55	20	632	410	90*	...	...	25·3	8·43	
0·55	20	632	409	90	499	133	25·1	8·37	
17·5	484	620	400	97	497	123	21·6	7·20	
17·7	488	623	410	91	501	122	25·1	8·37	
19·5	530	...	413						
20·9	562	623	410	92	502	121	25·0	8·33	
26·8	693	623	410	93	503	120	25·5	8·50	
30 ?	...	623	413	...	...	...	25·7	8·57	
46·5	1093	623	409	99	508	115	25·1	8·37	
52·5	1205	623	408	99	507	116	25·0	8·33	
63·0	1390	623	408	101	509	114	24·8	8·27	
73·2	1563	623	407	103	510	113	24·3	8·10	
			409	...	...	...	25·1	8·37	0·650
76·4	1617	623	410	101	511	112	25·5	8·50	
80·1	1680	(630)	414	(104)	(518)	112	25·1	8·37	
80·6	1685	630	430	89	519	111	25·1	8·37	
81·0	1693	640	440	90*	530*	(110)	...	...	0·633
65·3	1430	640	...	...	530*	112	25·5	8·50	
		(640)	452	(72)	(524)	116	25·5	8·50	
53·3	1220	640	452	71	523	117	26·5	8·83	
20·8	560	640	458	60	518	122	28·9	9·63	
20·65	555	640	450	65	515	125	24·7	8·23	
20·7	556	640	444	70	514	126	23·5	7·83	0·619
9·0	280	640	446	64	510	130	23·9	7·97	
2·0	78	645	446	64	510	135	24·1	8·03	
1·2	49	645	447	63	510	135	24·6	8·20	

already been mentioned, the gas in this part of the tube remained quite dark. But on allowing the current to fall gradually below the above value a brilliant yellow positive column began to rise up from the anode, and the potential-gradient in this part of the discharge increased very rapidly. It was at first thought that the tube had begun to leak rapidly until a direct measurement with the McLeod gauge disproved this. The cathode-fall had also only shown a very slight diminution. And on increasing the current the potential-difference (D − A) fell off again instantly to its former immeasurably small value.

While confirming the old well-known observation that at ordinary temperatures the cathode-fall increases with increasing current-density, this table also shows that, on the other hand, at high temperatures the cathode-fall diminishes with increasing current.

The measurements of the fall of potential along the discharge at different temperatures of the anode are collected in Tables XV. and XVI. at pressures of 1·83 and 0·63 mm. respectively. The effects of temperatures on the fall of potential close to the anode are shown in fig. 8. This "anode-fall" (K—D) shows a steady diminution with rising temperature. The changes of potential-gradient near the cathode were probably mainly due to its slow warming up, the amount of which could not, however, be measured.

Fig. 8.



It will be noticed that though the total potential-difference across the electrodes diminishes, yet the "anode-fall" (K—D) increases with increased current at all temperatures of the anode, though, perhaps, less markedly at high temperatures. The potential-gradient in the positive column, as we have noticed before, diminishes with increasing current.

I am glad of this opportunity to express my indebtedness to Professor Thomson for many encouraging suggestions during the progress of the work.

St. John's College, Cambridge.

LXXV. *Excited Radioactivity and Ionization of the Atmosphere.*

By E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, and* S. J. Allen, *M.Sc., Demonstrator in Physics, McGill University, Montreal*.*

THE experiments of Elster and Geitel[†] and C. T. R. Wilson[‡] have shown that a well insulated charged conductor placed inside a closed vessel gradually loses its charge, and that this loss of charge is due to a small spontaneous ionization of the volume of air inside the closed vessel. Wilson calculated from his results that about 19 ions per c.c. are produced in the air per sec. In a later paper[§] Wilson has shown that the ionization in different gases varies approximately as the density and pressure of the gas. These results point to the possibility that the ionization observed in gases may be due, in part at least, to the emission of an ionizing radiation from the walls of the containing vessel.

Recently Elster and Geitel[||] made the interesting discovery that a negatively charged conductor, placed in the open air, becomes temporarily radioactive. This radioactivity decays in the course of a few hours. The phenomena appear to be closely analogous to the "excited" radioactivity produced by the radioactive emanations of thorium and radium. The excited activity from the air can be concentrated on the negative electrode in exactly the same way as one of the authors[¶] has shown for thorium-excited activity.

In addition Elster and Geitel have shown that the substance responsible for the radioactivity can be removed by solution in acid. On evaporating the solution to dryness an active residue, which decays with time, is left behind in the vessel. This also is in striking agreement with what one of us (*loc. cit.*) had previously shown for thorium-excited activity.

In the experiments of Elster and Geitel, and Wilson, the amount of ionization of air has been determined by observing the rate at which the leaves of a charged electroscope of special construction fall together. This method, while very simple and advantageous for some experiments, is, in general, slow, and in many cases does not allow of sufficient variation of experimental conditions.

In the present investigation the authors have utilized a

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[*] Communicated by the Authors. [Communicated to the American Physical Society, Dec. 27, 1901; Abstract published in the *Phys. Zeit.* No. 11, 1902.

[†] *Phys. Zeit.* Nov. 24, 1900.

[‡] Proc. Roy. Soc. March 1901.

[§] Ibid. Dec. 1901.

[||] *Phys. Zeit.* iii. p. 76 (1901); xl. p. 590 (1901).

[¶] Phil. Mag. Feb. 1900.

sensitive quadrant electrometer for examination both of the ionization and excited radioactivity produced in air.

The electrometer employed is a modification of the Dolezalek electrometer which is described in *Instrumente Kunde*, Dec. 1901. It is of the ordinary quadrant type, with a very light needle of silver paper suspended by a fine quartz fibre. The apparatus, as constructed by Herr Bartels, of Göttingen, was for determination of small P.Ds. for electrochemical work. For our purpose it was necessary to completely alter the insulation and method of connexion of the quadrants. In the present experiments the needle was charged at intervals of two days by lightly touching the needle by a fine wire connected to a battery of 200 volts. It was found that the needle did not lose more than 10 per cent. of its charge in 24 hours. The damping of the needle, on account of its lightness, was fairly rapid, and no extra damping vane was required. The deflexion was observed by a telescope and scale at a distance of 2 metres. The zero point was found to be very steady. For the first suspension employed the electrometer gave a deflexion of about 1800 mms. of scale corresponding to one volt P.D. between the quadrants, when the needle was charged to 200 volts. This suspension was accidentally broken in the course of the experiments and was replaced by a quartz fibre which gave only about $\frac{1}{4}$ of this deflexion for the same voltage. When dealing with the very small rate of discharge which is produced by the spontaneous ionization of air, it is very essential that every precaution should be taken to guard against external electrostatic disturbances. The electrometer and all the connecting wires were inclosed in gauze cylinders connected to earth. The floor and woodwork in the immediate neighbourhood of the testing apparatus were covered with metal connected to earth. The separation of the quadrants was done by means of a special mercury key operated from a distance by a cord.

The insulating substances necessary in experimental arrangements were completely diselectrified by means of flames.

Production of Excited Radioactivity.

The simplest method of obtaining a large amount of excited radioactivity from the air is to expose a long insulated wire charged to a high negative potential in the open air. After exposure for several hours the wire is removed and wound on a frame, or in the form of a flat helix. The ionization produced by the radioactive wire in the testing vessel is then observed, by means of the electrometer, in the usual way.

Elster and Geitel in their experiments have used an electroscope to measure the ionization produced.

In order to produce a considerable quantity of activity on the conductor it is necessary to charge the wire to a high negative potential. Potentials varying from −5000 to −100,000 volts have been used in the experiments.

A positively charged wire remains quite inactive however long it may be exposed.

Decay of Excited Radioactivity.

The excited radiation from the air decays with the time in a manner similar to the excited radiation from thorium and radium, but at a different rate. The excited radiation from thorium falls to half value in about 11 hours, while the excited activity from air falls to half value in about 45 minutes for the range of voltages examined. It has been shown* that the excited radiation from radium decays in an irregular manner, the rate of decay depending on the time of exposure. The rate of decay is rapid at first, then nearly stationary for some time, and then a regular decay to zero, falling to half value in about 30 minutes. It is thus seen that the rate of decay of excited activity, due to the atmosphere, is more nearly allied to that from radium than to that from thorium.

In the experiments detailed below the excited activity was produced on a long insulated copper wire, 15 metres long, suspended outside the laboratory window about 15 feet from the ground.

The wire was kept charged by means of a Wimshurst machine driven by a motor. The potential of the wire was measured by means of the sparking-distance between two brass knobs.

In order to regulate the potential of the exposed wire to any desired value a needle-point connected to earth was placed near a small plate connected to the charged wire. The distance between the point and the plate was adjusted until the spark just refused to pass between the knobs. This method was found to be more satisfactory than varying the speed of the machine.

After the wire had been exposed a definite time, it was rapidly removed and wound on a rectangular metal frame 120 cms. long and 10 cms. wide.

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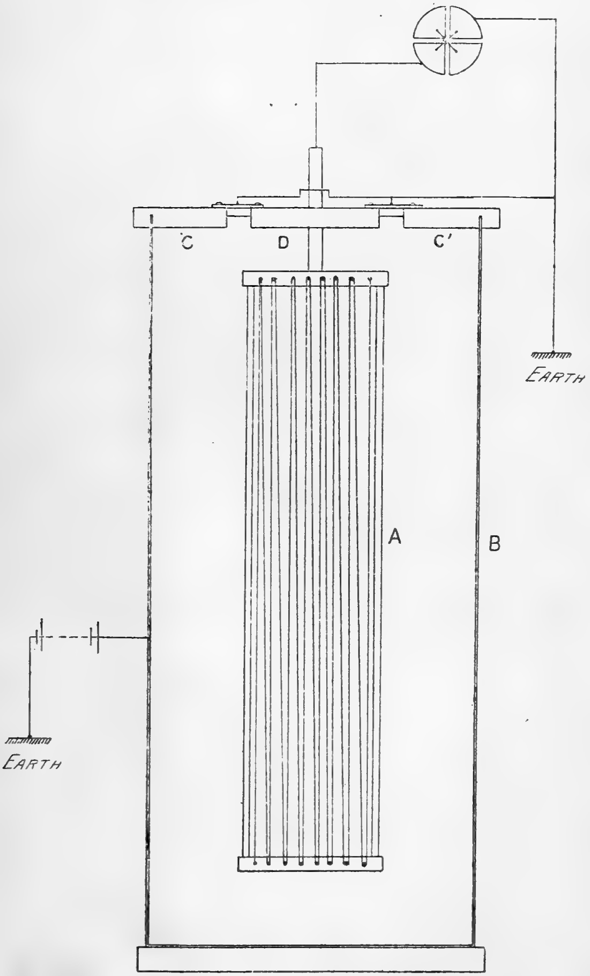
* Rutherford, *Phys. Zeit.* xii. p. 254 (1902); and Rutherford and Miss Brooks, Phil. Mag. July 1902.

The method of winding is shown in fig. 1, where the frame A is seen in position inside the testing cylinder B. The testing cylinder was of metal, about 150 cms. long and 30 cms. diameter. The outside cylinder was connected to a battery of 100 volts. In order to ensure that there was no conduction current between B and A over the supports the insulator CD was cut into two parts and separated by a metal ring connected to earth. The arrangement can be clearly seen from the figure.

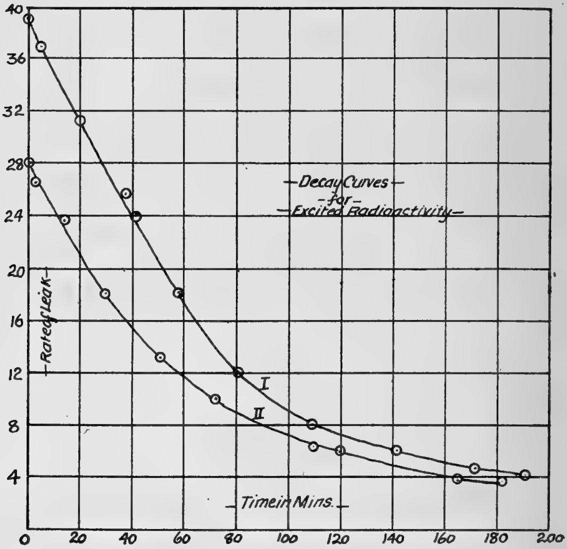
Fig. 1.



The radiation from the wire ionized the gas inside the testing cylinder and the current between the electrodes was observed with the sensitive electrometer in the usual way. On account of the weak ionization of the air by the radiation a P.D. of 100 volts was sufficient to remove all the ions to the electrodes before appreciable recombination, and to give the maximum current through the gas.

Fig. 2, I shows the decay-curve for a copper wire exposed 210 minutes inside the laboratory at a P.D. of −26000 volts; fig. 2, II the curve for the same wire exposed 270 minutes in the open air at −24000 volts. The ordinates represent divisions per sec. of the electrometer and the abscissæ time in minutes.

Fig. 2.

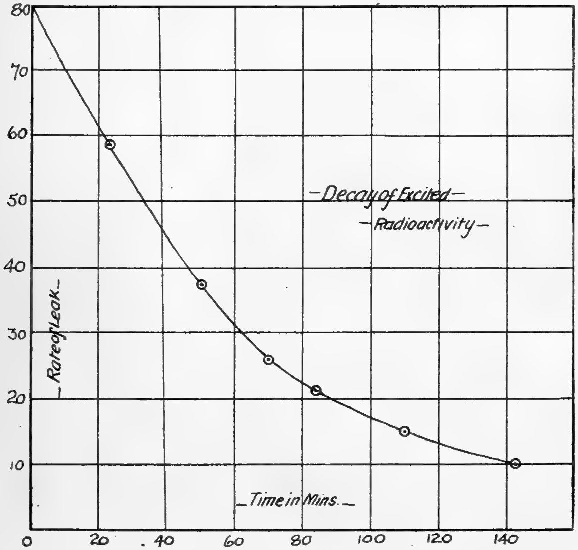


In most of the experiments (especially when the wire was exposed for several hours) it was found necessary to use a condenser in parallel with the electrometer to decrease the rate of movement of the needle.

There was always a current (about 2·5 divisions per sec.) in the testing vessel when the wire was inactive, due to the spontaneous ionization of the air in the cylinder. Allowing for this it will be seen that the current (which is proportional to the intensity of the radiation) falls off in a geometrical progression with the time, falling to half value for both cases in about 45 minutes.

Fig. 3 is a decay-curve for a lead wire exposed in an attic 190 minutes at −25000 volts. In this case the lead wire was wound in the form of a flat spiral and placed inside a testing vessel consisting of two parallel plates, one of which was connected to the electrometer and the other to the battery. This again falls to half value in about 45 minutes.

Fig. 3.



A large number of curves of decay have been determined under very varying atmospheric conditions, but no certain differences in the rate of decay have been observed, although the *amount* of excited activity in a given time varies greatly with the weather and amount of wind. The rate of decay was the same for a copper as for a lead wire, and was independent of the diameter of the wire. The rate of decay for a brass rod charged at −100,000 volts was about the same as for a lead or copper wire exposed at −5000 volts. The rate of decay for low voltages has not been investigated.

We may thus conclude that over the range examined the rate of decay is regular and independent of conditions. In this respect also it resembles the excited radiations produced by thorium and radium.

It will be seen, from these results on the rate of decay, that if the intensity of the excited radiation is initially I_0, the intensity I after a time t is given by

$$I = I_0 e^{-\lambda t}.$$

Since $I=\frac{1}{2} I_0$ when $t=45$ mins.

$$\lambda=\cdot 00026.$$

If the excited activity produced on the wire is due to a uniform rate of deposit of radioactive material the radiation from which decays with the time according to the above equation, it necessarily follows* that the intensity I after a time of exposure t is given by

$$I=I_0(1-e^{-\lambda t}),$$

where I_0 is the maximum value of the intensity reached after a very long exposure.

If this result is correct the amount of excited activity in a given wire for a fixed voltage should reach half its final value in 45 minutes.

Some experiments have been made on this point with wires exposed in the open air for different times. The amount of excited radioactivity in the air was found, however, to be too variable to test the truth of the equation. The results, however, showed that the amount of activity increased at first roughly in proportion to the time, but after three or four hours' exposure reached a practical maximum. More accurate experiments on this point are at present in progress, using a closed room instead of the open air, when the amount of excited activity is much more constant.

The amount of excited radioactivity from the air increased with the voltage of the exposed wire. On account of the variation of the amount of excited radioactivity in the air from hour to hour and day to day no definite results on the variation of the amount of excited radioactivity with the voltage were obtained.

Effect of Weather Conditions.

A large number of experiments were made on the effect of atmospheric conditions on the amount of excited radioactivity from the air. The wire was usually exposed for 30 minutes at a voltage of -25000 volts, outside a laboratory window, at a height of about 15 feet from the ground. The results showed that the amount of excited activity produced from the air varied very greatly with the atmospheric conditions.

Other conditions being the same, a bright clear day gave more excited activity than a dull cloudy day. The effect of temperature was not very marked. If anything slightly more activity was obtained on a bright day during the Canadian winter, with a temperature of about $-20°$ C., than

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* E. Rutherford, Phil. Mag. Feb. 1900, p. 180.

on a bright warm day in the spring. The most powerful factor in determining the amount of activity given to the wire is the presence or absence of wind. A windy day always gave much greater effects than a quiet day, when other conditions were the same. This is true whether the air was cold or warm, or the day bright or dull.

Most of the experiments were made during the Canadian winter, when there was about two feet of snow over the ground. The prevailing wind was from the north, and had been carried over snow-covered lands. The fact that the amount of activity was uninfluenced by the presence of snow shows that the excited activity is not likely to be due to any effect arising from vegetation. The amount of water-vapour in the air appears to have little influence on the result, for at $-20°$ C. the air is extremely dry.

Penetrating Power of Excited Radiation.

It has been shown in a previous paper* that the penetrating power of the excited radiations of thorium and radium was the same. As the penetrating power is one of the methods of distinguishing between the various radiations a special experiment was made to compare the penetrating power of the excited radiation from the air with that of other known radiations from radioactive substances.

Lead wire was employed in these experiments as it could readily be retained in the form of a flat helix. The wire was excited by exposure of two to three hours at $-30{,}000$ volts. It was then wound to form a flat helix and placed between a parallel plate apparatus. The ionization current between the plates was observed for different numbers of sheets of thin aluminium foil placed over the helix. The average thickness of the aluminium foil was $\cdot 00034$ cm.

The results are shown in Curve I. fig. 4 (p. 712) where the penetrating power of other known types of radiation are added for comparison.

The excited radiation due to air has greater penetrating power than any of the types of radiations, not deviated by a magnetic field, from the radioactive substances uranium, thorium, and radium, and is also more penetrating than the excited radiation produced by radium and thorium.

No special experiment has been made to determine the absorption of the excited radiation in its passage through the air, but its approximate amount can be readily deduced from known data. In all the different types of radiations examined

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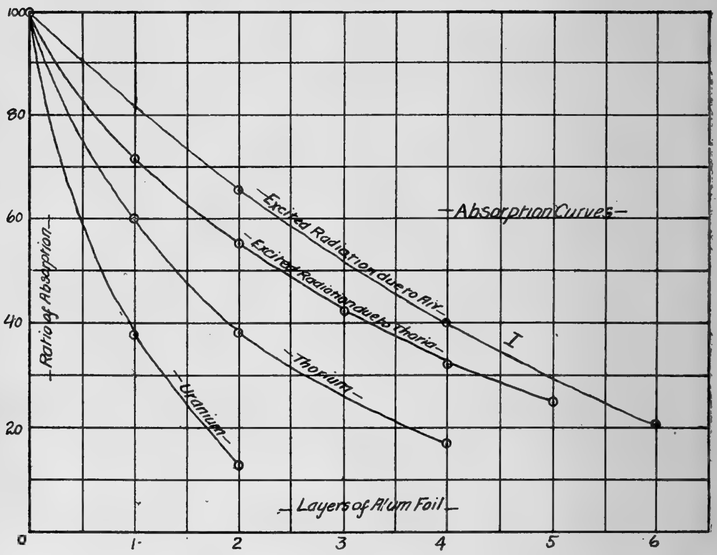
* E. Rutherford and Miss H. T. Brooks, Phil. Mag. July 1902.

it has been generally found that if one radiation is more easily absorbed than another, in aluminium for example, it is also more easily absorbed in air. Since the excited radiation from the air is slightly less absorbed in aluminium than that due to thorium, we can thus conclude that it is slightly less absorbed in air.

Fig. 4.



Now it is known that the intensity of the excited radiation from thorium falls to half value after passing through 1·6 cms. of air. It thus follows that the intensity of the excited radiation from air falls to half value after passing through about 2 cms. of air, and is almost completely absorbed in a distance of 10 or 12 cms.

From the differences observed for the penetrating power and ratio of decay we can conclude that the excited radiation from air cannot be ascribed to the presence of any known radioactive substance in the atmosphere.

Transmission of Excited Activity.

We have seen that the excited radiation from the air is similar in all respects to the known types of excited activity by thorium and radium. In both cases the activity is confined to the cathode in an electric field, and can be partly removed by rubbing with a cloth or by solution in acid.

The differences observed in the rate of decay and penetrating power of the radiations show that the effects obtained cannot be ascribed to the presence of a minute quantity of thorium or radium emanations in the atmosphere. The close resemblance in the phenomena, however, renders it probable that the excited activity from the air is due to a process similar in character to that which produces excited activity from the emanations of thorium and radium. One of the authors* has recently shown that in the case of radioactive substances the excited activity is due to a transmission of positively charged radioactive carriers to the cathode. These carriers travel in an electric field with about the velocity of the positive ions produced in air by Röntgen or Becquerel rays.

There seems to be little doubt that the excited activity is due to a deposit of a minute quantity of intensely active radioactive matter. Such an hypothesis is essential to explain the facts of solutions, and that the radioactivity can be transferred from the radioactive body to the cloth by rubbing. The production of excited activity from the air cannot be ascribed to any surface action on the conductor due to the electric field. A wire does not give any appreciable activity if it is confined in a cylinder where the volume of air is small, although the wire is subjected to the same voltage as in the open air. All the evidence obtained up to the present points strongly to the conclusion that the excited activity is derived from the volume of the air surrounding the charged wire. Since the activity is confined to the cathode, the carriers to which the activity is due must possess a positive charge. These carriers may obtain a positive charge either by the condensation of temporary radioactive matter of some kind round the positive ion already existing in the air, or by the expulsion of a negative electron from the carrier. The latter explanation seems the more probable, for we now know † that all the radioactive substances thorium, radium, and uranium, as well as the excited activity due to thorium and radium, possess the property of spontaneously expelling electrons.

There is as yet no definite evidence of the origin or mode of production of these radioactive carriers in the air, but assuming their presence, many of the experimental facts observed receive a simple explanation.

The higher the potential of the wire the greater the distance from which the carriers are conveyed to the cathode. The amount of excited activity on a wire exposed in free space, on this view, should increase rapidly with increase of voltage.

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* *Phys. Zeit.* x. p. 210 (1902).

† Rutherford and Grier, *Phys. Zeit.* xvii. p. 385 (1902).

There is strong evidence that a wire charged to a high potential attracts the carriers over a large volume of air. It was experimentally found that the amount of excited activity obtained from a wire charged to − 20,000 volts in a cylindrical vessel of volume 141,000 cub. cms., when outside air was drawn through it at a rate of 500 cms. per sec., was only a few per cent. of the amount obtained from the same wire in the open air.

The increase of excited activity observed on days on which a strong wind is blowing is, on this view, due to the continued supply of fresh carriers which are brought in the sphere of action of the electric field. Since the exposed wire merely acts as a collector of radioactive carriers under the influence of the electric field the amount and nature of the excited radiation should be independent of the nature of the conductor, and this is found to be the case.

It thus appears probable that radioactive carriers are continually produced from some constituent of the atmosphere, but at a rate depending on atmospheric conditions. Bright clear weather appears to be the most favourable condition.

Since the earth is nearly always charged negatively with regard to the upper atmosphere, it follows that these radioactive carriers are being continually deposited over the surface of the earth. We must thus regard the earth as covered with an invisible layer of intense radioactive material which ionizes the air strongly within a few centimetres of the surface. The presence of these carriers in the volume of the air will also cause the production of fresh ions throughout the atmosphere, for each carrier acts as a radiating centre. A hill or mountain peak, or any high mass of rock or land, concentrates the earth's electric field upon itself and consequently it will receive more excited radioactivity per unit area than the level plain. Elster and Geitel have pointed out that the greater ionization observed in the neighbourhood of projecting peaks, receives a satisfactory explanation on this view.

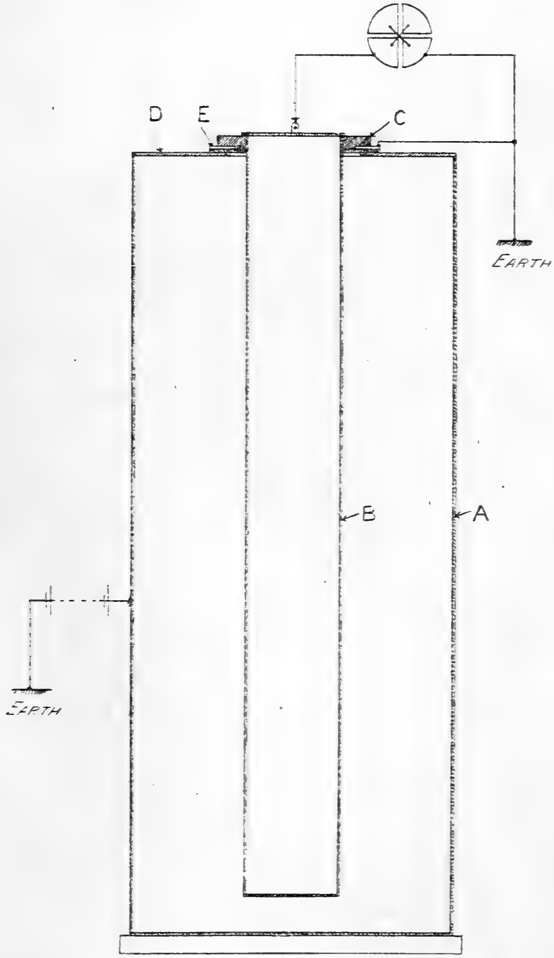
Spontaneous Ionization of the Air.

The experimental arrangement shown in fig. 5 was employed for determining the number of ions produced per c.c. per sec. in air and the variation of the ionization current with the strength of the electric field.

The current was observed by means of the electrometer between two concentric zinc cylinders A and B, 154 cms. in length, 25·5 and 7·5 cms. in internal diameter. The cylinders were placed vertical and the base of both cylinders closed.

The large cylinder was closed at the top by a zinc plate, in the centre of which was a circular opening slightly larger than the internal cylinder. A metal flange, fixed round the top of the inner cylinder, rested on an ebonite ring C.

Fig. 5.



Between the ebonite and the zinc plate D was placed a ring of thin metal E, connected to earth, which rested on a similar ring of a partial insulator like cardboard. The thin metal ring, connected to earth, served as a guard ring and ensured that even with a large P.D. between the cylinders, no current could leak across the insulator to the inner cylinder, which was connected to the electrometer in the usual way. The outer cylinder was connected to one pole of a battery of small storage-cells, the other pole of which was earthed.

The electrometer needle showed quite a rapid movement due to the ionization current between the electrodes with a P.D. of a few volts between the cylinders.

The cylinder was made fairly air-tight and allowed to stand undisturbed. Observations of the current between the cylinders were made at intervals for over a month. In order to avoid correction for the slight variations in sensitiveness of the electrometer from day to day, the ionization current between two paralleled insulated plates due to a standard sample of uranium oxide was observed at the same time. Previous experiments have shown that the uranium oxide is a very constant source of radiation.

The following tables show the variation of the current, due to the spontaneous ionization of the air, with the P.D. between the cylinders. Table I. is for air which has stood undisturbed for a month inside the vessel; Table II. for the ordinary air of the room several hours after it had been introduced into the apparatus.

Table I.

P.D. in volts.	Current in divisions per sec. of electrometer.
·4	·34
·8	·50
2·1	·59
4·2	·65
6·5	·67
13	·71
26	·72
52	·73

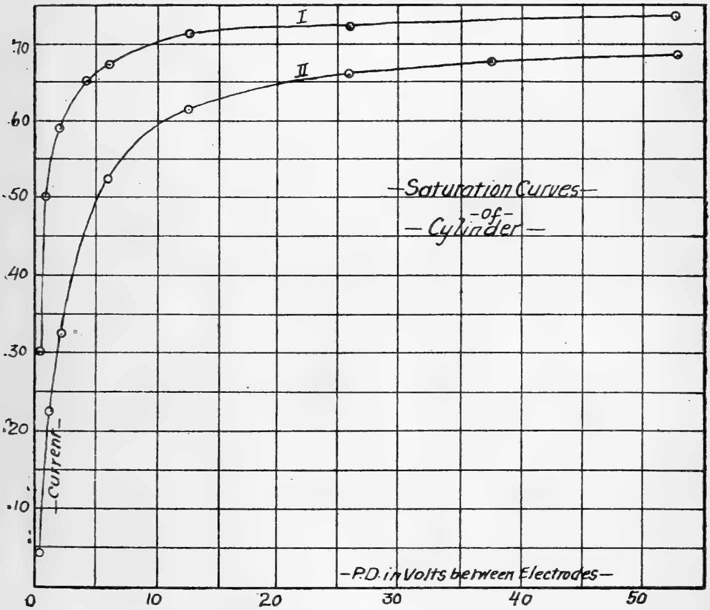
Table II.

P.D. in volts.	Current in divisions per sec. of electrometer.
·2	·04
1·05	·22
2·1	·32
6·5	·52
13	·61
26	·65
39	·67
52	·68

The results are expressed graphically in fig. 6, curves I. and II. respectively.

The curves are very similar to those observed when the air is ionized by Becquerel or Röntgen rays. The current first increases approximately directly as the voltage, but soon reaches a stage in which large variations of the voltage only cause a slight increase in the current. On account of the very small amount of ionization of the air and consequent slow rate of recombination of the ions, the maximum current is reached for a very small voltage. The current for 50 volts is not very different for the two samples of air, but in Curve I. the current reaches an approximate maximum much earlier than in Curve II. This difference is probably due to the presence of dust particles in the air in the latter case. Some of the ions in their slow passage between the cylinders give up their charges to the dust nuclei. This action causes an increase in the rate of combination of the ions and consequently a larger electric field is required to produce the maximum current.

Fig. 6.



The capacity of the electrometer, cylinder, and connexions, was 150 E.S. units when 1 mm. division of electrometer corresponded to ·00182 volt. The average value of the movement of the electrometer needle was 100 divisions in 132 seconds for 50 volts between the cylinders.

The current between the cylinders was thus

$$6{\cdot}9\ 10^{-4}\ \text{E.S. units}$$

$$\text{or}\quad 2{\cdot}3\ 10^{-13}\ \text{amperes.}$$

The volume of air between the cylinders was 71200 c.c. Taking the value of $6{\cdot}5\ 10^{-10}$ E.S. units, found by J. J. Thomson[*] as the charge on an ion, the number of ions produced per c.c. per second is 15.

[*] Phil. Mag., 1898.

This is not very different from the value of 19 found by Wilson for air inside a silvered glass vessel, using the electroscope method.

No certain difference was observed in the current for a period of time extending over one month. The production of excited radioactivity from the air suggested the possibility that a radioactive emanation was present in the air and that this might cause the ionization observed. If this is so, the radiating power decays at an extremely slow rate, or the emanation is being continuously reproduced in the inclosed space.

Application of the Ionization Theory.

In the spontaneous ionization of air we are dealing with an extremely slow rate of production of ions, and it is of interest to see how far the experimental results are in agreement with the ionization theory of gases, which has been previously tested in cases where the ionization is many thousands of times more intense than the present one. We have already noted that the variation of current with the voltage is in general agreement with the theory.

If q is the constant rate of production of ions per sec. and no electric field is acting, the number n of ions per c.c. increases until the rate of production is equal to the rate of recombination of the ions, or $q=\alpha n^2$, where α is the constant of recombination.

Now we have shown that $q=15$, and McClung* has found from the recombination of ions of Röntgenised air that

$$\alpha=3400\,e \text{ about},$$

where e is the charge on an ion.

Substituting these values, we find

$$n=2600,$$

i.e., when a steady state is reached, the number of ions per c.c. is 173 times the number produced per second. The time T taken for this number of ions to diminish to half, supposing the rate of production stopped, is given by

$$\begin{aligned} t &= \frac{1}{\alpha \mathrm{N}} \\ &= 174 \text{ seconds.} \end{aligned}$$

We can obtain a rough approximation of the agreement with theory of the current voltage curve shown in Curve I. (fig. 6) from the following considerations.

The electric field X, at any point distant r from the centre

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* Phil. Mag. March 1902.

of two concentric cylinders of radii *b* and *a*, is given by

$$X=\frac{V}{r\log_e\frac{b}{a}}=\frac{\cdot 82\,V}{r},$$

substituting values of *b* and *a* of cylinders in fig. 5.

Now if N is the maximum number of ions per c.c., the current *i* per unit length of cylinder over any cross-section, when a small P.D. V is applied, is given by

$$i=2\pi r\,.\,N\,.\,e\,.\,u\,.\,X,$$

where $u=$ sum of velocities of positive and negative ions in unit field.

Substituting the value of X

$$i=1\cdot 64\,\pi NeuV.$$

If I is the maximum current when all the ions produced reach the electrodes

$$I=qe\pi(b^2-a^2),$$

and

$$\frac{i}{I}=\frac{1\cdot 64\,N\,.\,u\,.\,V}{q(b^2-a^2)}.$$

Now for a P.D. of ·36 volt the current *i* is ·4 of its maximum value (see Table I. p. 716).

Now it will be shown later in the paper that the velocity of the ions produced in air is about the same as that of the ions produced by Röntgen rays. The value of *u* (the sum of the velocities of the positive and negative ions) for a gradient of 1 volt per cm. is thus about 3·2 cms. per sec.

Substituting these values, we obtain

$$\frac{N}{q}=32.$$

Taking into consideration that ·4 of the ions are removed by the current before recombination, it follows that when no voltage is acting

$$\frac{N}{q}=\frac{32}{\cdot 6}=53 \text{ roughly}.$$

Now we have shown that if α has the same value as that obtained for intense ionizations

$$\frac{N}{q} \text{ should equal } 174,$$

a value over three times as great.

There are, however, several causes at work which tend to make the observed value less than the theoretical. In the first place, no correction has been made for the disappearance of ions by diffusion to the sides of the vessel. This can be shown to be quite an important factor in causing a low value of $\frac{N}{q}$.

Curve II. (fig. 6) shows what an important influence the presence of dust has on the shape of the current voltage curves. In addition, it has been assumed, for simplicity of calculation, that the potential gradient is not disturbed by the movement of the ions. Experiment and theory have, however, shown that there is a sudden drop of potential near both electrodes and that the electric field some distance from them is less than if no ions were present. All of these three causes act in the same direction and tend to give too low a value of $\frac{N}{q}$. The agreement between theory and experiment is thus as close as could be expected under the experimental conditions.

The results show clearly that, when air is kept in a closed vessel and no electric field is applied, the number of ions per unit volume, when equilibrium occurs between the rate of production and dissipation, is more than 50 times the number produced per sec. per unit volume.

Velocity of the Ions.

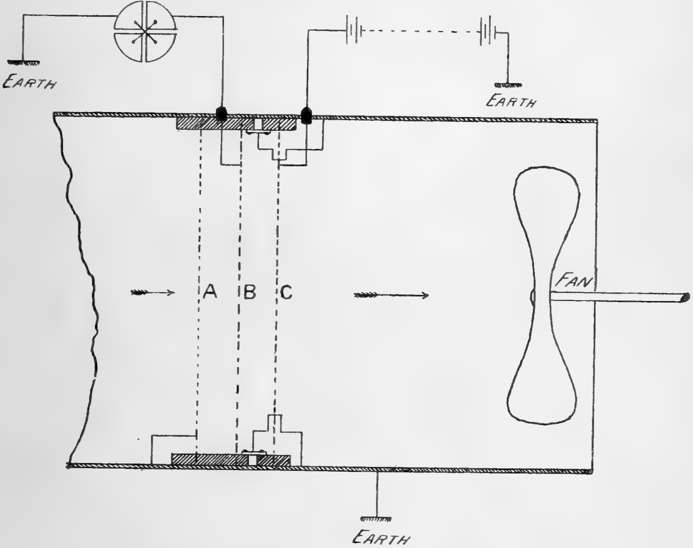
Some experiments were made to obtain an approximate estimate of the velocity of the ions which are spontaneously produced in air and at the same time to determine the number of ions per unit volume present in the outside air.

For this purpose, the apparatus shown in fig. 7 was employed. Air from the outside of the building was drawn through a zinc cylinder, length 200 cms., diameter 30 cms., by means of a fan driven by a motor.

The air in its passage through the tube passed through three circular parallel wire gauzes, A, B, C, 2 cms. apart and insulated from each other. The first gauze A was connected to earth, the second B to the electrometer, and the third C to one terminal of a battery of storage-cells, the other terminal of which was to earth. A guard-ring, connected to earth, was arranged between B and C to ensure there was no conduction leakage across the insulators between B and C.

Suppose gauze C is charged positive. The positive ions, carried with the current of air between the gauzes, start to travel up against the current of air, while the negative ions travel to the positive electrode with the current. If the velocity of the positive ions in the electric field is greater than the current of air, they will all reach the gauze B and for a given current of air the current observed with the electrometer will be unaltered when the strength of the electric field is increased.

Fig. 7.



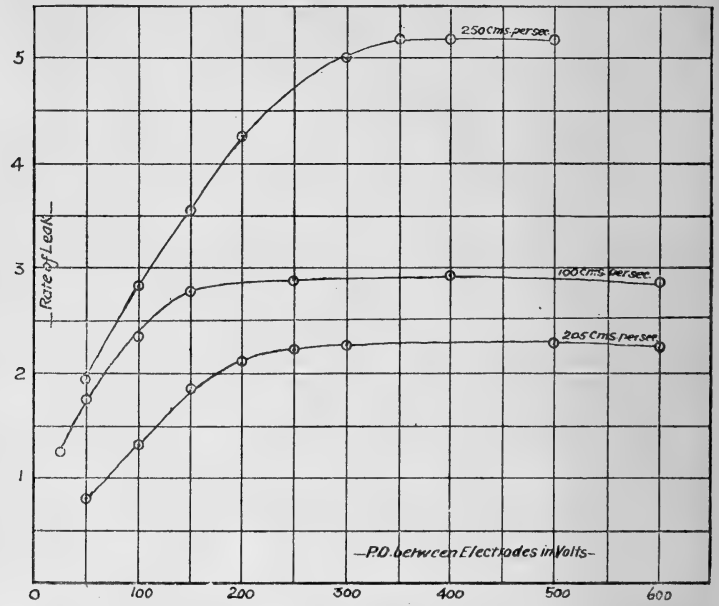
It was experimentally observed that even with a small electric field, there was some current to the gauze B. This amount increased with the voltage to a practical maximum. The experimental results are shown graphically in fig. 8 (p. 722) for velocities of the current of air of 100, 205, and 250 cms. per sec. respectively, when the gauze C was charged positively. It will be seen from the curves that, for a velocity of 250 cms. per sec., the maximum current is reached with a P.D. of about 350 volts. Since the gauzes were 2 cms. apart, the velocity K of the positive ions for a potential gradient of 1 volt per cm. is given by

$$K=\frac{2u}{V}=\frac{2\times 250}{350}=1{\cdot}4 \text{ cms. per sec.,}$$

where u is velocity of current of air and V the smallest P.D. for which the maximum current is reached. The other two curves also give a value of the positive ion of about 1·4 cms. per sec. It was not found possible to obtain more than an approximate result for the velocity of the ions, on account of the variation in the conductivity of the air drawn through in the course of a series of observations. The curves shown in fig. 8 were obtained on special days when the variation of the conductivity was small.

Observations made in a similar way, to determine the velocity of the negative ion, were not very definite on account of variations during an experiment. The results showed that the velocity of the two ions was about the same, but it was not possible to decide whether the negative ions move slightly faster than the positive, as is the case for ions produced by Röntgen and Becquerel rays in air.

Fig. 8.



The results obtained for the velocity of the ions are only approximate in character, but they point to the conclusion that the ions produced spontaneously in the atmosphere travel at about the same rate in the electric field as the ions produced in air by Röntgen and Becquerel rays. In a recent determination Zeleny * has shown that the sum of the velocities of the positive and negative ions, produced by Röntgen rays in dry air, is about 3·2 cms. per sec.

Variation of the Number of Ions in the Air.

By noting the *maximum* current between the gauzes, an estimate can be made of the number of ions per unit volume present in the air drawn through.

If A is the area of the cross-section of the cylinder, u the mean velocity of the current of air, N the number of ions per unit volume, the maximum current i observed by the electrometer is given by $i = A \,.\, u \,.\, N \,.\, e$,

where e is the charge on an ion.

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* Phil. Trans. Roy. Soc. 1900.

Substituting the observed values of i, A, and u in this equation, the value of N can be deduced. The value of N was found to be variable both from hour to hour and day to day. The following numbers illustrate a few of the results obtained.

Date.	Number of ions per unit volume.
Nov. 20, 1901	40
,, 21 ,,	30
,, 23 ,,	14
,, 27 ,,	16
,, 30 ,,	13

The temperature of the air in most of these cases was about −12° C.

A bright clear day was found to give a greater value of N than a dull day.

A very similar apparatus has been employed by H. Ebert[*] to determine the number of ions present in the air, only in his experiments the air was drawn between concentric cylinders, and an electroscope employed instead of an electrometer.

We see from the above results, that the number of ions per unit volume in the air varies considerably, but on three days was almost the same as the number produced *per sec.* in a closed vessel.

This is a surprisingly small number if we consider the outside air to be ionized at the same rate as the air inside the closed vessel; for we have shown earlier in the paper, that in a closed space the number of ions per c.c. increases to 50 times the number produced per sec. before the rate of recombination is equal to the rate of production.

After making due allowance for the causes tending to remove the ions, viz., the presence of dust and other particles in the outside air, and the electric field between the upper atmosphere and the earth, the number per unit volume is far lower than would be expected. It is possible that the spontaneous ionization of the air observed in closed vessels may be due (in part at least) to a *radiation* continuously emitted from the walls of the vessel. The spontaneous ionization of the outside air may, on this view, be much smaller than that observed in closed vessels, and the number of ions present per unit volume correspondingly less.

McGill University, Montreal,
June 9th, 1902.

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[*] *Phys. Zeit.* No. 46, 1901.

LXXVI. *Notices respecting New Books.*

Harper's Scientific Memoirs. Edited by J. S. Ames, Ph.D., Professor of Physics in Johns Hopkins University. 15 volumes. New York and London: Harper & Brothers, Publishers.

WE heartily commend the enterprise of the publishers in issuing this most timely series of reprints and translations of classical scientific memoirs. The 15 volumes published include the following:—

I. *The Free Expansion of Gases.* Memoirs by Gay-Lussac, Joule, and Joule and Thomson. Translated and edited by J. S. Ames, Ph.D.

II. *Prismatic and Diffraction Spectra.* Memoirs by Joseph von Fraunhofer. Translated and edited by J. S. Ames, Ph.D.

III. *Röntgen Rays.* Memoirs by Röntgen, Stokes, and J. J. Thomson. Translated and edited by George F. Barker, LL.D.

IV. *The Modern Theory of Solution.* Memoirs by Pfeffer, Van't Hoff, Arrhenius, and Raoult. Translated and edited by Harry C. Jones, Ph.D.

V. *The Laws of Gases.* Memoirs by Robert Boyle and E. H. Amagat. Translated and edited by Carl Barus.

VI. *The Second Law of Thermodynamics.* Memoirs by Carnot, Clausius, and Thomson. Translated and edited by W. F. Magie, Ph.D.

VII. *The Fundamental Laws of Electrolytic Conduction.* Memoirs by Faraday, Hittorf, and F. Kohlrausch. Translated and edited by H. M. Goodwin, Ph.D.

VIII. *The Effects of a Magnetic Field on Radiation.* Memoirs by Faraday, Kerr, and Zeeman. Edited by E. P. Lewis, Ph.D.

IX. *The Laws of Gravitation.* Memoirs by Newton, Bouguer and Cavendish; together with abstracts of other important memoirs. Translated and edited by A. Stanley Mackenzie, Ph.D.

X. *The Wave Theory of Light.* Memoirs by Huygens, Young, and Fresnel. Edited by Henry Crew, Ph.D.

XI. and XII. *The Discovery of Induced Electric Currents.* Vol. I.: Memoirs by Joseph Henry. Vol. II.: Memoirs by Michael Faraday. Edited by J. S. Ames, Ph.D.

XIII. *The Foundations of Stereo-Chemistry.* Memoirs by Pasteur, Van't Hoff, Lebel, and Wislicenus. Translated and edited by George M. Richardson, Ph.D.

XIV. *The Expansion of Gases by Heat.* Memoirs by Dalton, Gay-Lussac, Regnault and Chappuis. Translated and edited by Wyatt W. Randall, Ph.D.

XV. *The Laws of Radiation and Absorption.* Memoirs by Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen. Translated and edited by D. B. Brace, Ph.D.

The volumes are arranged on a uniform plan, which consists in having a general preface by the editor on the subject dealt with in the volume; this is followed by the memoirs, a biographical sketch of the author being appended to each memoir. The bibliography and index at the end of each volume form useful features.

In a few cases, where the papers seemed of excessive length, some portions have been left out; such omissions have, however, been indicated in every case, and as a good deal of judgment appears to have been exercised in the matter, the arrangement has not detracted from the value of the papers. We hope that the publishers will see their way to add to this most useful series of scientific classics.

Sichtbare und Unsichtbare Bewegungen. Von H. A. LORENTZ. Unter Mitwirkung des Verfassers aus dem Holländischen übersetzt von G. SIEBERT. Mit 40 eingedruckten Abbildungen. Braunschweig: F. Vieweg und Sohn. 1902. Pp. 123.

IT is not every distinguished man of science that condescends to write a popular book; and in many cases the attempt when made is hardly a success. But there are notable exceptions; and a perusal of the book before us has convinced us that Professor Lorentz's gift of clear exposition attains to the same high standard of excellence as that which characterizes his scientific work.

The book before us is the outcome of a course of seven lectures which the author was asked to deliver to a non-scientific audience, and forms most interesting reading. After expounding the leading principles of dynamics in the first three lectures, which are entitled respectively "Rectilinear Motion," "Curvilinear Motion," "Wave-Motion. Light-Waves," the author considers, in Lecture IV., the subject of Light in greater detail, especially in connexion with Spectrum Analysis. This is followed in Lecture V. by "Molecular Motion"—including a sketch of the kinetic theory of gases. Lecture VI,, on "Electrical Phenomena," is one of the most interesting in the book, as it contains a simple exposition of the electronic theory and the Zeeman effect. Lecture VII. is intended as a sort of *résumé* and expansion of the preceding lectures, considered with special reference to the principle of the Conservation of Energy.

The book is one which may be read with pleasure and profit by the advanced student as well as the general reader.

Electrochemical Industry. Vol. I. No. 1. 929 Chestnut St., Philadelphia, Pa., U.S.A., September, 1902.

THE appearance of a new periodical devoted entirely to the electrochemical industry is a healthy sign of the development of that industry in the United States. The first number promises well. It contains several interesting articles by well-known experts, one of the most striking of which is "Niagara as an Electrochemical Centre." We heartily wish the new periodical every success.

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