This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

THE

PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED BY

THE

AMERCAN PHYSICAL SOCIETY

VOL. III., SERIES II.

THE PHYSICAL REVIEW
LANCASTER, PA., AND ITHACA, N. Y.

1914

PRESS OF
THE NEW ERA PRINTING COMPANY
LANCASTER, PA.

CONTENTS TO VOLUME III., SECOND SERIES.

JANUARY, 1914.

FEBRUARY, 1914.

MARCH, 1914.

APRIL, 1914.

MAY, 1914.

JUNE, 1914.

Second Series *January, 1914* *Vol. III, No. 1*

THE

PHYSICAL REVIEW.

THE PHYSICAL PROPERTIES OF SELENIUM.

By P. J. Nicholson.

EVER since the discovery of the sensitiveness of the electrical resistance of metallic selenium to alteration in illumination, attention has been given to the problem of finding an explanation for the phenomenon. In late years, two views have been expressed regarding this. Pfund[1] introduced the idea that the effect is due to a resonance of the electrons in the atom, occasioning explosions which lead to an increase in the number of conducting electrons. This view has found favor with some investigators, particularly with Ries to whom a great amount of valuable work is due. It deserves attention for various reasons: First, the ultimate explanation found must be in terms of the electron theory if that theory is to remain a permanent part of our physical science. Again, the idea of resonance is a very plausible one to explain such an increase of conductivity. The second theory may be construed as quite in harmony with the first. Marc and others have obtained evidence that there exist at least two forms of metallic selenium of widely different electrical resistivity; and it is assumed that illumination brings about a transformation from the less to the more conducting of the two. This theory has been amplified and put in mathematical form by Brown,[2] who assumes the existence of three forms, selenium A, B and C.

As tests of these views, several lines of work suggest themselves, and the object of the present series of experiments was to obtain data that would be of help in the solution of the problem. Since the ultimate explanation must take into account the physical characteristics of the element, one of the first requisites is that satisfactory methods be obtained for the production of good films of selenium in its various forms. Accordingly, the first part of the work had that end in view. In the second

---

[1] Phys. Rev., XXVIII., 324, 1909.

[2] Phys. Rev., XXXII., 237, 252, 1911.

part, on the other hand, experiments having an immediate bearing on the theories to be tested were taken up.

SPUTTERING OF SELENIUM CATHODES.

There seems to be a great deal that is difficult to determine connected with the sputtering of selenium cathodes. Here, the observations of Longden[1] and later of Pfund,[2] that cathodes of metallic selenium do not yield films in the metallic form, was confirmed. When the current density is very small, films that are very thin but beautiful are yielded. Soon, however, the cathode becomes covered with a black powder which probably is some form of the element; and from that moment, satisfactory sputtering does not take place. Instead of continuous, semi-transparent films, layers appear that are wholly or in part granular in structure.

Since great difficulty has been experienced by different experimenters in obtaining semi-transparent films of metallic selenium by ordinary means, an effort was made to obtain them directly. The method that suggested itself at once was to keep the surface designed to receive the deposit at a temperature of 150° or thereabouts. This was done by using a small furnace of nicrome wire heated by a circuit that was taken through the base of the apparatus and insulated from it. For a variety of reasons, it was found very difficult to keep the pressure constant, and consequently, the temperature would vary. Nevertheless, several deposits were obtained whose surface possessed the appearance of metallic selenium; but their transmission, however, being reddish, showed the presence of some of the amorphous.

Accidentally, several films were obtained directly by sputtering from metallic cathodes which proved to contain at least a large fraction of the metallic form. One layer deposited on a platinum-on-mica grating was both conducting and light-sensitive. As its resistance was about 10^8 ohms, however, the cell was of little use. The conditions necessary for obtaining such deposits were not determined save that the cathode was always a metallic one that had been subjected to long heating near 200°, and that the current density was fairly great. It does not appear probable that this method will be of practical value in view of the ease with which good metallic layers can be obtained by the other process.

Films of amorphous selenium, on the other hand, can be formed by sputtering quite readily; but, if the current density is not very small, the cathode soon changes partly into the metallic state, and thereafter the films are granular, as before. It seemed desirable then to reduce the

---

[1] American Journ. of Sci., X., 55, 1900.

[2] PHYS. REV., XXVIII., 324, 1909.

heating effect within the apparatus to a minimum. With that end in view, a special cathode sputtering outfit was constructed. This will now be described.

Before the work had proceeded far, it was observed that alternating currents yielded quicker results than direct currents of equivalent voltage. This, no doubt, is due to the fact that the maximum voltage in the former is far in excess of the effective. It appeared better to use alternating current in all further work, but in order to decrease the heating effect, it should be rectified. This suggested the use of a point anode. The cathode was further cooled by a jacket of flowing water.

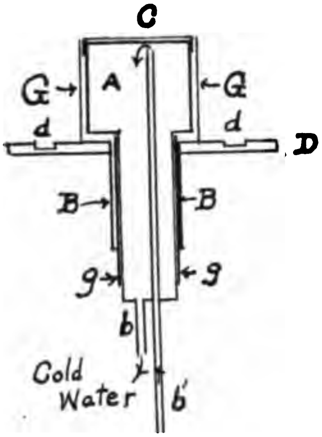


Fig. 1.

Section of cathode sputtering apparatus. *A*, brass chamber, fitted with brass tubes *b*, *b'* through which a steady stream of cold water was forced. *A* was fixed in brass tube *B* with cotinsky cement, and perfect insulation was assured by glass tube *g*. Top of chamber was made very thin and covered with a cap of aluminum foil *C*. Glass tube *G* kept discharge confined to top surface. Small bell-jar, fitted with point aluminum anode, was waxed into groove *d* in brass base *D*. Wire frame supported plate receiving the discharge from 1 cm. to 3 cm. above *C*, while a piece of aluminum foil covered with a layer of selenium was placed on *C*, serving as cathode for the discharge.

All who have ever tried to secure films of selenium by cathode sputtering must have observed that often small portions of selenium fall on the plate receiving the film and become nuclei for beautiful concentric rings which soon form around them. In order to obtain uniform films, then, this effect had to be eliminated; and sputtering upwards[1] was the obvious remedy. The apparatus was found very satisfactory with work on selenium, and moreover, proved to be more satisfactory than the commoner form for obtaining films of other metals. For example,

---

[1] This had been suggested by Dr. C. M. Sparrow for sputtering substances that cannot be made into continuous cathodes.

by its use, the time consumed in obtaining good mirrors of platinum was reduced by from one half to one third.

The vacuum found most advantageous was such that there was about one centimeter of dark space. As source of voltage a two thousand volt transformer was used. A large resistance was always used in series with the primary so that an E.M.F. of from a few hundred to two thousand volts was available. In no case could the latter be employed, for, as soon as its use was attempted, an emission of gas resulted that caused the pressure to rise above that which the work called for.

By means of this apparatus films of many kinds were obtainable. By using a fairly high current density, almost opaque films of amorphous selenium were deposited in less than one minute. It was found, however, that as a general rule, films deposited quickly were not as transformable as those deposited very slowly.

Other films were obtained that changed into semi-transparent metallic ones and stood long heating at a temperature near 200°. The pure metallic films were very easily distinguished by their plum-colored reflection and the absence of red in their transmission. Films with a good surface, but with some red in their transmission, are quite easily obtainable.

It was found that care should be taken to avoid having any sealing wax inside of the apparatus where the discharge might play on it. In addition to its emission of gas, this substance seems to have a special attraction for the selenium deposits, so that layers of the element accumulate on it in a very short time.

Transformation of Thin Films.

Considerable attention was paid to the transformation of selenium films, and this proved to be as enigmatical as the problem of sputtering. The question is here suggested whether transformation into the metallic state is ever complete or not. Some films, of considerable thickness, with beautiful red surfaces, withstood a temperature of 200° for twenty-four hours without showing any sign of transformation. Others would acquire a surface with the familiar plum-colored luster of the metallic selenium but whose transmission contained much red. Occasionally, a film was found which seemed to have transformed completely, having apparently no red transmission. These films were similar to that obtained by Pfund, whose optical constants were measured by him.

Some selenium films seem to vaporize quite readily. These could not be transformed satisfactorily, for it seemed that before transformation was complete, the continuity of the surface was destroyed. Others, again, changed into the metallic state quite readily, and these stood a heating up to nearly 200° for some hours. The conditions that must be fulfilled in order to transform thin films successfully seem to have partly to do with the process of heating and partly with the nature of the layer. One film on glass, about 2 inches square, was cut into small pieces, and each piece tried came over into the metallic state without difficulty provided the rate of heating was sufficiently slow. This indicates that the character of the films comes into play. All that can be said about the film is that it was yellowish in color, and was obtained when the rate of deposit was fairly slow while the glass plate was at a distance of nearly one inch from the cathode. All films so obtained, however, were not transformed, as the surface soon became broken, as mentioned above. It may be expected that if the pressure on the films were so increased as to cut down vaporization appreciably, transformation could be carried on successfully; and this is to be tested in a later experiment.

Ultra-Violet Absorption.

Several efforts were made to obtain a good semi-transparent film of selenium on quartz, with portions of two different thicknesses, so as to measure the optical constants in the ultra-violet. These, while untransformed, had absolutely no ultra-violet transmission. Although several films on quartz, of one thickness, were transformed, yet success was not met with in transforming films when portions were of different thicknesses. A rough determination of ultra-violet absorption was made, neglecting reflection; but so little of the light could be concentrated on a few square millimeters of film that the thermal couple deflections resulting were very small, and hence, not particularly reliable. It was established beyond doubt, however, that up to 230 $\mu\mu$ the absorption coefficient is not very different from what it is in the blue.

Ultra-Violet Sensibility.

It appears that no quantitative measurements of the sensibility of selenium cells to ultra-violet radiation have ever been made, and it was determined to extend the sensibility curve as far as possible into the region of short wave-lengths. The source of illumination first used was an improved form of water-cooled iron arc designed by Dr. Pfund. This was found to possess such intensity that thermal couple deflections of ten to twenty-five centimeters could be obtained quite readily around 300 $\mu\mu$, while the intensity around 250 $\mu\mu$ was considerable. The arc, however, did not possess the steadiness necessary for this work and it had to give way to a quartz mercury arc, kindly lent by Professor Wood, to whom I owe my best thanks. As only a small portion of the arc could be concentrated on the spectrometer slit, the intensity obtainable was much smaller than that yielded by the iron arc, but in the matter of steadiness it left nothing to be desired.

The apparatus was set up as in Fig. 2. The lens system *L* included a water cell that cut out infra-red radiation. Screens and diaphragms cut down all diffused radiation. The concave nickel mirror M_1 focused the light of the quartz mercury arc *Q* on the vacuum thermal couple *T*, while the plane nickel mirror M_2 was arranged in a frame in such a way that it could be slid down into the path of the beam so as to divert it on to the selenium cell *C*. The cell was covered with a piece of crystal quartz cut from a plate, the remainder of which furnished the window of the thermal couple *T*. This arrangement insured that the amount of absorption was the same in each case. Experiments were carried out with two cells made by Giltay, and the results found were not essentially different. In each case, the cell was connected through the galvanometer *G* with a storage battery *B* of, usually, twelve volts. Torsion was then applied to the galvanometer suspension so as to restore the zero of the instrument to its initial position. Change of conductivity caused by a certain illumination was noted as indicated by the change in galvanometer deflection.

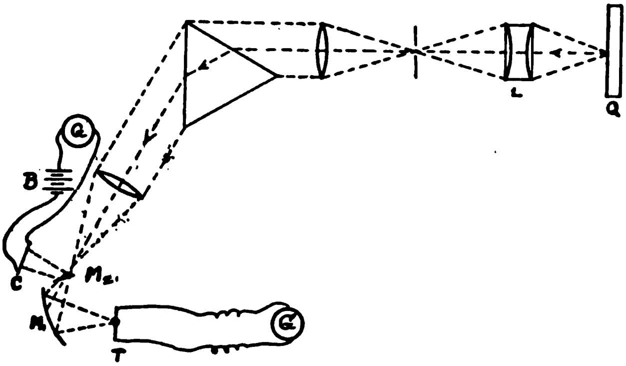


Fig. 2.

The galvanometer attached to the cell had a sensibility of 1.2×10^{-9}. It was found necessary to introduce a shunt cutting this down by a factor 3 so as to keep the deflections within the desired range. The thermal couple readings were made on the same scale, which was placed at a distance of two meters from the galvanometer.

A vacuum thermal couple was used and the chamber containing the element was joined to a vacuum[1] tube with charcoal anode, by means of which the vacuum was tested and maintained from time to time. This apparatus was kindly constructed by Dr. Pfund. The galvanometer used was one of the D'Arsonval type, and had a resistance of 20 ohms. This instrument was made by the writer. The sensitiveness of the galvanometer was 3×10^{-9} amperes while a candle placed a meter away from the thermal couple produced a deflection of 24 cm.

Limited exposure of the cell to the radiation was arranged for by using a sector rotated on the axis of the second hand of a small clock, a device used by Pfund in his latest experiments. In the same work, Pfund has shown that Talbot's law is applicable to the selenium cell, and hence, a rotating sector may be used to obtain beams of different energy. In this way, readings for unit, ½, ¼ and ⅛ energy were made. These readings indicated that the deflections for any wave-length obeyed with a very fair degree of accuracy the law

$$d = DI^{\frac{1}{2}}$$

established for the range from blue to yellow by Pfund in the work referred to above. Instead of spending much time in obtaining equal energy deflections in each case, a set of readings was made for every prominent group of lines in the Hg spectrum, using the most convenient energy readings. From these D, the change of conductivity corresponding to unit energy, was calculated, as shown in Curve 1. With each group of lines the maximum deflection for full energy was obtained. The inertia throughout the ultra-violet was observed to be small.

Sensibility Curves with Continued and with Limited Exposure.

Pfund[2] has shown that when selenium cells are exposed to monochromatic light for 12.5 sec., d, the increase in conductivity, varies with I, the intensity of the illumination, according to the law

$$d = DI^{\beta},$$

where D is a constant for any particular wave-length. β was found to be very nearly ½ for regions of the spectrum from the violet to the yellow. As the red is approached, however, β increases; so that with deep red and infra-red $\beta = 1$. For the shorter wave-lengths, this agrees with the results found by Rosse, Adams and Berndt. This relation was tested from 230 $\mu\mu$ to 900 $\mu\mu$ and found to hold with a fair degree of accuracy.

Most of these experiments, however, were carried on in mid-summer in Baltimore, where the temperature was very high, with very consider-

---

[1] See Pfund, Phys. Rev., XXXIV., 370, 1912.

[2] Phys. Rev., XXXIV., 370, 1912.

able variations and with great humidity. The results so obtained are accordingly not so reliable as would have been found under more favorable circumstances, and their agreement is not so good. Pfund, on the other hand, worked in winter, in a room in which the temperature was kept constant to one tenth of a degree. Changes in temperature are known to affect cells very markedly, while the observations of Ries and others indicate the dependence of cells on humidity. The Giltay cells are put up so that there is absolute communication between the outside air and the selenium surface, hence the variations. One cell was enclosed in an airtight box, with glass window, after it had been dried thoroughly, and thereafter it showed a marked improvement in its behavior.

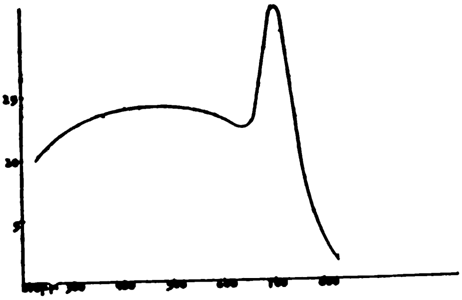


Fig. 3.

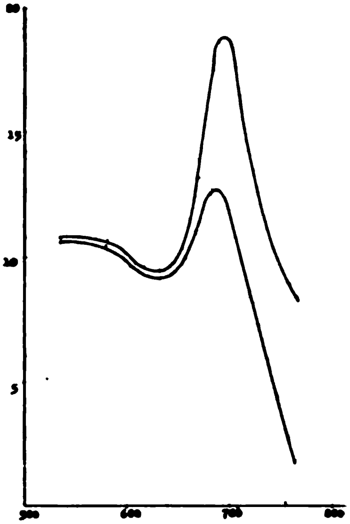


Fig. 4.

Curve 1. Sensibility of the Giltay cell extended into the ultra-violet. E.M.F. on cell, 12 volts. Time of exposure, 12½ seconds. Ordinates represent change of conductivity in terms of galvanometer deflections.

Curve 2. Showing sensibility when time of exposure was 15 seconds contrasted with the corresponding sensibility when time of exposure was unlimited. This shows the increase of inertia with the wave-length.

For the 12.5 sec. exposures the observations of Pfund were fully verified. The region in which the deflection varies as the square-root of the incident beam was found to extend into the ultra-violet, as far back as 230 $\mu\mu$. When the time of illumination was reduced to 10 sec., a noticeable increase in the value of β followed, with a small shift of the region in which β becomes 1 towards shorter wave-lengths. With the longer illuminations (15 and 20 sec.) the contrary was the result, as might be expected. Finally, with exposure until a steady state was reached, it was found that β was approximately constant and equal to .5 throughout the entire spectrum. There appeared, however, to be an appreciable minimum in the value of β about the region 600 $\mu\mu$, for here the value found in many sets of readings was about .4. The variation involved, however, may be seen to be comparatively small when we consider that it can be accounted for by a variation of less than 7 per cent. in one of the readings of deflection on which the value of β is based. The difficulties mentioned above make themselves particularly manifest here since the intervals between readings varied from about two minutes in the violet to from ten to twenty minutes in the infra-red; and as a result, conditions had an opportunity of changing very considerably during that time. If the interval between readings is not sufficiently long, fatigue makes itself manifest and the readings are affected. Curve 2 illustrates the difference between 15 sec. exposure and unlimited exposure.

VARIATION OF INERTIA WITH WAVE-LENGTH.

Fig. 4 shows that there is a very marked difference between the inertia of the red and infra-red as compared with the rest of the spectrum. It would be better, however, to show graphically the time required to reach say $\frac{3}{4}$ of saturation value of deflection in different parts of the spectrum, and this will be done shortly. The difference between the full deflection and that after a limited exposure is, apparently, constant from 230 $\mu\mu$ to near 700 $\mu\mu$; but here it very suddenly increases until it attains a value many times greater than before. The exact difference varies somewhat, corresponding to humidity and temperature, and very markedly to fatigue when the cell has not been allowed a sufficient rest between readings: but the general facts are always the same. This difference between the action of different parts of the spectrum led to the following experiments, suggested by Dr. Pfund.

EFFECTS DUE TO A STEADY ILLUMINATION USING BEAMS FOR WHICH k IS NEARLY CONSTANT.

The cell was subjected to a steady illumination, first of green light, and again of deep red, and, finally, of infra-red, and sensibility curves were taken as before. This was brought about by obtaining a parallel beam of light from a Nernst glower, and throwing it on the cell by means of a right-angled prism, through a window on the apparatus covered by an absorption screen. As is the case when the current passing through the cell is great owing to a high E.M.F., so it was found here that the conductivity of the cell was very unsteady when it had been increased five to ten times by illuminating it. It was, accordingly, found necessary to interpose an inclined piece of plate glass in the path of the beam so as to cut down the conductivity to the desired degree.

In one experiment with cell No. 2, the conductivity was increased about three times by means of a beam of red light. The absorption cell used was composed of equal parts of a 10 per cent. solution of sodium bichromate and a 1 per cent. cyanine solution. This had a slight transmission throughout the spectrum but only a very little up to 710 μμ. The results found can be summed up by saying:

1. The sensibility from the violet to the orange was slightly decreased. The red maximum, however, was almost entirely cut out, and the cell became practically insensitive at about 750 μμ.

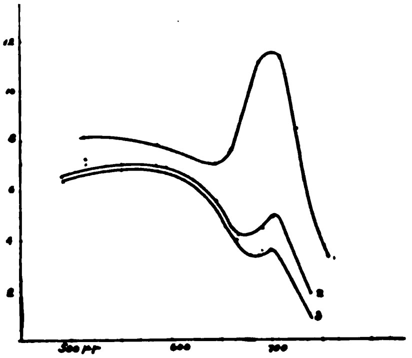


Fig. 5.

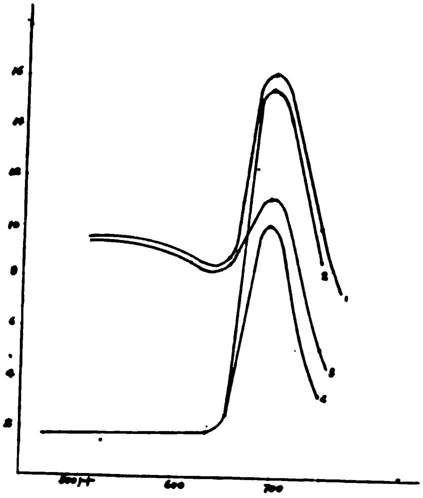


Fig. 6.

Curve 3. Cell subjected to a steady infra-red beam that increased its conductivity 2½ times. 2 and 3 show sensibility with unlimited and 15 sec. exposures, respectively. 1 gives corresponding ordinary sensibility curve.

Curve 4. Cell subjected to steady beam of green light that increased its conductivity 3 times. 2 and 4 show sensibility with unlimited exposures and 15 sec. exposures, respectively. 1 and 3 show corresponding ordinary curves. Cell unsteady. Inertia very marked in red and infra-red.

2. The inertia of the cell was very markedly decreased.

A second absorption cell whose transmission was strictly confined to the infra-red from 800 μμ to 1,950 μμ, was then used. This cell consisted of equal parts of a .6 per cent. solution of naphthol green and a 1 per cent. cyanine solution. The amount of radiation transmitted was such as to increase the conductivity about 2.5 times. The results here differed very little from those obtained using the red cell, save that the red maximum was cut out more completely and that the sensibility extended a little less far towards the infra-red. The results of this experiment are shown by Curve 3.

Finally, experiments were carried out using a saturated solution of copper chloride for the absorption cell. The transmission of this cell was not accurately determined; but it is well known that such solutions have a maximum transmission in the green while they are opaque to wave-lengths longer than .65 μ. The conductivity was now increased to three times its original value. The results that followed are shown in Curve 4, and were quite different from those hitherto obtained, for:

1. The sensibility was reduced almost to nil on the shorter wave-length side of the red maximum. The red maximum itself was reduced slightly as was the infra-red sensibility.
2. Inertia was quite marked.

Röntgen Rays.

To test further the laws stated above experiments were performed using Röntgen rays as exciting source.

To cut down the intensity of the rays by definite steps, a large rotating sector of heavy sheet lead was made. The quartz window of the cell was replaced by one of aluminum foil. By actual test, with the Röntgen ray tube in the position which it occupied throughout the experiment, the lead was of such thickness as to shield off all effects due to the rays.

A second piece of sheet lead was mounted in front of the rotating sector so as to allow only a narrow beam to strike the cell. The sector was rotated by means of an electric motor whose speed was quite high. By sliding the motor on its support, any portion of the sector could be brought in front of the hole in the lead sheet so that full, three quarters, one half or one quarter the intensity of the beam could fall on the cell.

As observed by other experimenters, the effect of Röntgen rays on the cell proved to be very slow. This rendered it an easy matter to take a reading with considerable accuracy when the exposure was of limited duration. Of course it was necessary that there should be two observers; one to observe the time, and the other to read the deflection of the galvanometer.

The results obtained from this experiment differ but little from those obtained using the long wave-lengths. With short exposures, an approximate first power law held. Exposure until a steady deflection was reached required a wait of from 15 to 30 minutes for each reading, and a still longer wait for recovery of the cell. The results indicated an approximate square root law as the following set of readings will show:

Intensity of Rays.	Deflection after 15 Sec.	Maximum Deflection.
1	3.40	11.50
2	7.70	17.00
4	15.30	24.10

ABSENCE OF SELECTIVE EFFECT.

The work of Pohl and Pringsheim on the external photoelectric effect of the alkali metals has shown that this effect depends on whether the incident light is polarized, and on the plane of polarization. Ries has found that the internal effect in selenium shows no such peculiarity through an experiment in which he allowed polarized light to fall on a cell at an angle of 45°, and observed that the deflections were of equal magnitude regardless of direction of current. A direct test of this had been made before the work of Ries was published.

A Nicol prism was introduced between the pair of lenses that focused the light of the Nernst glower on the slit of the spectrometer. A series of readings was taken throughout the visible spectrum, with the light polarized first in the plane of incidence, and then perpendicular to that plane. Suffice it to say that at no wave-length could a difference be detected between the deflection due to a given amount of energy, whether polarized in a particular plane or not. It is possible, however, that roughness of the selenium surface destroyed the polarization of the light; and to obviate this difficulty the experiment is to be undertaken with cells having mirror surfaces obtained by cathode sputtering. This observation may or may not have some value from a theoretical point of view; at any rate it seems desirable to place on record the fact that it was made.

THEORETICAL.

In the following pages an effort is made to calculate on the basis of the electron theory, the various effects that should be expected on the hypothesis put forward by Pfund that the increase of conductivity is an internal photo-electric effect. At best, such a theory can be only approximate, if extraordinary complications would be avoided. In the development of the equations, it is found necessary to leave out of account such effects as the following:

1. Variation in the coefficient of recombination. In view of the work of Plimpton[1] it is highly probable that this quantity is subject to large variation while selenium is undergoing changes due to illumination of varying intensity.

---

[1] American Jl. of Sci., XXXV., 39, 1913.

2. Diffusion of the electrons. If an appreciable amount of diffusion does exist, the expression developed for the number of electrons present in a layer is inaccurate. Many experiments have shown that the absorption coefficient of metallic selenium is very high. If we take $k = 6 \times 10^4$ as the average value in the visible spectrum as obtained by Pfund, we see that the intensity of a beam of light is reduced to 1/1,000 of its initial value after penetrating

$$\frac{\log 1{,}000}{6 \times 10} = 1.1 \times 10^{-4} \text{ cm.}$$

If diffusion is not very large, then, the effective depth of penetration of the light must be much smaller than this thickness. Brown[1] has deduced from his observations that the effective depth is 1.4×10^{-3} cm. for the Giltay cell, and if his assumptions are correct, diffusion must be a large factor. Further experiments relating to this point are under contemplation.

3. "Skin effect," owing to possible thinness of layer affected by light. It is possible, however, that no serious complication would enter from such a source, as the effect would be to bring in a constant factor in the relation between number of electrons present and current flowing.

4. Variation of coefficient of absorption when conductivity is increased. Such a variation would be expected on the electron theory. However, Amaduzzi[2] found no variation in the emissivity when selenium was illuminated, and Pfund, in an unpublished research, using elliptically polarized light, could detect no change in the optical constants when the metal was illuminated by a second beam of very great intensity. This effect, if it exists, must be very small.

5. Non-uniform distribution of electrons while selenium is in the dark. It is quite probable that the density of the electrons very near the electrode is greater than elsewhere. However, this would probably introduce no serious complication.

6. Losses of electrons due to external photoelectric effect. This[3] effect is probably very small, particularly in the visible spectrum.

7. Secondary ionization.[4]

This treatment may not be fundamentally different from that which assumes chemical effects as the cause of transformations which take place in the selenium; for such transformations, in so far as they cause an increase of conductivity, mean simply a liberation of electrons. The equa-

---

[1] Phys. Rev., XXXIV., 201, 1912.

[2] Accad. Lincei, XVII., 590, 1908.

[3] See Amaduzzi, Rend. di R. Accad. Bologna, XIV., 39, 1910.

[4] See Robinson, Phil. Mag., XXV., 115, 1913.

tions here given, however, possess the advantage of being in terms of quantities which have a definite physical meaning, not one purely arbitrary constant entering into the system. Accordingly, a field is opened for experimental tests which should be capable of either disproving or verifying the theory proposed.

THE VARIATION OF CONDUCTIVITY WITH INTENSITY OF ILLUMINATION.

Consider a layer of selenium whose depth is s and whose area is A. Let N denote the density of the electrons in it while in the dark. Let M^2 denote the number of electrons produced per second in unit volume, while in the dark. There will be present NsA electrons in the whole layer, and, if α^2 denote the coefficient of recombination, we have, while the selenium is illuminated

$$M^2 = \alpha^2 N^2; \quad \text{or} \quad M = \alpha N.$$

Let I denote the intensity per unit cross section of a uniform monochromatic beam of light passing normally into the surface of the selenium. Of this amount Ie^{-kx} will reach a layer a distance x from the surface, k being the coefficient of absorption. $Ie^{-k(x+dx)}$ will pass out through a surface a distance $(x + dx)$ from the top. Then j, the amount of light absorbed in the layer of thickness dx just considered, will be

$$j = AIe^{-kx} - AIe^{-k(x+dx)} = AIe^{-kx}(1 - e^{-kdx}) = AIke^{-kx}dx.$$

It is reasonable to suppose that the number of electrons expelled from their atoms due to resonance will be proportional to j—say $\mu j = \mu AIke^{-kx}dx$. There will also be a spontaneous expulsion of electrons amounting to AM^2dx in this layer whether the surface be illuminated or not. If n represents the density of the electrons in the layer there will be a loss of α^2n^2Adx due to recombination. The total change per second in the number of electrons present in the layer will be

$$\frac{d}{dt}(nAdx) = AM^2dx + \mu AIke^{-kx}dx - \alpha^2n^2Adx$$

So that

$$\frac{dn}{dt} = M^2 + \mu kIe^{-kx} - \alpha^2n^2 \qquad (1)$$

$$= M^2 + c^2e^{-kx} - \alpha^2n^2,$$

$$= q^2 - \alpha^2n^2,$$

c and q being introduced to reduce the mathematical complication.

The solution for this equation may be put in this form:

$$n = \frac{q}{\alpha}\left\{ 1 - \frac{2}{\dfrac{q+M}{q-M}e^{2\alpha qt} + 1} \right\}. \tag{2}$$

Now, if we denote the total number of electrons present in the whole body by m, we have

$$m = \int_0^s A n dx = -A \int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \frac{q}{\alpha}\left\{ 1 - \frac{2}{\dfrac{q+M}{q-M}e^{2\alpha qt} + 1} \right\} \frac{2qdq}{q^2-M^2}.$$

It is seen immediately that the steady state following illumination, corresponding to $t = \propto$, is given by the first term of the integral. The second term is quite difficult to integrate; but an approximation to its value can readily be obtained if we consider the state of affairs when t has a considerable value. Then the term can be developed into a very rapidly converging series, of which the first term alone need be considered, so that

$$m = \frac{2A}{\alpha k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \left\{ \frac{-q^2dq}{q^2-M^2} + \frac{2q^2}{(q+M)^2} e^{-2\alpha qt}dq \right\} \tag{6}$$

$$\begin{aligned} &= \frac{2A}{\alpha k}\Bigg[(c^2+M^2)^{\frac{1}{2}} - (c^2e^{-ks}+M^2)^{\frac{1}{2}} + \frac{M}{2}\log\frac{M+(c^2e^{-ks}+M^2)^{\frac{1}{2}}}{M-(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ &\qquad\qquad \times \frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} \\ &\qquad - \frac{(c^2e^{-ks}+M^2)}{\alpha t\{(c^2e^{-ks}+M^2)^{\frac{1}{2}}+M\}^2} e^{-2\alpha t(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ &\qquad + \frac{(c^2+M^2)}{\alpha t\{(c^2+M^2)^{\frac{1}{2}}+M\}^2} e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}} \Bigg], \end{aligned} \tag{7}$$

neglecting all terms involving the factor $e^{-4\alpha qt}$; and since the quantity e^{-ks} is vanishingly small for cells that are opaque

$$\begin{aligned} m = \frac{2A}{\alpha k}\Bigg[&\left\{ (c^2+M^2)^{\frac{1}{2}} - M + \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} + \frac{M}{2}\cdot ks \right\} \\ &- \frac{1}{\alpha t}\left\{ \frac{1}{4}e^{-2\alpha Mt} - \frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2} e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}} \right\} \Bigg]. \end{aligned} \tag{8}$$

After steady state has been reached, *i. e.*, when $t = \propto$, the second term has vanished. Of the first term, the quantity

$$\frac{2A}{\alpha k}\cdot\frac{Mks}{2} = \frac{MAs}{\alpha} = NAs$$

obviously represents the total number of electrons present when cell is in the dark. The increase in the number of electrons owing to illumination of intensity I then is

$$m - m_0 = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)^{\frac{1}{2}}}\right]. \quad (9)$$

If M is very small as compared with c this reduces to

$$m - m_0 = \frac{2Ac}{\alpha k} = \frac{2A\sqrt{\mu k I}}{\alpha k} = \frac{2A}{\alpha}\sqrt{\frac{\mu I}{k}}. \quad (10)$$

As M increases in value, the proportionality between $m - m_0$ and c becomes less and less accurate.

Now, let us consider the relative value of c and M in a practical case. The number of electrons ejected by light of intensity I, according to our assumption, in an opaque layer is

$$\int_0^\infty k\mu I e^{-kx}dx = \mu I = \frac{c^2}{k}.$$

The number of electrons ejected, as indicated by the increase in conductivity, is usually of the same order of magnitude as the number produced spontaneously whether the cell is illuminated or not. Hence c^2/k is of the same order of magnitude as M^2. But, as seen, k is a very large number; hence c^2 is large compared with M^2, and in many particular cases, c will be large compared with M. We should, therefore, expect proportionality to exist between the increase in conductivity and the square root of the intensity of illumination, *i. e.*,

$$d = D\sqrt{I}.$$

This is the law verified by Rosse, Pfund, Adams, Berndt and the writer. It must be borne in mind, however, that D involves the coefficient of absorption, k, as well as μ, both of which are functions of the wavelength; hence the law will not hold for unresolved or partially resolved light. A different relation, therefore, should be expected for every source of unresolved light used. In order to obtain a complete expression connecting change of conductivity, intensity of illumination, and wavelength, it is necessary only to express μ and k as functions of the wavelength, correct I for loss of reflection, and insert its value in the equation. This problem does not at all seem hopeless.

DEPENDENCE OF SENSIBILITY ON DARK CONDUCTIVITY.

Referring to equation (9) it can readily be seen that $m - m_0$, to which the increase in conductivity is proportional, decreases as M increases.

Hence, for cells of high resistance, high sensibility would be expected. This, as a rule, is true of selenium cells. Assuming μ to be constant when the temperature is varied, we should expect a change in sensibility corresponding to temperature changes in resistance. Now μ should measure the external photoelectric effect, and this has been shown to be independent of temperature in the case of good conductors. The work of Amaduzzi[1] indicates a decrease of photoelectric effect of selenium with rising temperature, but his experiments were not carried below ordinary temperatures. However, if μ has not increased very markedly when the resistance is increased by lowering the temperature, we should expect a large increase in sensibility. This was verified by Miss McDowell[2] with a number of cells whose resistance increased several hundred times when their temperature was lowered to that of liquid air.

An experiment performed by Pochettino[3] does not admit of so ready an explanation, however. This physicist used a cell whose resistance fell very noticeably when its temperature had been lowered; but its sensibility increased somewhat, nevertheless. Cells whose resistance decreases at low temperatures are rather unusual, and to explain this effect a change in α, k or μ must be assumed.

Light-Negative Selenium.

Similar considerations lead to a possible explanation of light-negative selenium. We have, when steady state is reached,

$$m = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2} \log \frac{c^2}{4M^2} \cdot \frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)} + \frac{Mks}{2} \right]. \quad (11)$$

It is seen by substituting for c values of the same order of magnitude as M that the first term, representing the sensibility, is now small, while the last term, which represents the dark conductivity, is large. Now, if through the action of light α increased slightly, so that the second term would be slightly decreased, that decrease could easily be of such magnitude as to more than compensate for the first term which represents the change due to illumination. The latest work[4] on the value of α for gases indicates that when the distribution of ions is not uniform α is very much greater than it is for a uniform distribution. The impinging of light on selenium violently disturbs the distribution of electrons in the element; hence, an increase in a is plausible. Effects of this kind could not be expected to be great in agreement with the fact that the sensibility of light-negative selenium has always been found to be very small.

[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.

[2] Phys. Rev., XXXI., 524, 1910.

[3] Rend. R. Accad. dei Lincei, XI., 286, 1904.

[4] Plimpton, American Jl. of Sci., XXXV., 39, 1913.

INERTIA.

We next consider the case when t has a considerable value, but a steady state has not been reached. In such a case we have the additional term

$$\frac{2A}{\alpha^2kt}\left\{\frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}}-\tfrac{1}{4}e^{-2\alpha Mt}\right\}. \tag{12}$$

The quickness with which a steady state is reached depends on the quickness with which these terms disappear. Hence the inertia of a cell on illumination is seen to depend on the three coefficients,

$$\frac{1}{\alpha^2k},\quad \frac{1}{\alpha(c^2+M^2)^{\frac{1}{2}}}=\frac{1}{\alpha(\mu kI+M^2)^{\frac{1}{2}}}\quad\text{and}\quad\frac{1}{\alpha M}.$$

We should expect, then, that the rate at which a maximum deflection is approached should be:

1. Least for regions of smallest absorption. This is a well-known fact, verified throughout the present work. This also explains the slow action due to Röntgen rays.

2. Least when illumination is faintest. This has been mentioned by Pfund, Miss McDowell and others, and observed by the writer again and again.

3. Least for least value of dark conductivity. This was verified by Miss McDowell,[1] who found that the action at liquid air temperatures, where the dark conductivity is very low, became very sluggish.

POSSIBLE EXPLANATION OF ANOMALOUS EFFECTS.

We have seen that in ordinary experiments c is great compared with M; hence, the effect of the second term in equation (12) will be manifest long after that due to the first. When t is very small, however, the latter is the greater term. The quantity M, on the other hand, is widely different for different preparations, from the light-negative variety up to Ruhmer's soft and hard selenium. With a suitable choice of M the first term could be made to predominate for a moment. Under such conditions, we should expect a maximum deflection to be reached in an instant, followed by a slow decrease. Effects of this kind have been observed since the earliest work done on the element.[2]

DECREASE OF INERTIA WITH STEADY RED ILLUMINATION.

An explanation of the disappearance of inertia due to red light when a cell is illuminated steadily with light of shorter wave-length can be

---

[1] PHYS. REV., XXXI., 524, 1910.

[2] Ries, Die elektrischen Eigenschaften und die Bedeutung des Selens für die Elektrotechnik, p. 27.

obtained from similar considerations. Such an explanation is attempted in preference to a complete mathematical deduction owing to the great complications that arise in the solution of the equations. Here, steady illumination of the cell may be considered, on the average, with certain limitations, as being equivalent to a large increase in M. When the change in conductivity due to the incidence of a small amount of red light is then considered, we have the exponent of the first term small, since

$$c = \sqrt{k\mu I}$$

and μ is most probably small in regions of long wave-length. The two terms would, therefore, approach one another in value, so that the effect of both would be expected soon to disappear. On the other hand, the fact that μ and k are large for regions of shorter wave-length may explain satisfactorily the fact that there is no appreciable change in inertia in these regions.

Effect of Steady Illumination by Approximately Monochromatic Beam on Sensibility.

This theory is capable of development for the case just discussed when there is a steady illumination on the cell while its sensibility curve is taken. For this case the equations become extremely complicated and nothing is gained by reproducing them since a few simple considerations are sufficient to explain the facts. First, considering the case when there is a steady green illumination. As seen, we have the approximate law

$$d = D\sqrt{I},$$

D being a function of k and μ. Hence,

$$\frac{d}{dI}d = \frac{1}{2}\frac{D}{\sqrt{I}},$$

so that the sensibility to a given amount of illumination decreases as the total illumination is increased. If μ and k were constant, we should expect this decrease to be manifest throughout the spectrum, regardless of the steady illumination on our cell. But, as seen, D involves μ and k, both of which are functions of the wave-length. In regions of shorter wave-length, k being approximately constant, sensibility should disappear. In the regions of long wave-length, on the other hand, k is small. As a consequence, red light falling on a cell illuminated by green light will penetrate into its interior, to parts unaffected by green light, hence giving rise to an increase of conductivity that is almost unaffected by the presence of the green illumination.

When the cell is subjected to a steady beam of light whose coefficient of absorption is small while its sensibility is measured, the case is quite different. Obviously, the sensibility to light whose absorption is approximately the same as that of the steady beam will be very small, provided the value of μ is not very different. When a beam of light of shorter wave-length falls on such a cell, its action will be confined to a thin layer; but μ being tremendously greater here, the effect of the steady beam is hardly appreciable. This explains the retention of the blue and green sensibility when a cell is subjected to a steady beam of red or infra-red radiation.

INITIAL RATE OF CHANGE OF CONDUCTIVITY DUE TO ILLUMINATION.

Having discussed the rate of increase of deflection after light has been falling on the cell for a considerable length of time, but before the steady state is reached, it remains for us to discuss the initial rate of change. We have

$$\frac{dm}{dt} = -\frac{2A}{\alpha k}\frac{d}{dt}\int_{(c^2-M^2)^{\frac{1}{2}}}^{(c^2e^{-kt}+M^2)^{\frac{1}{2}}} \left\{\left(1-\frac{2}{\frac{q+M}{q-M}e^{2\alpha qt}+1}\right)\frac{q}{(q^2-M^2)}\right\}dq$$

which becomes, when $t = 0$,

$$= -\frac{8A}{k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-kt}+M^2)^{\frac{1}{2}}} \frac{q^3(q+M)(q-M)^2\,dq}{(q-M)(q+M+q-M)^2(q^2-M^2)}$$

$$= \frac{A}{k}c^2 = A\mu I.$$

The initial rate of change of conductivity is, therefore, proportional to the intensity of the incident beam.

If the time considered after incidence of light on the cell be small compared with the time required to reach a maximum deflection, we should expect the change of conductivity to be approximately proportional to the intensity. When the light used is of long wave-length, or when the intensity of the beam is very small, while time of exposures is about ten seconds, then, this relation would be expected to hold. This explains the first power law established by Pfund in regions of great wave-length. Stebbins[1] assumes the same relation in his work on stellar photometry, where the intensities used were very small, and, no doubt, the law was verified by him for such cases.

---

[1] Astrophys. Jl., XXXII., 185, 1910.

Recovery.

To find the expression representing the recovery of selenium, we proceed as follows:

When the illumination is cut off, there will still be produced M^2 electrons per unit volume per unit time. The rate of recombination will remain as before. Representing the density of electrons by n, as before, we have

$$\frac{dn}{dt} = M^2 - \alpha^2 n^2,$$

for which we have the solution

$$n = \frac{M}{\alpha}\left\{ 1 - \frac{2}{\dfrac{M + N'}{M - N'} e^{2\alpha Mt} + 1} \right\},$$

where N' denotes density of the electrons when $t = 0$, *i. e.*, when selenium was in a steady state under illumination.

Now, glancing at a previous equation we see that

$$N' = \frac{q}{\alpha} = \frac{1}{\alpha}\{c^2 e^{-ks} + M^2\}.$$

Having substituted this value and introduced a number of obvious approximations we obtain the solution in the form

$$m = NsA + \frac{4AM}{\alpha k}\left\{ 2 \log \frac{M\alpha + (c^2 + M^2)^{\frac{1}{2}}}{M\alpha + M} e^{-2\alpha Mt} - \frac{ks}{2}\left(\frac{1}{2} - \frac{1}{\alpha}\right) e^{-2\alpha Mt} \right.$$
$$\left. + \frac{1}{\alpha} \log \frac{c^2}{4M} \cdot \frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)^{\frac{1}{2}}} e^{-2\alpha Mt} \right\}.$$

The deductions to be made from this are not greatly different from the results of the former equation, viz.,

1. Rate of recovery greatest when absorption is greatest, amply verified by experiment.
2. Rate of recovery greatest for great values of I and μ.
3. Rate of recovery greatest with cells of high conductivity, a fact often observed and verified by Miss McDowell in her low temperature experiments.

Glancing at the terms involving t, we see that that quantity appears only in the expression $e^{-2\alpha Mt}$. Moreover, this quantity is associated with coefficients of considerable magnitude. Turning to equation (8) on the other hand, we see that the term controlling the time required to reach a steady state under illumination is $\frac{1}{2\alpha^2kt}e^{-2\alpha Mt}$. The latter, therefore, disappears much more quickly than the former. This is in agreement with experiment, for it is well known that it takes a longer time to return to the initial conductivity after a cell has been illuminated than it does to reach a steady state under illumination.

BEARING ON EFFECTIVE DEPTH OF PENETRATION.

The agreement between the above deductions and experiment indicates that the view expressed is correct that μ increases with decreasing wave-length. The only experimental evidence on this point is the work of Amaduzzi[1] who found that μ had a value in the ultra-violet but that it was too small to be measured in the visible spectrum. As seen, the approximate sensibility law is

$$d = D\sqrt{I},$$

where D is a function only of μ, α, and k. Moreover, k is nearly constant on the short wave-length side of 550 $\mu\mu$. This law would, accordingly, require a steady increase of sensibility as μ increased, and this is not borne out by experiment. It would seem, then, that a factor not taken into account in the above discussion enters into the problem. This strengthens the view of Pfund that the effective depth of penetration is so small here that Ohm's law fails to hold and it is necessary to introduce an undetermined factor in the relation between conductivity and number of electrons present.

TIME TAKEN IN REACHING A STEADY STATE.

The equations given above fail to represent the facts concerning the time taken to reach a steady state under illumination. The equations would indicate that this should be extremely short—less than a second, in an average case, probably. As a matter of fact, the time required by a selenium cell to reach a steady state is considerable, varying from about 20 seconds to several hours. It is probable that a distinction should be made between lag proper to the selenium owing to the change in conductivity caused by the illumination and the lag, due to Joule heating, and potential effects. At best, however, a considerable disparity exists on this point. A plausible explanation of it may be found in the fact that diffusion has been neglected in the development of the equations. Even if diffusion were so small that its effect had little influence on the general conclusions derived from the equations, it is quite possible that,

---

[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.

if its influence be taken into account in the latter, the time required to reach a steady state would be found to be lengthened considerably.

When this factor is taken into account, equations result as given below, for which a solution has not yet been obtained. Let n' denote density of atoms that have lost an electron, and C, the coefficient of diffusion of electrons. The reasoning used above will apply here, so that we have

$$\frac{\partial n'}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 nn'.$$

For electrons the equation will be somewhat different. $AC(\partial n/\partial x)$ electrons will enter the layer considered above through the top surface, in unit time. $AC[(\partial n/\partial x) + (\partial^2 n/\partial x^2)dx]$ will pass through the lower surface. The layer will gain, accordingly, $-AC(\partial^2 n/\partial x^2)dx$ electrons in one second, and we should have

$$\frac{\partial n}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 nn' - C\frac{\partial^2 n}{\partial x^2}.$$

SUMMARY.

1. Considerable information has been collected regarding the sputtering of selenium cathodes, and an improved form of sputtering apparatus has been used.

2. Many semi-transparent films of amorphous selenium have been transformed into the metallic state.

3. The ultra-violet absorption of metallic selenium was roughly determined.

4. Selenium cells have been found to retain a large sensibility down to 230 $\mu\mu$, and the sensibility curve for short wave-lengths was determined.

5. Sensibility curves were obtained when exposure was limited and of varied duration, as well as when steady state was reached. If change in conductivity be represented by d, energy of incident beam by I, while β and D are constants, the law $d = DI$ was found to hold with considerable accuracy in every case. When exposure is between 12.5 sec. and 20 sec. Pfund's results are confirmed that $\beta = 1$ in red and infra-red but $\beta = \frac{1}{2}$ for shorter wave-lengths. For unlimited exposures it was found that $\beta = \frac{1}{2}$ throughout the spectrum.

6. Sensibility curves were obtained with a cell permanently exposed to illumination of different wave-lengths, and different peculiarities were noted.

7. The law $d = DI^{\beta}$ was found to hold with considerable accuracy when the exciting source was Röntgen rays. For short exposures, $\beta = 1$, while $\beta = \frac{1}{2}$ when time of exposure is unlimited.

8. Experiments conducted with home-made cells indicate that they obey the same laws as the Giltay cell.

9. A mathematical deduction has been made, with the electron theory as a basis, from which the most important facts known regarding the behavior of selenium cells have been deduced. The facts accounted for are as follows:

(*a*) Variation of change in conductivity with square root of intensity for long exposures.

(*b*) Variation of change in conductivity directly with the intensity when time of illumination is short compared with that required to reach a steady state.

(*c*) High sensibility of cells of high resistance.

(*d*) Decrease of inertia with increasing intensity of illumination, absorption coefficient, and "dark conductivity." This also explains variation of sensibility with temperature and other disturbing factors.

(*e*) Dependence of rate of recovery upon the same causes.

(*f*) Change in sensibility when cell is illuminated continuously with a beam of light for whose constituents k is nearly constant.

(*g*) Decrease in inertia when this beam is red, or infra-red.

(*h*) Possible explanation of "light-negative" selenium and anomalous effects.

In conclusion I beg leave to express my best thanks to Professor Ames and the entire staff of the physical laboratory of the Johns Hopkins University for interest taken in the work; also to Mr. S. M. Burka, who assisted me in the construction of apparatus and in taking readings. I feel that special mention should be made of Dr. Pfund, who suggested the work and spared no pains in aiding me in every possible way.

CHARACTERISTICS OF CRYSTAL RECTIFICATION.

By Alan E. Flowers.

IN an article published in the Physical Review[1] some of the peculiarities of the uni-directional resistance between a conducting point and a rectifying crystal surface were described. Most of the measurements were made with direct current and the resistance showed a well-defined tendency to increase with time of current flow in the highly resisting direction and to decrease with time of current flow for the direction of easy current flow. Frequently, upon sudden reversal of current direction the initial resistance corresponded more nearly to the value just previous to reversal than to the final value for this direction of current. In most of the crystals examined some spots rectified well, and nearby portions of the surface rectified but little, if at all, or even gave rectification in the reverse direction. It was also found possible to produce rectifying spots on the surface of non-rectifying galena crystals by treating the surfaces with hot sulfur.

In view of these peculiarities it seemed desirable to subject crystals to very low and very high frequencies to see if time or energy were required to build up a resisting film upon change of current to the direction giving the higher resistance. Also it seemed desirable to determine the magnitude of the rectification at the high frequencies used in wireless telegraphy.

Two series of tests were carried out. One at Cornell University in December, 1910, was made possible by a grant from the Telluride Association, and another was carried out in the protective apparatus laboratory of the General Electric Company through the courtesy of Mr. E. E. F. Creighton, during the summer of 1912.

In the tests at Cornell University five different sources of supply were used. One of these was the 60-cycle lighting circuit. This was made the standard of comparison in every case. A double pole double throw switch was arranged so that the rectifier could be connected immediately either to this 60-cycle circuit or to the high frequency supply. The usual procedure was to measure the rectification on the 60-cycle circuit, then on a high frequency circuit, and again on the 60-cycle circuit as a check.

---

[1] 1909, Vol. XXIX., p. 445.

It is worth noting that the readings taken on the 60-cycle circuit in this way check with each other very well indeed, indicating a much greater constancy of rectification on alternating current than was to be expected from the variable values found when measuring the resistance with direct current. This method of checking both before and after the readings on high frequency eliminated chance effects such as, jarring, change of contact pressure, change of contact spot, etc. The contact point in these tests was a blunt ended piece of No. 13 B. & S. copper wire and the pressure on the point was about 250 grams. These values were such that considerable variations of either contact area or contact pressure would affect the rectification but slightly, if at all.

The effective value of the current was measured by means of a thermo-couple consisting of crossed wires of copper and constantan approximately 0.002 cm. in diameter. The current to be measured upon being passed through the copper-constantan crossover raised its temperature sufficiently to produce a thermal E.M.F. and a uni-directional current through a d'Arsonval galvanometer connected to the two ends of the crossed wires at right angles to the current path. A precaution to be observed in the use of this crossed-wire thermo-couple is to see that the crossed wires are well soldered together, otherwise the resistance of the contact causes current to flow directly through the galvanometer when calibrated with direct current or when being used for a partly rectified current. The deflections are then affected by the direction of the current through the couple and one may get a calibration curve that is nearer a straight line than a parabola. In taking measurements with this thermo-couple reversed readings were taken on the galvanometer to eliminate any slight error from this cause.

The average current was measured with a Weston permanent-magnet-type direct current mil-ammeter which gave full scale deflection for 20 milliamperes. For currents of 20 to 50 milliamperes this meter was shunted by non-inductive resistances.

Some of the results of these tests are presented in Table I.

A supply of approximately 2,000 cycles was obtained from an inductor alternator built by the Peerless Electric Company and belonging to the physics department. The wave shape given by this alternator is not known but is fairly smooth. The test results given in Table I. show a rectification ratio on 2,030 cycles very slightly poorer than on 60 cycles. The average difference from a number of such tests amounted to only 1 per cent. and could easily be attributed to wave shape. At the suggestion of Professor Frederick Bedell the effect of widely different wave shapes was tried making use of a complex wave consisting principally of

20-cycle and 60-cycle components which could be combined in different relative phase positions by varying the position of an induction motor rotor used as a transformer. The effective value being kept the same, the wave with the higher form factor should give the poorer rectification. This conclusion was confirmed by Tests Nos. 9 to 17 in Table I. The form factor for the wave given by rotor in position −20 was 1.154, while for the rotor in position 170 the form factor was 1.204. These values were calculated from the equations to the curve. I am indebted to Mr. Anderson, at that time a graduate student in Cornell University, for the use of this variable wave shape apparatus and for the equations to the curve. The difference in rectification was even greater than was to have been expected from the form factors. The effect of wave shape was even more marked on the poor rectifying spots where reverse rectification occurred.

In making the tests with very high frequencies use was made of a 500-volt direct current quenched spark oscillator. The arc played between electrodes lying in a powerful magnetic field and surrounded by an atmosphere of illuminating gas. This apparatus had been set up by Mr. F. H. Kroger, then of the electrical engineering department of Cornell University, who very kindly allowed its use for the purpose of carrying out these experiments. A diagram of the connections is shown in Fig. 1.

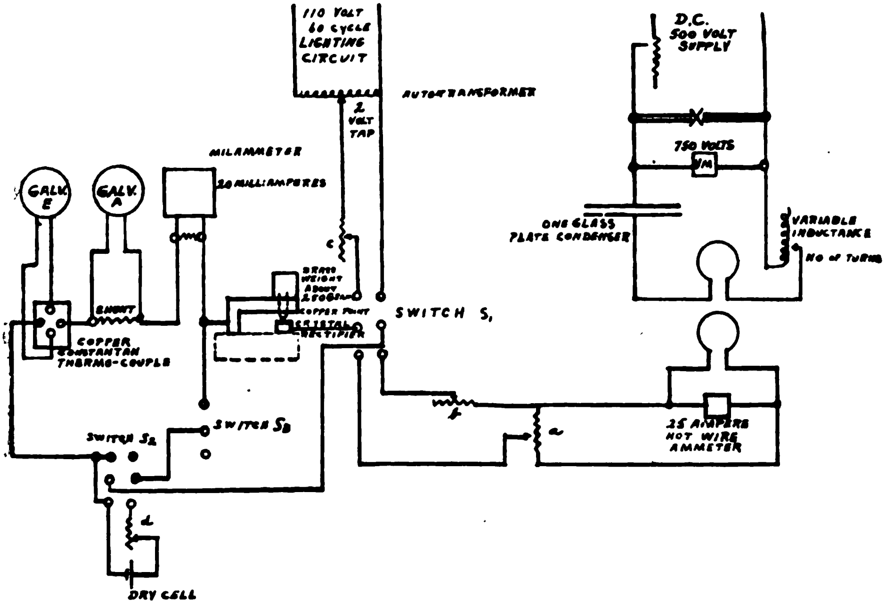


Fig. 1.

Diagram of Connections for Oscillatory Tests at Very High Frequencies.

The arc was somewhat unsteady, consequently a number of readings were averaged in obtaining the results tabulated.

In every case the rectification was found to be better on the oscillating circuit than on the 60-cycle circuit. In several cases this effect was quite pronounced particularly when inductance was placed in series with the supply to the rectifier. The intermediate frequency of approximately 268,000 gave in all cases the best rectification. Tests 21 and 22 show that no disturbing effects were produced by the mere presence of the oscillating arc when the rectifier switch was closed on the 60-cycle circuit. The measuring circuit was inductively linked with the oscillating circuit and well insulated from it but it is possible that in some way leakage may have occurred, and caused part of the D.C. meter deflections. None of the attemps to detect such leakages resulted in discovering anything which caused a decrease in the readings of the meter which indicated effective values or an increase in the readings of the D.C. meter used to get the average or rectified current values.

The results of these tests indicate increased rather than decreased rectification for high frequency oscillating currents. It must be borne in mind, however, that these currents consist of more or less damped wave trains and that rectification varies with the magnitude of the current and the potential difference as will be shown later.

In the tests caried out in the protective apparatus laboratory of the General Electric Company a 60-cycle lighting circuit was again used as a standard to see that no permanent alteration had occurred in the crystal or contact. The high frequency supply was obtained from inductor type alternators giving frequencies up to 100,000 cycles per second for one machine and up to 200,000 cycles per second for the other machine. Some tests were also made using a spark discharge oscillating circuit inductively linked with the measuring circuit.

Effect of Contact Pressure.

It was deemed wise to try the effects of considerable variation in contact pressure to settle definitely the question as to the possibility of variations caused by pressure changes being included in the other effects studied.

Variations of contact pressure on a blunt No. 13 B. & S. copper wire contact between 40 and 550 grams caused very small variations in the ratio of average to effective value of the current when using the 60-cycle supply. The rectification ratio, as just defined, varied between 57.3 and 59.6 per cent., and not more than half of this difference can be definitely ascribed to change of pressure. Another test made later at 100,000 cycles per second showed that the effects of very considerable changes of pressure on the contact-point was negligible when the rectified current was as large as 20 milliamperes. Some observations with very small contact areas and very light pressures will be described later on.

EFFECT OF ROOM TEMPERATURE.

The effect of temperature through a very wide range was described in the article already referred to (published in the PHYSICAL REVIEW, November, 1909). The results showed a decrease of rectification with increased temperature; the rectification becoming unstable or disappearing at temperatures between 200 and 300 degrees centigrade. The change for room temperature variations was small and this was checked by a test made during the course of these experiments which showed a decrease from 58.9 per cent. to 57.9 per cent. when the temperature was raised approximately 10 degrees centigrade above the initial room temperature of 22 degrees. This difference is small enough to be negligible in comparison with the effects obtained in the course of this work.

EFFECT OF FREQUENCY.

The small effect of change of frequency is illustrated by the curves in Fig. 2. It is to be noted that a small but measurable increase in rectification occurred at the frequency of 100,000 cycles for the larger values of rectified current, but that for the smaller currents the rectification decreased slightly. Changes of wave shape may have had some effect, but such effect could not have been large for the alternator was run at low and high speeds for the readings, the current kept constant and hence

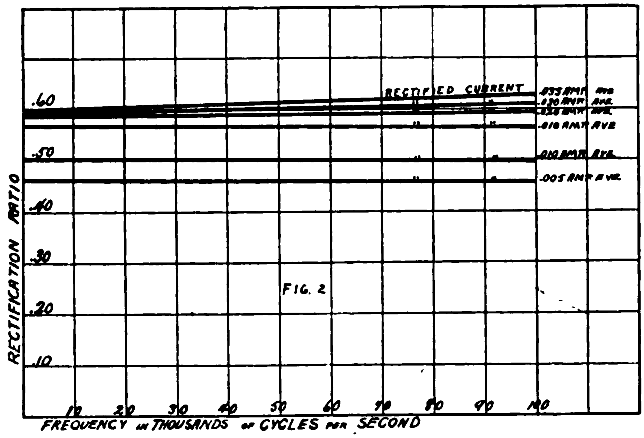


Fig. 2.

Effect of Frequency on Rectification Ratio for Various Rectified Currents.

the reaction of the current on the field must have been almost exactly constant.

Another thing to be noted about the curves is that they show in general a better rectification for the larger currents. The rectification tended to increase with increase of current at 60 cycles per second and a similar effect was found at 100,000 cycles.

Some tests were made with a high frequency supply from an oscillating circuit. The oscillating circuit was excited by a Tesla coil, a sphere spark gap and a high voltage condenser. The oscillating circuit had a frequency of about 120,000 cycles per second as measured with a cymometer and was inductively linked with the rectifier and meters by a single turn air core coil.

The galena crystal which had been giving a rectification ratio of about 60 per cent. on the 60-cycle lighting supply or on the 100,000 cycle alternator gave only 3 per cent. to 5 per cent. rectification on the oscillating circuit. When reconnected later to the 60-cycle supply gave only 35 per cent. to 40 per cent. rectification. These results lead one to think that the high peak in the first wave of the oscillating wave train may have been sufficient to partially break down the rectifying film.

EFFECT OF CURRENT AND CURRENT DENSITY.

The noticeable decrease in rectification for small currents led to the attempt to measure the rectification ratio for exceedingly small currents. For these measurements the 60-cycle lighting circuit supply was employed and the value of the alternating curent measured by means of a separately excited dynamometer. The exciting current for the dynamometer was kept constant at 5 amperes and its phase adjusted by means of a phase shifting transformer to give the maximum deflection of the dynamometer. Trial showed that the position of the phase shifter for maximum deflection on the dynamometer was the same for either small or large currents. An instrument of this type really measures the average value of the current without regard to the direction of current flow; consequently the limit of the rectification ratio, as employed here, would be 100 per cent. for complete rectification of a sine wave, while the limit for a sine wave whose effective value was measured would be 91 per cent. This drawback would not greatly affect different readings all taken on the same dynamometer and under the same conditions.

The curve given in Fig. 3 shows that for currents of the order of 1 to 2 microamperes of rectified current the rectification ratio is less than 10 per cent. The same conditions (No. 13 B. & S. blunt copper wire point and 276 grams contact pressure) gave rectification ratios of over 80 per cent. for rectified currents of 500 microamperes. This is shown in

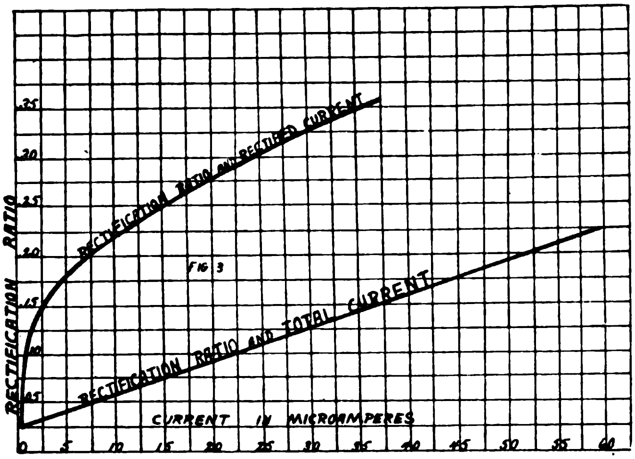


Fig. 3.

Relation of Rectification Ratio and Current at 60 Cycles for Very Small Currents. No. 13 blunt copper wire contact. 276 grams contact pressure. Total current measured with separately excited dynamometer.

Fig. 4 where the results for the whole range of currents are shown in one curve. The rectification ratios in the tests shown in Figs. 3 and 4

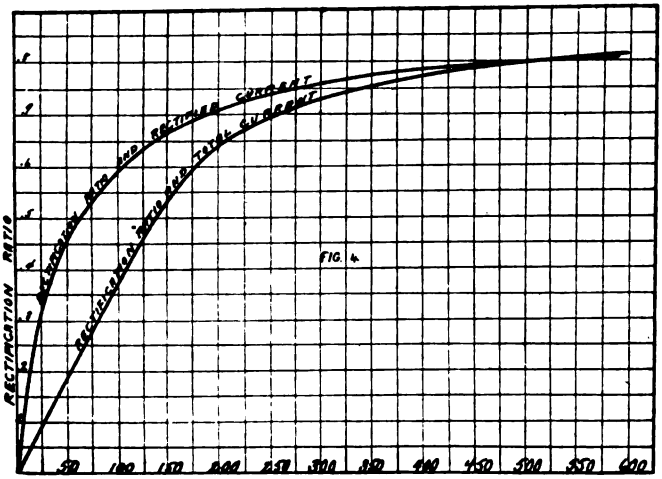


Fig. 4.

Relation of Rectification Ratio and Current at 60 Cycles. No. 13 blunt copper wire contact, 276 grams contact pressure. Total current measured with separately excited dynamometer.

vary as the *square* of the rectified current and as the *first power* of the whole current throughout a considerable range.

EFFECT OF CONTACT PRESSURE ON RECTIFACTION OF VERY SMALL CURRENTS.

The preceding test which showed that the rectification ratio was very low for small currents suggested that the current density must be a large factor, consequently other tests were made with normal and reduced pressures on the No. 13 B. & S. blunt copper wire point. The tests already described using larger currents had shown but little influence of pressure between 38 and 276 grams. For small currents, however, it was found in this test that quite considerable differences in rectification existed for small rectified currents. The lighter pressure on the point gave an appreciably better rectification, as is shown in Fig. 5.

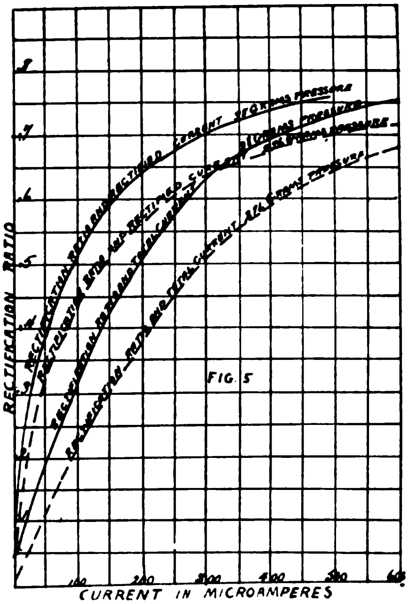


Fig. 5.

Effect of Contact Pressure and Current on Rectification Ratio for Small Currents. 60-cycle supply No. 13 B. & S. blunt copper wire contact. Total current measured with separately excited dynamometer.

EFFECT OF SIZE OF CONTACT POINT.

In order to still further investigate the question of current density tests were made with very fine wires giving small contact areas and with a contact made by a drop of mercury about 3 mm. in diameter. The contact area must bear some relation to the cross section of the wires except possibly in the case of the No. 13 copper wire which was too large to touch over its whole surface area.

The results tend in general to show that, for very small currents at least, the reduction in size of contact points improves the rectification ratio very markedly. It was noted, however, that much larger voltages had to be employed to get the same current.

Fig. 6 shows the results for a 7 mil (0.0178 cm.) copper wire. The section area of this wire was 2.49×10^{-4} cm., and the curve shows the fairly large rectification ratio of 63 per cent. for very minute rectified currents, *i. e.*, values of 2 to 3 microamperes. For larger rectified currents the rectification ratio was even higher. Even for 0.7 of a microampere this small copper wire gave a rectification ratio of 35 per cent. For currents over 50 microamperes the readings taken gave rectification ratios that indicated practically complete rectification.

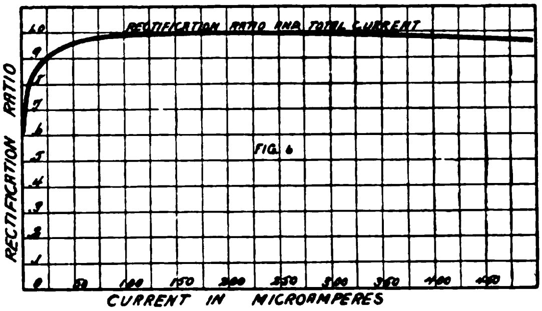


Fig. 6.

Relation of Rectification Ratio and Current at 60 Cycles for a Small Copper Wire Point, .0178 cm. in Diameter. Total current measured with a separately excited dynamometer.

A still smaller silver wire 0.0025 cm. in diameter, section area 4.9×10^{-6} sq. cm. while requiring a still higher voltage to give readable currents gave rectification ratios of the very small currents not quite so good as in the preceding test. Another peculiar action which occurred with this extremely small silver wire point was *reverse* rectification on the first application of voltage followed by a sudden decrease in the value of the current, then a change of direction of rectified current to the direction usually found accompanied by very good rectification. On decreasing the supply voltage and thus reducing the current there was a decided tendency for reversal of rectification to proceed of itself as soon as the total current lowered to a value less than 75 to 100 microamperes. Reversed rectification ratios of 35.5 per cent. or more were obtained in this way. In one case 65 per cent. reversed rectification ratio was obtained with 7 microamperes total current. This was obtained, however, by using the smallest obtainable value for the supply voltage.

The current was not stable when using this 0.0025 cm. silver wire and when the results were plotted as in Fig. 7 the curve brings out only the marked tendency to drift towards reverse rectification for low voltages and small total currents.

A check test with a 0.005 cm. copper wire gave results similar to those of the 0.0178 copper wire already described and no reversal of rectification such as was observed with the 0.0025 cm. silver wire.

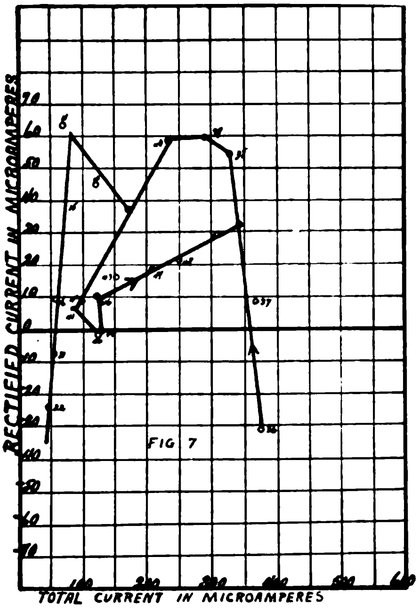


Fig. 7.

Rectification with an Extremely Small Silver Wire Point, .0025 cm. in Diameter. 60-cycle supply. Total current measured with a separately excited dynamometer.

A check test with the large blunt copper point made of No. 13 B. & S. wire gave again results similar to those obtained in the earlier tests under the same conditions. The effect of very large size contact areas giving a very low current density was investigated by the use of a drop of mercury about 3 mm. in diameter, having thus a contact area of 0.07 sq. cm. The results are plotted in Fig. 8.

The highest rectification ratio obtainable with this large contact area was about 10 per cent. and even this required a total current of 60 milliamperes. For currents between 150 and 2,500 microamperes the rectification ratio was less than .1 of 1 per cent. For total currents less than 150 microamperes it was found that the crystal alone gave a direct E.M.F. that affected the galvanometer, giving from 12 to 14 mm.

deflection corresponding to a direct current of 0.12 to 0.14 microampere, so that the apparent rectification ratios rose again to something over 1 per cent. for total currents less than 15 microamperes.

This test gave also an opportunity to compare the readings of the dynamometer with those obtained by the thermo-couple. When in series the current as calculated was 0.00298 ampere for the heated thermo-couple and 0.002455 from the dynamometer reading. The values as read on the dynamometer are therefore smaller than the effective value of the current, and, according to this one check, even somewhat smaller than the ratio of average to effective value of a sine wave. This would, however, tend to make the real rectification ratios *higher* for all the small currents where such low values were found. The validity of this conclusion in regard to the method of measuring the total current is further checked by the higher rectification ratios obtained for currents greater than half a milliampere.

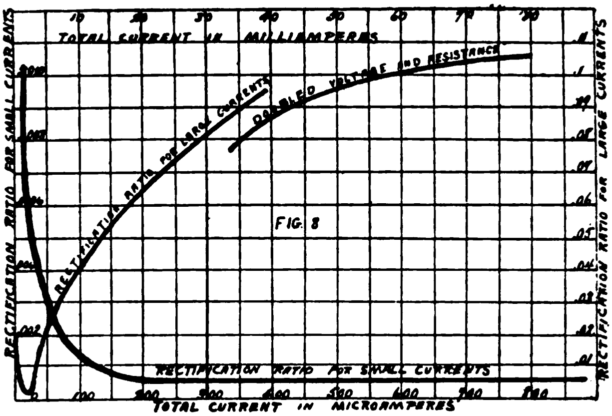


Fig. 8.

Effect of Current on Rectification for Very Large Contact Area. 3 mm. mercury drop contact. Total current measured with a separately excited dynamometer.

Effect of Frequency and Low Current Density.

If high frequency currents were less well rectified than currents of low frequency such an effect should be most marked with the combination of large contact area, small current, and high frequency. It has already been shown that small currents of normal frequency are but imperfectly rectified when the contact area is large.

Fig. 9 shows the results of tests at different frequencies using the 60-cycle lighting circuit and the high frequency alternator, for several values of rectified current. The rectified current was kept constant and the frequency changed. The effective current was measured in this case with the crossed-wire thermo-couple. These results show, as before, small rectification ratios particularly for the small currents; but the effect of increasing the frequency to 100,000 cycles per second is negligible even for this large contact area and extremely small current density.

The rectification curve for the highest frequency obtainable from the 100,000 cycle alternator lies only a very little below that for the lowest frequency obtainable from the same machine. Both these curves show, however, higher rectification than on the 60-cycle circuit. As far as possible the circuit conditions were kept the same, particularly with regard to resistance, the voltage control being obtained by the use of step-up or step-down transformers, moderate changes of field current, and finally by shunt and series rheostats for fine adjustments.

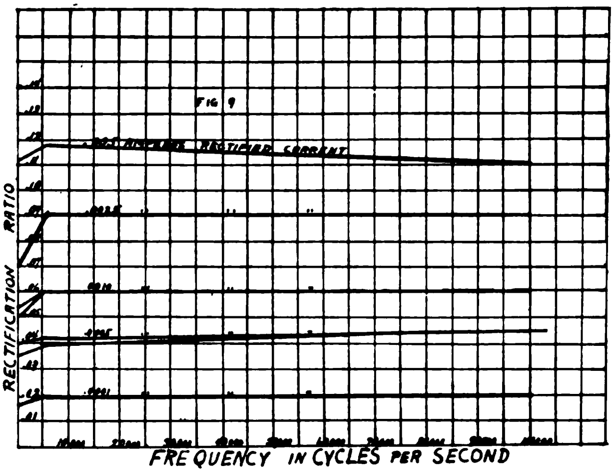


Fig. 9.

Effect of Frequency on Rectification for Small Current and Large Current Area. 3 mm. mercury drop contact.

It is also fairly evident from the trend of these curves that larger currents (involving higher voltage) would give very much better rectification. This was proven by later tests which showed rectification ratios of 30 per cent. to 40 per cent. for 2 to 2.5 volts on the crystal rectifier and 1/2 to 3/4 ampere total current. This result is stated here in order to show that the low rectification ratios found with the large contact areas (7 sq. mm.) are due to the low current density and not to accidently touching upon a non-rectifying spot. There is always considerable likelihood with the crystal rectifiers of getting on non-rectifying spots. This particular crystal had been found to have, about 18 months previous to these tests, on its top surface, *one part* which would give reversed rectification. The whole surface at the period of these tests gave rectification in the usual direction. This change is particularly interesting in view of the results obtained by R. H. Goddard and published in the Physical Review for Feb., 1912, Vol. 34, p. 149, showing the absence of rectification on surfaces freshly broken in a vacuum where they would be quite free from oxidizing influences.

Volt-Ampere Characteristics.

The rectification of small currents is better with small contact areas, but this improvement is obtained at the expense of higher applied voltages. In view of this fact further tests were made in which the applied voltage was kept constant. Hot wire voltmeters and ammeters were used in these tests to measure the effective values of voltage and current. The rectified current was measured by a permanent-magnet moving-coil-type meter.

The volt-ampere characteristic when using the blunt No. 13 B. & S. copper point on 60 cycles per second gave a nearly linear increase of rectified current with increase of voltage, but a more rapid increase of total current so that the rectification ratio decreased markedly as the voltage across the rectifier was raised from 1 to 3 volts.

The volt-ampere and rectification characteristics with the very large contact area of 7 sq. mm. obtained when using the mercury drop for a contact gave the fairly high rectification ratios of 30 to 45 per cent. when the total current reached values of .3 to .4 ampere. The better rectification occurred at the high frequency of 180,000 cycles. Possibly the skin effect at this frequency would give increased current density at the outer edges of the drop and so produce a better rectification.

The nominal current density for maximum rectification ratio of 35 to 45 per cent. varies between 5 and 6½ amperes per sq. cm. with this large contact of 7 sq. mm. irrespective of frequency.

A comparison of the tests at 60 cycles per second show nominal current densities for maximum rectification ratio as follows, the maximum rectification ratio corresponding in all case to nearly complete rectification.

Point.	Nominal Current Density for Maximum Rectification.
No. 13 B. & S. copper wire point	7 –
.0178 copper wire point	½ to 5
.005 copper wire point	6
.0025 silver wire point	16

The currents range from 50×10^{-6} amp. for the smallest wires to nearly half an ampere, a range of variation of 1 to 10,000 and the areas vary through a similar range, but even these approximate calculations give only a moderate change of optimum current density.

It is hoped that this work may be followed by other more precise measurements which will make it possible to settle upon definite quantitative values for optimum current density.

If the contact area be very large, the optimum current density may not be reached even when the voltage approaches the critical value, consequently the rectification ratio may be limited to low values.

EFFECT OF FREQUENCY ON RECTIFICATION AT CONSTANT VOLTAGE.

The first tests were made with a No. 13 B. & S. blunt copper wire point under 276 grams pressure resting on the same crystal that had been used in the preceding tests. The high frequency supply was taken from the inductor type alternator and the low frequency standard supply from the 60-cycle lighting circuit. Fig. 10 shows that for these conditions the rectification ratio, the total current, and the rectified current, increaes slightly at the highest frequencies. The best rectification as given in Fig. 10 is 65 per cent. at 180,000 cycles per second.

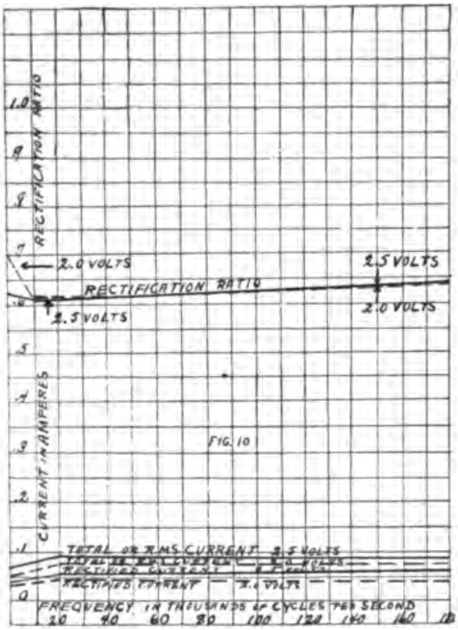


Fig. 10.

Effect of Frequency on Rectification at Constant Voltage. No. 13 blunt copper wire contact, 276 grams contact pressure.

The resistance of the hot-wire mil-ammeter was rather large (about

16 ohms) and the effect of this resistance in decreasing the rectification was quite marked.

The results at high and low frequency were very similar, as might be expected from the results already given in Fig. 2 but both rectified and total current were somethat greater than at 60 cycles. The difference was greatest at the higher voltages. At 2.5 volts the current values at 180,000 cycles were about 30 per cent. higher than at 60 cycles but the rectification ratio was very nearly the same; 61 per cent. at 60 cycles and 63 per cent. at 180,000 cycles. The numerical values for current and rectification ratio obtained with these hot wire meters should not be given too much weight, because the calibration corrections as given for these meters are rather large and the ammeter measured also, necessarily, the current required by the voltmeter for its deflection and this correction to the ammeter readings had to be applied in all these tests. The voltmeter was connected directly across the rectifier thus excluding meter drops. These drawbacks do not affect the value of the *comparisions* on low and high frequency.

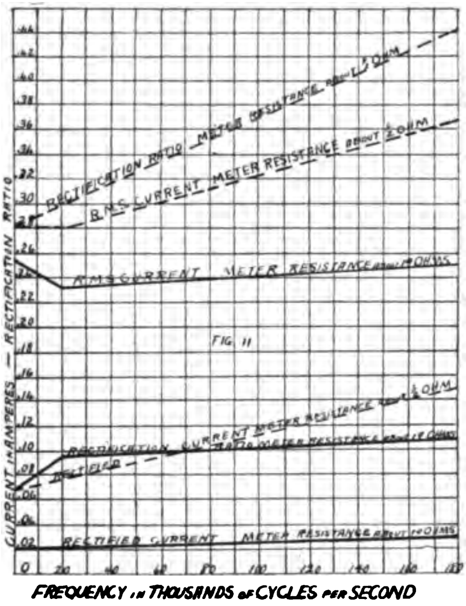


Fig. 11.

Effect of Frequency and Meter Resistance with Large Contact Area and 1.8 Volts on Rectifier. 3 mm. mercury drop contact. Meter resistance 19 ohms and ½ ohm.

In order to get the combined effect of low current density and high frequency other tests were made at constant voltage using the same crystal but with the contact consisting of a mercury drop about 3 mm.

in diameter resting on the top surface of the crystal. Part of the results in terms of current and rectification ratio are plotted in Fig. 11 (for 1.3 volts across rectifier) to show the effect of frequency at constant voltage.

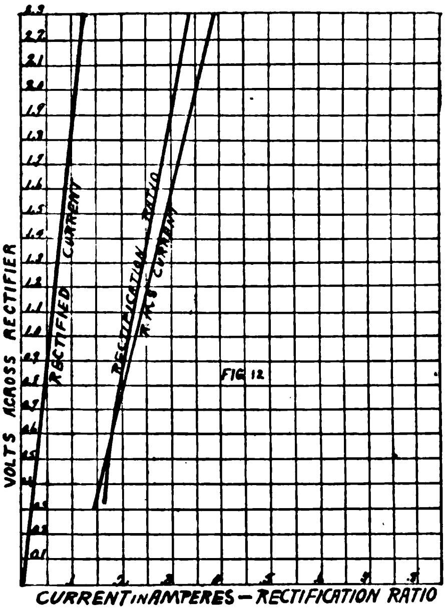


Fig. 12.

Low Frequency Volt-Ampere and Rectification Characteristic with Large Contact Area. 3 mm. mercury drop contact. 60-cycle supply. Meter resistance ½ ohm.

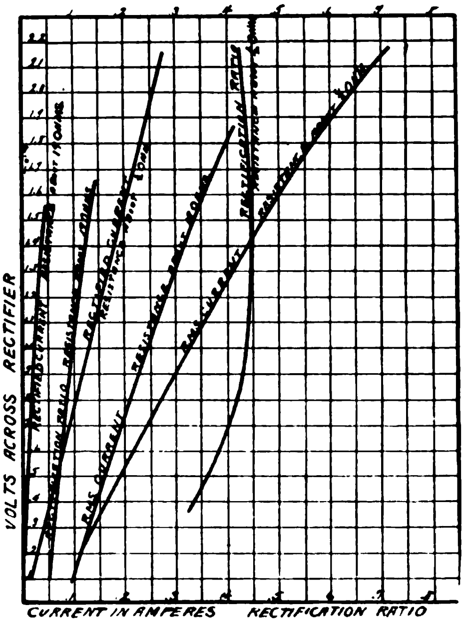


Fig. 13.

High Frequency Volt-Ampere and Rectification Characteristic with Large Contact Area, at 180,000 Cycles per Second. 3 mm. mercury drop contact.

The effect of reducing the circuit resistance by making use of low resistance meters is very marked, particularly on the rectification ratios. The shorting of two meters, one the hot-wire mil-ammeter (0.25 ampere full scale deflection) having 16 ohms resistance and the D.C. mil-ammeter (0.20 ampere full scale deflection) having 2.5 ohms resistance thus reduced the resistance of the circuit 18.5 ohms; that is, from about 19 ohms to about 0.5 ohm. This reduction in resistance made a moderate increase in the total current but a very great increase in the rectified current and consequently in the rectification ratio. Apparently the difference is not due to the elimination of the inductance of the D.C. meter the resistance of which was small (2.5 ohms), but is largely due to the elimination of the reistance of the small scale hot-wire mil-ammeter which had a resistance of 16 ohms as determined by test during the course of these experiments. This conclusion is based upon the values obtained

TABLE I.

Effect of Frequency and Wave Shape on Rectification.

	Date of Test.	Rectifier.	Frequency Cycles per Second.	Current.		Rectification Ratio.
				Effective Value Milli-amp.	Average Value for Current Milli-amps.	
1.	Dec. 21, 1910	*M*	60	8 to 38		.544
		P	60	21.9		.568
2.	Dec. 28, 1910	*P*	60	41.5	25.75	.619
		P$_1$	2,030	40.4	24.90	.616
3.	Dec. 29, 1910	*P*$_1$	60	34.35	19.6	.571
4.			2,020	34.35	19.47	.567
5.	Dec. 29, 1910	*M*	60	21.4	13.7	.640
6.			2,150	21.4	13.4	.626

Set Contact on Area for Reversed Rectification.

7.	Dec. 29, 1910	*M*$_1$	60	45.4	1.5	.0331
8.			2,150	43.1	.45	.0104

Effect of Wave Shape.

9.	Dec. 29, 1910	*P*$_1$	60	28.6	18.4	.633 standard
10.			20+60	30.28	18.7	.618 flat-topped wave
11.			20+60	30.28	14.5	.479 peaked wave

Effect of Wave Shape Using Spot Having Reversed Rectification.

12.	Dec. 29, 1910	*M*	60	47.5	.8 Unsteady	.01685
13.			20+60	46.6	.4	.00858 flat-topped wave
14.			20+60	46.5	.25	.00538 peaked wave

Effect of Wave Shape with Point Reset for Usual Direction of Rectification.

15.	Dec. 29, 1910	*M*	60	28.35	18.55	.654 standard
16.			20+60	8.20	5.35	.652 flat-topped wave
17			20+60	9.73	5.00	.513 peaked wave

High Frequency Supply from Quenched Spark Oscillating Circuit.

21.	Dec. 30, 1910	*M*	60	59.4	35.23	.5935
22.			60	58.9	34.97	.5955
23.			268,000	36.95	28.18	.763
24.			60	56.	33.40	.597
24'.			60	36.9	21.60	.586
25.	Dec. 31, 1910	*M*	60	49.02	29.56	.603
26.			678,000	52.18	32.70	.626
27.			268,000	37.50	28.60	.7688
28.			60	50.81	30.66	.603
29.			60	30.62	18.48	.604
30.			268,000	25.52	18.70	.7326
31.			678,000	26.31	18.56	.7053
32.			678,000	32.56	20.42	.638
33.			678,000	54.13	32.55	.605
34.			60	29.95	18.24	.6088

TABLE I.—*Continued.*

High Frequency Supply from Quenched Spark Oscillating Circuit.

Date of Test.	Rectifier.	Frequency Cycles per Second.	Current.		Rectification Ratio.
			Effective Value Milli-amp.	Average Value for Current Milli-amps.	
35. Dec. 31, 1910.	M	268,000	25.02	18.45	.7375
36.		678,000	27.27	17.98	.661
Air Core Induction Coil in Series with Supply to Rectifier.					
37. Dec. 31, 1910	M	60	29.79	18.17	.6103
38.		268,000	17.68	17.44	.986
39.		678,000	14.09	9.46	.6744

when first one and then the other of these two meters was short-circuited. In this connection it should be stated that the hot-wire voltmeter was connected directly across the terminals of the rectifier so that none of these changes of ammeter resistance could affect the accuracy of the values taken for the potential difference across the rectifier. In all cases the A.C. ammeter readings have had subtracted from them the values corresponding to the current through the voltmeter. The values for these corrections to the ammeter readings were obtained by a separate experiment. The magnitude of these corrections is well brought out by the data recorded in Tables II. and III.

The results in Table II. and in Fig. 10 have been corrected for voltmeter current but the values *given* for the hot-wire A.C. ammeter calibration errors have not been used in calculating the results. In Table III. and in Figs. 11, 12, and 13 the effect of the voltmeter current and also the calibration errors of the ammeters have been allowed for. There is some doubt as to the values that should be used for the calibration corrections. The omission of the calibration corrections gives somewhat larger values for the effective current and lower values for the rectification ratio, particularly for the smaller currents.

SUMMARY AND CONCLUSIONS.

1. The rectification at high frequency tends to be greater than at low frequency with the larger currents, and but very little different for small currents.

2. For very small currents the rectification tends to disappear, particularly for large contact areas and low current densities.

Table II.

Volt-ampere. Rectification Characteristics at Low and High Frequency.

Galena Crystal M, No. 18 B. & S. with Blunt Copper Wire Point and a Contact Pressure of 276 Grams.

Rectified or Direct Current.		**Total Current.**		**Voltage on Rectifier.**	**Voltmeter Current, Amp.**	**Net Current through Rectifier, Amp.**	**Rectification Ratio.**
No. 3,815. .020 Sc., 2.5 Ohm, Amp.	**No. 263, .5 Sc., .08 Ohm, Amp.**	**No. 5,535, 2 Scale, .26 Ohm, Rdg. Amp.**	**No. 47,201, .25 Sc., 16 Ohm, Rdg. Amp.**	**No. 47,203 5 Scale, Volts.**			
60-cycle Lighting Circuit Supply, Meter 3815.							
.0073	.0075	?	.032	.5	.015	.017	.430
.0127	.013	.1 est.	.054	1.0	.031	.023	.550
.0205	.0205	.1 est.	.085	1.5	.0475	.0375	.547
Meter 263.							
Shorted	.024	.1 est.	.090	1.5	.0475	.0425	.565
	.035	.2 est.	.128	2.0	.0625	.0655	.534
	.045	.2	.161	2.5	.080	.0810	.555
	.036	?	.130	2.0	.0625	.0675	.533
	.025	?	.091	1.5	.0475	.0435	.575
	.0165	?	.062	1.0	.0310	.0310	.533
	.036		Shorted	1.0	.0310		
	.059			1.5	.0475		
	.085			2.0	.0625		
	.118	.28 est.		2.5	.080		
.0193	.019	?		.5	.016		
180,000-cycle Supply from Inductor Alternator.							
.0122	.012		.044	.5	.015	.029	.421
.0189	.018		.064	1.0	.031	.033	.572
Shorted	.019		.063	1.0	.031	.032	.594
	.024		.078	1.2	.0355	.0425	.565
	.031		.099	1.5	.0475	.0515	.602
	.041		.129	1.8	.056	.073	.562
	.046		.143	2.0	.0625	.0805	.572
	.052		.161	2.2	.069	.092	.565
	.057		.175	2.4	.076	.099	.576
	.060		.180	2.5	.080	.100	.60
	.053		.165	2.2	.068	.097	.547
	.047		.146	2.0	.0625	.0835	.573
	.033		.106	1.5	.0475	.0585	.564
	.021		.070	1.0	.031	.049	.428
20,000-cycle Supply from Inductor Alternator.							
.012	.012		.044	.6	.018	.026	.462
.0163	.016		.060	1.0	.031	.029	.562
Shorted	.018		.067	1.0	.031	.036	.500
	.028		.099	1.5	.0475	.0515	.544
	.036		.125	1.8	.056	.069	.522
	.043		.144	2.0	.0625	.0815	.527
	.050		.165	2.3	.0725	.0925	.541
	.0545		.179	2.5	.080	.099	.55
	.043		.145	2.0	.0625	.0825	.521
	.030		.103	1.5	.0475	.0555	.540
	.020		.070	1.0	.031	.039	.645?

TABLE II.—*Continued.*

Check on 60-cycle Lighting Circuit.

Rectified or Direct Current.		Total Current.		Voltage on Rectifier.	Voltmeter Current, Amp.	Net Current through Rectifier, Amp.	Rectification Ratio.
No. 3,815. .020 Sc., 2.5 Ohm, Amp.	No. 263, .5 Sc., .08 Ohm, Amp.	No. 5,535, 2 Scale, .26 Ohm, Rdg Amp.	No. 47,201, .25 Sc., 16 Ohm, Rdg. Amp.	No. 47,203, 5 Scale, Volts.			
10	.010		.040	.5	.015	.025	.40
15	.015		.056	1.0	.031	.025	.60
Shorted	.016		.060	1.0	.031	.029	.552
	.026		.093	1.5	.0475	.0455	.572
	.037		.132	2.0	.0625	.0695	.532
	.046		.165	2.5	.080	.085	.541
	.037		.135	2.0	.0625	.0705	.525
	.026		.095	1.5	.0475	.0475	.548
	.021		.063	1.0	.031	.032	.656
	.0105		.044	.5	.013	.031	.339
	.021		Shorted	.5	.013		
	.037			1.0	.031		
	.060			1.5	.0475		
	.093			2.0	.0625		
	.120			2.5	.080		
	.099			2.0	.0625		
	.041			1.0	.031		

3. The rectification ratio for small currents is nearly proportional to the square of the rectified current and nearly proportional to the first power of the total or R.M.S. current.

4. Even very large contact areas will rectify well with large currents.

5. The rectification *ratio* for very small currents may be improved by the use of very small contact points but a much larger potential is required to get the same amount of current.

6. The current density must be equal to or greater than a given minimum value for good rectification.

7. Resistance in series with the galena crystal rectifier greatly decreases the rectification ratio even for the same potential difference on the terminals of the rectifier.

OHIO STATE UNIVERSITY,
November, 1913.

REFERENCES.

Streintz and Wellik, Physikalische Zeitschrift, Vol. 12, p. 845.
Streintz, Physikalische Zeitschrift, Vol. 13, p. 673.
Binder, Elektrotechnik und Maschinenbau, Sept. 22, 1912.
Branley, Comptes Rendus, Vol. 155, p. 933.
Stark, Physikalische Zeitschrift, Vol. 13, p. 585.
Merritt, Physical Review, Vol. 32, p. 630.
Pierce and Evans, Proceedings of the American Academy of Arts and Sciences, Vol. 47, March, 1912.
Doelter, Zeitschrift für Anorganische Chemie, Vol. 67, p. 387.
Martin, Physikalische Zeitschrift, Vol. 12, p. 41.
Eccles, Philosophical Magazine, Vol. 19, p. 869; Philosophical Magazine, Vol. 20, p. 128.
Beilby, Proceedings of the Royal Society, Series A, Vol. 82, p. 599.

Table III.

Volt-ampere and Rectification Characteristic at Low and High Frequency.
Galena Crystal M. 60-cycle Supply. 3 mm. Mercury Contact.

Direct or Rectified Current.		Total Value or Effective Value of Current.				Potential on Rectifier, No. 47,203, 5 Scale, Volts.	Voltmeter Current, Amp.	Net Current through Rectifier.	Rectification Ratio.
No. 3,815 (Weston), .020 Scale, 2.3 Ohms, Amp.	No. 263 .5 Sc., .2 Ohm.	No. 5,535, 2 Scale, .26 Ohm.		No. 47,201, .25 Scale, 16 Ohm.					
	Amp. Rdg.	Amp. Rdg.	Amp. Value.	Amp. Rdg.	Amp. Value.				
1	2	3	4	5	6	7	8	9=4 or 6–8	10
.015	.015	.250	.22	.208	.223	1.0	.030	.220	.068
.0196	.020	.300	.27	.239	.260	1.3	.040	.199	.100
Shorted	.031	.220	.190	Shorted		.5	.015	.175	.177
this meter	.050	.280	.250	this meter		1.0	.030	.220	.227
	.080	.410	.360			1.5	.046	.314	.254
	.113	.510	.460			2.0	.062	.400	.283
	.135	.650	.610			2.5	.079	.530	.255
	.113	.450	.390			2.0	.062	.330	.347
	.080	.400	.340			1.5	.046	.294	.272
	.052	.320	.280			1.0	.030	.250	.208
20,000 Cycle. R = 19.16 Ohms.									
.0021	.002			.067	.055	.1	.003	.052	.0403
.0033	.003	?		.084	.075	.15	.007	.068	.0485
.0074	.0075	.1		.132	.129	.3	.009	.120	.0616
.00955	.0095	.1		.161	.163	.5	.015	.148	.0645
.01640	.0170	.23		.213	.228	1.0	.030	.198	.0828
.01780	.0180	.24	.21	.217	.234	1.1	.033	.201	.0886
.02000	.0200	.26	.23	.233	.259	1.2	.037	.222	.0901
R = 16.66. Voltage rose because D.C. meter was short-circuited.									
Shorted	.0250	.30	.27	.248	.283	1.38	.042	.241	.1037
	.0190	.26	.23	.228	.251	1.20	.037	.214	.0889
Shorted this meter, making the resistance of the meters .66 ohm. This reduction of resistance increased the meter readings until the supply was readjusted.									
	.127	.47	.41			1.73	.053	.36	.353
	.043	.22	.19			.5	.015	.175	.246
	.063	.29	.26			1.0	.030	.23	.274
	.079	.33	.29			1.2	.037	.25	.316
	.093	.40	.34			1.38	.042	.30	.310
	.098	.42	.37			1.50	.046	.32	.306
	.123	.48	.43			1.73	.053	.38	.324
	.113	.48	.43			1.90	.059	.37	.307
	Tapped lightly								
	.127	.49	.44			1.9	.059	.38	.334
	.130	.50	.45			1.73	.053	.40	.325

Table III.—*Continued.*

20,000 Cycle. R = 19.16 Ohms.

Direct or Rectified Current.		Total or Effective Value of Current.				Potential on Rectifier, No. 47,203, 5 Scale, Volts.	Voltmeter Current, Amp.	Net Current through Rectifier.	Rectification Ratio.
No. 3,815 (Weston), .020 Scale, 2.5 Ohms, Amp.	No. 263, .5 Sc., .2 Ohm.	No. 5,535, 2 Scale, .26 Ohm.		No. 47,201, .25 Scale, 16 Ohms.					
	Amp. Rdg.	Amp. Rdg.	Amp. Value.	Amp. Rdg.	Amp. Value.				
1	2	3	4	5	6	7	8	9=4 or 6-8	10
	.143	.55	.51			1.90	.059	.45	.318
	.151	.58	.53			2.0	.062	.47	.321
	.108	.45	.39			1.5	.046	.34	.318
	.069	.33	.29			1.0	.030	.26	.265
	.042	.23	.20			.5	.015	.18	.233
180,000 Cycles.									
.0058	.006			.117	.112	.2	.006	.106	.0557
.0116	.0115	.180	.15	.161	.163	.5	.015	.148	.0784
.0195	.0195	.25	.22	.223	.244	1.0	.030	.214	.0911
Shorted this meter	.0275	.30	.27	.250	.287	1.24	.038	.249	.1104
	.0150	.20	.17	.183	.189	.50	.015	.174	.0862
	.022	.27	.24	.223	.239	1.0	.030	.209	.1052
	.026	.28	.25	.244	.277	1.2	.037	.240	.1083
	.184	.50	.45	Shorted this meter		1.45	.045	.410	.445
	.081	.26	.23			.6	.018	.21	.385
	.125	.36	.31			1.0	.030	.28	.449
	.137	.40	.34			1.1	.033	.31	.442
	.149	.43	.38			1.2	.037	.34	.438
	.078	.25	.22			.6	.018	.20	.390
	.124	.37	.32			1.0	.030	.29	.428
	.135	.40	.34			1.1	.033	.31	.436
	.147	.43	.38			1.2	.037	.34	.432
	.178	.49	.44			1.4	.043	.40	.445
	.204	.55	.51			1.6	.049	.46	.443
	.234	.62	.57			1.8	.056	.514	.455
	.257	.69	.67			2.0	.062	.61	.422
	.275	.75	.72			2.2	.068	.65	.423
	.303	.87	.86			2.5	.079	.78	.389
	.258	.71	.67			2.0	.062	.61	.423
	.208	.59	.54			1.6	.049	.49	.425
	.185	.51	.46			1.4	.043	.41	.452
	.157	.45	.39			1.2	.037	.35	.448
	.129	.40	.34			1.0	.030	.31	.416
.0190	.019	.25	.22	.220	.239	1.0	.030	.209	.091
.0121	.012	.20	.17	.176	.181	.5	.015	.166	.073
.0061	.006	.1 Est.		.121	.116	.2	.006	.110	.055

SOME OBSERVATIONS ON SELECTIVE REFLECTION FROM SOLUTIONS IN THE INFRA-RED.

By A. K. Ångström.

DRUDE'S[1] theoretical considerations led him to regard the ultra-violet absorption lines as due to the vibration of particles of the size of an electron, while the particles giving rise to the infra-red absorption bands have a mass of the order of magnitude of the molecule.

In accord with the theory the investigations of Pfund,[2] Morse,[3] Langford[4] and others, and specially the comprehensive works by Coblentz[5] indicate that the mechanism giving rise to strong maxima of reflection in the infra-red spectrum, in the case of salts, is localized within the acid radical. Salts of the same acid have characteristic reflection-maxima, whose positions are more or less independent of the positive radical. Further investigations have shown that a change of the positive radical generally gives rise to a slight change in the period of the vibration, in such way that an increase in the molecular weight of the base causes a shift of the absorption (reflection) band to longer wave-lengths. Several relations have been tried in order to express this shift as a function of the molecular weight of the constituents; none of them seems to be of general applicability.

Under conditions, where the absorption coefficient is unusually large, as is the case for most crystals at several points in the infra-red spectrum, and for water in the infra-red, the *reflecting power* gives an important means of detecting the position and slight variations in the absorption bands, a method; first used in the classical investigations of Rubens and Nichols.

In the present note, I will describe some measurements with aid of the spectrometer and the Nichols' radiometer, where the selective reflection properties of water have been used in order to detect slight variations in the free period of vibration, when different compounds are dissolved

---

[1] Annalen der Physik, *14*, 677, 1904.

[2] Astrophysical Journal, XXIV., 19, 1906.

[3] Physical Review, *25*, 500, 1907.

[4] Physical Review, *33*, 137, 1911.

[5] Coblentz, Investigations of Infra red Spectra. Publ. by the Carnegie Inst. of Washington. Parts IV. and V.

in the water. These observations are closely connected with the problem of the rôle of the solvent in solutions, a problem that has been extensively studied by H. C. Jones and his collaborators at Johns Hopkins University. The observations of Guy, Shaeffer and Jones[1] indicate that under special conditions there occurs a shift of the spectral bands of the solvent to the long wave-lengths with an increase in the concentration of the dissolved substance. They observed further that the absorption power of the solution was sometimes considerably less than the absorbing power of the water present in the solution. This seems to be the case when this dissolved substance is a strongly hydrated salt, and the view held by the authors is that this shift and this change in the absorption power is due to a chemical reaction taking place in the solution, a part of the water combining with the dissolved substance to form hydrates. Such a hypothesis will evidently account for the observed facts. It has, however, since been pointed out by G. H. Livens,[2] that the results obtained by Guy, Shaeffer and Jones can be derived from the dispersion and absorption theory in the form given by Lorentz without any hypothesis in regard to intramolecular changes taking place in the solution. The point brought forward by Livens seems well worth the attention of the upholders of the solvate theory. From the purely physical point of view, it seems however difficult to account for the fact that the observed shift only occurs in measurable degree in the case when the dissolved substance is a strongly hydrated salt.

Before the results of Jones and the theoretical considerations of Livens were communicated, I had begun a study of the influence of the dissolved substance upon the strongly marked water band at 3 μ, that gives rise to a very sharp and definite reflection maximum at 3.18 μ. The absorption of water in this region is such that a layer of only 3 μ thickness absorbs almost totally, and it is therefore preferable to use the reflection properties as an indicator of the selective conditions.

As the study has brought forward some facts that require to be taken into consideration in forming a view upon the question, some preliminary results are here published.

INSTRUMENTS.

The general arrangement of the apparatus is shown in Fig. 1. A reflection spectrometer with mirrors of 6 cm. aperture and 54 cm. focal length was used. By aid of the Wadsworth mirror prism arrangement, the spectrometer arms could be kept fixed and an adjustment for minimum

---

[1] American Chemical Journal, *49*, 265, 1913.

[2] Physikalische Zeitschrift, *14*, 660, 1913.

deviation of one wave-length (*D*-line) held for all. The adjustment for minimum deviation was made in accord with Coblentz' description,[1] and a check on the adjustment was obtained by noting the position of the carbon dioxide band in the bunsen flame and the unchanged position of the selective reflection maximum of water at 3.20 μ during the observations.

Concerning the spectrometer, it may be mentioned, that the angle through which the prism table was rotated was measured with aid of telescope and scale, the tiny mirror being fastened to the top of the prism. The sensibility of the arrangement was such that 1 mm. on the scale corresponded to 1.5 minutes' rotation of the prism table. As one minute's rotation corresponds to about 0.12–0.15 μ in the investigated interval and the readings were made accurately to 0.1 mm., the accuracy in the wave-length determinations is about 0.01–0.02 μ.

The advantage of this way of determining the deviation over a direct reading on the spectrometer circle, lies in the possibility of the observer keeping as far away as possible from the heat-sensitive instrument during the observations. In the beginning and end of every observation series, the readings on the telescope scale were checked with the direct readings on the spectrometer circle. The spectrometer and the heat-measuring instrument, the radiometer, were both enclosed in a way that totally protected against air currents.

The Nichols' radiometer was surrounded by cotton and a blackened metal case, in the manner described by other observers. The mica vanes had a width of 0.80 mm., which corresponded to the same width of the spectrometer slit. The sensitiveness was such that a meter candle gave rise to a deflection of about 750 mm. The vacuum corresponded to maximum sensitiveness. The leak was so small that the sensitiveness remained practically the same during several days. When the writer returned after three months' absence, it was found that the sensitiveness of the radiometer had only diminished by 20 per cent. through increase of the pressure. Slight variations in the sensitiveness arose from temperature changes.

A 110-volt Nernst glower fed by the current from a 120-volt storage battery was used as source of radiation. The glower was well protected against air currents. The radiation was found to be constant within 1.5 per cent.

Method of Observing.

The following observation series were taken: (1) Reflection from a silvered plane mirror, whose reflecting power was assumed to be unity. (2) Reflection from the water surface. (3) Reflection from the solution.

---

[1] Coblentz, loc. cit., Part I.

In some cases a second determination of the energy distribution in the spectrum of the Nernst glower was made. This second determination gave, as a rule, results that agreed within 0–2 per cent. with the former determination.

The main purpose being to detect occurring shifts in the position of the reflection maximum, no attempt was made to measure the absolute value of the reflecting power.

RESULTS.

1. *Salts.*

Several solutions of different salts in water were investigated: NaCl, Na_2SO_4, KNO_3, $CuSO_4$, $SrCl_2$ and $CaCl_2$. Among these NaCl, Na_2SO_4, KNO_3 and $CuSO_4$ produced no shift in the position of the reflection maximum possible to detect. Fig. 1 shows the reflection curve of a saturated solution of Glauber's salt as compared with the same curve for water. The selective characteristics are somewhat weakened but the position of the reflection maximum remains the same as for the pure solvent.

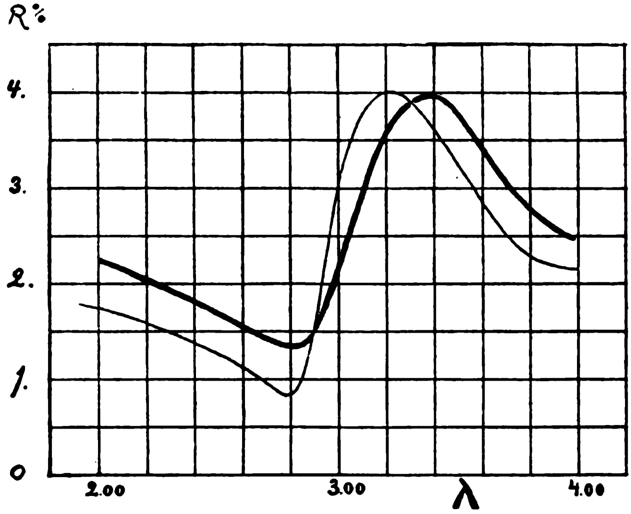


Fig. 1.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of Na_2SO_4.

In the case of the strongly hydrated salts $SrCl_2$ and $CaCl_2$, the conditions are different. As the curves (Fig. 2) show, the selective properties have here been subjected to a considerable shift to the longer wavelengths. As both the maximum and the minimum are shifted by about the same amount, the shift must be a consequence of a real change in the position of the absorption band.

Such a shift evidently corresponds to what is to be expected in the case where a part of the water molecules combine with the dissolved substance to a dissolved hydrate. The hydroxyl-group is now combined with a positive radical of larger atomic weight than before, and analogous with the conditions of sulphates and carbonates, a shift to the longer wave-lengths is to be expected.

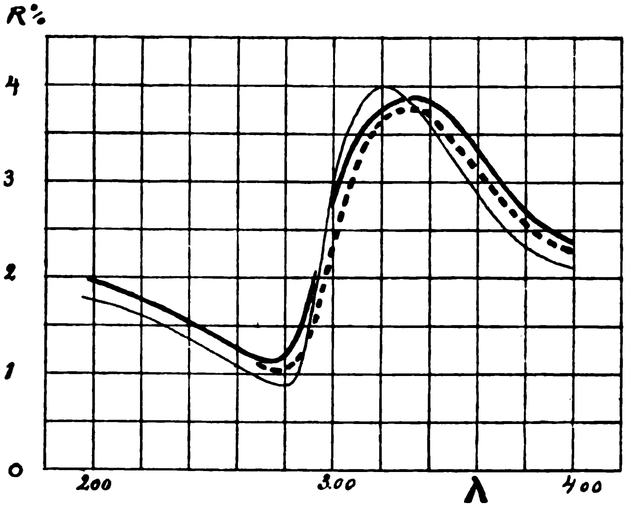


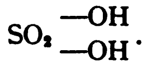
Fig. 2.

Light curve: Reflection from H_2O.
Heavy smooth curve: Reflection from saturated solution of $CaCl_2$.
Heavy dotted curve: Reflection from saturated solution of $SrCl_2$.

2. *Hydrates.*

After this result was obtained, it was found desirable to look for a similar shift in the cases where the dissolved substance is a real hydrate. For, when it has been shown that the same phenomenon occurs when known hydrates are dissolved in the water, the results obtained for the hydrated salts may be said to lead to a certain hypothesis. Consequently NaOH and KOH were investigated.

Figs. 3 and 4 give the results of an examination of concentrated solutions of sodium and potassium hydrate. The selective characteristics are evidently shifted to the longer wave-lengths by a considerable amount. For KOH the maximum occurs at 3.4 μ, for NaOH at 3.35 μ. For water the maximum and the minimum occur at 3.20 and 2.80 μ respectively.



3. $SO_2\begin{matrix}\text{—OH}\\ \text{—OH}\end{matrix}$.

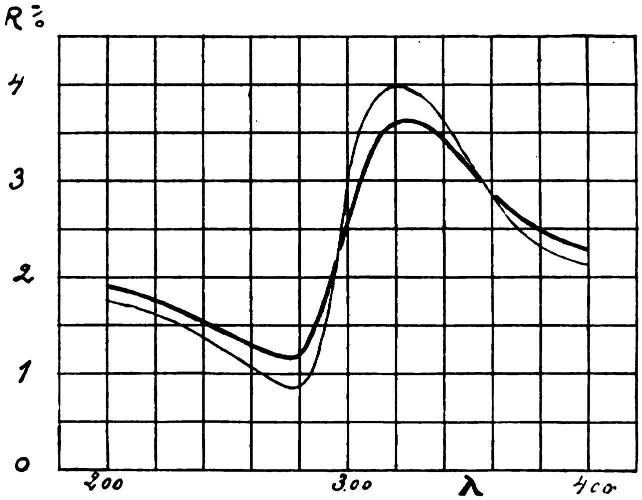


Fig. 3.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of KOH.

Under certain conditions we may also regard sulphuric acid as a hydrate. As will be seen from Fig. 5 some interesting changes in the reflection properties occur when the acid is diluted.

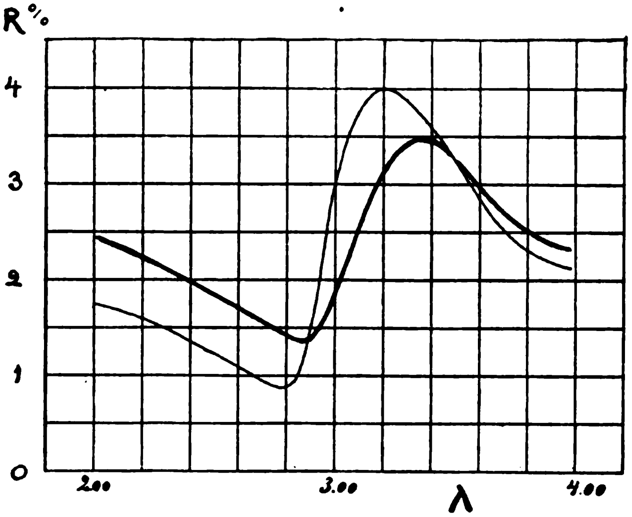


Fig. 4.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of NaOH.

Fig. 5 shows the relation between reflected energy and deviation for various solutions of H_2SO_4 in water.[1] The reflection maximum decreases with an increase in the concentration. At the same time a considerable shift to the longer wave-length is noticed. When a concentration of about 75 per cent. is reached the reflection has a minimum. Between 75 per cent. and 100 per cent. the reflection maximum increases rapidly, showing that the concentrated acid has a marked reflection maximum at 3.55 μ corresponding to a strong absorption band at about 3.20 μ.

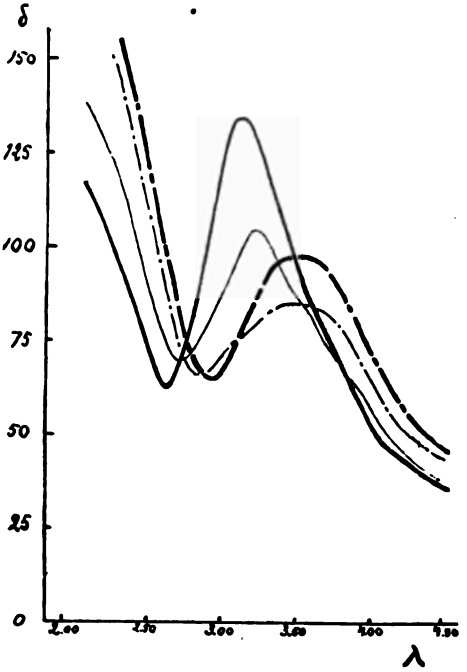


Fig. 5.

Heavy smooth curve: Energy reflected from H_2O.
Light smooth curve: Energy reflected from 32 per cent. $H_2SO_4 + H_2O$.
Light dotted curve: Energy reflected from 75 per cent. $H_2SO_4 + H_2O$.
Heavy dotted curve: Energy reflected from 98 per cent. H_2SO_4.

That sulphuric acid has a strong absorption band at about 3.20 μ, together with the fact that an absorption band at about 3.00 μ is characteristic of all compounds containing the hydroxide groups, seems to indicate that in the *undissociated sulphuric acid molecules* the hydrogen and oxygen are combined in such a way as to have the optical properties

---

[1] The form of the curve depends upon the energy distribution in the spectrum of the Nernst lamp.

of the hydroxide group. That the absorption band which in the case of water occurs at 3.0 μ is here somewhat shifted to the longer wave-lengths is only a natural consequence of the greater molecular weight of the acid.

The reflection curves show another interesting feature. It has been shown by Coblentz,[1] that the reflecting power of a compound in solution is practically proportional to the concentration, provided that no changes occur in the part of the molecule in which the mechanism giving rise to the reflection maximum is localized. If no such changes take place in the solution, the reflection power of the solution ought always to lie between the reflecting power of the constituents. From the data obtained from various solutions of sulphuric acid, it is obvious that the reflecting power of a 75 per cent. solution between the wave-lengths 3.2–3.6 μ is considerably less than the reflecting power of the constituents. At 3.28 μ, for instance, the reflecting power is only 85 against 105 for the water and 97 for the concentrated sulphuric acid. This disappearing of the reflection band reminds one strongly of similar conditions found by Pfund[2] for the reflection maxima of sulphuric acid at wave-lengths between 8 and 11 μ.

In our present case, it is interesting to notice this disappearing of the reflection maximum at 3.2 μ in connection with the generally accepted hypothesis that this band is due to the presence of the hydroxide group. In the undissociated H_2SO_4 molecules, the hydrogen and the oxygen are combined in such a way that it seems natural that they should show the optical properties of the hydroxide group. When the acid is dissolved in a dissociating solvent, the molecules are first broken down into $H\ H^{\cdot}SO_4$ ions and finally into $H_2^{\cdot}SO_4$ ions—complete change to the latter taking place at infinite dilution. The connection between the hydrogen and the oxygen forming the hydroxide group is consequently broken through the dissociation of the molecule. The concentration of the OH group—we consider the part furnished by the acid—is not proportional to the concentration of the acid, but decreases more rapidly with increased dilution. Such a dissociation process will evidently account for the observed weakening in the reflection maximum. We must, however, here take into consideration that the conditions probably are complicated through the formation of complexes, the acid molecules combining with the water molecules to dissolve hydrates. In such a process, similar to what we may suspect in the case of $SrCl_2$ and $CaCl_2$, a part of the water used as solvent is probably not present in the solution as water, but enters

---

[1] Coblentz, loc. cit., Part IV., p. 106.

[2] Loc. cit.

as a constituting part in a new compound that does not necessarily have the properties of its constituents.

Summary.

It has been shown in this paper:

1. That the selective reflection maximum of water at 3.20 μ is shifted to the longer wave-lengths when the strongly hydrated salts $CaCl_2$ and $SrCl_2$ are dissolved in the water.

2. That no appreciable shift occurs when NaCl, Na_2SO_4, KNO_3 and $CuSO_4$ are dissolved in the water.

3. That the reflection maximum is shifted by a considerable amount toward the longer waves when a real hydrate (NaOH, KOH) is in the solution.

4. That concentrated sulphuric acid shows the reflection maximum characteristic for the OH group.

5. That this maximum tends to vanish when the molecule is broken down through dissociation.

Cornell University,
November, 1913.

BENJAMIN OSGOOD PEIRCE

Benjamin Osgood Peirce, Hollis professor of mathematics and natural philosophy in Harvard University, Past-president of the American Physical Society and recent member of the editorial board of the Physical Review, died at Cambridge, Massachusetts, on the fourteenth day of January, 1914, in his sixtieth year.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SIXTY-NINTH MEETING.

THE regular Thanksgiving meeting of the Physical Society was held in Ryerson Physical Laboratory of the University of Chicago on Friday and Saturday, November 28 and 29, 1913.

The Friday afternoon session was in charge of a local committee consisting of R. A Millikan, A. A. Michelson and Henry Crew. The program consisted of the following symposium on the Quantum Theory:

The Quantum Theory and Radiation. C. E. **Mendenhall.**

The Quantum Theory and Photoelectric Effect. R. A. **Millikan.**

The Quantum Theory and Statistical Mechanics. **Max Mason.**

The Quantum Theory and Atomic Structure. **Jacob Kunz.**

The Quantum Theory and Specific Heats. A. C. **Lunn.**

The presentation of each topic was followed by a twenty-five-minute general discussion.

On Saturday there was both a forenoon and afternoon session and the following program of papers was presented. In the absence of president and vice-president, A. P. Carman was called to the chair and later R. A. Millikan.

The Relation between Photo-potentials and Frequency. W. H. **Kadesch.**

A Study of Contact P.D.'s between Metal Surfaces Prepared in Vacuo; the Effect of Ultra-violet Light upon these P.D.'s; and the Mutual Relation between Positive Potential and Contact P.D.'s. **Albert E. Henning.**

Anomalous Temperature Effects upon Magnetized Steel. N. H. **Williams.**

Experimental Determination of the Earth's Rigidity. A. A. **Michelson.**

A New Maximum in the Wave Length Sensibility Curves of Selenium. F. C. **Brown** and L. P. **Sieg.**

Evidence of a Diurnally Reversing Convectional Circulation of the Atmosphere Over the Upper Peninsula of Michigan. **Eric R. Miller.** (By title.)

Polarization of Long-wave Infra-red Radiation by Wire Gratings. A. D. **Cole.**

Glow Discharge in a Magnetic Field. R. F. **Earhart.**

A Polarization Spectrophotometer Using the Brace Prism. **Harvey B. Lemon.**

Certain Experiments in Sound Diffraction. G. W. STEWART and HAROLD STILES.

Effect of Space Charge and Residual Gases on the Thermionic Current in High Vacuum. IRVING LANGMUIR.

Arrival Curves with Artificial Long Lines. CARL KINSLEY.

An Attempt at an Electromagnetic Emission Theory of Light. JACOB KUNZ.

Theory and Use of the Molecular Gauge. SAUL DUSHMAN.

A Modified Method of Measuring e/m and v for Cathode Rays. L. T. JONES.

An Experimental Determination of the Correction to the Law of Stokes for Falling Bodies, and of the Value of the Elementary Charge "e". JOHN Y. LEE.

On the Coefficient of Slip Between a Gas and a Liquid or Solid. R. A. MILLIKAN.

Note on the Electron Atmospheres (?). CARL R. ENGLAND.

Vapor Pressure of Molybdenum and Platinum. IRVING LANGMUIR.

Disappearance of Gas or Clean-up Effect in Vacuum Tubes. IRVING LANGMUIR.

A New Principle in the Application of Selenium to Photometry. F. C. BROWN and L. P. SIEG.

Determination of e/m from Measurements of Thermionic Currents. SAUL DUSHMAN.

Rate of Decay of Phosphorescence at Low Temperatures. E. H. KENNARD.

Determination of the Sun's Temperature. G. A. SHOOK. (By title.)

The Theory of Photoelectric and Photochemical Action. O. W. RICHARDSON. (By title.)

Photoelectric Potentials of Cathode Films. P. H. DIKE.

The Temperature Coefficient of Young's Modulus of an Iron Wire. H. L. DODGE.

The Temperature Distribution in an Incandescent Lamp Filament near a Cooling Junction. A. G. WORTHING.

Further Experiments on Magnetization by Angular Acceleration. S. J. BARNETT.

Production of Gases in Vacuum Tubes. G. WINCHESTER.

A Precision Relay. CARL KINSLEY.

A Thermopile of Bismuth Alloy. W. W. COBLENTZ.

ALFRED D. COLE,
Secretary.

A Thermopile of Bismuth Alloy.[1]

By W. W. Coblentz.

THE most recent investigation of Haken[2] and of Gelhoff and Neumeier[3] show that an alloy of Bi + 9 to 10 per cent. Sb gives a maximum E.M.F. which is of the order of 77 to 87 microvolts. The writer has found however that alloys containing more than 5 per cent. of antimony are too brittle for thermopiles. Moreover, different samples of this alloy supposed to contain the same amount of antimony did not give the same E.M.F., which varied from 61 to 85 microvolts. Apparently the physical structure has an influence upon the E.M.F. This alloy was therefore discarded, and pure bismuth was employed as in previous thermopiles. The best bismuth wire against silver gives an E.M.F. of 81 microvolts.

Tests showed that an alloy of bismuth containing 5 to 6 per cent. of tin gave a uniform (for different melts) value of 44 to 45 microvolts. A thermoelement consisting of the best bismuth and an alloy of Bi + 5 to 6 per cent. tin gives an E.M.F. of 125 to 127 microvolts per degree.

The bismuth (and in the near future, bismuth-tin alloy) may be obtained from Hartmann and Braun in fine pliable wire from 0.06 to .10 mm. diameter. This may be further reduced in size by cutting the wire in short lengths and pressing it flat between plates of glass. These flat pieces are then cut into narrow strips of the desired width.

The wire of bismuth-tin alloy is not yet on the market. It is made by spattering the molten metal, by allowing it to drop from a height upon a smooth perfectly clean glass plate.[4] Pfund[5] goes a step further, and by hurling the molten metal over a glass plate produces much longer filaments. The spattered material is quite pliable. The wide strips increase the emissivity, so that for the same resistance of the round as compared with the flat material, the best width to balance emissivity and conductivity must be found by experiment.

A thermopile was constructed as shown in Fig. 1. The receivers are of platinum 0.005 mm. in thickness and 1.8 by 3.0 mm. in area. The bismuth wire is 0.1 mm. diameter; the alloy was selected and estimated of a slightly greater area of cross-section. The thermopile is constructed by melting a globule of pure tin (0.05 mm. diameter) to the receiver by means of soldering solution. The receivers are then glued upon a piece of cardboard; properly spaced as shown in Fig. 1. The bismuth wire (joined to the silver wire by means of tin as described in previous publications) is joined to the tin on the receivers. The wires of bismuth-tin alloy are then placed on the receivers (see Fig. 1) and secured with Wood's alloy, care being taken that the fusible alloy does not affect the bismuth wire, thus producing a brittle juncture. The cardboard

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society,

[2] Haken Vesh, Phys. Gesell., 12, p. 229, 1910.

[3] Gelhoff and Neumeier, Phys. Gesell., 15, p. 876, 1913.

[4] Coblentz, Bull. Bur. Standards, 7, p. 248, 1910.

[5] Pfund, Phys. Rev., 34, p. 228, 1912.

is then placed over the holder, the end-wires are attached to the binding posts by means of Wood's alloy and the card is removed by soaking in water. The front side of the receivers is painted with a mixture of lamp black and chemically precipitated platinum black, as previously described.[1]

The wires are joined in series-parallel thus reducing the resistance by one fourth from what would be obtained by joining all the elements in series. The silver or copper end-wire is used for three purposes: (1) to maintain a low resistance, (2) to maintain symmetry by having all the E.M.F. junctions close together, freely in contact with the air, (3) greater strength. The bismuth wire cannot be easily attached to binding posts, and although pliable it is not advisable to subject it to torsional strains. The additional length of wire (of negligible resistance) at the ends of the bismuth adds pliability which is needed in a commercial instrument, subjected to rough usage. No shellac is used except for covering the silver wire and for insulation at the overlapping edges of the central line of receivers. This produces a very quick acting instrument.

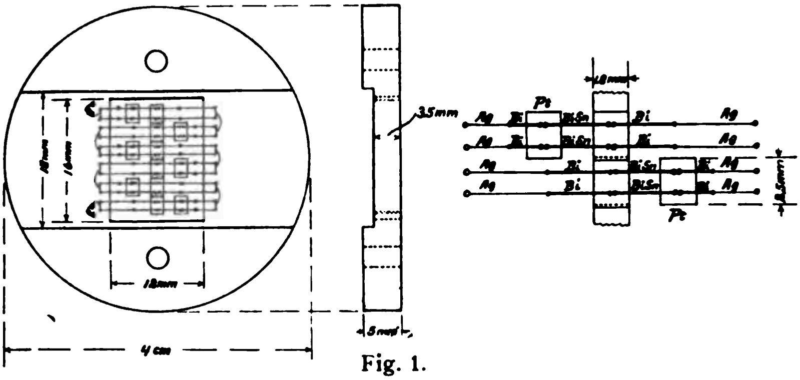


Fig. 1.

The radiation sensitivity of this thermopile was not quite as high as was hoped to attain. However, as a first attempt at this design, the knowledge gained indicates where improvements may be made. The resistance was 3.8 ohms. The thermal sensitivity was about 55 per cent. greater than the bismuth silver thermopile. The radiation sensitivity was 30 to 31 per cent. greater than the average sensitivity of a number of bismuth-silver thermopiles. For some researches it will therefore be of advantage to construct a thermopile of bismuth and of bismuth-tin alloy.

The efficiency of these thermopiles is such that one microwatt of radiant energy produces a rise in temperature of 15 to 16 × 10^{-6} degree in the receiver. The E.M.F. developed depends upon the number of junctions attached to the receiver and their manner of connection; whether all in series or in series-parallel as in this design. The voltage test was made with a Leeds and Northrup "type K" potentiometer, having a 100th shunt so that one division on the slide wire represents one microvolt, the standard lamp being at a distance of two meters. From this it may be seen that this type of thermopile may be

---

[1] Coblentz, Bull. Bur. Standards, 9, p. 7, 1912.

used in photometric and other investigations with rather insensitive auxiliary apparatus.

WASHINGTON, D. C., November 21, 1913.

AN ATTEMPT AT AN ELECTROMAGNETIC EMISSION THEORY OF LIGHT.[1]

BY JACOB KUNZ.

THE phenomena of light in discussion are explained by means of the following fundamental assumptions:

1. Light arises from oscillating electric charges. Each charge is connected with its own electromagnetic field, which has a material physical existence. These atomic fields carry mass, momentum and energy with them.
2. Maxwell's equations hold for these fields.
3. The velocity of light is always $-$ C.
4. Only relative motions can be defined and detected.

A MODIFIED METHOD OF MEASURING e/m AND v FOR CATHODE RAYS.[1]

BY L. T. JONES.

THE method used is the result of an attempt to eliminate as nearly as possible the errors that accompany the experimental determination of e/m by the usual method of electrostatic and magnetic deflections. The tube through which the rays are passed is made by drawing a scratch on a slip of iron and pressing it against the upper of the two electrostatic plates. The undeflected beam thus passes at grazing incidence to this plate. The upper electrostatic plate has a piece of soft iron, of the same dimensions as that on which the scratch is drawn, inlaid in it so that the cathode beam while passing through the tube is wholly surrounded by iron.

This method differs from those ordinarily employed in the position of the photographic plate. This is placed flat on the lower electrostatic plate. Sufficient potential is applied to deflect the beam downward to strike it. The electrostatic deflection is thus constant and may be determined accurately. With the distance between the electrostatic plates small in comparison with their linear dimensions the deflected beam may be made to fall wholly within a uniform electrostatic field.

The magnetic field is furnished by a solenoid with its axis perpendicular to the surfaces of the electrostatic plates. The solenoid encloses the whole apparatus and is of such length that the field is uniform and its strength may be calculated.

The cathode beam when deflected by the electrostatic field alone produces a straight line parallel to the undeflected beam. When the magnetic field is applied this line is displaced to the right or left according to the direction of the magnetic field and takes the form of the arc of a circle.

The measurements taken from the photographic plate are the horizontal distance of travel of the electron and its corresponding magnetic displacement.

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

The greatest source of error is in the measurement of the magnetic deflection which enters, as usual, to the second power. The other factors, with the exception of the dielectric constant of the photographic plate, may be very accurately determined. The dielectric constant of the glass enters the equation in such a way that any error in its value affects only very slightly the resulting value of e/m.

Laboratory of Physics,
University of Illinois, November 14, 1913.

Certain Experiments in Sound Diffraction.[1]

By G. W. Stewart and Harold Stiles.

THE experiments undertaken resulted in interesting confirmations of sound theory. The four cases studied were the diffraction about a sphere whose circumference is equal to the wave-length, the alterations in the intensity passing through a narrow slit when the dimensions of the slit are changed, the intensities obtained by diffraction through circular openings of different sizes, and the variation of the intensity with the number of circular openings, the size of each being the same.

In the first experiment, the distortion of the intensity distribution about the sphere, due to the absorption brought about by resonance, was eliminated and the experimental results agreed with the theoretical predictions within the limit of experimental error.

In the last three experiments the changes in the openings modified the resonance of the tube which conducted the sound to the measuring instrument, and there was introduced an error which could not be eliminated with the apparatus used. In spite of this fact, it was found that the theory for the slit which shows that the total intensity is much more sensitive to changes in the length of the slit than in the width, was satisfactorily verified within a reasonable limit. The experiments with the circular openings also showed that the "conductivity" of the opening was approximately proportional to the area and that with equal circular openings used simultaneously the conductivity was proportional to the square of the number of openings. The range of the experiments should be extended.

Evidence of a Diurnally Reversing Convectional Circulation of the Atmosphere Over the Upper Peninsula of Michigan.[1]

By Eric R. Miller.

CLIMATIC maps show the following abnormalities in the upper peninsula of Michigan and northeastern Wisconsin: Heavy rainfall in the interior and light on the coasts and great range of temperature in the interior, with late frosts in fall and early in spring.

An explanation of these abnormalities is found in the hypothesis of a convectional circulation of the atmosphere arising from the unequal heating and cooling of adjacent bodies of land and water. The rainfall is ascribed to the

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society,

dynamic cooling of a column of air ascending over the land by day; the great range of temperature and extreme susceptibility to frost, to excessive radiation of heat from the ground through unusually clear sky produced by dynamic warming, and evaporation of cloud, in the column descending over the land by night.

The winds and weather of the upper Lake Region are usually undei the control of passing cyclones but statistical analysis of wind records affords a verification of the foregoing hypothesis by showing the existence of a diurnally reversing component of the wind.

Anomalous Temperature Effects upon Magnetized Steel.[1]

By N. H. Williams.

SMITH and Guild, in experimenting with short steel rods of high carbon content, found that, upon heating the specimens, the magnetism was reversed in the neighborhood of 200° C. Their explanation ascribed the reversal to the difference in action of the self-demagnetizing field of the magnet upon the iron and the carbide components of the steel.

The present paper deals with experiments which suggest an entirely different explanation.

It is found that the reversal is dependent upon the method of magnetizing the rod and that it can be prevented entirely by preventing an oscillatory discharge through the magnetizing coil.

The Positive Potential in the Photo-Electric Effect.[1]

By W. H. Kadesch.

TWO main sources of error have been especially troublesome in work on the positive potential. These are due, first, to the relatively short range of frequencies to which the easily manageable metals are sensitive, and secondly, to the effect of ageing of surfaces, and of photo-electric fatigue. The use of the strongly electropositive metals as electrodes in this research made it possible, not only to illuminate with light of greater wave-length than has hitherto been used but also to expose a new surface with the greatest readiness whenever desired.

Cylindrical electrodes of sodium and potassium were fixed to the rim of a wheel which could be rotated by means of an electro-magnet, the shaft of the wheel carrying a soft iron armature. In the plane of the wheel, and at opposite ends of a diameter, were placed a Faraday cylinder, and an auger-like knife operated by means of a second electro-magnet. To make an observation the electrode was turned first toward the knife, by means of which a slice of any desired thickness was taken off, then toward the Faraday cylinder, in position to receive the illumination. The source light was a spark about 2 mm. in length between iron terminals. The analyzing device was a quartz spectrometer.

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society,

The Faraday cylinder was joined to one pair of quadrants of an electrometer, while the electrode was given any desired potential by means of potentiometer scheme. The positive potential corresponding to any wave-length was determined, either by giving the electrode a potential just sufficient to prevent the escape of electrons, or by varying the potential applied and then plotting curves with this, and the corresponding photo-electric current, as cöordinates. In the former method fresh surfaces were frequently cut, especially when the balancing potential was approached. In the latter, for each potential applied the current given by surfaces of different age was determined, a fresh one being cut for each exposure. The current for zero age was then found by extrapolation. This precaution was found to be unnecessary, however, since the slope of the age-current curves fell to zero at the balancing potential.

The range of wave-lengths employed was that from 2155 to 3970 A.U. Longer waves could not be used, with the quartz arrangement, because of the small dispersion. The positive potential was found to vary directly as the frequency of the light. This relation is expressed by the equation,

$$V = kn - V_0.$$

The value of k found for sodium was 3.87, that for potassium 3.83. The true value is somewhat higher, every source of error tending to reduce the value given by experiment.

THE THEORY OF PHOTO-ELECTRIC AND PHOTO-CHEMICAL ACTION.[1]

BY O. W. RICHARDSON.

IN this paper it is shown that the following equations are valid for all substances at all temperatures:

$$\int_{\nu_0}^{\infty} \frac{F(\nu\nu_0)h\nu^3}{e^{\frac{h\nu}{RT}} - 1}\left\{\varphi(\nu) - \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}} - 1} - RT^2\frac{\partial \log F(\nu\nu_0)}{\partial T}\right\}d\nu = 0, \qquad (10)$$

$$\int_{\nu_0}^{\infty} \frac{F(\nu\nu_0)h\nu^3 d\nu}{e^{\frac{h\nu}{RT}} - 1} = A_1 T^{\frac{1}{2}} e^{\int^T \frac{w}{RT^2} dT} = \Phi(T)e^{-\frac{h\nu_0}{RT}}, \qquad (16)$$

$$\int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1}\left\{\frac{F(\nu\nu_0)}{RT}\left(\frac{\partial w}{\partial \nu_0}\right)_T + \frac{\partial F(\nu\nu_0)}{\partial \nu_0}\right\}d\nu = 0, \qquad (17)$$

$$\int_{\nu_0}^{\infty} \frac{\nu^3 T_\nu F(\nu\nu_0)}{e^{\frac{h\nu}{RT}} - 1} h d\nu = 2RT\Phi(T)e^{-\frac{h\nu_0}{RT}}, \qquad (27)$$

where the notation is the same as in Phil. Mag., Vol. 24, p. 570 (1912), except that T is written for temperature instead of θ, $F(\nu\nu_0)$ is written for $\epsilon F(\nu)$, $\varphi(\nu)$ is the energy abstracted from the radiation by an atom which is liberated under the excitation of radiation of frequency ν and $\Phi(T)$ may be regarded as defined by the right-hand one of the two equations (16). ν_0 is the value of ν at which $F(\nu\nu_0)$ becomes zero.

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

It is also shown that the following values of the functions involved are consistent with all of the equations (10), (16), (17) and (27), viz.:

$$\left.\begin{aligned} \varphi(\nu) &= h\nu, \text{ universally,} \\ F(\nu\nu_0) &= \frac{A_1 h}{R^2}\left(1 - e^{-\frac{h\nu}{RT}}\right)\frac{\nu - \nu_0}{\nu^3}, \quad \nu_0 < \nu < \infty, \\ T_\nu &= h(\nu - \nu_0), \\ h\nu_0 &= \omega - \tfrac{3}{2}RT, \\ \Phi(T) &= A_1 T^2. \end{aligned}\right\} \quad (43)$$

Palmer Physical Laboratory, Princeton, N. J.

Determination of e/m from Measurements of Thermionic Currents.[1]

By Saul Dushman.

In a paper on "The Effect of Space Charge and Residual Gases on the Thermionic Current in High Vacuum,"[2] Dr. I. Langmuir has developed the following formula for the thermionic current from a heated filament to a coaxial cylindrical anode.

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{\frac{3}{2}}}{r} = \frac{k \cdot V^{\frac{3}{2}}}{r}. \qquad (1)$$

The formula has been tested experimentally by measuring the thermionic currents from a heated tungsten filament 10 mils diameter to a molybdenum anode, 7.62 cm. long and 2.54 cm. diameter. All end corrections were avoided by making use of two auxiliary anodes over the ends of the filaments, on the guard-ring principle.

The glass tube containing these electrodes was thoroughly exhausted by means of a molecular pump, the tube being heated to 360° C. and liquid air interposed between it and the pump. The anodes were freed from gases by bombardment with electrons of high velocity. This was secured by applying a very high potential of four or five thousand volts to the heated filament (cathode) and molybdenum cylinders (anode).

After the electrodes had been treated in this manner it was found that the space charge formula given above held very accurately over the range of voltages tested: 35 to 130. In each case the filament was heated to a temperature so high that in accordance with the Richardson equation very much higher currents could be obtained (provided a sufficiently high voltage was used).

Substituting for e/m in the above equation, the most probable value, 1.76×10^7, the constant k becomes 14.6×10^{-3}, where i is expressed in milliamperes per cm. length, V in volts, and r in cms. The values of i actually obtained for different values of V agreed with those calculated by means of this value for k, to within one per cent. These results were obtained under conditions in which

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

[2] Phys. Rev., December, 1913.

no attempt was made to secure a high degree of accuracy. It would therefore seem as if the above method ought to prove highly applicable for the determination of e/m with an accuracy perhaps greater than that obtainable by any other method.

THEORY AND USE OF THE MOLECULAR GAGE.[1]

BY SAUL DUSHMAN.

FURTHER details are given regarding the construction of the vacuum gage previously described by Dr. I. Langmuir.[2] The theory of the instrument is developed for both the case of low pressures and that of higher pressures. At low pressures where the mean free path is larger than the distance between the mica disc and rotating aluminum plate, the theory shows that the angle of torque of the mica disc is proportional to the rate of rotation of the aluminum plate and to the function $p\sqrt{M/RT}$, where p is the pressure, M the molecular weight of the gas, R the gas constant and T the absolute temperature.

The method of calibration and correction factors to be introduced are discussed in detail.

The instrument has been used to measure the vapor tension of mercury at room temperature, and that of ice at − 78°, and results obtained in agreement with those previously obtained by other investigators.

The pressures obtainable with a Gaede molecular pump were also measured by means of this instrument. A liquid air trap was inserted between gage and pump and the regular ground joint connection was used.

The speed of the pump was maintained at 8,100 r.p.m. With a pressure of 10^{-2} mm. on the rough side, the best vacuum obtainable without using liquid air or heating the gage was 0.15 micron. But by heating the gage to 300° C. for one hour and putting a liquid air flask over the trap, it was found possible to obtain a vacuum which was certainly lower than 0.005 micron (the gage was not sensitive to any smaller pressure). Under these conditions it was possible to increase the pressure on the rough side to 0.1 mm., without increasing the pressure on the high vacuum side, and on increasing the rough side pressure to 19 mm., the pressure in pump had increased to only 0.3 micron, giving a value of 57,000 for the ratio of pressures.

THE TEMPERATURE DISTRIBUTION IN AN INCANDESCENT LAMP FILAMENT NEAR A COOLING JUNCTION.[1]

BY A. G. WORTHING.

THE differential equation representing the distribution of temperature in a uniform cylindrical filament heated by a steady electric current, on the assumption of a constant current density, is

---

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

[2] PHYS. REV., April, 1913.

$$\frac{\partial^2 T}{\partial l^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{k}\frac{\partial k}{\partial T}\left[\left(\frac{\partial T}{\partial l}\right)^2 + \left(\frac{\partial T}{\partial r}\right)^2\right] + \frac{i^2\rho}{k} = 0,$$

where T represents temperature; l, distance parallel to the filament axis; r, radial distance; i, current density; ρ, resistivity, and k, thermal conductivity.

The assumption of a new scale of temperature, so chosen that the corresponding value for thermal conductivity is constant for all temperatures, enables one to rewrite the differential equation as

$$\frac{\partial^2 T'}{\partial l^2} + \frac{\partial^2 T'}{\partial r^2} + \frac{1}{r}\frac{\partial T'}{\partial r} + \frac{i^2\rho'}{k'} = 0,$$

where T', ρ' and k' in the new system correspond to T, ρ and k in the original equation.

The above equation has been applied to a tungsten filament 0.25 mm. in diameter heated by a 6.4 amp. current to about 2440° K. (Kelvin) using the temperature scale of Mendenhall and Forsythe. In this instance the term $i^2\rho/k'$ has been found approximately proportional to T', that is,

$$\frac{i^2\rho'}{k'} = a^2 T'.$$

The differential equation thus conditioned becomes linear and a particular solution may readily be found. The further working out of the problem consists in building up a series from such terms in such a fashion that the experimental and theoretical boundary conditions are satisfied.

The following table indicates some of the more interesting results:

Temperature Distribution near a Cooling Junction, in a 0.25 mm. Tungsten Filament Heated by a 6.4 Amp. Current.

Distance from the Cooling Junction in cm.	Surface Temperature in °K.	Angle at the Surface between Temperature Gradient and Filament Axis in Degrees.	Axial Component of the Temperature Gradient in Degrees per cm.	Temperature Difference between Axis and Surface in °C.
0.2	1764	0.18	2250	0.04
0.7	2323	4.6	420	0.21
1.2	2421	31	70	0.27
1.7	2437	76	11.4	0.27
∞	2440	90	0.0	0.28

In any single filament the temperature variation from the axial temperature, across any right section, varies quite closely with the square of the radial distance. In different sized filaments of the same material operated under the same conditions at the same maximum temperature, the temperature differences between the axes and the surfaces in the neighborhood of that maximum temperature vary quite closely as the radii.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

Physical Laboratory,
National Lamp Works of General Electric Co.,
Nela Park, Cleveland, O.

THE ILLUMINATION-CURRENT RELATIONSHIP IN POTASSIUM PHOTO-ELECTRIC CELLS.[1]

By Herbert E. Ives.

IT has been commonly believed that the photo-electric current is directly proportional to the intensity of illumination. The relationship has been experimentally studied by Elster and Geitel, Lenard, Griffith and Richtmyer. Lenard concluded the relationship to be linear, although his results plot as a shallow curve, convex toward the illumination axis. Griffith found the curve to increase more rapidly than the illumination. Elster and Geitel and Richtmyer found the linear relation. On the assumption of this linear relation the photo-electric cell has been suggested as a physical photometer.

The problem of the present investigation was to develop absorbing screens to use with alkali metal cells, probably rubidium or cæsium, to reduce the wave-length sensibility to that of the normal eye.

After carefully determining the conditions under which the quadrant electrometer could be used to measure current, a number of potassium cells were constructed and studied. It was found that no two showed the same illumination-current relationship. When plotted, the results showed all varieties of curves, from convex to the illumination axis to concave. Further work with special cells showed this relationship to be a function of voltage, electrode distance and gas pressure.

The wave-length sensibility curves were different for the various cells, probably due to varying relative strength of the normal and selective effects.

It is concluded that the photo-electric cell, at least as at present made, is only applicable to photometry if accurately calibrated for every illumination intensity used. The application of absorbing screens to produce a visual luminosity curve sensibility is not feasible.

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, December 30, 1913.

Second Series. *February, 1914* *Vol. III., No. 2*

THE

PHYSICAL REVIEW.

THE ELECTRICAL DISCHARGE FROM LIQUID POINTS, AND A HYDROSTATIC METHOD OF MEASURING THE ELECTRIC INTENSITY AT THEIR SURFACES.[1]

By John Zeleny.

1. The discharge of electricity from pointed conductors has been studied heretofore only from points made of metal. The assumption is generally made that all of the features of the discharge are independent of the kind of metal of which the point is made. In support of this view may be mentioned the results of Precht,[2] who found that, after a steel needle had been plated with a thin coating of copper, the potential at which the discharge ceased from the needle as well as the current obtained with any voltage, remained the same as before. In a study of the discharge from cylindrical points of different diameters, the writer[3] used platinum points for the two smallest diameters while the others were made of brass, and the results from both kinds of points could be expressed well by the same empirical formula, indicating that the nature of the metal is of no consequence.

2. There are a number of phenomena, however, attending the discharge from pointed conductors which can only be explained by attributing some importance to the surface from which the discharge is taking place. Thus Röntgen[4] found that the potential at which the discharge from a gilded needle began was dependent upon whether a current had been flowing from the point shortly before. Precht[5] gives an example where the beginning potential rose by 25 per cent. at the end of a number of successive determinations.

---

[1] A preliminary paper on this subject was read before the American Physical Society on December 30, 1910.

[2] J. Precht, Wied. Annalen, 49, p. 150, 1893.

[3] J. Zeleny, Phys. Rev., 25, p. 305, 1907.

[4] W. C. Röntgen, Göttingen Nachrichten, p. 390, 1878.

[5] Loc. cit.

Warburg and Gorton[1] found that the passage of a current from points made of various metals permanently increased the potential at which a discharge begins above that first required when the points were newly made. Subjecting such aged points to various radiations had the effect of temporarily reducing the beginning potentials to their original values. Similar effects were obtained by heating the points in a flame or by heating them to a glow by means of an electric current when they were immersed in oxygen or hydrogen. In some of the cases recorded, the potential increased by over fifty per cent.

Again, it is well known that some impulsive discharges of short duration and at considerable intervals of time may take place from a point at potentials much lower than are required for the first continuous discharge. Precht[2] cites the case of a point cut from a piece of aluminum leaf which gave the first impulsive discharges at + 1,871 and − 1,065 volts, while the continuous currents did not begin until the potentials were raised to + 4,173 and − 2,971 volts.

Such effects as these cannot be ascribed to changes in the circumambient gas, but must be attributed either to some chemical change at the metallic surface, to the accumulation there of some foreign material gathered from the gas, to the formation of or changes in an electric double layer, to changes in the amount of gas absorbed by the point or to changes in the layer of occluded gas. Some of the effects are most likely due to one cause and some to another. In any case, the changes mentioned involve the character of the discharging surface.

3. Although no systematic study has yet been made with points of different metals, it would seem that, for the investigation of influences arising from conditions at the surface of discharge, it would be well not to confine the experiments to metallic points, since metals in general may not differ greatly among themselves as regards some crucial property. In choosing between various materials it was decided to experiment first with liquids because of their radical difference from metals and because of some advantageous properties. A small hemispherical drop protruding from the end of a fine capillary tube may serve as the liquid point. The discharging surface may readily be renewed in this case by simply removing the drop. The chemical nature of the surface may be made quite different by a change of liquid; and this without changing the geometrical shape of the point. The surfaces of such liquid points are necessarily perfectly smooth,[3] but have the disadvantage of being liable to distortion.

---

[1] E. Warburg and F. R. Gorton, Ann. der Physik, 18, p. 128, 1905.

[2] Loc. cit.

[3] The results of Precht (loc. cit.) and the writer (loc. cit.) indicate that the presence of

Apparatus Used.

4. The essential parts of the apparatus which was used in the experiments are shown in diagram in Fig. 1. The discharge took place in air at atmospheric pressure at the end of the point *A*, and the current passed to the brass disc *D* (6.3 cm. in diameter), situated 1.5 cm. below the end of the point, unless otherwise stated. From the disc the current passed first through a telephone receiver, used for detecting intermittence, and then to earth through a shunted D'Arsonval galvanometer whose greatest sensitivity was 3 × 10^{-9} amperes per scale division. The point *A* consisted of a cylindrical glass tube whose diameter was nearly constant for a length of 3 cm. and usually did not exceed one millimeter. The free end was broken off squarely across, and the upper end, with the piece of larger tubing from which the fine point had been drawn out, was connected at *B* by means of a piece of rubber tubing to the glass tube *T*. This mode of attachment made it easy to exchange points. Finally, the tube *T* was joined to the glass part *F* by the rubber tube *R*.

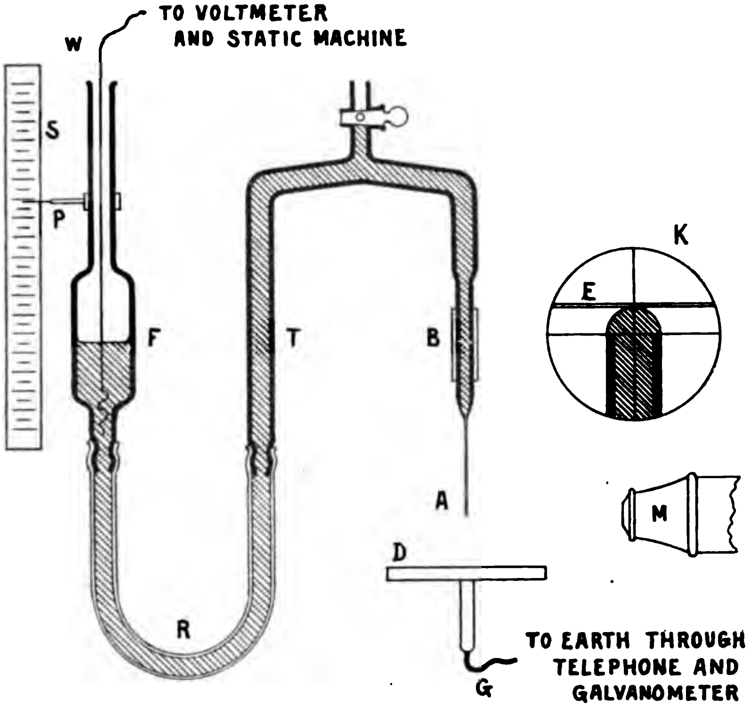


Fig. 1.
Diagram of apparatus.

minor irregularities on the surface is of no consequence and that the general geometrical shape is alone determinative for both the beginning potentials and the current obtained with any potential.

The liquid in the apparatus was connected by the wire W to a high capacity static machine and the voltmeter. The static machine was provided with 15 Leyden jars for steadying the potential, which could be regulated by shunting a part or all of the current to earth through a variable india-ink on paper resistance which was devised for such purposes in this laboratory.[1] A Braun voltmeter reading to 10,000 volts was usually used for measuring the potentials of the points. Its accuracy was tested by comparing its readings with other Braun voltmeters and Kelvin vertical electrostatic voltmeters of various ranges, some of which had been checked for the lower voltages by means of a high potential storage battery. The glass piece F could be raised or lowered by a rack and pinion motion on the stand to which it was clamped. Changes in the vertical position of the liquid surface at F were determined by a cathetometer or from readings of the pointer P on the fixed scale S.

The end of the discharge point was observed with a low power microscope which had an ocular micrometer and was itself carried on a micrometer slide. The latter permitted the measurement of the diameter of a point while in position. With the ocular micrometer a distance was measured from the end of the point equal to the height of meniscus it was proposed to use. The movable cross hairs were left in this position, shown at E in a picture of the field of view drawn at K, and the meniscus was simply raised to the point of tangency to ensure its being of the proper height.

5. The end of a point best suited to the purpose should have a sharp continuous edge, which moreover should lie in a plane which is perpendicular to the axis of the cylinder. Ground ends are not serviceable because the act of grinding breaks off minute chips from the edge and the meniscus on such a point can rarely be raised to a hemispherical form without the liquid crawling over the edge and running up the outside of the tube. The method adopted was to make a fine short scratch on the side of the tube and then break off the tube by a gentle pull. In a rather small fraction of cases the break was sufficiently straight across to permit of use. The roughened portion of the edge, due to the scratch, caused much trouble owing to the overflow of the drop at this point under certain conditions.

The choice of liquid to be used in the apparatus is confined to such liquids as do not leave a residue on evaporation, because the rapid evaporation at the surface of the point soon causes any salt solution to become saturated at this place and to form a deposit. In the experiments to be described in this paper, only one kind of liquid was used, and that

---

[1] F. Aust, Physik. Zeitschrift, 12, p. 732, 1911.

was a very dilute solution of hydrochloric acid. The conductivity of this was large enough so that no account had to be taken of any fall of potential existing between the voltmeter and the end of the point. Some measurements of the various quantities with which this paper is concerned were made using distilled water and strong hydrochloric acid, and in each case the values obtained were essentially the same as those obtained with the very dilute acid.

Procedure in Experiments.

6. When the liquid surface in *F*, Fig. 1, is on a level with the end of the tube *A*, the meniscus at the latter place is flat, it being presupposed that no electric charges are present. As *F* is raised gradually the meniscus at *A* bulges out more and more. The vertical height between the meniscus and the surface level in *F* is a measure of the hydrostatic pressure in the liquid drop. This pressure is a maximum when the radius of curvature of the meniscus is a minimum, which is the case when the meniscus becomes hemispherical.

Knowing r, the radius of the tube *A*, and h, the height of the liquid necessary to make the meniscus hemispherical, the surface tension T of the liquid can be found from the relation

$$T = \frac{rhdg}{2},$$

where d is the density of the liquid and g the gravity constant. This method of determining T is capable of giving fair results when a well-made point of small diameter is used.

7. If the liquid is gradually charged, the electric force acting at the surface of the meniscus tends to pull the drop outward. This tendency may be counteracted by lowering *F* until the meniscus is of the same height as it was before being charged. The distance p that the liquid surface was lowered is a measure of the electric pull per unit surface on the meniscus. Expressing this latter in terms of f, the electric intensity at the surface,

$$\frac{f^2}{8\pi} = pdg, \quad \text{or} \quad f = \sqrt{8\pi pdg}.$$

The electric intensity at the surface of the meniscus is thus determined by simply measuring the length of the liquid column whose hydrostatic pressure just counteracts the mechanical pull exerted by the electric field on the surface of the liquid. The electric intensity measured is evidently the largest value obtaining on any part of the liquid surface. If inequalities exist, equilibrium is attained by a distortion of the surface.

The method permits the measurement of the electric intensity in all cases where a definite meniscus can be maintained and has been used for determinations when no current is flowing, when a current is flowing, and under the conditions of the initial current from points.

No difficulty was experienced in getting the pressure reading when the point was charged to a considerable potential, but a great deal of difficulty was experienced with most of the points prepared in obtaining the pressure required to form an uncharged drop whose height approached that necessary to make it a hemisphere. This difficulty arose from the ease with which a drop of such a height overflows up the sides of the tube, the place at which this overflow starts being the scratch on the glass made for breaking off the tube as already mentioned in § 5.

8. The arrangement of a point opposite a plane does not permit of the calculation of the electric intensity at the surface of the point for any voltage. Determinations of the value of this quantity for various potentials below that necessary to start a current were made by the method described with a number of points with hemispherical menisci whose radii ranged from .021 cm. to .054 cm., and where in each case the distance between the end of the charged point and the earthed plane was 1.5 cm.

The results obtained may be stated in the following form: The electric intensity at the end of a point of the form used is sixty per cent. of the intensity that exists at the surface of the inner of two concentric spheres,[1] the smaller of which has a radius equal to the radius of the point in question and is charged to the same potential, while the larger has a radius equal to the distance between the point and plane (1.5 cm.) and is at zero potential.

Measurements of the electric intensity at the point for other distances than 1.5 cm. between the point and plane, made with one point only, gave for the above percentage, 57 per cent. for a distance of 3 cm., and 67.5 per cent. for a distance of 0.5 cm.

These results may be used for finding the electric intensity at the end of metal points of the same shape under the given conditions.

CHARACTERISTICS OF THE DISCHARGE.

9. Some of the phenomena which attend the starting of a current from the points deserve first consideration. Suppose the potential of a liquid point, which has not been used for some minutes, to be increased gradually while the meniscus is kept in a fixed position by proper adjustment of the liquid pressure. When the potential has reached a certain value,

---

[1] Maxwell, Electricity and Magnetism, Vol. I., 3d ed., p. 189.

whose magnitude depends not only on the diameter of the point but also upon how long the surface of the liquid has stood unused, a momentary discharge takes place, a single click being heard in the telephone receiver and the galvanometer indicating a slight ballistic throw. A faint flash of light appears and the meniscus of the point jerks back into a more flat position, showing that some change has taken place which has resulted in an increase in the surface tension.

This solitary discharge is not repeated at the same voltage (not within some minutes at least) even after the meniscus has been brought to its initial position by added pressure. A second solitary discharge only occurs after the potential has been raised one or more hundred volts. This, too, is accompanied by a fall of the meniscus. Further discharges of the same kind are obtained on increasing the potential by constantly diminishing steps, except that this first stage changes after a few discharges into a second stage where, instead of one discharge following a rise in voltage, several take place at increasing intervals, finally stopping altogether. Going up in potential from this value, a third stage[1] is reached where discharges continue indefinitely, say, at the rate of about one a second. With further increases in voltage the discharges occur closer and closer together until the individual discharges cannot be distinguished either by the galvanometer which shows a steady deflection or by the telephone where a continuous sound is heard, or by the jerks of the meniscus whose upper surface simply appears very blurred through the microscope.

At a still higher potential, a fourth stage is reached with the positive discharge where the meniscus suddenly becomes perfectly motionless, the sound in the telephone ceases, and the galvanometer deflection assumes a smaller steady value. This last stage continues through increases of potential up to the limit used, which was 10,000 volts.

On lowering the potential of the point from its highest value, the steady state (stage four) passes back as suddenly into the intermittent one but this occurs at a somewhat lower voltage than at which it began.

The voltage at which the intermittent current stops is nearly the same as that at which the continuous intermittent stage (stage three above) begins, but is usually a little higher owing to the fact that this stage on the first trial begins at a lower potential than on succeeding trials. However, after a current of some magnitude has been allowed to flow from the point, the voltages at which the intermittent stage stops and then

---

[1] A slightly different intermediate stage has also been noted where keeping the potential constant, a continuous series of discharges takes place, each consisting of a few discharges in rapid succession, the series being separated by an interval of rest of a second or two.

begins again are usually identical.[1] Potentials obtained under these conditions and the corresponding electric intensities determined at the same time have been taken as the values of these quantities which are necessary to start the discharge. This means that these quantities were measured for the surface conditions existing after the treatment noted.

After the current from a point has been stopped, the initial solitary discharges, mentioned under stage one above, may again come into evidence if the point is left standing for several minutes. The conditions have not been determined under which the first of these solitary discharges would occur at the lowest possible potential. Under the usual procedure of starting an experiment, the liquid surface is agitated during the manipulations and for such a surface the discharge usually begins with the continuous intermittence stage. The removal of one or more drops from the end of the point brings the initial discharge voltage nearly up to the value it has after a current has been flowing.

10. The following examples will give an idea of the range of voltages over which the various types of discharge extend. Thus a point with a hemispherical meniscus whose radius was 0.025 cm. gave the first momentary discharge at + 4,000 volts, the next came at 4,110, the next at 4,200, and so in turn others until at 4,700 volts the discharges came continuously. The intermittent stage changed to the steady stage at 5,125 volts. On lowering the voltage the intermittent stage was resumed at 5,000 volts and the current ceased at 4,750 volts. After raising the voltage to 8,500 and then lowering it, the steady stage repeatedly changed to the intermittent at 5,000 volts as at first, but the current now stopped at 4,800 volts. At the transition stage the steady current of 4.9×10^{-8} amperes changed to an intermittent current whose mean value was 5.8×10^{-8} amperes.

With another point having a radius of 0.034 cm. the first discharge was observed at + 4,100 volts, the next at 4,250, and so on until at 5,250 discharges passed continuously about one a second, and at 5,350 the rate had increased to several per second. At 5,750 volts the intermittent current of 9.8×10^{-8} amperes changed to the steady current of 6.2×10^{-8} amperes.

A still larger point of radius, 0.045 cm., gave the first momentary discharge at + 4,500 volts with others in turn as before. The intermittent current changed to the steady form at 6,050 volts. With decreasing potentials the steady current changed back to intermittent at 6,025 which ceased at 5,760.

---

[1] If the current is diminished very rapidly to zero, it is apt to stop at a higher voltage than is otherwise the case.

In some cases the stopping potentials obtained on different days varied by as much as 3 or 4 per cent., but the condition accountable for this has not been ascertained.

Luminous Appearance.

11. The luminous effects which are seen in a dark room near the end of a liquid point at once decide that the positive discharge is of quite a different character when intermittent from what it is while a steady current is passing. In the latter case, for the larger currents the whole hemispherical surface is covered with a coating of steady purplish light of imperceptible thickness, and with the smallest current at which this form of discharge exists, usually less than half of the hemisphere is covered with the luminous coat.

When the current is intermittent, however, in place of the luminous coat, there is seen at each discharge a fibrous like brush of light which starts from a small area on the liquid surface and reaches out half way to the plane. Near the surface of the liquid, the light is confined to a narrow region and here it is much brighter than in the brush part proper. The general appearance is seen from the drawing *a* in Fig. 2. It appears to be a real positive brush discharge. Just before the intermittent form changes into the steady form the luminous effects of both kinds of discharges are seen at times. They either coexist or there is a rapid succession of changes of one kind into the other.

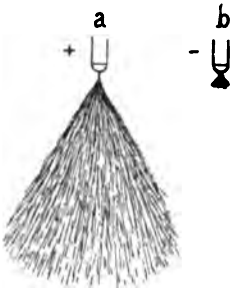


Fig. 2.
Appearance of intermittent positive discharge and of negative discharge.

12. The negative discharge is nearly always an intermittent one (occasionally no intermittence was observed) and in the dark the light from it has the appearance of a short stubby brush. The brush starts from a very small area of the surface and is especially bright at this initial point. Its appearance is shown at *b* in Fig. 2, and it is seen to be a typical negative brush discharge.

Oscillations of Meniscus.

13. The character of the oscillations of the meniscus during the intermittent stage of the discharge has been studied by making observations in light from the spark of a Leyden jar. Drawings of some of the instantaneous outlines, observed in this way during discharge from a point of 0.034 cm. diameter, are shown in Fig. 3.

For the smallest positive currents the oscillations usually are confined to the limits indicated in *a* and *b*, although now and then the form *c* was seen, the pointed top flying off in a drop having a diameter about one tenth of that of the tube. The outlines *d*, *e*, *f*, *g*, *h* and *i* show some of the forms seen with larger positive currents. When the current was about to change from intermittent to steady, the meniscus showed the agitated appearance indicated in *k*, the meniscus tossing about from side to side and drops of liquid flying off from its end. Without intermittent light this has the appearance *l*, as if the surface were breaking into spray. The contrast is very remarkable when the meniscus of so much commotion suddenly becomes a perfectly still and clear-cut hemisphere as the current changes to the steady form.

14. In the case of the negative discharge the appearance for small currents was much the same as with the positive, forms *a*, *b*, *d* and *e* being seen, but form *c* was not observed. With large currents (many times larger than the positive ones with which the form *k* was observed) using potentials above 8,000 volts, the meniscus was comparatively steady, although moving about as shown at *j*. Excessive pressure in a meniscus always results in large drops flying off, and it is difficult to know what external pressure should be applied which would make the meniscus hemispherical were it not in motion. Thus with the negative discharge just considered, where the applied pressure remained unchanged throughout, during the range of voltages from 6,000 to 8,000, large drops were thrown off from the meniscus, while this was not the case for lower or higher voltages than these. The conclusion is drawn that with this discharge, the electric intensity at the point, after the current has started to flow, first increases considerably with increase of potential and then falls again to the initial current value or still lower.

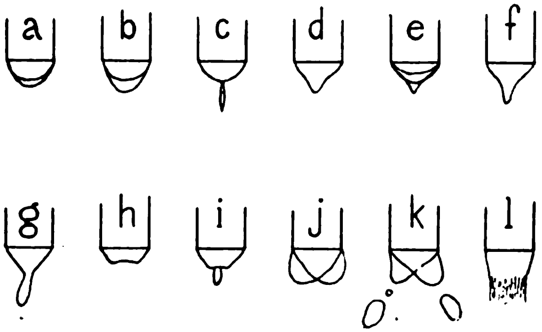


Fig. 3.

Oscillations of meniscus during intermittent discharge.

15. The oscillations of the meniscus are doubtless attributable to the intermittent character of the discharge, the electric force at the surface being smaller with the current flowing than without a current. The fact that during an intermittent discharge, this is of such a character that it is limited to a very small area on the surface, must produce differences of

surface tension over the surface which help to upset its equilibrium. Changes in surface tension actually occur after the first momentary discharges, as already described.

ELECTRIC INTENSITY AT A DISCHARGING SURFACE.

16. The principle of the method used for measuring the electric intensity has been described in § 7. The difference in level of the liquid surface in *F*, Fig. 1, when the point is at the potential under observation and when uncharged, must be measured, the meniscus at the end of the discharge point being of the same height in both instances.

For the steady positive currents, this pressure can easily be measured. The intermittent stage of the positive discharge is included in a rather short range of voltages and in the lower part of this range also, the pressure can be obtained quite accurately.

When the momentary discharges occur but slowly, it is noticed that just before each discharge the center of the meniscus rises slightly and forms a portion of greater curvature from which the discharge takes place, following which the whole meniscus flattens in the way already described in § 9. A little uncertainty arises from not knowing to just what height the meniscus should be forced in this case. The method adopted was to bring the meniscus to such a point that it rose to the adjusted cross hair (*E*, Fig. 1) at each discharge. However, a slight increase in pressure only was necessary to raise the meniscus from the position named to where it touched the cross hair before the sudden elevation preceding discharge, just noted, took place.

17. The measurement of the pressure within a high meniscus when at zero potential offered two difficulties. The first is the one already mentioned due to the ease with which the meniscus overflowed the sides of the tube. Running the discharge for a time helped matters considerably, unless the scratch on the side (§ 5) was too prominent.

The second difficulty arises from the way the surface tension of the meniscus changes on standing, while no discharge is passing. It was necessary to determine the pressure in the meniscus for zero potential immediately after the discharge was stopped in order that the surface tension might be as nearly as possible of the same value as during the discharge. The pressure thus obtained was usually a little larger than was found with a surface made fresh by the removal of one or more drops. It is possible that ordinarily some impurities collect on the outside of the glass tube and are able to pass gradually to the liquid, whereas the discharge dries this glass surface so thoroughly that it takes time before a layer of moisture, sufficient for permitting the passage of impurities to the meniscus, can form.

different day from the preceding, the atmospheric pressure being less and the temperature higher. Some results obtained on that day with a distance of 1.5 cm. are represented by crosses on the horizontal part of the pressure curve for $d = 3$ cm., and it is seen that the pressures are again identical during the discharge.

These results show that the increase in the volume charge in the gas between the point and the plane almost exactly neutralizes all effect of increase of voltage of the point upon the electric intensity at the discharging surface. Since more ions are produced with the higher voltages this limiting electric intensity must extend farther into the gas, the larger the current. Hovda[1] has shown that in the space between the point and plane the electric force is very nearly proportional to the square root of the current. This proportion evidently does not hold at the discharging surface.

21. The relation between the currents i and the applied voltages V is not expressed well for these points by Warburg's formula,[2]

$$i = aV(V - M),$$

where M is the minimum potential at which a current flows. In most of the cases, M must be given a value larger than the observed minimum potential to make the equation applicable.

To illustrate the effect of changes in the height of the meniscus upon the current flowing from a point, some results are given in Table I. which were obtained with a point of radius 0.0281 cm. The heights of the menisci are expressed as before in terms of the radius of the tube. The numbers show that the shape of the meniscus does not influence greatly the current flowing from the point, for voltages removed considerably from the starting potential, which itself is changed considerably by a change of meniscus.

TABLE I.

Variation of Current with Voltage for Menisci of Different Height.

Height of Meniscus.	Starting Potential.	Currents in 2.9×10^{-7} Amperes.		
		6,000 Volts.	8,000 Volts.	10,000 Volts.
1/3 radius.	4,900 volts.	7.8	29.0	59.9
2/3 "	4,900 "	6.8	27.7	59.0
1 "	4,750 "	7.2	29.3	58.2
2 " [3]	4,200 "	8.0	27.2	56.5

---

[1] O. Hovda, PHYS. REV., 24, p. 25, 1912.

[2] E. Warburg, Wied. Annalen, 67, p. 69, 1899.

[3] When the current is flowing from its surface, a drop may be drawn out in cylindrical form to an astonishing length.

22. The counteracting pressure during discharge was not found in all cases to be so nearly the same for all values of the current as in the example given in Fig. 4. The observed pressure was found in some cases to increase with voltage and in other cases to decrease, depending upon the height of the meniscus and upon the diameter of the point used. Some variations of this kind are shown in Fig. 5, by the curves giving results obtained with points of three different radii, whose values are indicated on the right side. Two or more heights of meniscus are represented in each case, the height *h* being given with each curve in term of the radius of the glass tube from which the meniscus protrudes. At *A* are drawn three menisci of the heights indicated, to picture more clearly the differences. The first reading at the left end of each curve is that corresponding to the voltage required to start the current, except that with the middle point some values are given on the downward slope of the pressure curve preceding the beginning of the current.

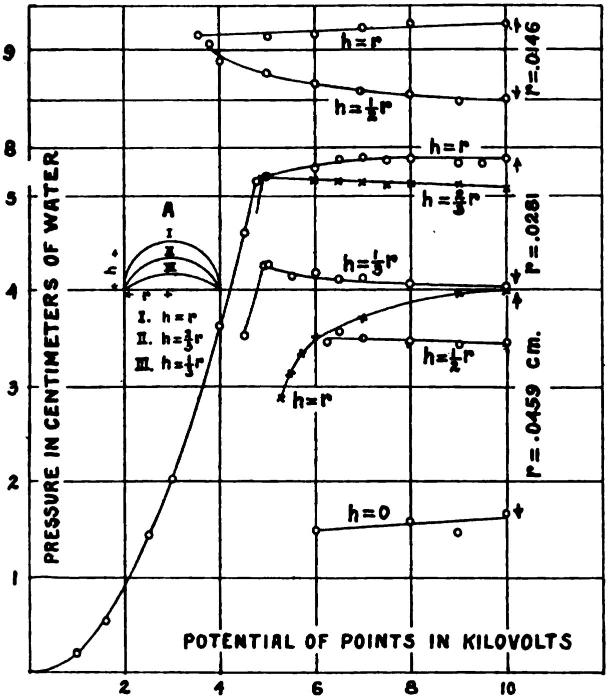


Fig. 5.

Effect of height of meniscus and size of point upon the electric force at the surface.

Considering first the smallest point, $r = 0.0146$ cm., it is seen that the pressure for the initial current is nearly the same in the two cases given, but while for $h = r$ the pressure increases slightly with increase of voltage, for $h = \frac{1}{2}r$ on the other hand the pressure diminishes considerably, more especially during the first part of the range.

With the second point, $r = 0.0281$ cm., the initial pressures are alike for $h = r$ and $h = \frac{2}{3}$, and for increasing voltages the values remain nearly alike, increasing somewhat with voltage in the first case and diminishing in the second case. When the meniscus is lowered to $h = \frac{1}{3}r$, the pressures for all of the voltages are smaller by twenty per cent.

In the case of the largest point, $r = 0.0459$, it is to be noted particularly, that with $h = r$ the pressure increases quite rapidly at first with increase of voltage. The curve for $h = \frac{1}{2}r$ starts higher and is nearly horizontal. A curve for a flat meniscus, $h = 0$, is also added, but this is not directly comparable to the others since the discharge here took place from the sharp edge of the tube.

The facts to be noted are that with increasing diameter of point the pressure which overcomes the electric pull diminishes, and that with the smaller points, the pressure where the current starts is almost the same for menisci differing considerably from the hemispherical shape. Since the electric intensities vary as the square roots of the pressures which have been plotted, the ratio differences between the intensities at various voltages or under different conditions are only about half as large as exist between the pressures.

23. In Fig. 6 are plotted pressure-voltage curves for positive discharge from some of the points of different sizes which were used, the height of the meniscus being in each case equal to the radius of the tube. The whole range of sizes used is included, the radius corresponding to each curve being given in centimeters at its right end. The first observation recorded at the left end of each curve represents the voltage at which the discharge stopped and began again. It will be noted that these plots are nearly straight lines for the smaller points, and that they become more curved and show a greater rise in pressure with voltage as their size increases.

Mention should be made of a peculiarity observed at times with some of the smaller points but not shown by any of the curves given. In these cases, as the voltage was increased above the minimum potential, the pressure at first fell rather rapidly by a small amount to the nearly constant value which obtained over a wide range of higher voltages.

The different character of the pressure curves for points of different sizes needs explanation. The difference may arise simply from the fact that with the larger points the meniscus differed considerably from the hemispherical shape at the starting potential and while small currents only were flowing, although with the larger currents the shape was as nearly hemispherical as the eye could judge. At *A*, near the bottom of Fig. 6, a curve drawn inside of a semi-circle shows approximately the appearance of the meniscus at the starting potential with large points. This distortion does not exist when the meniscus is not charged and hence acts to give too low a value to the pressures which have been plotted, since the increased curvature of the surface partly counteracts the electric pull on the surface. The pressure for zero potential with the distorted meniscus might be calculated from the known surface tension by measuring the curvature at the end of the meniscus and from this the true value of the electric pull might be determined. Again it might be assumed, from analogy with the small points, that the pressure at the high voltages where the meniscus is hemispherical is nearly what it would be at the starting potential for a meniscus of the same shape.

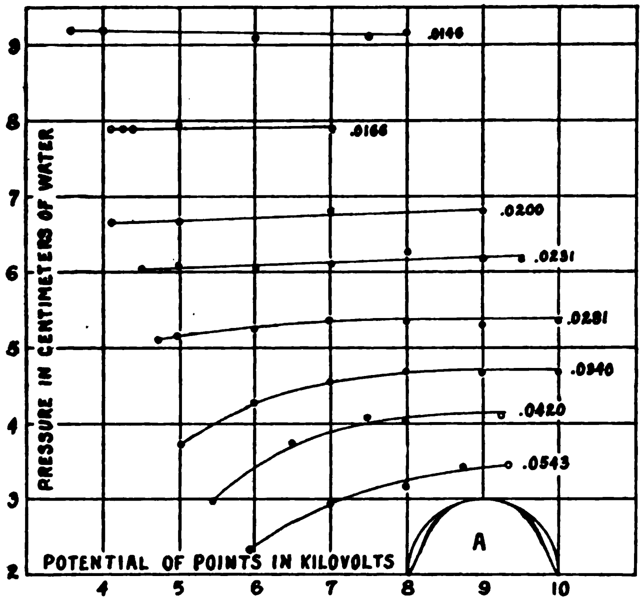


Fig. 6.

Electric intensities at the surfaces of various sized points, during discharge.

With these large points the currents, as indicated by the coating of light on the surface, only spread very gradually to the whole area of the hemisphere, and it is possible that this is the chief reason for the different shapes in these cases of the pressure curves under consideration.

24. An experiment was tried to see if any effect upon the electric intensity at the starting potential could be observed owing to the different

TABLE II.

Electric Intensity at Discharging Surface.

1	2	3	4	5	6	
r	n	f (water)	$f\sqrt{r}$	T	f (brass)	
					+	−
0.0146 cm.	21	471	56.8	73.8	508	482
.0166	3	436	56.2	68.5	474	....
.0178	3	416	55.5	69.0	443	430
.0185	3	414	56.3	70.7	435	....
.0200	18	405	57.2	70.5	415	409
.0229	13	382	57.8	72.8	390	....
.0250	6	353	55.8	66.2	374	376
.0281	1	356	59.7	....	351	....
.0340	10	309	57.0	72.6	318	....
.0370	1	294	56.6	71.2	304	....
.0419	4	270	55.3	76.0	285	....
.0451	4	276	58.6	73.7	275	....
.0543	3	241	56.2	79.0	250	....
Average....	....	....	56.9	72.0	....	....

cases by more than two per cent. from the mean value given. The barometric pressure was usually close to 74 cm. of mercury with a maximum variation from this of about 5 mm. The temperature during most of the observations was about 22° C., although the extremes were 20° and 26°.

It is seen that the value of f for the smallest point is about twice that for the largest point. The results can be represented very well by the empirical relation $f\sqrt{r}$ = a constant. The values of this product are given in column 4, the average being 56.9.[1] There are no systematic variations in column 4 from this value, and the larger deviations which exist may be attributed to the lack of perfection in the ends of the points.

It must be remembered however that the considerations given in § 23 raise the question whether the values obtained for the electric intensity with the larger points are not really too low.

30. Column 5 in Table II. gives the values obtained by the method described in § 6 for the surface tension T of the liquid used (water very slightly acidulated with hydrochloric acid). The average of the values given for all of the points is 72.0. By the capillary tube method, the surface tension of the same solution was found to be 71.3.

The larger deviations from the true value are an indication of the

---

[1] Combining this relation with the equations in §§ 6 and 7 it can be shown that $p = 9/10\ h$ nearly. This means that at the potential for which a current starts the liquid surface in F (Fig. 1) is always situated a small distance only above the level of the discharge point.

difficulty experienced in some cases of getting the true pressure owing to the readiness with which the liquid overflowed the sides when not charged, but in some cases they arise from the meniscus being somewhat distorted because of the unevenness of the edge of the glass tube. A distortion of the kind just mentioned, while it would result in giving an incorrect value of the surface tension, would not affect the determination of the electric intensity if it did not change its character with the charging of the liquid.

31. Chattock[1] found the relation $f.r^{0.45} = 85$ to represent his determinations of the electric intensity at the surfaces of platinum points when a positive current just ceased to flow. The size of the points used is not stated, but his formula when applied to the extreme limits of size used in the present experiments gives values over 20 and 30 per cent. larger respectively for the smallest and largest points. Whether this difference between the results with water and platinum surfaces is a real one arising from some inherent difference in the two kinds of surfaces or whether it is to be ascribed to some inaccuracy in one or the other of the methods used in making the measurements, remains to be determined.

Some of the results obtained by the writer[2] for the minimum potentials of brass points of various sizes were gotten under like conditions to those obtaining in the present experiments, except that the point was situated in a metal vessel. The method explained in § 8 should therefore be applicable to those results and the electric intensity at the surface of the cylindrical brass points with hemispherical ends may be calculated from the minimum potentials. Values of f thus computed from the results taken from Figs. 2 and 5 of the paper cited, are given in column 6 of Table II. The values for the brass points are on the whole several per cent. larger than for the water points, the divergence being largest for the smallest points.

Preferable to computing the electric intensities for the brass points, a more direct method of comparing the behavior of the two kinds of points would have been to compare the values of the minimum potentials. This is not done because the determinations of the minimum potentials with the liquid points show some peculiarities not fully understood. Thus the value obtained might be different by over a hundred volts on some occasions without any similar change in the electric intensity. This much may be said of the potentials obtained, and this should be contrasted with the relative values of the electric intensities given above, that for the lower half of the range of sizes used the minimum potentials

---

[1] A. P. Chattock, Phil. Mag., 20, p. 266, 1910.

[2] J. Zeleny, Phys. Rev., 25, p. 305, 1907.

for the liquid points are almost the same as for the brass points, being a little higher in a few cases, but for the largest points used the minimum potentials are about six to seven per cent. lower.

32. Any discussion of the results which have been presented in this paper will be postponed until the results of some other experiments which have been completed are published. These further experiments deal with the discharge from various kinds of liquid surfaces; with the discharge in different gases at various pressures; and with the effect of intense X-rays and alpha rays upon the discharge from both liquid and metal points.

SUMMARY.

33. The electrical discharge from points whose discharging surfaces consist of slightly acidulated water when placed opposite a metal plate have been studied. The positive discharge was found to begin with a momentary current, which was repeated only by an increase in the potential of the point. At higher potentials the discharge current is intermittent and this is followed by a steady current at still higher potentials. In the last case the liquid meniscus is quiescent and the luminosity covers the surface and is confined to its immediate neighborhood.

With the intermittent form of positive discharge the liquid meniscus is agitated and the light starts from a small area on the surface and extends half way to the plate in the arrangement used.

The negative discharge is always in the form of a brush discharge and the current is almost always intermittent and the meniscus in motion. The light in this case, however, while starting from a small area of the surface also, extends out into the gas a distance which is only about equal to the diameter of the point.

The momentary discharges, which first take place from the liquid surface, produce some effects there which result in an increase in the surface tension. This arises, most likely, from the surface being cleansed of some material collected there. It is probable that some such effect is likewise produced when metal surfaces are used.

A hydrostatic method is given for measuring the electric intensity at the surface of liquid points both before and during discharge. The surface tension of the liquid may also be obtained with the same apparatus. The product of the electric intensity at the discharging surface when a current just ceases to flow by the square root of the radius of the point, was found to be a constant equal to 56.9. The radii of the points used range from 0.0146 to 0.0543 cm.

The electric force under these conditions, as well as the potentials at which the currents cease to flow, were found to be the same for the negative and for the positive discharges.

For the small points of the range given the electric intensity at the surface of a hemispherical meniscus, when a current of any magnitude is flowing, is nearly the same as at the minimum potential, but for the larger points the value increases with current, becoming nearly constant at higher values of the latter.

The electric force at the surface of the smaller points used was influenced to a small extent only by changing the height of the liquid meniscus considerably from the hemispherical form. This intensity was not affected by such changes in the distribution of the electric field as are brought about by changing the distance between the point and plane or by using a hemispherical electrode in place of the plane, or by charging the plane instead of the point itself.

With potentials considerably above the minimum value; the current flowing from a given point was found to vary but slightly when the height of the meniscus was changed greatly.

The temperature of the liquid of the meniscus during the discharge was measured and found to be slightly lower than it was while no discharge was passing.

Results were obtained which permit the calculation of the electric force under certain conditions at the surface of a point while no discharge current is passing.

The action of the beta and gamma rays from three milligrams of radium was found to lower slightly the starting potential.

The values obtained for the electric intensity at the minimum potential with liquid points are considerably smaller than those obtained by Chattock with platinum points and somewhat smaller than those calculated by the writer from some of his measurements on brass points.

Physical Laboratory,
University of Minnesota,
December 19, 1913.

NOTES ON QUANTUM THEORY.

A THEORY OF ULTIMATE RATIONAL UNITS; NUMERICAL RELATIONS BETWEEN ELEMENTARY CHARGE, WIRKUNGSQUANTUM, CONSTANT OF STEFAN'S LAW.

BY GILBERT N. LEWIS AND ELLIOT Q. ADAMS.

THE importance to science of a simple and established set of units has led to the almost universal adoption of the system based upon the centimeter, the gram and the second. These units themselves, however, have no rational significance. The centimeter was intended to be a certain simple fraction of the earth's circumference; the gram to be the weight of one cubic centimeter of water at the temperature of its maximum density, and the second is a certain fraction of the mean solar day. But neither the size of the earth nor its velocity of rotation is unique or even constant; nor does water in any notable way stand by itself among substances.

It has sometimes been assumed that there is some peculiar appropriateness in choosing three and only three fundamental units. This is by no means the case. It happens that the branch of physics which was first developed was the mechanics of rigid bodies. That science may be represented by a manifold of five dimensions, in which the three dimensions of space, one of time and one of mass,—or density,—are the five independent variables. In general for the treatment of such a manifold, five fundamental units would be necessary, but owing to the symmetry of the space of Euclidean geometry it is possible and convenient to adopt a single unit—that of length—in the discussion of all problems in three-dimensional geometry. The number of units required by the mechanics of rigid bodies is thus reduced to three. When, however, we consider other branches of physics, other units are necessary. Thus in the theory of heat it is customary to introduce new units, such as the unit of temperature, without attempting in the first instance to determine the dimensions of these units in terms of the units of mechanics. On the other hand, when important relations between existing units are discovered, the number of units which are to be regarded as fundamental is reduced, as we have pointed out in the case of the units of geometry.

Since it was, in fact, in the science of geometry that such a reduction in the number of fundamental units first occurred, it may be well to consider in this simple case the nature of the assumptions made.

In the first place, owing to the existence of rigid and movable measures of length, it was assumed that distances in all directions can be expressed in terms of a common measure. But fixing the unit of length does not determine immediately the unit of area, or of volume. The units actually chosen are the area of a square of unit side and the volume of a cube of unit edge, but many different units might have been proposed. Unit area might have been defined as the area of a circle of unit radius, or diameter, or circumference.[1] These units would be to the one actually chosen in the ratios π, $\pi/4$ and $1/4\pi$ respectively. There are numerous reasons for preferring the units actually in use, not the least important of which is the fact that an area or volume may be built up of squares or cubes, but not of circles or spheres. Admitting, then, that the choice is a wise one, it must nevertheless be emphasized that it is a choice of a somewhat arbitrary character.

Having made this choice, however, it is important to make a similar choice wherever a similar occasion arises, and thus to adopt consistently a system of "square" units.[2] In the case of angles the choice of unit has not been unanimous. In one system a simple fraction or multiple of a right angle is the unit, in the other the unit is the angle subtended by a circular arc equal to the radius of the circle and in this latter system a right angle is $\pi/2$. In our sense we shall speak of the former unit as a "square" unit just as the latter is commonly known as the "circular." We shall have occasion to notice how frequently the choice between two fundamental units involves the introduction or omission of some simple function of π.

When we add to the three dimensions of space the one dimension of time we obtain the four-dimensional manifold of kinematics. The science of kinematics involves geometry and a further degree of extension in time. Kinematics, therefore, in the broadest sense, includes all of

---

[1] The second of these units is actually in use in stating the cross section of circular wire, which is said to be one circular mil when the diameter is one mil.

[2] We might make an even more fundamental classification, for the axioms and propositions of geometry may be divided into those which depend upon parallel translation and those which depend upon rotation [cf. Wilson and Lewis, "The Space-Time Manifold of Relativity," Proc. Amer. Acad., *48*, 389 (1912)]. The parallel geometry is more general and is common to Euclidean geometry and to the non-Euclidean geometry of relativity. In this parallel geometry we may divide a given plane into unit parallelograms, and such conceptions as density can be readily introduced; but a field possessing radial symmetry about a point could not be adequately treated. For the most part, the square units we shall adopt will be identical as far as this is possible with those which could be obtained from the parallel geometry alone.

Euclidean geometry as a special case. In other words, geometry may be regarded as a cross-section of zero extension in time, through the manifold of kinematics.

In classical kinematics the units of length and of time were regarded as independent. The first great step toward the realization of the essential interdependence of these two units was made by Maxwell when he discovered the identity between the velocity of light and the ratio of the electromagnetic to the electrostatic units. Maxwell inferred that this identity was merely an evidence of the electromagnetic nature of light, but the development of the principle of relativity has led us to a more fundamental conclusion, which perhaps can best be stated in the following form: The constant c, known as the velocity of light, is merely a number imposed upon kinematics through the arbitrary choice of the centimeter and the second as units of length and time. In other words, all the equations of physics may be simplified by choosing a unit of time which is to the second in the ratio of 1 to 3×10^{10}. As examples we may cite the Maxwell equations of electricity and magnetism or the equation for the pressure of a beam of light in terms of the energy emitted or received per second, or any of the equations of non-Newtonian mechanics, in all of which cases every term which has the dimensions of time to any power contains the factor c to that power.

Not only has the principle of relativity shown the existence of this relation between the fundamental units of time and space, but it has enabled us to construct for kinematics a four-dimensional geometry which is as satisfactory as the Euclidean geometry of ordinary space. "Suppose that a student of ordinary space, habituated to the interpretation of geometry with the aid of a definite horizontal plane and vertical axis, should suddenly discover that all the essential geometrical properties of interest to him could be expressed by reference to a new plane, inclined to the horizontal, and a new axis inclined to the vertical. Whereas formerly he had attributed special significance to heights on the one hand and to horizontal extension on the other, he would now recognize that these were purely conventional and that the fundamental properties were those such as distance and angle, which remain invariant in the change to a new system of reference."[1]

In the four-dimensional geometry of kinematics an interval of time is a length, and we have the same reason for adopting a single fundamental unit in kinematics as in geometry. We shall use the centimeter provisionally as this unit. The dimensions of any kinematic quantity must therefore be represented by a power of a single dimension. This di-

---

[1] Wilson and Lewis, l. c.

mension, representing a one-dimensional interval in space or in time, will be denoted by $[I]$. Thus the dimensions of area are $[I]^2$, of volume $[I]^3$; both angle and velocity have zero dimensions; acceleration is $[I]^{-1}$, angular velocity $[I]^{-1}$ and angular acceleration $[I]^{-2}$.

Of the secondary units of kinematics the most important is that of velocity and there can be no dispute as to the desirability of choosing in this system the velocity of light as the unit of velocity, every other velocity is therefore a proper fraction, but in the case of other secondary units the choice is not always obvious. Thus the unit of angular velocity to be chosen depends upon the previous choice of unit angle.

In mechanics a new variable appears, and the choice of mass, energy, density, force, momentum, or any other simple mechanical quantity to serve as this new variable is quite arbitrary. Since it is customary we will regard mass as this primary variable and take, provisionally, the unit of mass, the gram, as independent of the unit of kinematics. All mechanical quantities may therefore be assigned dimensions in terms of interval $[I]$ and mass $[M]$. Thus energy and momentum have the dimensions $[M]$, force is $[M][I]^{-1}$; density and pressure $[M][I]^{-3}$, etc. The secondary units which have been universally adopted for these quantities seem to be unquestionably the best. In our system the gram is the unit of momentum and of energy as well as of mass, and the unit of force is one gram per unit interval, which may be derived from any of the older expressions for force, namely, energy per unit distance, momentum per unit time, or mass times acceleration.

The theory of heat involves at least one new variable. Since the discovery of the "mechanical equivalent of heat" the dimensions of thermal quantities can be expressed in terms of mechanical dimensions and of temperature. Thus it is customary to regard entropy and "heat capacity" as having the dimensions of energy divided by temperature. If now in addition to the "mechanical equivalent of heat" we find another very fundamental relation between thermal and mechanical quantities we shall be justified in eliminating temperature as a fundamental dimension. Such a relation is in fact furnished by the constant of the gas law, a law which is valid for all substances in the gaseous state at a sufficient degree of attenuation. This equation is ordinarily written: $PV = nRT$, where n is the number of mols. Since R is a universal constant we could, by using in place of the Centigrade degree a unit R times as small, simplify the formula to $PV = nT$. Since, however, the molecule seems a more desirable unit than the mol, and since the number of molecules, N, in one mol is now known about as accurately as the molecular weights, we will write for the number of molecules in n mols

$m = nN$, and the gas law becomes $PV = m(R/N)T = mkT$, where k is another universal constant. Now this constant appears not only in the equation for gases, but also in other important formulæ, and always to the same power as T, for example in the so-called Rayleigh equation for the distribution of energy in black radiation, $E_\lambda = c\lambda^{-4}kT$. We may therefore eliminate this constant once for all by writing $\theta = kT$, where the unit of θ is k times the Centigrade degree. The gas law becomes $PV = m\theta$. Any dimensions which k may have possessed are now incorporated in the temperature θ, and temperature therefore has the dimensions of energy or mass.

This process of reducing the number of fundamental units, or dimensions, which has been proposed only recently[1] for the thermal quantities, was adopted at the outset in the case of electrical quantities. If in the first instance electric charge had been measured in some arbitrary unit, then Coulomb's law would have contained a universal constant, like c or k. Charges were, however, so defined as to make this constant unity, and on the assumption that it is also free from dimensions the electrostatic system of units was developed. Another important system of units, the electromagnetic, becomes identical with the electrostatic when we take the velocity of light as unity. The adoption of the electrostatic system led to a number of equations in which the prominence of the factor π led Heaviside to suggest another unit of charge which is to the former as $1 : \sqrt{4\pi}$ and which Heaviside called the rational unit. The difference between the electrostatic and the Heaviside units is like the difference between the circular and square units of area; Coulomb's law expresses the force between two charges, each of which determines a field of radial symmetry while the Heaviside unit is so chosen that the capacity of a unit cubical condenser is unity.

In the preceding discussion of the methods by which geometrical, kinematical, mechanical, thermal and electrical quantities may be expressed in terms of a few fundamental dimensions or units, we have attempted to point out the difficulties attending the choice of secondary or derived units, but also to indicate, in spite of these difficulties, the way in which we may hope to diminish still further the number of fundamental independent dimensions. Having expressed all of the quantities hitherto considered in terms of two arbitrary units of interval and mass, it is necessary only to find *one* more relation of a universal

---

[1] Planck, Vorlesungen über die Theorie der Wärmestrahlung. First edition, p. 164. We should call attention here to the fact that Planck has suggested a system of units from which the arbitrariness of the ordinary units has been eliminated by the use of a sufficient number of universal constants. Planck did not, however, attempt to make his units rational in the sense in which we use the term.

character in order to express one of these units in terms of the other, or *two* more such relations to determine absolutely both of these units. We shall then have a system of units all of which are in a sense dimensionless. An interesting question now arises. Supposing that instead of finding two such, we found three or more such relations, would we not then have several different sets of rational units between which the choice would be purely arbitrary? Our answer to the question can best be expressed by stating our belief that these different sets of units will be dependent upon one another in a very simple way, and that if in the manner suggested we obtain the ultimate units of interval and of mass by the aid of two universal and fundamental relations, then all universal constants will prove to be pure numbers, involving only integral numbers and π, just as we have seen that in geometry several different units of angle, area and volume may be chosen, which, however, differ only by such a factor. This we shall call the *theory of ultimate rational units.*

There are a number of important constants from which to choose the two which are to determine the ultimate units: the constant of gravitation, the charge of one electron, the mass of an isolated electron, the constant of Stefan's law, the constant h of the Planck radiation equation, and several others which may posses universal significance. Indeed, the properties of any other atom are as universal, presumably, as those of the electron, but in the present state of our knowledge the electron appears to be unique in a sense in which the other atoms are not. Thus if it were decided to choose the mass of some atom as unit mass the mass of the electron would be the most promising choice. While each atom has a different mass, there is however one property of the electron which is in every sense unique, and that is its charge. Unlike the mass of the electron, the charge of the electron is constant under all circumstances. Because of these facts, and because of the success which has attended the various attempts to regard other branches of physics as parts of the science of electricity, we have without hesitation decided to take the electron charge as the first of the two fundamental constants needed for the final determination of the ultimate units.

The dimensions of electric charge become in our system $[M]^{\frac{1}{2}}[I]^{\frac{1}{2}}$ and it is interesting to note that two of the other constants mentioned above have, as dimensions, powers of the dimensions of electric charge, for Planck's h has the dimensions $[M][I]$ and the constant a of Stefan's Law, $[M]^{-3}[I]^{-3}$. We must expect, therefore, that the square of the electron charge, Planck's h, and the reciprocal cube root of a, will differ only by simple numerical factors.

The charge of one electron in ordinary electrostatic units we may call ϵ.

If we call the same charge in Heaviside electrostatic units ϵ', then $\epsilon' = \sqrt{4\pi}\epsilon$. Numerous other systems of electrical units might be invented, and we shall refer to one other in which the electron charge is $\epsilon'' = 4\pi\epsilon$, and which has advantages in certain cases. For example, the energy emitted per second by a simple harmonic oscillator, which has played so large a part in the modern theory of radiation, is in the three units, repectively

$$-\frac{dE}{dt} = \frac{8\pi^2}{3}\frac{E}{M}\epsilon^2\nu^2 = \frac{2\pi}{3}\frac{E}{M}\epsilon'^2\nu^2 = \frac{1}{6}\frac{E}{M}\epsilon''^2\nu^2,$$

where E is the energy, M the mass, and ϵ the charge of the oscillator of frequency ν. Our opinion as to the relative desirability of these units may be modified as the properties of the electron become better understood. Formerly, when electricity was regarded as a continuum, the Heaviside system was unquestionably superior. We have seen that in geometry the unit square is a more satisfactory measure of area than the unit circle, and that in general we must attempt to choose consistently units similar to the unit square and the unit cube. Thus we regard a uniform vector field as simpler than one which possesses radial, that is to say spherical, symmetry. The Heaviside system was based upon the properties of the uniform electric field between the plates of an infinite plane condenser. Whether our present recognition of the atomic nature of electricity deprives the Heaviside system of its advantages is a question which merits the most careful scrutiny.

As ordinarily expressed the dimensions of ϵ^2 are energy times length. According to the choice of the electrical unit it will be natural to choose ϵ^2, $4\pi\epsilon^2$ or $(4\pi\epsilon)^2$ as the unit of energy times interval with the dimensions $[M][I]$. For convenience in the following calculation we shall continue to express the energy in ergs. In terms of this unit we shall expect to find the constants a and h to be simple numbers.

Let us consider first the constant a of Stefan's law, which reads

$$E = aVT^4,$$

where E is the energy (ergs) in the volume V (c.c.) at the absolute temperature T (deg. Cent.). We may put this equation in the form

$$E = ak^{-4}V(kT)^4 = ak^{-4}V\theta^4. \qquad (1)$$

Both E and θ are now expressed in ergs.

Hence $a = k^4(E/V\theta^4)$, where the quantity in parenthesis is measured in reciprocal (erg cm.)^3. If we choose now a new unit of energy times length, namely, ϵ^2, ϵ'^2 or ϵ''^2, we may express the factor in parenthesis in these units by writing:

$$a = \frac{k^4}{\epsilon^6}\left(\frac{E\epsilon^6}{V\theta^4}\right) = \frac{k^4}{\epsilon'^6}\left(\frac{E\epsilon'^6}{V\theta^4}\right) = \frac{k^4}{\epsilon''^6}\left(\frac{E\epsilon''^6}{V\theta^4}\right). \tag{2}$$

And we may expect to find that the three quantities in parenthesis are simple numbers. In fact, it will be seen presently that the third of these numbers is unity, that is,

$$\frac{a\epsilon''^6}{k^4} = \frac{a(4\pi\epsilon)^6}{k^4} = \frac{E\epsilon''^6}{V\theta^4} = 1. \tag{3}$$

The constant a cannot involve π except in so far as this factor is introduced in the unit of energy times length, and therefore only as π^{3p} where p is an integer. The reason for this statement lies in the uniformity of distribution of energy in the hohlraum. There is nothing in the nature of the problem to require the use of any but square units. If Stefan's law were expressed in some other form, for example, if we should write $dE/dt = bT^4$, where dE/dT is the rate of emission of energy from a black sphere of unit radius at the temperature T, b, like a, would be a universal constant, but would contain intrinsically the factor π, since it involves quantities which cannot be completely expressed in square measure. While the constant a therefore does not contain intrinsically the factor π, it might obviously contain some simple coefficient such as 2 or 3/4. This is a more difficult question, but we shall attempt presently from *a priori* considerations to show that no such coefficient is to be expected in the constant a. Meanwhile this will be regarded as an empirical fact on the basis of the following calculations.

The results of numerous experimental determinations of the constant of Stefan's law are extraordinarily discordant. Without considering the earlier measurements, the following results have been published during the last two years for the value of $\sigma \times 10^5$ (where $\sigma = ac/4$): 5.67,[1] 5.80,[2] 5.45,[3] 5.96,[4] 5.54,[5] 5.89,[6] 6.33.[7] The mean of all these values is 5.81, or 5.72 excluding the incomprehensibly high value of Féry and Drecq. Coblentz[8] after a very careful and critical survey of the various determinations gives as the probable value 5.7.

Let us now calculate the value of σ from our assumption (equation 3) that $a = k^4/\epsilon''^6 = k^4/(4\pi\epsilon)^6$. The recent determination of the elementary

---

[1] Shakespear, Proc. Roy. Soc., *A 86*, 180 (1912).

[2] Gerlach, Ann. d. Phys., *38*, 1 (1912).

[3] Kurlbaum, Verh. d. phys. Gesell., *14*, 576 (1912) (recalculated from older result).

[4] Puccianti, Nuov. Cim., *4* (6), 31 (1912). See also Nuov. Cim., *4* (6), 322 (1912).

[5] Westphal, Verh. d. phys. Gesell., *14*, 987 (1912).

[6] Keene, Proc. Roy. Soc., *A 88*, 49 (1913).

[7] Féry and Drecq, Journ. de Phys. (5), *3*, 380 (1913).

[8] Coblentz, Jahrb. d. Radioakt., *10*, 340 (1913).

charge by Millikan[1] for which he claims an accuracy of 0.2 per cent., a claim which seems to be warranted by the extreme care of his measurements, give $\epsilon = 4.774 \times 10^{-10}$. From the value of ϵ, k can be obtained at once from the equation $k = R\epsilon/F$, where F is the Faraday equivalent in the same units as ϵ. Hence $k = 1.372 \times 10^{-16}$, and since R and F are known with a very high degree of accuracy, the percentage error in k is the same as in ϵ. We thus find $a = 7.60 \times 10^{-15}$ in which the percentage error is twice that in ϵ, as is obvious if we write $a = R^4/(4\pi)^6\epsilon^2F^4$. From this value of a we find $\sigma = 5.70 \times 10^{-5}$.

We believe that the value of a thus obtained is the true constant of Stefan's law, subject only to such uncertainties as are due to the experimental errors in R, F and ϵ.

This result may be presented in a different way. If the equation of the perfect gas be written in the form $PV = m\theta$ and Stefan's law in the form $E = V\theta^4$, these two equations suffice to determine the value of a unit of energy times length, and this unit would then prove to be, within the limits of experimental error, equal to the unit which we have called ϵ''^2. It may be asked why the coefficient of the energy equation representing Stefan's law should be simpler than the coefficient of the corresponding entropy equation, $S = \beta V\theta^3$, where S is the entropy of a hohlraum of volume V at temperature θ, and β is another universal constant, namely $\beta = 4a/3$. Why, then, should we expect a to be unity rather than β? In the units we have chosen, the energy of a unit volume of a hohlraum at unit temperature is equal to two thirds of the energy of one molecule (possessing three degrees of freedom), of any perfect gas at unit temperature. No statement of similar simplicity can be made with respect to the entropy of the hohlraum and that of a molecule. While the average energy at a given temperature is the same for all molecules, and independent of all other conditions, the average entropy of a molecule depends upon the concentration and the chemical nature of the molecule as well. For this reason we should expect a simplicity in the energy equations which the entropy equations do not possess.

We may next proceed to a discussion of the constant h, which appears in the Planck equation for the distribution of energy in the spectrum of a black body, and which must appear in any radiation formula of which the Wien equation is a limiting case. If the Wien equation is in fact true in the limit, the constant h, the "Wirkungsquantum," must be a significant universal constant, irrespective of the validity of any more general expression, such as that of Planck.

If the Planck equation is correct it is possible to calculate h directly

[1] Millikan, PHYS. REV. (2), 2, 79 (1913).

from a, by means of the equation obtained by integrating the Planck equation:

$$a = \frac{8\pi^5 k^4}{15 c^3 h^3}. \tag{4}$$

If, now, we write, as before,

$$a = \frac{k^4}{\epsilon''^6}$$

then $15c^3h^3 = 8\pi^5\epsilon''^6$, or

$$h = \frac{\epsilon''^2}{c}\sqrt[3]{\frac{8\pi^5}{15}} \tag{5}$$

and substituting we find $h = 6.56 \times 10^{-27}$.

Now the constant of the Wien equation, $c_2 = ch/k$ has been determined with considerable accuracy. The latest value obtained by Coblentz[1] as the mean of several determinations in the Bureau of Standards at Washington is 1.4456 ± .0004, while Warburg, Leithäuser, Hupka and Müller[2] in the Reichsanstalt at Berlin obtain as a mean 1.437 ± .004. The value of c_2 calculated from h as given above is 1.434.

If one admits that the Planck formula is correct, the close agreement between this value and those obtained experimentally affords strong evidence of the correctness of our calculation of the constant of Stefan's law. On the other hand the agreement does not demonstrate the validity of the Planck formula. Numerous substitutes for that formula might be suggested which would agree equally well with the experimental facts and which would not only satisfy the Wien displacement law, but also approach at the two limits the Wien and the Rayleigh radiation formulæ. Indeed it seems hardly likely that if h is a quantity of really fundamental significance it is represented by so complicated a formula as (5).

We hope to revert to this question of the true radiation formula and the significance of the constant h, in a later publication. At present it need only be pointed out that the fundamental quantum in the theory of electricity and of radiation is the quantum of electricity, and that the so-called "Wirkungsquantum" is merely the square of this fundamental quantum with a simple numerical coefficient, depending upon the units chosen.

We shall not attempt at this point to decide finally as to the choice of the ultimate rational units, but the two experimental data by which these units will be determined will be the charge of the electron and the mass of the isolated electron. It is to be hoped that a further study of

---

[1] Jahrb. d. Radioakt., *10*, 340 (1913).

[2] Ber. Berl. Akad., *2*, 35 (1913).

the law of gravitation will soon enable us to obtain the constant of that law in terms of the chosen ultimate units, as a pure number.

We have attempted in this paper to show the relation between the so-called fundamental and derived units of geometry and physics, and have outlined a theory of ultimate rational units in accordance with which we have obtained relations between several important universal constants. In particular we have derived from this theory a value for the constant of Stefan's law which we believe to be far more accurate than any of the values of this quantity obtained by direct experiment. We have shown that the fundamental quantum in physics is the charge of the electron.

In a following paper we shall attempt to show that the numerous theories of the so-called energy quantum which have recently been advanced are unnecessary for the explanation of the phenomena with which they deal.

CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA,
November 13, 1913.

DISCHARGE IN A MAGNETIC FIELD.

By Robert F. Earhart.

SIR J. J. THOMSON, in the "Discharge of Electricity through Gases" discusses the motion of an ion in a magnetic field.[1] Among the special cases treated is the one where the ion moves in the direction of the magnetic field. The forces are such as to cause a charged particle to travel along a helical path. In a later chapter (pp. 575–579) a résumé of experimental work on the effect of a magnetic field upon a discharge is given. Birkland[2] found that when a discharge tube was placed in a magnetic field and oriented so that the direction of the field coincided with the line joining the electrodes, the potential required to produce the discharge was lowered.

Almy in 1901[3] made a more careful and quantitative study of the case. His experiments were conducted at low pressures and he too found the action of a longitudinal field lowered the discharge potential. Among other things he noted that when the field was applied, the discharge was for the most part concentrated along limited paths and instead of the glow filling the entire tube it was concentrated into stream-like lines.

Willows[4] extended the experiments with some variations and operated with transverse fields as well.

Paalzow and Neeson[5] made some experiments with a tube in the shape of a Greek cross. There were four electrodes pointing toward the intersection of the cross arms. This was placed in a magnetic field in such a manner that the field could be made parallel or at right angles to the electric force. The electrodes consisted of pointed wires, and from their description neither the electric field nor the magnetic field was uniform. They established several interesting points, among others the fact that at some pressures a weak field facilitates the discharge while stronger fields diminish the discharge. The diminution of current strength or increase as the case may be is given in terms of scale divisions of the galvanometer employed. There is a description of the magnet used to

[1] Second edition, pp. 111–116.

[2] Comp. Rendus, CXXVI., p. 586, 1898.

[3] Proc. Cam. Phil. Soc., XI., p. 183.

[4] Phil. Mag., VI., 1, p. 250, 1901.

[5] Wied. Ann., I., XIII., p. 207, 1897.

produce the fields but the variations produced by the magnetic field are stated only in terms of the current through the magnetizing coils. In 1901 Reicke[1] made an experiment in which he determined current-potential or characteristic curves for discharge in a magnetic field. In his experiment the discharge chamber was placed near one end of a cylindrical magnet and in a diverging field. His record shows the values of the field strength at several points along the discharge path. The longitudinal component of the magnetic field did not exceed 100 C.G.S. units at the electrode farthest removed from the magnet.

Recently there has been a renewed discussion of the effect produced by a longitudinal field both in high vacua and pressures ranging up to one or two millimeters. An article by Strutt[2] reviews some work done by C. S. E. Phillips[3] and extends his experiments along some lines. Both Phillips and Strutt noticed, among other things, that when two cylindrical iron electrodes are in high vacuo a discharge passes for a greatly reduced potential when the iron electrodes are magnetized.

In some cases the discharge potential was reduced from several thousand volts to between 350 and 400, only slightly more than the cathode fall in potential.

J. S. Townsend[4] comments on Strutt's experiment and believes the reduction in potential is due to the increase in path which electrons will have in a magnetic field of this kind. A helical motion will increase the effective path through which they move, thereby increasing the number of collisions which in turn will produce a supply of ions necessary for the maintenance of a current.

F. Horton[5] also comments on Strutt's work as well as on some results recently obtained by himself and in the main agrees with Townsend. He suggests that with strong fields ions may be diverted by the field and a critical field will be obtained when the loss from one effect balances the gain resulting from increases in collision.

The very interesting articles of More and Reiman,[6] More and Mauchley[7] and Righi[8] discuss the possible effects of a magnetic field on the discharge potential.

More and Mauchley maintain that the effect of a longitudinal field is not to produce a new type of ray but that the effect of a longitudinal

[1] Ann. d. Phys., VI., 4, p. 592.

[2] Proc. Roy. Soc., A 89, Aug., 1913, p. 68.

[3] Roy. Soc. Proc., 189, Vol. 64, p. 172.

[4] Phil. Mag., VI., 26, Oct., 1913, p. 730.

[5] Phil. Mag., VI., 26, Nov., 1913, p. 902.

[6] Phil. Mag., Nov., 1912, p. 840.

[7] Phil. Mag., Aug., 1913, p. 252.

[8] Phil. Mag., Nov., 1913, p. 848.

field upon the production of the so-called magnetic rays is to reduce the cathode fall in potential so that a moderate potential will effect a discharge. These possess peculiarities which lead Righi to designate them magnetocathodic rays but More and his colleagues evidently regard them as cathode rays with some features accentuated and these peculiarities are brought out by a delicate adjustment of pressure, potential and a magnetic field but that the latter is not essential.

The article by More and Reiman suggested to the author the desirability of finding out the effect of a magnetic field on a discharge when the conditions were simplified to a greater extent than in some of the previous work. The author has no criticism of previous experiments but wishes to point out that the conditions in many of them were not reduced to the most simple terms. An effort was here made to produce a discharge between plane parallel electrodes having the electric and magnetic field parallel and uniform. The measurements made consisted of the potential required to maintain a steady current whose magnitude was measured while the magnetic field was varied from 0 to 10,000 C.G.S. units. Furthermore, these were obtained under different pressure conditions and for several gases. Fig. 1 indicates the arrangement of the discharge chamber in its relation to the two fields. The discharge chamber *D* was a glass tube 14 mm. long and 12 mm. diameter. This was closed at the ends by the electrodes *A* and *B* which were brass plates 8 cm. in diameter. The chamber *D* was placed in the region where the field would be most uniform. The electrodes were backed with fiber 1/32 inch thick and mounted on the faces of the magnet poles *MM* by means of fiber collars *FF*. The tapered pole pieces were 5.08 cm. across the face. An exploring coil showed that the magnetic field in the central region between the

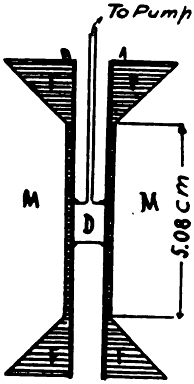


Fig. 1.

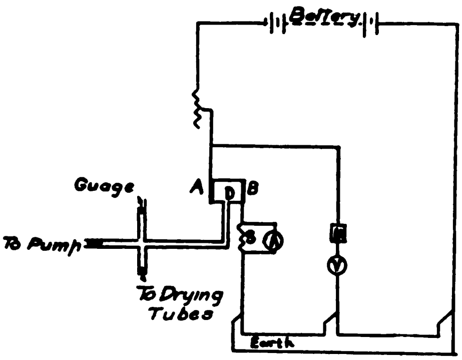


Fig. 2.

poles was uniform. Fields of 10,000 C.G.S. units were obtainable with this gap.

Fig. 2 indicates the electrical arrangement. One terminal of a battery of 400 storage cells was earthed while the other was connected to the electrode *A* of the discharge chamber through a high variable resistance. The second electrode of the chamber was earthed through a low resistance which formed a shunt, *S*, for a D'Arsonval galvanometer, *A'*. This served to measure the current passing through the discharge chamber. A Weston voltmeter, *V*, with a multiplier, *M*, measured the P.D. between *A* and the earth. The discharge chamber was connected with pump, McLeod gauge and drying apparatus through a small glass tube. Confining the discharge to the central portion of rather large electrodes and in the central portion of the magnetic field approximates rather closely the end desired, viz., to secure uniform and parallel fields. The glass walls enabled changes in the appearance of the discharge to be readily noted.

The motion of the ions under the pressures used, is no doubt a complicated one. In developing the theory of the path which ions follow, it is assumed that saturation is not attained; but in the luminous discharge saturation is attained. It is customary to regard intense ionization as a condition for luminosity. Hence while the magnetic and electrical fields may be applied in the most simple way the results of collisions will no doubt make the motion of the ions a very complicated one.

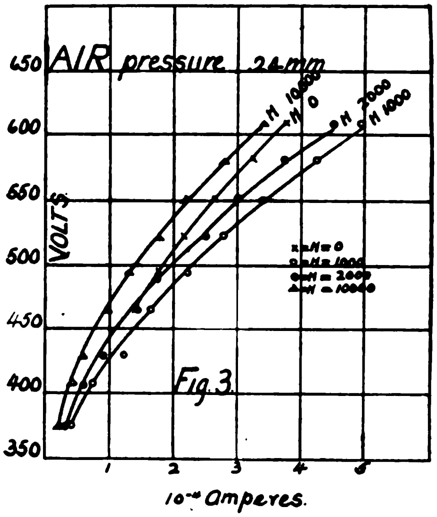


Fig. 3.

Fig. 3 indicates the effect of applying a magnetic field at a pressure less than the critical pressure. The line designated $H = 0$ gives the current and potential values for zero current in the field coils. The core of the magnet was of very soft iron and the current was reversed with diminishing values until the circuit was broken. However, there is probably some residual magnetism and the field was not strictly zero. It will be noted that with fields up to 1,000 units the discharge current for any potential is increased. In fact at this pressure a potential which will not produce a discharge under the action of the electric field alone

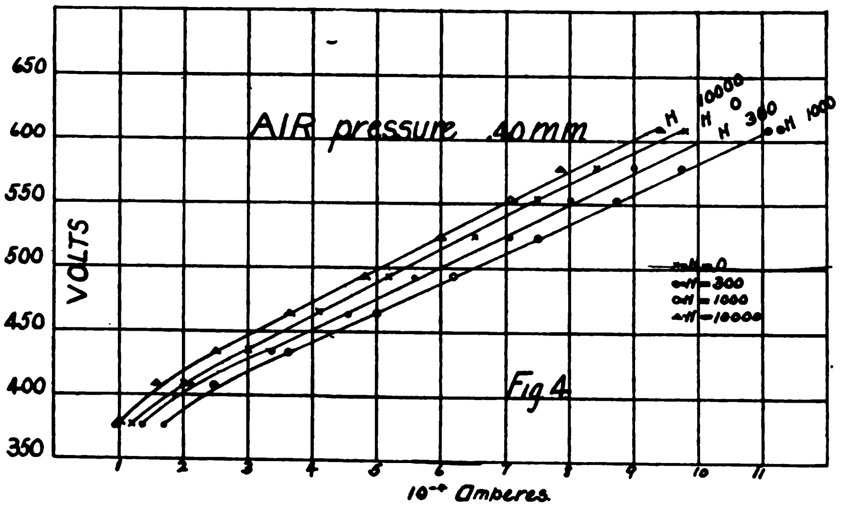


Fig. 4.

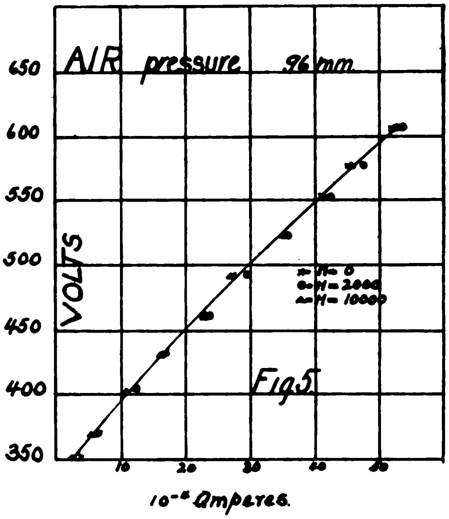


Fig. 5.

will, upon applying a magnetic field, cause the discharge to pass. Reversing the polarity of either electric or magnetic field does not modify the current. I noted, as Almy had previously noted, that when the field was applied, the appearance of the discharge changed. Instead of a soft glow filling the tube a series of blue stream-like filaments appeared along the axis of the tube and while the glow did not disappear it was visibly affected by the magnetic field. The current for a given potential increased with field strengths up to 1,400 units; beyond that the current

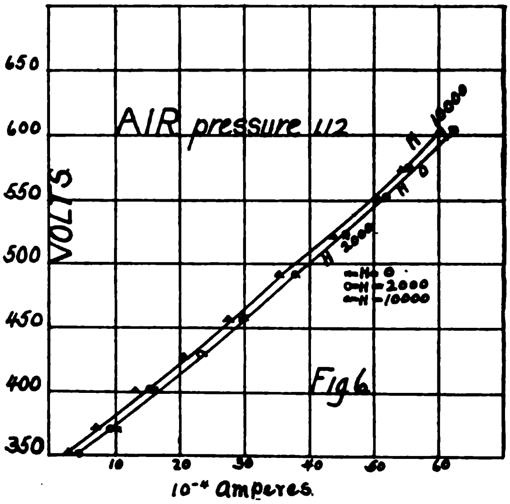


Fig. 6.

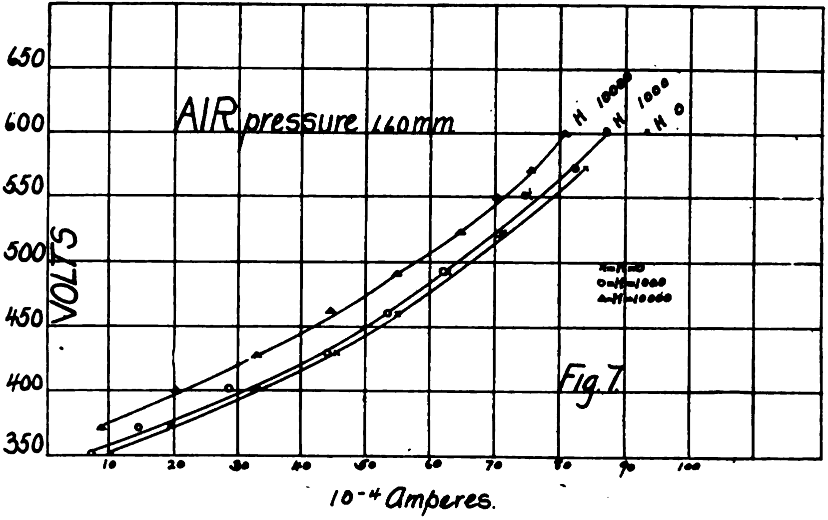


Fig. 7.

decreased. In some earlier experiments a less powerful magnet was employed with which fields of only 4,500 units could be obtained. The same effect was noted, viz., that above a critical value of the field the current became less with increase in field strength but the field was not sufficiently strong to reduce the current to the value for $H = 0$. With the larger magnet using 10,000 C.G.S. units the current value was reduced below the values for zero field.

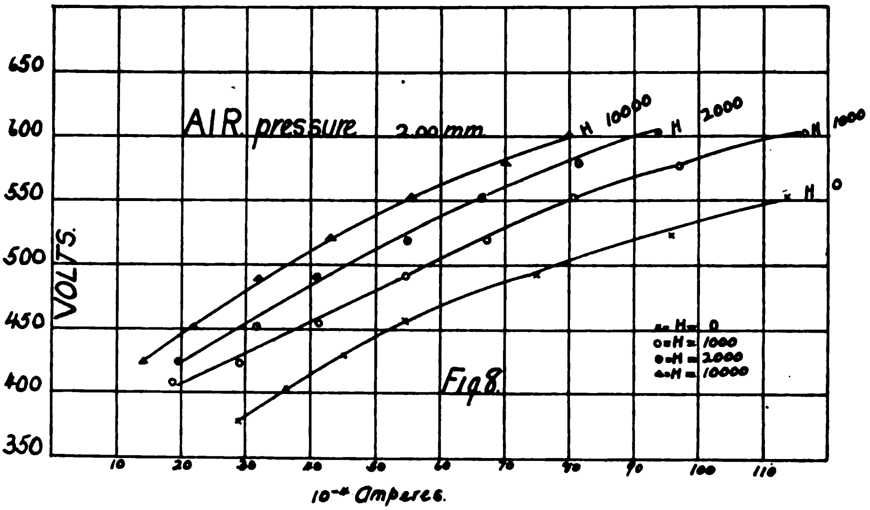


Fig. 8.

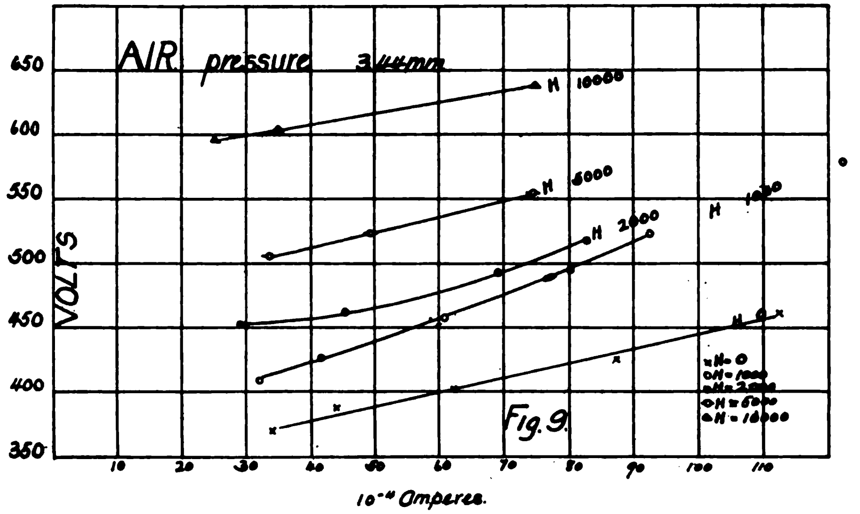


Fig. 9.

The figures which follow indicate the influence of pressure change.

It may be noted (Fig. 4) that when the pressure is .40 mm. a field of 1,000 units increases the current, 2,000 units (not shown in figure) produces no further increase but rather a slight diminution. With 10,000 units the current is reduced decidedly below the value for no field. These experiments were performed before some of the recent discussions to which reference has been made occurred, but the trend of the curves indicates that for low pressures increasing the magnetic field would lower the discharge potentials and this would continue until rather strong

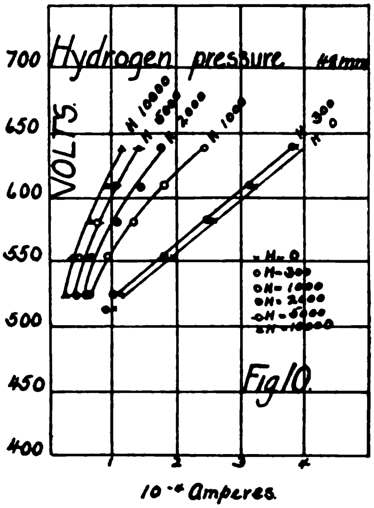


Fig. 10.

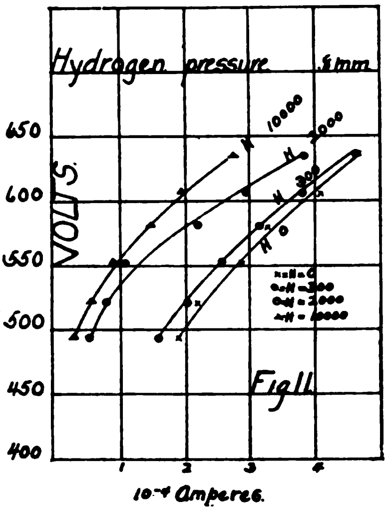


Fig. 11.

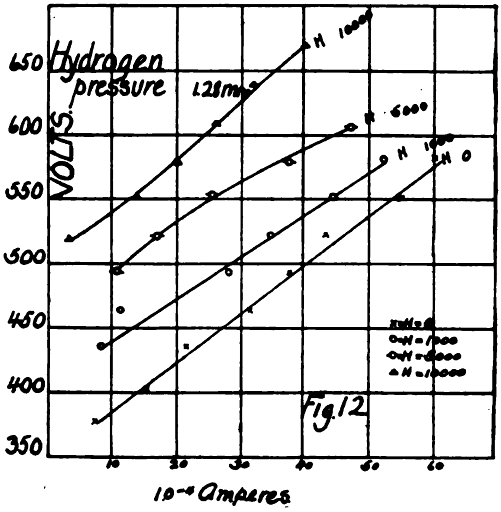


Fig. 12.

fields were produced. It would be necessary, for example, at pressures lower than .24 mm. to obtain a field of strength greater than 1,400 units before further increase in field caused a decrease in current and a very intense field to reduce the current to the value secured when H was 0. From my own experience in this experiment it seems that More and Mauchley are quite correct in stating that at pressures of .1 mm. the effect of the magnetic field is to reduce the effective cathode fall in potential.

At pressures of .96 mm. and 1.12 mm. (Figs. 5 and 6) the effect of the magnetic field is very small. A set of measurements made at a pressure of 1.04 mm. show variations of less than one per cent. A curve for this pressure is not shown, however. The readings taken persistently indicate that for the higher potentials the effect of the field is to increase the current slightly while for the lower potentials the current is reduced. These variations are small and would not appear in the graph on the scale chosen. It must be borne in mind that the potentials used were not greatly in excess of the cathode fall in potential and that the potential gradient between the electrodes for a portion of the distance is not the total potential difference divided by the distance separating the electrodes. It may be possible then, that a change in potential from 375 to 400 volts will double the gradient which occurs over a considerable part of the path. This pressure range is very near the critical pressure. Increasing the gas pressure above the critical pressure causes a very large increase in current under normal conditions. Attention is called to the fact that the value of the abscissæ differs in the various figures. It is

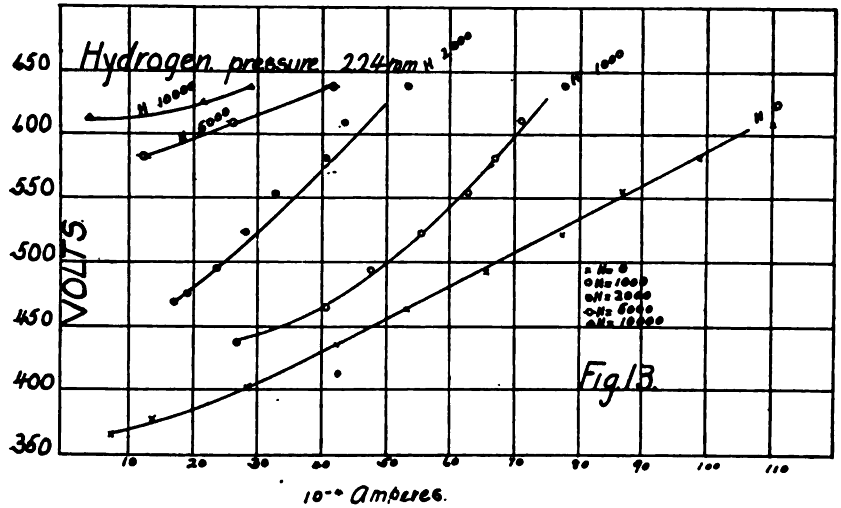


Fig. 13.

quite impossible to plot these on the same scale on account of the large changes in current produced by pressure variation. At pressures above the critical pressures the effect of the field is to greatly reduce the current.

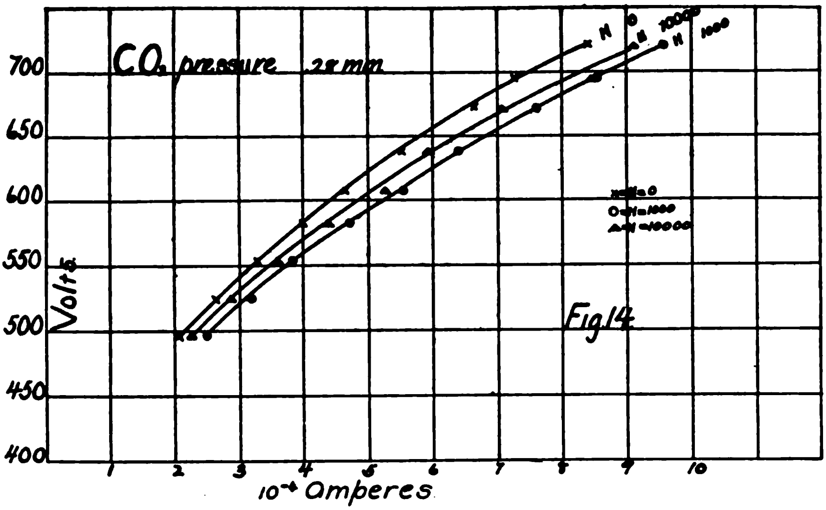


Fig. 14.

In fact at pressures of 3 mm. or more the battery was not sufficient to start the discharge in the presence of a moderate field. It was necessary

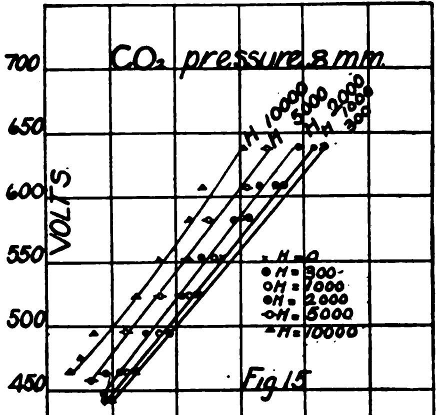


Fig. 15.

to start the discharge, then to apply the field. Unless the potential was maintained at sufficiently high value the discharge would be quenched. This is exactly the reverse of what occurs at the low pressures for in that case a discharge could be started in a magnetic field which could not be maintained when the field was withdrawn.

Figures 10 to 13 show the results of some experiments on hydrogen. The hydrogen prepared in a Kipp apparatus was purified and dried. At the lowest pressure used, a field of 300 gauss reduced the discharge current. A very feeble field, however, would increase it slightly. At higher pressures all fields applied reduced the current. The author is skeptical about the purity of the hydrogen but prepared it in the usual manner. Carbon dioxide shows the same general results as air. At the lowest pressure .28 mm. the application of a field of 1,000 units increased the current, 2,000 units increased it still more. With 5,000 units a diminution of current occurred which was not reduced to the value obtained for $H = 0$ with the application of 10,000 units. In few cases are all of the data plotted. Measurements were made with fields of strength 0, 300, 1,000, 2,000, 5,000, 10,000 C.G.S. units. Many intermediate values are omitted in the plotted results. They have served, however, as a satisfactory check upon the other values. In so far as consistent results were obtained they were made possible by operating on a seasoned gas. In order to obtain results which can be repeated and checked several or any number of times it seems necessary to thoroughly dry the gas and to let the discharge pass through it for an hour or more. After such a period of seasoning the gas appears to attain a steady state and the quantitative results can be duplicated with an accuracy of less than one per cent. from day to day. This is not true for a fresh gas.

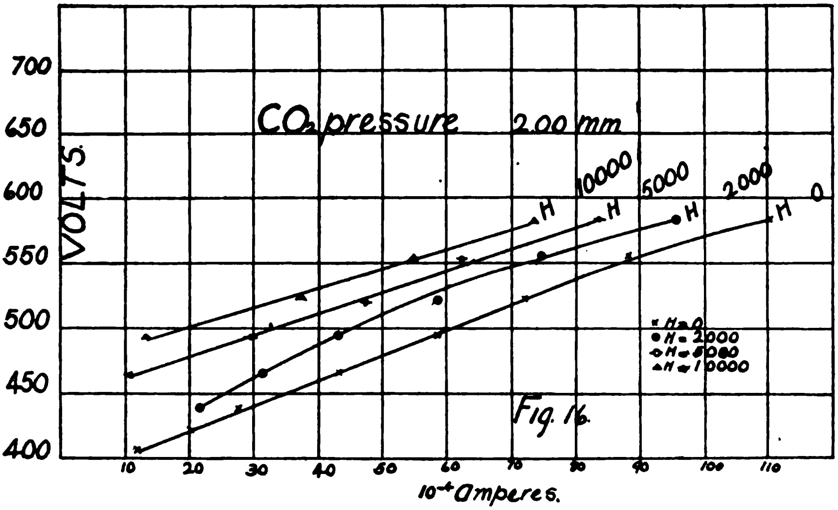


Fig. 16.

Before the discussion of Townsend and of Horton appeared the author had entertained much the same view as to the cause of the changes [illegible] the magnetic field. For pressures below the critical value [illegible] motion of the electrons will increase the effective path and [illegible] will be increased. There is also a force tending to [illegible] from the field if their motion should have a transverse [illegible] the higher fields the loss due to their diversion would [illegible] the loss due to their diversion becomes greater than [illegible] of fresh ions the stronger fields would cause an [illegible] diminution. For pressures above the critical pressure there [illegible] conditions a rapid ionization and the increase due to the [illegible] is more than offset by the large number diverted. [illegible] of a large number of cases leads me to believe there is no [illegible] pressure at which the magnetic field is ineffective at all voltages. [illegible] particular pressure there is a field value that will produce no effect [illegible] certain potential but for potentials slightly above this an increase [illegible] current will occur while for lower potentials a reduction of the current [illegible] obtained. Some experiments are in progress to test the questions [illegible] It appears that by increasing the area of the electrode, *i. e.*, using a discharge chamber of larger section, the current density would not be altered by the factor which increases the ionization, *i. e.*, the helical motion of the electrons projected from the cathode, but the factor tending to reduce the current due to the diversion of the ions would be decreased. The discussion of More and Righi on the magnitude of the fields necessary to reduce the cathode fall in potential at low pressures has caused the work so far performed to be published perhaps a little prematurely.

SUMMARY.

1. Quantitative measurements on the effect of a longitudinal magnetic field on a luminous discharge have been made in three gases above and below their critical pressures.

2. Measurements in a uniform magnetic field varying from 0 to 10,000 C.G.S. units have been made.

3. The results indicate that at pressures below the critical pressure a weak field increases the current obtained by a given potential difference while strong fields reduce it. They are shown quantitatively.

4. The lower the gas pressure the greater must be the critical value of the magnetic field to secure a reduction of the current.

5. Pressures close to the critical pressures show small effects due to magnetization but above the critical pressure the longitudinal field reduces the current.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY,
COLUMBUS, OHIO, November 24, 1913.

ANOMALOUS TEMPERATURE EFFECTS UPON MAGNETIZED STEEL.

By N. H. Williams.

A SOMEWHAT striking case of anomalous magnetization was described about a year ago by Smith and Guild.[1] Steel rods 7 cm. long were magnetized and then heated. In all cases in which the carbon content was greater than .15 per cent. the magnetism was reversed in the neighborhood of 200° C. The effect was most marked when the percentage of carbon was .85 of one per cent. In that case the negative intensity at 210° was about 10 per cent. of the maximum residual intensity before heating. With further rise of temperature, this negative flux very gradually decreased and finally disappeared at about 700° C.

If, after the temperature had been raised to 210° and a negative magnetic moment established, the specimen were allowed to cool, it partially regained its former positive magnetism.

The explanation of the phenomenon by the authors can be gathered from the following quotation from their paper: "The facts, therefore, suggest the following view of the course of events within each rod. Withdrawal of the magnetizing field leaves the rod subject to the influence of its own self-demagnetizing force, which at first is considerable. This force, acting upon the iron and upon the carbide tends to reverse the polarity of both. The alignment of the iron is more easily disturbed than that of the carbide and a greater amount of reversal is produced in the former. The reversing field diminishes continuously, and when it becomes incapable of producing further change, the feeble residual polarity is made up of a small positive polarity due to the carbide and of a still smaller negative polarity due to the iron.

"When the rod is heated, the polarity of the carbide diminishes more rapidly than the opposite polarity of the iron for several reasons. One of the most important is that the carbide is approaching its transition temperature more rapidly than the iron, and another is that, until the zero moment in the neighborhood of 200° is passed, the demagnetizing field tends to maintain the negatively magnetized constituent."

If this explanation be accepted, we must imagine an intimate mixture

---

[1] Proceedings of the Physical Society of London, August 15, 1912.

of two different kinds of particles in which the magnetic induction is in one sense in one constituent of the mixture and in the opposite sense in the other; moreover, the reversal of the polarity of one constituent was accomplished by the action of the other.

So long as we think of the substance composing the magnet as a continuous homogeneous medium of definite permeability, it is perfectly correct to say that at an interior point the only field acting is the demagnetizing field due to the ends but when we conceive of the magnet as made up of discrete particles of two kinds of substance in intimate mixture we are no longer entitled to treat the substance of the magnet as a homogeneous, continuous medium. The field brought to bear upon a molecular magnet within the iron would be the field existing in the intermolecular space, which is by no means a demagnetizing field.

Hopkinson's experiments show a large increase of susceptibility of iron and steel to *small* magnetic fields when the temperature is raised. This would lead us to expect considerable self-demagnetization with rise of temperature, but it would not account for the reversal.

The work described in the present paper was undertaken in the hope of furnishing further data upon which to base an explanation of this curious phenomenon.

A solid bar of steel 7 cm. long and having a cross-sectional area of 1.75 sq. cm. was used. The steel contained .85 of one per cent. of carbon. The bar was magnetized by placing it within a helix of many turns of wire, the current being supplied from a storage battery. After the bar was magnetized it was fastened within a frame upon which a test coil was arranged to slide so that it could be brought quickly to a position where it surrounded the magnet. The test coil was connected to a ballistic galvanometer and the frame and coil were immersed in an oil bath. It was assumed that the throw of the galvanometer when the coil was thrown over the magnet or when it was suddenly taken off would be proportional to the residual flux in the metal. The conclusions drawn from the work are not affected if this assumption is considered as only approximately correct. The oil was heated by Bunsen burners and the temperature was measured by a mercury thermometer. In this way the residual flux was measured at brief intervals as the temperature increased from 20° to 220°.

The experiments upon this specimen showed the reversal of polarity that was expected but the magnitude of the reversed flux was not as large in comparison with the maximum residual flux as was obtained by Smith and Guild. Fig. 1 shows the results. Temperatures are plotted as abscissæ and galvanometer deflections (proportional to magnetic flux) as ordinates. The reversed deflection at 195° was about 5 per cent. of that due to the maximum residual flux and upon cooling, the specimen recovered about a quarter of its original positive magnetism. However, the experiment may be so arranged as to avoid the appearance of this anomalous behavior. Fig. 2 shows results obtained under the same conditions as those pertaining to Fig. 1 with this exception: This time after magnetizing the steel it was removed from the coil without opening the magnetizing circuit, whereas in the former case the circuit was broken at the switch before the iron was removed from the helix.

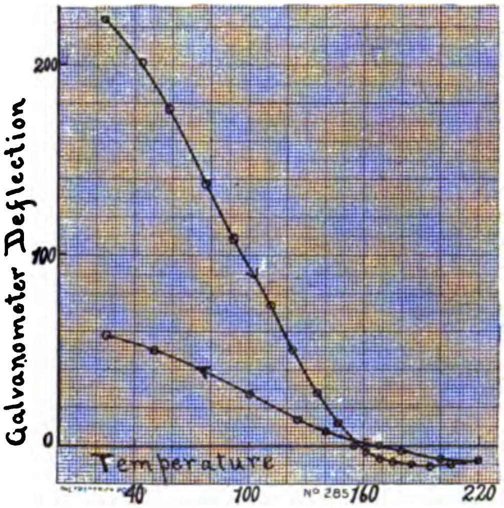


Fig. 1.

It will be observed that in Fig. 2 the flux starts at a very much higher value and diminishes as the temperature rises, coming to zero at about 190°, but that it does not reverse. If the end effects were responsible for the reversal there should have been a larger reversed magnetization in the second case than in the first, since the residual flux which produced the end effect was twice as large in the second case as in the first. Since, however, there was none at all we seem justified in the conclusion that end effects are not the cause of the reversal but that the explanation is to be found in the oscillatory spark at the switch when the circuit is opened. The condition that the discharge shall be oscillatory in a given system is expressed by the relation $R^2/4L^2 < 1/LC$, R being resistance, L inductance and C capacity.

The circuit, here considered, consisted of a storage battery, a coil of wire and a knife switch. The capacity is therefore extremely small and we may be certain that the above condition is fulfilled and that an oscillatory current will flow through the coil when the switch is opened. The period of this oscillation is

$$T = \frac{2\pi}{\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}}$$

or approximately $2\pi\sqrt{LC}$. Since C is extremely small the period is also extremely small.

The effect of such a current on the magnetism of the steel core would

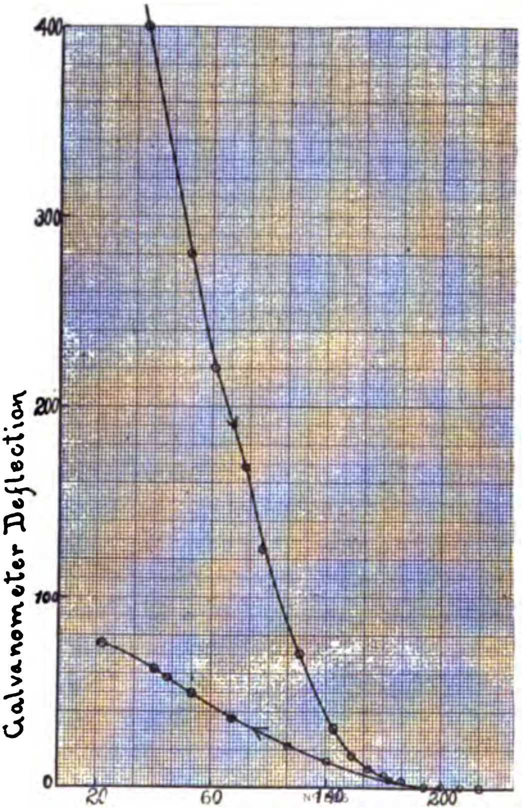


Fig. 2.

be confined to a thin surface layer, the eddy currents in the outside layers being sufficient to protect the inner portion of the core from its action. The first reversed current of this oscillatory discharge would be larger than any subsequent current in either direction and the magnetic effect of this current in conjunction with the demagnetizing field due to the ends might produce a reversal of the outside layers of the core.

It is almost inevitable that steel with such high percentage of carbon should be slightly harder in its outside layers than at the interior of the specimen. We should then expect that with rise of temperature the magnetism of the outer layers would persist after that of the softer interior had disappeared and hence that the resultant magnetic moment would be reversed at the high temperature.

The authors previously mentioned also studied the effect of a rise of temperature upon a specimen that had been first magnetized strongly and then subjected to a demagnetizing field just strong enough to leave the specimen apparently demagnetized. They stated that under these conditions the negative magnetism that developed with rise of temperature was much stronger than in the other cases and that it occurred after a very slight rise of positive magnetism. The author has been unable to reproduce these results. What has happened in each case is a rise of positive magnetism, *i. e.*, a flux in the direction of the original strong magnetizing field and whether the flux finally reverses at 190° is again determined by the method of magnetizing and demagnetizing the specimen.

Fig. 3 shows the results when the specimen was first highly magnetized then demagnetized; in both cases the steel being removed from the coil before the switch was opened thus avoiding entirely the effects of oscillatory currents. With rise of temperature the positive magnetism develops, reaches a maximum at about 80°, then decreases reaching zero at about 200°. On cooling, the steel recovers over 80 per cent. of its maximum flux. There is no indication of a reversal.

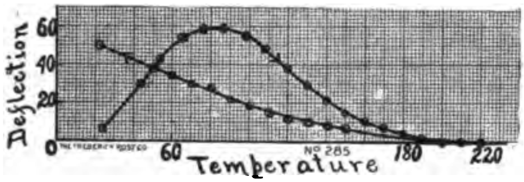


Fig. 3.

Two other cases naturally suggest themselves: (*a*) The specimen might be magnetized and the circuit broken at the switch, then demagnetized without breaking the circuit. We should expect then a reversal of magnetism at high temperatures. (*b*) The specimen might be magnetized and removed from the coil without breaking the circuit, then subjected to a demagnetizing field, the circuit being opened at the switch in the latter operation. The effect of the oscillating current would be to reverse the outer layer with respect to the final field, *i. e.*, to magnetize it in the direction of the original field, which we have called positive. So in this case we should not expect a reversal of magnetism with rise of temperature nor indeed should we expect to be able to reduce the flux to zero in the neighborhood of 200°.

Figs. 4 and 5 represent data obtained under the conditions described under (*a*) and (*b*) respectively, and they are in accordance with the statements there made as to what should be expected.

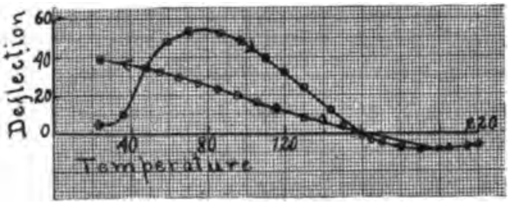


Fig. 4.

A good illustration of the effect of the oscillatory current was found while obtaining data similar to those of the last two curves. The specimen was magnetized strongly in the positive direction and then subjected to a negative field such that if the bar were slowly withdrawn from the field, it retained negative polarity sufficient to produce a throw of the galvanometer equal to − 102. This same negative field was again applied and the current interrupted at the switch, thus giving rise to oscillations. The residual magnetism was then found to be positive and sufficient to produce a deflection + 60. Again the field was applied without permitting oscillations and the residual flux produced a deflection of − 106. Another application of the same field followed by a break at the switch caused positive residual magnetism, and so on indefinitely.

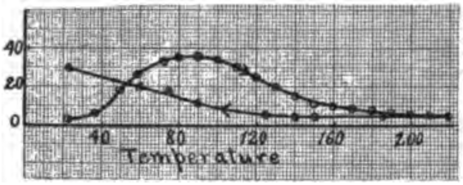


Fig. 5.

If the explanation proposed for this apparent anomaly be correct, the phenomena may be classified with other cases which have been described in detail in a recent paper by B. O. Peirce, on "The Anomalous Magnetization of Iron and Steel."[1]

UNIVERSITY OF MICHIGAN,
ANN ARBOR.

---

[1] Proceedings of the American Academy of Arts and Sciences, March, 1912.

CALCULATION OF A DAMPING RECTANGLE TO PRODUCE CRITICAL DAMPING IN A MOVING COIL GALVANOMETER.

By Paul E. Klopsteg.

If a moving coil galvanometer is used ballistically, it is ordinarily desirable to have the coefficient of damping small, principally because much damping reduces the throw produced by a given quantity of electricity; there are, however, certain conditions under which it is expedient to have the instrument critically damped. When the galvanometer is to be used for steady deflection work it is often not only expedient but imperative to have the motion just aperiodic. The advantages of critical damping have been discussed by O. M. Stewart[1] and Jaeger.[2]

The usual procedure in changing from a ballistic to a deflection galvanometer is to increase the damping to aperiodicity by attaching to the coil a closed wire rectangle, usually of the same mean area as the coil. However, since a certain coil may be used with different kinds and lengths of suspension fibers and, furthermore, since there is considerable initial damping when the galvanometer is used on a closed circuit of high resistance, the damping rectangle usually furnished by the manufacturers may or may not make the coil just aperiodic. In most cases the boundary condition between periodic and aperiodic motion is not realized. A method is given in this paper by means of which the proper diameter of a wire for a damping rectangle may be found in order that, for given conditions, the galvanometer may be critically damped.

We shall assume at the outset that the magnetic field in which the coil is suspended is uniform, *i. e.*, that the damping rectangle which is to be attached to the face of the coil will swing in a field of the same strength as does the "mean" turn of the coil. In a previous paper[3] the author

---

[1] Phys. Rev., 16, O.S., 1903, p. 158.

[2] Ztschr. f. Instrumentenk., 23, 1903, pp. 261 and 353.

[3] Klopsteg, Phys. Rev., 2, N.S., 1913, p. 390. After the publication of the paper here cited, and after the present paper had been submitted for publication, my attention was called by Dr. I. Fröhlich of Budapest to his paper, which I had overlooked, appearing in "A Mathematikai és Természettudományi Értesítö", Vol. VII, 1889, p. 44, under the title, "Zárt elektromos vezetök lengése homogén mágnesi térben", dealing with the vibrations of a closed conductor in a homogeneous magnetic field. Dr. Fröhlich develops an equation

developed an equation for field intensity, based upon critical damping, of the form

$$H = \frac{2\sqrt{10^9 I_0}}{nld}\sqrt{\frac{R_0}{T_0}(\pi - \lambda)}, \tag{1}$$

in which I_0, n and ld are, respectively, the moment of inertia, number of turns and mean area of the coil, T_0 is its period and λ its logarithmic decrement on open circuit, while R_0 is the total resistance in ohms of the circuit containing the galvanometer. The resistance R_0 is such that damping is critical. If in this equation we place $n = 1$ and solve for R_0, the result will be the resistance of a single closed turn of wire such that the induced current in it due to the cutting of the field may be of proper magnitude to bring about the desired effect. The equation becomes

$$R_0 = \frac{(Hld)^2 T_0}{4 \times 10^9 I_0(\pi - \lambda)}. \tag{2}$$

The damping rectangle having the same mean area as the coil, the total length of wire will be $2(l + d)$; the diameter of the wire is then, in centimeters,

$$D = \sqrt{\frac{8\rho(l + d)}{\pi R_0}}, \tag{3}$$

ρ being the specific resistance of the metal from which the wire is drawn. Combining (2) and (3),

$$D = \frac{1}{Hld}\sqrt{\frac{3.2 \times 10^{10}\rho I_0(l + d)(\pi - \lambda)}{\pi T_0}}. \tag{4}$$

In galvanometer fields of the type represented in Fig. 1, with the usual

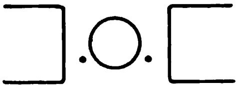


Fig. 1.

which gives the relationship between the intensity of the field and quantities to be obtained by measurement or calculation from the closed conductor. Briefly, his method is based upon the difference in the periods of the closed conductor when vibrating in zero field and in the field under investigation, whereas my formula makes use of the difference in the logarithmic decrements when the coil vibrates on open and closed circuits, respectively. In my paper (p. 392, eq. (10)) it was shown that the difference in periods corresponding to any two logarithmic decrements is very small, which fact alone would make the method of Dr. Fröhlich impracticable; on the other hand, the comparatively large differences in the logarithmic decrement are readily measurable with great accuracy. Another objection to using a closed conductor is the inflexibility of the method, on account of the fixed resistance of that conductor. For the best results by such a method, the damping must be great enough to make an appreciable difference in the period, but not so great as to make the vibrations die out rapidly. This means, in its practical application, that any one closed conductor could be used over a very limited range only; whereas, in the description of the damped coil method, it was shown that it is entirely practicable to use the same coil for measurements of a few gausses up to several thousand. Dr. Fröhlich gives no experimental data. Had he tried his method he would have been at once confronted by the above mentioned limitations.

type of coil used in such fields, the vertical wires of the rectangle are approximately in the position shown by the dots in the figure when the coil is undeflected. The damped coil method[1] of determining H for equation (4) gives as its value the field intensity at the position of the "mean" turn of the coil at rest. Evidently the value so obtained is higher than the field strength at the position of the rectangle, consequently equation (4) will give a value of D which is too small. To correct for this difference, the field was measured in several galvanometers of this type both at the null position of the coil and at the position of the rectangle. The ratio between these two values was found[2] to be 1.30. Usually the damping rectangle is made of copper wire; in this case $\rho = 1.69 \times 10^{-6}$ (15° C.); introducing this value and the ratio 1.30 into equation (4) it becomes

$$D = \frac{170}{Hld}\sqrt{\frac{I_0}{T_0}(l + d)(\pi - \lambda)}. \tag{5}$$

To apply formula (5), H is determined by the method mentioned above, l and d are readily found by means of a stage microscope, while λ and T_0 are obtained in the usual manner. It should be observed that λ is not necessarily the logarithmic decrement on *open* circuit; when, for example, the galvanometer is used on a closed circuit of such resistance that damping is not critical, λ is the logarithmic decrement for this special condition. I_0 is found by the method of comparing the periods of the coil and of a disk of known moment of inertia, each in turn suspended from the same fiber. The value of D having been calculated, the wire gauge corresponding most nearly with this value is selected for the rectangle.

The addition of the mass of the rectangle to that of the coil has the effect of increasing to some extent the values of both I_0 and T_0. It is unnecessary to make a second approximation because of the fact that the value of the fraction I_0/T_0 is changed only slightly and that this fraction is under the radical sign, the percentage change being thereby halved. Practically, one is also limited to the standard wire gauges, which admits of some latitude in the value of D. To determine the effect of the added mass of the rectangle, an experiment was tried, using an

---

[1] Loc. cit.

[2] For any particular type of field or depth of coil (distance from face to back) the ratio between field strengths may be determined by the damped coil method, the equation for the ratio being

$$\frac{H}{H'} = \sqrt{\frac{T_0'}{T_0}\,\frac{\Lambda - \lambda}{\Lambda' - \lambda'}}$$

when the same value of R is used in both cases. The value 1.30 is understood to refer to the case only which is discussed above.

"open" rectangle of the wire gauge given by one calculation, and redetermining the quantities appearing in the equation. There was a slight change in the new value of D, but not sufficient to necessitate using a different wire gauge. The size found by the first calculation produced damping as nearly critical as could be judged.

When the number of turns in the galvanometer coil is known, a formula more simple in its application—one which involves the determination of neither H nor I_0—may be found by making use of the equation[1]

$$H = \frac{2\sqrt{10^9 I_0}}{nld}\sqrt{\frac{R}{T_0}(\Lambda - \lambda_0)}, \tag{6}$$

where Λ is the logarithmic decrement corresponding to a total resistance R in the circuit which is not sufficiently small to make damping critical, and λ_0 is the logarithmic decrement on open circuit. The other quantities are defined as before. From this equation and (2) we find

$$R_0 = \frac{R}{n^2}\frac{\Lambda - \lambda_0}{\pi - \lambda}, \tag{7}$$

which equation, when combined with (3) gives

$$D = \sqrt{\frac{8\rho n^2(l + d)(\pi - \lambda_0)}{\pi R(\Lambda - \lambda_0)}}. \tag{8}$$

Introducing the constant 1.30, explained in connection with (5), and substituting for ρ the value before given, we find that for a copper wire damper

$$D = 0.00269n\sqrt{\frac{(l + d)(\pi - \lambda)}{R(\Lambda - \lambda_0)}}. \tag{9}$$

Evidently, when the galvanometer is used in open circuit work, λ_0 and λ of equations (8) and (9) are equal; when the coil is on closed circuit, λ is, as before, the logarithmic decrement for this condition, while λ_0 remains the logarithmic decrement on open circuit.

The results obtained by equations (5) and (9) were found in good agreement in all cases tried, which included several types of moving coil galvanometers and three kinds of upper suspensions, viz.: 3-mil and 1.5-mil phosphor bronze strip and 1.5-mil phosphor bronze wire.

SUMMARY.

In brief, this paper gives the development of two equations for finding the proper size of wire to be used in damping rectangles in order that critical damping may be obtained in moving coil galvanometers. The

---

[1] Loc. cit.

first equation is used when the number of turns in the coil cannot be ascertained, the second when this number is known.

The suggestion is made, in conclusion, that manufacturers be requested to furnish with their galvanometer coils the values of n, l, d and I_0. Such data would minimize the number of quantities to be determined by the experimenter in measuring fields by the damped coil method; and would greatly simplify the obtaining of data for calculations such as are mentioned in this paper.

Physical Laboratory,
The University of Minnesota,
December, 1913.

CHANGE OF PHASE UNDER PRESSURE.

I. THE PHASE DIAGRAM OF ELEVEN SUBSTANCES WITH ESPECIAL REFERENCE TO THE MELTING CURVE.

BY P. W. BRIDGMAN.

CONTENTS.

INTRODUCTION.

THIS paper is the first of a projected series of papers dealing with the various problems offered by the phenomena of change of phase under pressure. At high pressures we are concerned with phase changes of only two types, from the fluid to the solid (or crystalline) phase, and from one solid phase to another, since at high pressures the gaseous phase no longer has an independent existence. It is the first of these changes, that from the liquid to the solid, that is to be the special subject of this paper. The problem presented by the change from liquid to solid involves for its complete solution a description of the molecular arrangement of the liquid and the crystal and of the nature of the forces that produce crystallization. Hitherto one narrow aspect of this problem has received almost exclusive attention, the question as to the general shape of the melting curve. Evidently an answer to this question would go far in pointing the way to the essential difference between a liquid and a crystal. Two answers to this question have been regarded as most probably correct; the first is that the liquid-solid curve ends in a critical point, and the second, directly opposed to the first, is that the melting curve passes through a maximum temperature, so that if pressure is raised sufficiently high at constant temperature we may first freeze the liquid to the solid and then melt it again to the liquid. The more particular object of this paper is to settle definitely, with the help of new data, this long discussed question as to the shape of the melting curve.

The data hitherto available have covered a pressure range of about 3,000 kgm. These data are mainly due to Tammann, who measured the relation between pressure and melting temperature over this pressure range, and also measured for some of his substances, with considerably less accuracy, the difference of volume between solid and liquid along the melting curve. The data presented here cover a pressure range up to 12,000–13,000 kgm. per sq. cm., and a temperature range from 0° to 200°. Over this entire range the relation between melting temperature and pressure has been measured, and the difference of volume between solid and liquid has also been determined. These two kinds of data are necessary and sufficient from a thermodynamic point of view to settle the point at issue. Eleven substances have been experimented on, including simple and complicated organic compounds and three elements. These all indicate the same answer to the question in hand.

For the immediate purposes of this first paper those substances were selected which had only one known modification of the solid, in order not to complicate the study by the entrance of a second solid phase. But four of the substances studied have been found to have new solid modifications at high pressures. It may be, therefore, that polymorphism at high pressures is a common instead of an exceptional phenomenon. The data given in this paper include data that will be used later in the discussion of the relation between different solid modifications. And similarly, some of the data to be presented in future papers may be expected to have a bearing on the narrower question to be discussed here.

Summary of Previous Work and Present State of the Problem.

It is proposed to quote here only those papers bearing on the question at issue, the true character of the melting curve. This will omit a few papers giving measurements only, and also much of the earlier work, which was occupied with experimental proof of the validity of the formulas deduced by thermodynamics, at a time when complete confidence apparently was not felt in thermodynamic arguments. Most of the early speculators on the true nature of the melting curve seem to have been guided mostly by analogy with the then recently established critical point between liquid and vapor, and assumed the existence of a similar critical point between liquid and solid. Poynting[1] was one of the earliest of these. He predicted by analogy between water and its vapor that there were two critical points between water and ice; one at − 120° and 16,000 atmos., the other at + 14° and some high negative pressure. Practically no experimental evidence was given. Planck[2] thought that there was a critical point, and deduced some thermodynamic relations which must hold if such a point exists. Peddie[3] also gave thermodynamic relations for a critical point if it exists, and quoted observations of Bunsen on paraffine suggesting the possible existence of such a point. Amagat[4] then contributed some actual observations up to 1,100 atmos. on the solidification of CCl_4, and stated that the appearance was as if a second liquefaction took place at a higher pressure than that required to produce solidification. In his opinion a critical point seemed likely. Two papers by Damien[5] with new experimental data gave the subject new impetus from the experimental side. His results reached to 200 atmos. and he claimed to have found for several organic substances, not a critical point, but a maximum melting temperature. At temperatures below the maximum the continually increasing application of pressure first freezes the body to a solid and then melts it again. This seems to have been the first suggestion in the literature of such a phenomenon. Barus[6] in 1892 published investigations up to 2,000 atmos. on a number of organic liquids, but his results did not become known until later. He found no evidence of a maximum up to 2,000 atmos., but there was a certain cyclic character in the transformation solid-liquid which reminded him of the unstable part of the isotherms of James Thomson. He seems to have been of the opinion that at high enough pressures there is a critical point. Amagat[7] then published data on water, obtained with the same apparatus as for CCl_4, up to 1,000 atmos. He was of the opinion, although his results do not suggest it particularly strongly, that at high enough pressures there might be an inversion point beyond which ice is more dense than water, so that at high pressures the melting point of ice would be raised by pressure instead of lowered; that is, a minimum point, the reverse of Damien's maximum. Demerliac[8] in two papers next subjected Damien's results to further experimental scrutiny up to 300 kgm. Demerliac's results are usually quoted as supporting Damien's theory, but only because of a misunderstanding. Demerliac found that for the lower pressures of his range his results could be very accurately represented by a formula which predicts a maximum, but that at the higher pressures the results no longer fitted the formula, the temperature tending to approach more and more closely to a limiting value. Demerliac's opinion, therefore, was that the melting curve tends to approach a horizontal asymptote. He nearly reached the asymptote for several substances. The years 1898–99 marked great activity in this field, several of the results appearing without knowledge of the others. Heydweiller[9] published results showing that there could not by any possibility be a maximum at pressures as low as Damien supposed, and was of the opinion that there must be a critical point at high enough pressures. He chose substances to investigate that might be expected to be near their critical points, but he could find no critical phenomena up to pressures estimated to be between 1,000 and 3,000 atmos. At the same time he observed effects of another kind on menthol which he thought were indicative of a critical point. Mack[10] published results up to 2,100 atmos. on several organic substances, and could find evidence of neither a critical point nor of a maximum. His melting curves were nearly linear. Hulett[11]), inspired by Ostwald who was of the opinion that there was a critical point, investigated liquid crystals up to 300 kgm. It seemed natural to suppose that liquid crystals might be near the critical point, but he found on the contrary that the difference between liquid crystal and the liquid became more strongly accentuated at increasing pressure. If there were a critical point, it could exist only at negative pressures. About this time Tammann[12] began to publish his experiments and theory, and he has since then almost monopolized the field. His results cover a range of 3,000 kgm., higher than had been reached hitherto. One of his first services was to explain the remarkable discrepancies between previous experimental results by calling attention to the effect of dissolved impurities. Damien provides a particularly striking example of this; his medium of compression was air, which is dissolved more and more at high pressures. The cycles found by Barus are also similarly explained by the action of impurities. Tammann's theory is well known, and will be described again only briefly. It is, in part, that all substances show a maximum melting point, but this maximum is very much higher than supposed by Damien. Tammann himself was never able to reach it, but supposed that it might be in the neighborhood of 10,000 kgm. for a number of substances. In support of this theory, Tammann shows that we must consider all the thermodynamic elements of the phenomena of melting, the change of volume and the latent heat, as well as the melting curve itself. His data show that the change of volume decreases along the melting curve, while the latent heat increases or remains nearly constant. Now at a critical point the change of volume and the latent heat must vanish together, but at a maximum the change of volume vanishes, while the latent heat remains finite. The data are unquestionably more favorable to the second than to the first of these alternatives, and this constitutes the evidence for a maximum. Still the evidence, even from Tammann's own data, is by no means conclusive, and there have been at least two upholders since then of the idea of a critical point. Weimarn[13] in 1910 argued from the behavior of colloids to the probable existence of a critical point. His argument is briefly as follows. At any pressure, no matter how high, the temperature may be raised so high that the dispersive forces due to the intense molecular agitation overcomes the orienting forces, so that the substance can exist only in the form of very finely disperse crystals. When the crystals become molecular in dimensions we have achieved continuous passage between the two states, or have reached the critical point. Van Laar[14] also, from an entirely different point of view, has deduced a theory demanding a critical point. This has been described in greater detail elsewhere; briefly, the difference between a liquid and a solid consists in an association of the molecules in the solid, which produces a second loop in the isotherm of James Thomson, with the possibility of a critical point. For substances which contract on freezing, this theory demands that there shall always be a critical point solid-liquid, but never a maximum. Because of an error in one of the figures of the original article, the author stated in a previous summary of van Laar's theory that under some conditions a maximum might occur. In 1911 the author published two experimental papers bearing on this subject,[15] over a pressure range considerably higher than previously reached. The evidence of the first paper, on mercury to 12,000 kgm., was against the existence of Tammann's maximum, but left open the question of a critical point. The second paper, on water to 20,000 kgm., did not give so valuable evidence because of the many abnormalities of water. However, all the evidence suggests that these abnormalities disappear at high pressures. If water can be regarded as really normal at high pressures, then the evidence of water is that there is neither critical point nor maximum, but that the melting curve continues rising indefinitely. Van Laar[16] has since this published a short paper in which he regards the evidence of the mercury as on the whole favorable to his theory, but apparently regards water as too abnormal to make its evidence of much value.

APPARATUS AND EXPERIMENTAL METHOD.

Apparatus.—The apparatus is in essentials the same as that used in previous work[15] and needs only brief description. Some slight changes have been necessitated by the higher temperature reached here, 200° instead of 80°. The apparatus finally used consists of an upper and a lower cylinder, connected by a heavy piece of tubing. The upper cylinder contains the moving piston, actuated by a hydraulic press, by which pressure is produced. The motion of the piston, measured with a micrometer, may be combined with the cross section to give the change of volume of the substance under investigation in the lower cylinder. The upper cylinder also contains the coil of manganin wire, from the change in the resistance of which the pressure is determined. The upper cylinder contains one feature not found in the previously used apparatus. The compressibility of some of the substances was so high that a single stroke of the piston would not have given the maximum pressure desired. The difficulty was avoided by starting the experiment with initial pressure. To accomplish this, a very minute by-pass was provided at the upper end of the cylinder connecting the interior of the cylinder with an auxiliary pressure pump. The by-pass connects with the interior of the cylinder only when the piston is withdrawn to the extreme position. In this position, pressure was raised to the desired amount, 2,000 or 3,000 kgm., by the auxiliary pump acting through the by-pass, and then the auxiliary pump cut off by advancing the piston slightly beyond the by-pass. It is necessary that the by-pass be very small indeed, otherwise the rubber packing on the moving piston gets blown into it as the piston moves by. A sufficiently minute hole was made by drilling and tapping a hole through the side of the cylinder, and then screwing into the hole a tightly fitting screw, across the threads of which a lateral scratch had been made. The upper cylinder, together with the lower part of the hydraulic press, was placed in a thermostat maintained at about 35°. In this way all temperature corrections of the manganin coil were avoided. A temperature as high as 35° was necessary because the conduction of heat along the connecting tube from the lower cylinder sufficed (when the lower cylinder was as high as 200°) to keep the upper thermostat at nearly 35°.

The lower cylinder contained the substance to be investigated. It was held suspended in another thermostat by the connecting tube, led through a water-tight stuffing box in the bottom of the upper thermostat. The temperature of the lower thermostat was systematically run to 200°. For the higher temperatures, "Crisco," a substitute for lard by the Proctor and Gamble Co., was chosen for the bath liquid, because of its comparative freedom from odor. The temperature regulation was by means of an ordinary mercury contact device. This worked well for the few hours occupied by a single run, but at the higher temperatures trouble might arise if longer runs were necessary, because of a slow drift of temperature due to the very gradual distillation of mercury from the temperature regulator. The difficulty can be largely avoided by carefully designing the mercury bulb. The substance to be investigated, if it was such as not to be attacked by the kerosene which transmitted the pressure, was placed in an open cup, or if it were attacked by the kerosene, it was placed in a steel bulb with a mercury seal, of exactly the same design as was used in investigating the thermal properties of twelve liquids.[17]

The dimensions of the various parts of the apparatus were as follows. The upper cylinder: length 8 inches, outside diameter 4½ inches, inside diameter 17/32 of an inch, length of stroke of piston 3½ inches. The connecting pipe: length 16½ inches, outside diameter 1½ inches, inside diameter 1/16 of an inch. The connections at the end of this tube were especially heavy, the minimum outside diameter at places where the pressure was entirely internal was ¾ of an inch. The lower cylinder had the dimensions: length 10½ inches, outside diameter 4½ inches, inside diameter 11/16 of an inch, depth of interior cavity 9 inches. All parts of the apparatus were made of the Halcomb Steel Co.'s electric furnace chrome-vanadium steel, which has proved itself the best yet found for the purpose.

The apparatus in the form just described was not the form first used. In the first form there were three pressure cylinders and two connecting pipes. In the one cylinder the pressure was produced by the moving piston, in the second was placed the manganin coil with which pressure was measured, and in the third was the liquid under investigation. There was only one thermostat, around the third cylinder. Conduction of heat to the second cylinder was avoided by a water jacket with running water around the connecting tube. The temperature fluctuations in the second cylinder were not large and could be readily corrected for. The fatal weakness in this original apparatus was in the connecting pipes. The connections were of a type in which the end of the tube was turned down to 5/16 of an inch and threaded with a 32 thread, bringing the minimum outside diameter of points where there is only internal pressure to about ¼ of an inch (the inside diameter was 1/16 of an inch). The result was that the tubes were invariably torn apart at the connections, sometimes at pressures as low as 7,000 kgm. The high temperature has a perceptible weakening effect on the tubing, since the same type of connection had been previously used to 12,000 kgm. in the work on mercury at 20°. Various other types of connection were tried with this first form of apparatus, but none with permanent success. Finally, after six explosions, the attempt to use this form of apparatus was entirely given up, since for one thing, the labor of drilling each new piece of tubing with a hole 1/16 of an inch in diameter and 16 inches long is considerable. However, the data obtained at the lower pressures with this apparatus are perfectly reliable, and form an important part of the data of this paper.

To prevent rupture of the connections, a piece of apparatus much like that finally used was constructed, but which had no connections, everything being made out of one piece of steel. This necessitated drilling a hole 1/8 of an inch in diameter through a piece of steel 30 inches long and 5 inches in diameter, turning the steel to 1½ inches over the middle third, and to the dimensions given above for the cylinders at the two ends, hardening in oil, seasoning by subjecting to 17,000 kgm. at 200°, and finally machining to the final size after the preliminary stretching. Some measurements had already been made with this apparatus when a flaw developed in the steel which made the whole apparatus valueless. The flaw developed rapidly into a crack through which the kerosene could be forced in a stream.

The risk of flaws in the steel, as exemplified by this accident, is one which is apparently unavoidable in work at very high pressures. Several pieces of Krupp's best chrome nickel steel have previously developed flaws under high pressure, but it was a great surprise to find a flaw in this apparently perfectly homogeneous product of the electric furnace. That the flaw was very small is shown by the fact that the steel had withstood the first application of 17,000 kgm. at 200°.

Rather than run the risk and lose the time of making another piece of apparatus, an attempt was then made to design a form of connection which should not have the weakness of the other, and the attempt was entirely successful. The packing is a thin ring of lead confined between two Bessemer rings. The lead gives the initial tightness, and at the high pressures the soft Bessemer rings become sufficiently deformed to give tightness. The connection has not leaked or broken once in several months of use.

Besides the two forms of apparatus described above for high pressure a third form was used to find points at approximately atmospheric pressure. The necessity of this was not contemplated in the original plan of the work, but an examination of the existing data showed rather large discrepancies in the values for the change of volume (ΔV) on melting at atmospheric pressure, so that a redetermination of these data became necessary. The chief possibility of error in previous work, apart from impurity, seems to have been the formation of unfilled cracks, and uncompensated capillary effects. To avoid this, these determinations were made at a slight pressure, about 60 kgm., and then extrapolation made from 60 to 1 kgm. The change of ΔV with pressure is so small that this can be done without danger. The readings with this apparatus may also be used to give by extrapolation an approximate value of the freezing temperature at atmospheric pressure, but the extrapolation is sometimes uncertain, and the freezing point determined in this way is not so good as that directly measured. However, the freezing point so found may be of some value, and it is given in those cases where it was not determined by direct measurement.

The apparatus for the low pressure measurements is in essentials the same as that used for high pressures. First there is a cylinder of known cross section in which there is a moving piston. This piston was actuated by a screw instead of by a hydraulic press, and the connection between the screw and the piston was a positive one, so that the piston could be either advanced or withdrawn. The position of the piston was measured as usual with a micrometer. To avoid error from the distortion of the piston or the wearing away of the packing, the piston was made hollow, and a rod was led through the piston and through the packing to the washer retaining the packing at the inner end. The position of the free end of this rod evidently gives directly the position of the upper surface of the liquid in the cylinder. This cylinder connects with a pressure gauge (a Geneva Bourdon gauge was accurate enough) and a second cylinder, containing the substance to be investigated, which was placed in a thermostat. The procedure in making measurements was to vary the temperature at constant pressure, instead of to vary the pressure at constant temperature as in the high pressure measurements. The data give the means of plotting volume against temperature, from which the discontinuity of volume at the freezing temperature may be found graphically. Because of the low pressures used with this apparatus, it was possible to enclose the liquid under investigation in a glass bulb with a mercury seal, instead of a steel bulb, as was necessary at the higher pressures. In this way somewhat greater purity was ensured. The use of the glass also allowed examining the liquid after the experiment, to be sure that none of the transmitting fluid had found its way to it. In no case had this happened. To further ensure purity, no glass bulb was used more than once. The bulbs were filled by boiling the liquid into them under reduced pressure, in the same way as for the steel bulbs. The liquid transmitting pressure in this low pressure experiment was a mixture of water and glycerine, instead of kerosene, which was used at the high pressures. Corrections for the thermal expansion of the glycerine and water on passing from one clyinder to the other were determined and applied in the same way as for the kerosene at high pressures.

Procedure.—This was in most respects like that used either in the work on ice[18] or on twelve liquids[17]. A brief summary will suffice. The purified liquid was boiled into the bulb under reduced pressure to exclude all air, and its quantity determined by weighing. The apparatus was then assembled, the upper thermostat adjusted to 35°, the zero of the manganin coil determined, initial pressure of 1,000–2,000 kgm. applied through the by-pass, the by-pass shut off by pushing in the piston, and then the lower thermostat adjusted to the desired temperature. Pressure was now increased beyond the freezing point sufficiently far to ensure complete freezing, and then the pressure decreased, and readings made of the position of the piston for about 700 kgm. on each side of the melting point. Ordinarily four points were found above the melting point and three below it, with two determinations of the equilibrium pressure, one from above and one from below, with the liquid about two thirds melted. The results were plotted on a large scale, and the change of volume calculated from the discontinuity at the melting point. The temperature was then changed and the next point found in a similar manner. Ordinarily the points were obtained with increasing pressure and temperature. During one experiment on a single substance the apparatus was left with the pressure continuously at least as high as the initial value. This might be for three or four days. The procedure in finding the point at approximately atmospheric pressure has been indicated, the temperature being varied a few degrees at a time at constant pressure, instead of the pressure being varied at constant temperature.

Corrections.—Several corrections were to be applied, but these have been so carefully described in previous papers that a mere enumeration will suffice; a correction for slight variations in temperature of the manganin coil (in the final form of apparatus there was no such correction), a correction for the distortion by pressure of the cylinder containing the moving piston, a correction for the thermal expansion of the transmitting fluid on passing from one cylinder to the other,* a correction necessary only with the first form of apparatus for slight variations of temperature of the cylinder containing the manganin coil, and finally corrections not peculiar to this particular work, such as corrections for the lack of uniformity of the bridge wire, or corrections for the thermometers, which were mercury thermometers, calibrated at the Reichsanstalt or at the Bureau des Poids et Mesures.

Accuracy.—The accuracy of the melting curves, *i. e.*, the curves showing the relation between melting temperature and pressure, was limited only by the accuracy with which pressure could be determined with the manganin coil. This was as good as .1 per cent. at the higher pressures. The coil was calibrated several times during the course of the experiment by determining with it the freezing pressure of mercury at 0°, the coil being at 35°. There was no change in the coil of so much as 0.1 per cent. during the experiment. The freezing pressure of mercury at 0° was taken as 7,640 kgm., and the relation between pressure and change of resistance was assumed to be linear. (For further particulars on this matter see Proc. Amer. Acad., vol. 47, No. 11, Dec., 1911.)

The accuracy of the values for ΔV is not so high as that for the equi-

---

* This is the most important correction, and may be as high as 6 per cent.; it was entirely overlooked by Tammann.

librium pressures, chiefly because it is seldom possible to entirely eliminate a slight rounding of the corner at the discontinuity of the curve of volume against pressure. This source of error has also been always present in all previous determinations of ΔV at atmospheric pressure. All the indications are that the special form of apparatus used here avoids this effect at atmospheric pressure more successfully than has yet been accomplished. Of course the error varies greatly with the nature of the substance. Several substances were tried and discarded because they could not be obtained sufficiently pure. Some of the substances show no perceptible rounding of the corners. The order of accuracy can be judged for each separate liquid from an examination of the curves in detail.

The general accuracy of the results is further vouched for by the fact that we have here three independent pieces of data, obtained with different pieces of apparatus at different times; the first with the original high pressure apparatus up to 7,000–10,000 kgm., the second at nearly atmospheric pressure with the low pressure apparatus, and the third with the final high pressure apparatus up to 12,000–13,000 kgm. The inconsistency between the three sets of data is not greater than the discrepancies between readings with the same apparatus.

In addition to the directly measured quantities p, t and ΔV, there are tabulated the latent heat of the change of state and the difference of internal energy between solid and liquid. The latent heat, ΔH, was computed from Clapeyron's equation,

$$\Delta H = \frac{\tau \Delta V}{\frac{d\tau}{dp}}.$$

The computation involves, therefore, the slope of the melting curve. Now the slope of an experimental curve is known with somewhat less accuracy than the points of the curve themselves. To avoid as much as possible error in finding the derivative, two independent methods were used; first the derivative was obtained directly graphically from a large scale drawing, and secondly the melting curve was approximated to by two straight lines, the difference curve drawn, the slope of the difference curve found graphically, and combined with the slope of the straight lines to give the slope of the original melting curve. The two methods agreed very well, usually better than 0.5 per cent., so that we may feel confident that there is no large error in computing the derivatives from the actual melting curves. But aside from the error usually met in finding a derivative, there is here a special source of error operative only at the low pressures. The curvature of the melting curve decreases rapidly as pressure increases, so that to find the initial curvature as accurately as the curvature at high pressures, a large number of observations would be necessary at the lowest pressures. But the form of apparatus used made it impossible to obtain points at much less than 1,200 kgm. This was due to the sticking of the piston and has been alluded to elsewhere. To avoid it, especially constructed apparatus would be necessary. As a result, the slope at atmospheric pressure of all the curves, and hence the latent heat, is much more in doubt than at any higher pressure. The agreement between the latent heat at atmospheric pressure, computed in this way, and that found by other experimenters by direct experiment, is not very good. In those cases in which reliable direct measurements of the latent heat exist, they have been accepted, and the most probable value of the initial slope computed backward from the accepted value of the latent heat. But unfortunately, the latent heat has been directly measured for only a few of the substances used here. For the other substances it must be borne in mind that the initial latent heat listed here may be subject to correction. The numerical details are given under the separate substances.

The change of internal energy differs from the latent heat only by the external work ($p\Delta V$) during change of state. This involves only quantities directly measured, so the errors in the change of energy are the same as those in the latent heat. In particular, the latent heat and the change of energy are practically the same at atmospheric pressure.

In order to avoid the troublesome work of changing units, and to permit the direct substitution of the values given here in Clapeyron's equation, the latent heat and the change of internal energy are given here in mechanical units, kgm. m. per gm. instead of the familiar gm. cal. per gm. To change kgm. m. to gm. cal. multiply by 2.3442.

Materials.—It is of the utmost importance that the materials be as pure as possible; erroneous results by other experimenters have been obtained because of this, as for example when Tammann announced two solid modifications of carbon dioxide, but later found the effect was due to impurity. The materials to be used were selected by running through a catalogue of chemicals and choosing those which were not prohibitively expensive, which it was known could be obtained fairly pure, which had freezing points within the desired range, and for which only one solid modification was known. These were then subjected to further purification, either by fractional distillation or by crystallization from the melt, or in those cases that were practicable, by both methods. The details of the purification by distillation do not require comment. The purification by crystallization was performed with more care than is perhaps usual. The substance to be purified was placed in the melted condition in a closed glass vessel, within a larger glass vessel, which dipped into a bath kept at constant temperature by a thermostat. The thermostat was then adjusted to a temperature a few tenths of a degree, or perhaps as much as 1.5° (depending on the purity of the substance) below the freezing point of the pure substance. After temperature equilibrium had been attained and the substance was in a slightly subcooled condition, it was inoculated with a minute crystal, and crystallization allowed to take place. Transfer of heat from the bath to the substance took place across an air space, and was therefore slow. Crystallization might continue in some cases for a couple of days. The remaining liquid was then drained off by inverting the glass vessel. The draining occupied several hours. During the draining the temperature of the thermostat was raised a few tenths of a degree in order to melt off more perfectly any layer of impurity clinging to the crystals. The advantages of the method are the very slow crystallization, and the fact that one can be perfectly sure that there is not enough impurity present to depress the freezing point as much as the depression artificially maintained by the thermostat.

No special analysis is necessary to show the amount of purity finally attained, because the conditions of the experiment themselves impose one of the sharpest tests that could be applied. If the substance is perfectly pure it will all freeze sharply at one temperature, but if it is impure, the impurity will remain in the liquid as crystallization progresses, becoming more and more concentrated, so that the freezing temperature will drop as freezing proceeds. Or if the freezing takes place at constant temperature, as here, the freezing pressure will increase as the liquid approaches complete solidification. This will be shown by a rounding of the upper corner (where melting begins) of the curve of volume against pressure. It has been already stated that in only a few cases was it possible to entirely get rid of the rounding, but it was never allowed to become large enough to raise doubt; if it did the liquid was discarded, or further purified. It was very seldom that the rounding was perceptible more than 200 kgm. beyond the freezing point, and the curve from which extrapolation was made was usually run 700 kgm. beyond the point.

One other effect of impurity is to greatly slow the reaction, so that it may be necessary to wait hours for equilibrium. The reason for this is evident. As the liquid crystallizes the pure substance separates, leaving an excess of impurity in the neighborhood of the freshly formed crystal. Further freezing cannot now continue until the excess of impurity has been removed by diffusion into other parts of the liquid. But at high pressures the diffusion takes place very slowly because of the greatly increased viscosity. One striking example of this was found while working on monochloracetic acid. After setting up the apparatus the acid was found to become gradually impure by attacking the steel envelope. Three points at high pressure were determined. The progressive gain of impurity was shown not only by the much greater rounding of the corners at the last reading (which was at lower pressure than the first two), but by the exasperating slowness of the reaction. The impurity of this one substance finally became so great that it was not worth while to attempt any more readings.

The slowness of the reaction furnishes, therefore, a further rough test of the purity of the substance. Thus Tammann mentions that he was troubled by the slowness of freezing of a number of his substances, while no such trouble was found here. The presumption is that Tammann's materials were impure. An example is the case of sodium. Tammann found a very slow reaction, while in the present work the reaction ran as rapidly and as cleanly as one would expect from a metal, as rapidly as for mercury, for example.

In some cases actual experiment showed that the commercial materials were pure enough. Examples are phosphorus and sodium. The details of the purification are to be found under the data for the separate liquids.

Unsuccessful attempts were made to purify acetophenone and para-xylol. Two crystallizations of acetophenone did not raise the freezing point more than 0.5°, from 19.1° to 19.6°, although the pure substance melts at 20.5°. Two distillations of para-xylol failed to give a liquid that approximated to a constant boiling point. An attempt was also made to purify acetone. This was Kahlbaum's best, "from bisulfite," and would have been judged to be perfectly pure from the constancy of the boiling point, but the freezing under about 10,000 kgm. was spaced over a wide pressure interval. Monochloracetic acid was also tried and discarded because it collected impurities from the pressure apparatus, not because it could not be sufficiently purified initially.

Depression of Freezing Point under Pressure.—One question of interest in this connection is as to the variation of the depression of the freezing point by impurity with pressure. It admits of simple thermodynamic treatment as follows.

We shall find it easy to deduce this relation by considering first the equilibrium between pure liquid and pure solid, both being at the same temperature, but the hydrostatic pressure on one being different from that on the other. Let us suppose that the liquid (1) and the solid (2) are in equilibrium under normal conditions at p and t. The temperature of both phases is now raised by Δt, and the pressure on the liquid kept at its original value. We require to find the increment of pressure (Δp) on the solid, so that the liquid at p and $t + \Delta t$ may be in equilibrium with the solid at $p + \Delta p$ and $t + \Delta t$. The relation may be found by an obvious thermodynamic cycle to be

$$\frac{\Delta t}{\Delta p} = \frac{-v_2 t}{\Delta H},$$

where ΔH is the latent heat of transformation. Δt and Δp are, therefore, of opposite sign.

We now apply this formula to determine the depression of the freezing point. Given pure (1) and (2) in equilibrium at p and t, and impure (1) in equilibrium with pure (2) at p and $t - \Delta t$. We require to find Δt. The direct contact between pure (2) and impure (1) may be separated by an intermediate step. Impure (1) at p and $t - \Delta t$ shall be in equilibrium with pure (1) at $p - \Delta p$ and $t - \Delta t$, and the pure (1) at $p - \Delta p$ and $t - \Delta t$ shall be in equilibrium with pure (2) at p and $t - \Delta t$. Under these conditions we shall evidently also have impure (1) at p and $t - \Delta t$ in equilibrium with pure (2) at p and $t - \Delta t$. The decrement of pressure is evidently the osmotic pressure of the dissolved impurity. Now the formula deduced above gives a relation between Δt_1 and Δp (see Fig. 1). We have, therefore, the two equations

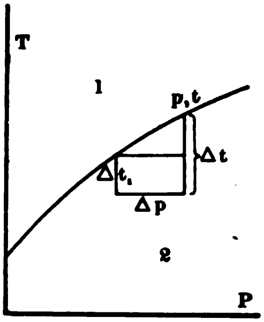


Fig. 1.
Diagram for the depression of the freezing point by impurities.

$$\frac{\Delta t_1}{\Delta p} = \frac{v_2 t}{\Delta H},$$

and

$$\Delta t_1 = \Delta t - \Delta p \frac{d\tau}{dp}.$$

Whence

$$\frac{\Delta t}{\Delta p} = \frac{v_2 t}{\Delta H} + \frac{d\tau}{dp} = \frac{v_1 t}{\Delta H},$$

and finally,

$$\Delta t = \frac{v_1 t}{\Delta H} \Delta p.$$

This gives the depression of the freezing point in terms of the osmotic pressure of the dissolved impurity. Now Δp does not change much with increasing pressure, since for impurities of slight concentration it is equal to the pressure that would be exerted by the impurity in the form of a gas occupying the same volume. ΔH changes only slightly on the melting curve, as will be shown later. v_1 decreases and t increases as pressure increases; the two partly neutralize each other. We need expect, therefore, that the depression of the freezing point due to a given quantity of dissolved impurity will not change markedly on the freezing curve, what change there is probably being in the direction of an increase.

(*To be continued in following number, p. 153.*)

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SEVENTIETH MEETING.

A JOINT meeting of the Physical Society with Section B of the American Association for the Advancement of Science was held in the physics lecture room of the Georgia School of Technology, Atlanta, Ga., December 29, 1913, to January 3, 1914. The presiding officers were Past-President E. L. Nichols (in the absence of President B. O. Peirce, of the Physical Society) and Vice-President A. D. Cole, of Section B.

The annual business meeting of the Physical Society was held Thursday forenoon, January 1, 1914. Messrs. A. Zeleny and N. E. Gilbert acted as tellers and reported the result of the mail ballot for officers for 1914.

No nominee for president having a majority of all votes cast, the Society chose Ernest Merritt president by ballot.

As Mr. Merritt had been elected Vice-President by the mail ballot, a new ballot resulted in the choice of K. E. Guthe as Vice-President.

The following officers were declared elected by the mail ballot:

Secretary: A. D. Cole.

Treasurer: J. S. Ames.

Members of the Council: D. C. Miller and G. K. Burgess.

Managing Editor: Frederick Bedell.

Members of Editorial Board: A. G. Webster, C. E. Mendenhall, H. A. Bumstead.

The secretary presented the reports of the treasurer and of the managing editor of the PHYSICAL REVIEW. These reports will be printed and mailed to all members.

It was announced that the Council had voted to continue the existing arrangement with the publishers of Science Abstracts for the year 1914.

The session of Tuesday afternoon, December 30, was in charge of Section B, and was devoted to papers of general interest as follows:

Address of the Retiring Vice-President of Section B, "The Methods of Physical Science; to what do they Apply?" A. G. WEBSTER. (Read by A. D. Cole.)

The Factors of Climatic Control. W. J. HUMPHREYS.

Isostasy and the Size and Shape of the Earth. WM. BOWIE.

On Thursday forenoon there was a joint session with Sections B and C, with this program:

Geochemical Research. **John Johnson.**

The Ternary System; Lime—Alumina—Silica. **G. A. Rankin.**

Seismology. **Otto Klotz** (Dominion Observatory, Ottawa, Canada).

The Present Status of the Magnetic Survey of the Earth. **L. A. Bauer** (presented by W. J. Humphreys).

At the other three sessions of the meeting the following papers were presented:

The Illumination-Current Relationships in Potassium Photo-electric Cells. **Herbert E. Ives.**

Range of Alpha-Particles in Air at Different Temperatures. **Alois F. Kovarik.**

Counting the Transmitted and Reflected Beta-Particles. **Alois F. Kovarik** and **L. W. McKeehan.**

An Absolute Method of Determining the Ballistic Constant of a Moving-coil Galvanometer. **Paul E. Klopsteg** (presented by Anthony Zeleny).

Contributions to the Thermodynamics of Saturated Vapors. **J. E. Siebel.**

Experimental Tests on an Artificial Cable at 700 Cycles. **H. G. Heil.**

The Energy Absorption of Condensers for High-frequency Oscillations excited by the Lepel Arc. **A. D. Cole.**

Binaural Beats and the Character of the Sound-conducting Paths between the Ears. **G. W. Stewart.**

The Mobility of Ions at Different Temperatures and Constant Gas Density. **H. A. Erikson.**

Thermo-electromotive Force produced when the Two Metals forming a Junction are not at the Same Temperature. **S. L. Brown.**

Why some Winters are Warm and others Cold in the Eastern United States. **W. J. Humphreys.**

Physical Characteristics of the Vowels. **Dayton C. Miller.**

Absorption of Beta-Rays by Gases. **Alois F. Kovarik.**

Calculation of the Size of Wire for a Damping Rectangle to Produce Critical Damping in a Moving-coil Galvanometer. **Paul E. Klopsteg** (presented by Anthony Zeleny).

A New Fuorescence Spectrum of Uranyl Chloride. **Edward L. Nichols** and **Ernest Merritt.**

Preliminary Note on Fluorescence Spectra of Aqueous Solutions of Uranyl Salts at Low Temperatures. **Edward L. Nichols** and **Ernest Merritt.**

A System of Color Standards for the Practical Measurement of Color. **H. E. Wetherill.** (By title.)

On the Thermions Produced by Platinum. **Charles Sheard.** (By title.)

Discharge Potentials across Very Short Distances. **Edna Carter.**

Adjournment Thursday noon, January 1, 1914.

A. D. Cole,
Secretary.

ON THE THERMIONS PRODUCED BY PLATINUM.[1]

BY CHARLES SHEARD.

THE results presented here are in continuation of the work reported in the PHYSICAL REVIEW for October, 1913.

1. The positive thermionic currents obtained on the *initial* heating of the wire over the range of temperature from 530–850° C. followed the Richardson law $i = AT^{\frac{1}{2}}e^{-b/T}$.

2. Upon heating the wire under positive potential until the "steady-valued" or "slow decay" current condition obtained and upon using the current values thus found in the Richardson formula, two distinct linear relations held between $\log i - \frac{1}{2} \log T$ when plotted against $1/T$, (where i = thermionic current and T = absolute temperature). The ratio of the tangents of the angles which these lines make with the temperature axis was found equal to about 0.6. The first range of values covered temperatures from about 600 to 725° C.; the second from 725 to 850° C.

3. With continued heating under positive potential it was found that the slope of the line at high temperatures gradually changed and assumed a position nearly parallel with that of the temperature-current relations obtained at the lower temperature range. This is interpreted to mean that there are two sources capable of producing ionization and is in agreement with data obtained by Richardson indicating a value of $e/m = 32$–36 for the initial period of heating and giving, under further treatment, a value of $e/m = 25$.

4. With further heating under potential a condition was reached in the lower temperature range in which the ionization currents were smaller at higher temperatures than those obtained at the preceding lower temperatures.

5. The effect of moisture upon the positive thermionic currents has been carefully investigated. At a definite temperature the positive decay with time curve was obtained; when the steady-valued current period was reached the wire was dipped in distilled water. This process was repeated seriatim some half dozen times. In each instance a very considerable increase in ionization currents was produced, the effect being the greatest in the case of the initial addition of water. This increased ionization fell away very quickly with time. Upon testing the curves thus obtained by plotting the logarithm of the difference between the actual current and the steady leak versus the time, two straight lines were obtained in each case, the slope of the line obtained from the readings during the first few minutes being greater than that of the second line representing the decay with time from the fifth minute on. In all cases the lines intersect at the time point 2.5–3.5 minutes. These and similar results, it is believed, are sufficient to show the effect of the presence of traces of *water vapor* on the initial positive ionization. It will be shown that the results of Richardson[2] as to the so-called activity induced by air and the activity

---

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, January 1, 1914.

[2] Phil. Mag., Vol. VI., 1903.

induced by hot wires at higher pressures as well as the recent work of Klemenciewicz[1] on the restoration of thermionic emission when metals are heated in various gases, can be wholly explained as due to the presence of water vapor.

6. Following the experiments with water vapor, the wire was removed and washed in nitric acid. When again tested at the same temperature as that used in the water experiments it was found that the initial current-time curve was almost identically duplicated. This and other facts point to the conclusion that the dissociation of water vapor until temperature and potential produces positive H ions and that the oxygen in turn forms oxides removable in hot nitric acid. Heating the wire without the application of potential does not give the effects referred to above.

7. With continued usage, however, the ability of the wire to produce increased ionization when cleaned in acid fell off markedly, indicating that there are present in the wire one or more substances which give thermions not due to chemical action.

8. The effect of heating the wire in hydrogen and carbon dioxid was investigated when the wire was in a condition of producing extremely small thermionic currents. Increased currents were obtained after ten minutes' heating in hydrogen which fell off to values of the order of the currents obtained before such treatment in the course of two or three minutes. The same effects in general were obtained in carbon dioxide. These effects do not point to the conclusion of Horton and others that heating in hydrogen, etc., causes a subsequent emission of the absorbed gases as ions. Rather is it to be believed that small traces of water vapor or hydrogen (due to its reducing action on the surface of the wire or to its recombination with oxygen producing water at the surface of the wire) constitute the cause of this increase.

9. The wire when initially tested, and for some time after, showed an increased positive emission after the wire had been heated for a few minutes under negative potential and at such temperatures as to cause a negative ionization current. In time, however, the wire reached a condition in which such a treatment produced no effect on the subsequent positive currents. These effects may be due to—(1) previous removal of material in the wire capable of producing ions or (2) to the inability of the surface of the wire after oxidation to further combine with oxygen, hence permitting no permanent dissociation of water vapor.

10. The wire was finally gotten into a condition such that with increase of temperature by stages of 20° from 550–900° C. the ionization currents rose to a maximum at a certain temperature within the range 600–675° C. and then fell off with increase of temperature until the higher temperature range of 825–900° C. was reached. In this latter region the current values rose with increase of temperature, but the current value at 900° C. was in most cases several times less than at 600–650° C. This maximum at lower temperatures did not, under many repetitions, appear at the same temperature but did occur within the 600–650° range. A time effect was looked for and it was found that this

---

[1] Ann. der Phys., 1911.

maximum was reached in 7–10 minutes of heating without any apparent connection with increase of temperature. The paper, when published, will present and discuss three possible explanations.

11. There are, then, apparently two general sources of thermions: (1) external, not permanent but very effective in the initial stages, and (2) internal, permanent. The first source is probably chiefly water vapor, the second consists of impurities present in the form of salts.

Ohio State University,
December 27, 1913.

THE CHARACTER OF INTERAURAL SOUND CONDUCTION INDICATED BY BINAURAL BEATS.[1]

By G. W. Stewart.

SOUND conduction of the bones of the head is well known. Experiments in sound localization with two tones of the same frequency but of different phase, presented one to each ear, have shown the importance of interaural sound conduction. Rostosky assumes a conduction with a lag due to longer path; Wilson and Myers assume in addition a change of phase of 180°. These theories do not account for the maxima of apparent intensity found when two tones differing slightly in frequency are presented one to each ear. The maxima as observed first by Rostosky and later independently by the writer occur as follows:

1. With rapid cycles of recurring equal phase, the cycles being less than one or two seconds, a maximum of apparent intensity occurs at zero phase difference, as has long been known, but with the cycle of greater length additional maxima appear at phase differences $180° - \delta$ and $180° + \delta$, the former occurring apparently in the ear having the tone of greater frequency.

2. With cycles greater than one second in length, the additional maxima increase in intensity with increasing cycle length until they appear of greater intensity than the original maximum.

The additional facts found by the writer are:

3. The quality of the tone at zero phase maximum is the same as that of the exciting tones, but the quality of the tone at the additional maxima is noticeably different, being less pure.

4. The value of δ is independent of the duration of one cycle, depending only on the frequency of the tones.

5. The values of δ with varying frequency as determined by Dr. Stiles and the writer are: with 256 d.v., 64.8°; 128 d.v., 54°, and 64 d.v., 32.4°.

6. Theoretical considerations assuming simple sound conduction and using the sum, the ratio, and the differences of intensities at the ears, and also the individual intensities, do not produce results consistent with the experimental facts.

---

[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

From a detailed consideration not outlined here, there appear the following conclusions:

1. That the causes producing the zero maximum are not those which produce the additional maxima.

2. That conduction from one ear to the other produces a resulting variation of intensity in each ear, and that the maximum and minimum occurring with rapid cycles can be accounted for if the sum of the two ear intensities be regarded as the determining factor. (The importance of this factor has already been pointed out by the writer.)

3. That the experimental values of δ given agree with the theory that the additional maxima are caused by forced vibrations, for tan δ is proportional to the frequency within experimental error. This agreement is striking and demands further investigation.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.

AN ABSOLUTE METHOD FOR DETERMINING THE BALLISTIC CONSTANT OF A MOVING-COIL GALVANOMETER.[1]

BY PAUL E. KLOPSTEG.

FROM the equation for damped periodic motion of a galvanometer coil, expressing the condition for the discharge of a quantity Q of electricity through the coil at rest, the value of the first maximum displacement is found by the usual method of differentiation. This value represents the ballistic throw of the slightly damped galvanometer. From the expression so found the equation for the ballistic constant is obtained. In the transformation a substitution is made which is based upon the equation for the damped coil method of measuring magnetic fields. The resulting expression is

$$K_1 = \pi \sqrt{\frac{I_0 \epsilon^{\lambda}}{10^7 R T_0 (\Lambda - \lambda)}},$$

this value of K_1 being equal to the number of coulombs per radian. I_0 is the moment of inertia of the coil, T_0 its period and λ its logarithmic decrement on open circuit, and Λ its logarithmic decrement with R ohms in the galvanometer circuit.

When the value of λ is about 2.5 per cent. of π, the value of K_1 is too large by 0.1 per cent., the difference increasing as λ grows larger. The following more exact formula may then be used:

$$K_2 = \epsilon^{\frac{\lambda}{\pi} \tan^{-1} \frac{\pi}{\lambda}} \sqrt{\frac{I_0}{10^7 R T_0} \frac{\pi^2 - \lambda^2}{\Lambda - \lambda}}.$$

An explanation is offered for the frequently observed difference between the

---

[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

values of the ballistic constant in a given instrument with a strip or ribbon upper suspension, on the two sides, *A* and *B*, of the scale. This difference is due principally to a certain amount of torsion in the lower suspension which necessitates a corresponding amount of "counter torsion" in the upper suspension in order to keep the coil in the position of the null reading. The effect of torsion in a strip suspension is to shorten it, the case resembling that of a bifilar suspension for angles less than 180°. For a throw in one direction, say *A*, the coil must be raised; in the opposite direction the turning moment of the force of gravity acts in the same direction as the electromagnetic torque. Consequently with a given quantity of electricity the throw in the direction *B* is greater than in the direction *A*.

The same "bifilar effect" introduces an error into the determination of I_0 of a coil by the comparison of vibrations method when a strip is used as the suspension fiber, unless the masses of the coil and of the comparison disk, as well as their amplitudes, are the same. The error due to this effect becomes negligible if a wire of circular cross-section is used as the suspension fiber.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

RANGE OF α-PARTICLES IN AIR AT DIFFERENT TEMPERATURES.[1]

BY ALOIS F. KOVARIK.

THE range of α-particles in any substance depends on the nature and the number of atoms in the path. And we find, therefore, that the range varies inversely with the pressure of a gas; similarly, we should expect that the range varies inversely with absolute temperature. This has been tacitly assumed to be true. In some experiments on the ionization by the α-particles I have found it convenient to test this experimentally between 90° and 362° absolute. The apparatus and method were after Geiger and Nuttall. Bulbs used as ionization vessels were of two sizes, 5 cm. and 9 cm. radius, respectively. The bulbs were metallic. The temperature was obtained by means of a thermocouple placed near the center of the bulb. The α-ray substance used was a polonium plate of about 4 mm. diameter. The lowest temperature was obtained by immersing the bulb in liquid air and the highest temperature by immersing the bulb in boiling water. Intermediate temperatures were at room temperature and the temperature obtained when the apparatus was packed in ice. The pressure-ionization curves gave sharp breaks for the ordinary temperatures, but at the low temperature the change was not as abrupt, a rounded bend being obtained. This was no doubt due to some convection currents (which must have existed as the neck of the bulb protruded from the liquid air). However, the pressure at which the α-particle just reached the walls of the bulb could be fairly accurately determined from the

---

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, December 30, 1913.

straight lines below and above this pressure. The following table shows the experiments tried and the results obtained:

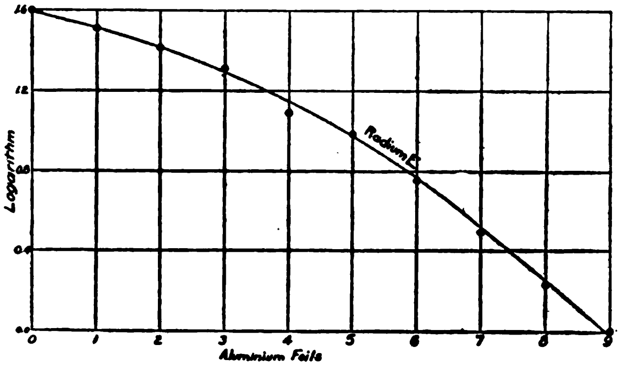
Temp. Absolute.	Size of Ionization Vessel.	Range / Abs. Temp.
90.0	5 cm.	0.0125
273.7	5 cm.	.0130
297.3	5 cm.	.0130
298.0	5 cm.	.0129
298.0	9 cm.	.0129
300.0	9 cm.	.0129
362.0	9 cm.	.0131

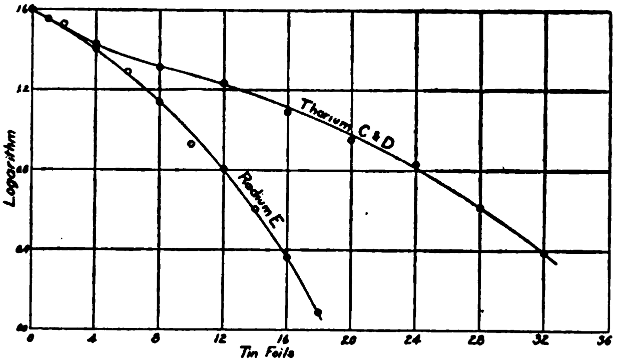
Physical Laboratory,
University of Minnesota.

COUNTING THE TRANSMITTED AND REFLECTED β-PARTICLES.[1]

By Alois F. Kovarik and Louis W. McKeehan.

RECENTLY Dr. H. Geiger announced a simple method for counting α- and β-particles.[2] This method depends on the point discharge set up when a few ions are produced near a point at a potential close to that required for a continuous discharge.





---

[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

[2] Verh. d. Deut. Phys. Ges., XV., p. 534, 1913.

Measurements, by this method, on the number of β-particles transmitted and reflected by thin foils of aluminum and of tin were made, using for the source radium E and thorium active deposit. The results show that the number of β-particles transmitted decreases more rapidly than if the exponential law held as it does hold in measurements of absorption by the ionization method. In the reflection experiments, the ratio of the number of reflected β-particles to the number incident was found smaller than the ratio of the ionization of the reflected rays to the ionization of the incident rays, as found by Schmidt and one of us.[1] In both classes of experiments, the absorbing or reflecting material was close to the source of rays and at some distance from the counting chamber.

The figure shows that the logarithmic curves deviate from the straight lines to be expected from the exponential law. The increase of ionizing power with the decrease of velocity of the β-particles, due to passage through matter, doubtless explains the effects observed.

The comparatively small number of β-particles counted in these experiments (60,000) makes it undesirable at present to state the results quantitatively.

Discharges from the point due to γ-radiation were small in number under the conditions of the experiments, but were always measured and corrected for.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

ABSORPTION OF β-PARTICLES BY GASES.[2]

BY ALOIS F. KOVARIK.

THE preliminary work on the absorption of β-particles, namely from radium D and radium E, was reported at a previous meeting of this society. The principle of the method used in the investigation is to allow the particles to pass through a definite distance in the gas before entering a shallow ionization chamber (2 or 3 mm. deep). By increasing the pressure of the gas, the absorption becomes greater, but the ionization in the ionization chamber also becomes greater. If the pressure is within twenty atmospheres the ionization is proportional to the pressure. All measurements were made within this pressure. Consequently, the ionization reading is reduced to what it would be at one atmosphere. The mean path of the β-particles is found graphically. By changing the pressure the absorption curve is obtained. The values obtained for the coefficient of absorption for different distances of the active material from the ionization chamber were concordant when the metallic pressure apparatus was lined with thick paper, thus minimizing the reflected radiation effect. This also shows that the graphical method of finding the mean path of the β-particles is feasible. The measuring instrument was C. T.

---

[1] Schmidt, Ann. d. Phys., XXIII., 671, 1907; Kovarik, Phil. Mag., XX., 849, 1910.

[2] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

R. Wilson's inclined electroscope in some experiments, ordinary Dolezalek electrometer and Erikson's modification of Dolezalek's electrometer. The rate method and Townsend's null method were both used in taking readings, the null method being found the more satisfactory.

The radiations examined are those from radium D, radium E, uranium X, actinium active deposit, thorium active deposit. The soft radiation was studied by obtaining the differential curve and it was found rather difficult to obtain accurate results.

The results are given in the table below for the two gases used, air and carbon dioxide.

	Coefficient of Absorption in—	
Substance.	Air.	Carbon Dioxide.
Radium E	0.0151 cm.	0.0298 cm.
Radium D (hard)	0.086	0.157
Radium D (soft)	0.64	1.48
Uranium X (hard)	0.0063	0.0116
Uranium X (soft)	0.12	0.24
Actinium Active Deposit (hard)	0.0091	0.0175
Actinium Active (Deposit (soft)	0.35	
Thorium Active Deposit (hard)	0.00683	0.01293
Thorium Active Deposit (soft)	0.09	0.14

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

THE MOBILITY OF IONS AT DIFFERENT TEMPERATURES AND CONSTANT GAS DENSITY.[1]

BY HENRY A. ERIKSON.

THE mobility of ions at different temperatures and at constant pressure was determined by Kovarik and by Phillips. The agreement in their results is quite close. The writer has felt that a determination of the mobility at constant gas density ought, however, to be made as the conditions to which the ions are subject at the lower temperatures at least are not necessarily the same in this case as in the case of constant pressure.

The α rays from polonium were used as the ionizing agent. The ions were drawn towards a wire grating through which some of them passed and became subject to an alternating field. The time required to charge the electrometer to a given potential was measured. The reciprocal of this time, *i. e.*, the current is proportional to the frequency. By using various values for the frequency and plotting, the frequency (n) necessary to give no current is obtained and the mobility calculated from the relation

$$k = \frac{4d^2n}{v},$$

where d is the distance from the grating to the plate connected to the electrometer and v the difference of potential.

---

[1] Abstract of a paper presented at Atlanta meeting of Physical Society, December, 1914.

The vessel was air tight and was immersed in CO_2 snow and liquid air during the measurement at the two lowest temperatures. The results obtained thus far are as follows in centimeters per gradient of one volt. The density being that of air at 0° C. and 76 cm. pressure.

Temp. °C.	k_+	k_-
20	1.35	1.89
− 64	1.34	1.82
−180	1.20	1.24

Physical Laboratory,
University of Minnesota,
December 22, 1913.

Second Series. *March, 1914* *Vol. III., No. 3*

THE

PHYSICAL REVIEW.

CHANGE OF PHASE UNDER PRESSURE.[1]

I. The Phase Diagram of Eleven Substances with Especial Reference to the Melting Curve.

By P. W. Bridgman.

Details of Experiment and Computations.

The detailed presentation of data follows. Besides giving the data actually found in this present investigation (which in most cases are shown with sufficient accuracy by the points on the diagrams), the attempt has been made to collect all previous data bearing on the point, and to give some discussion of the most probable values. This would not be necessary if it were the only object of this paper to find the most probable course of the melting curve.

In addition to numerical data, any details of manipulation or of computation peculiar to the individual substances are given; in particular the extent of the region through which search was made for other solid forms.

Potassium.—The potassium was obtained from Eimer and Amend. The first sample used was very carefully purified by the following method. The commercial lumps were placed under gasolene in a glass receiver, the gasolene removed with an air pump, and the potassium melted and run into a connecting vessel. This connecting vessel was constructed so as to form part of a still, from which the potassium was distilled at high vacuum into a third vessel. The third vessel was then sealed off from the still and placed in the thermostat, where about two thirds of the potassium was allowed to crystallize slowly. The liquid metal was then drained off and the pure crystals used for the first run. But subsequent work showed all these precautions to be unnecessary; the commercial metal is pure enough if the scum of oxide is removed by the first of the processes described above.

---

[1] Continued from page 141.

Three sets of measurements were made; one with each of the three pieces of apparatus. The first set comprises observations to 7,800 kgm. and 150°, the second two observations at atmospheric pressure, and the third five observations between 7,400 kgm. and 12,000 kgm. The direct experimental results are shown in Fig. 2 and the computed values of the latent heat and the change of internal energy in Fig. 3. The numerical values of these quantities are given in Table I.

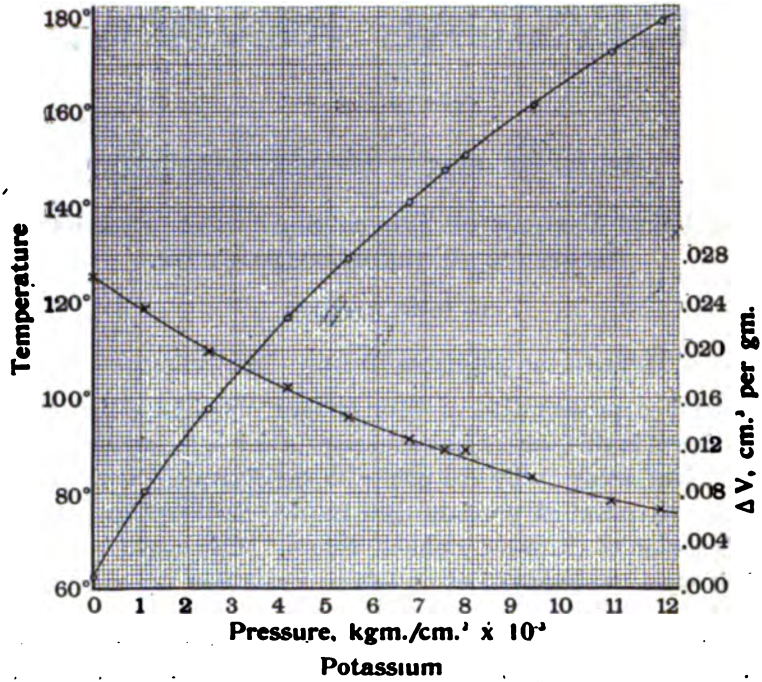


Fig. 2.

Potassium. Freezing curve and the change of volume curve. The observed freezing temperatures are shown by circles, and the observed changes of volume by crosses.

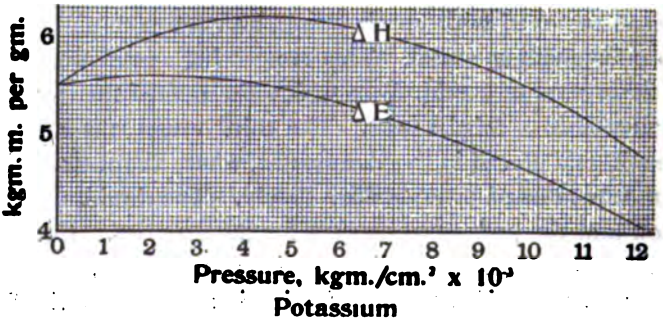


Fig. 3.

Potassium. The computed values for the change of internal energy and the latent heat when the solid melts to the liquid.

Table I.

Potassium.

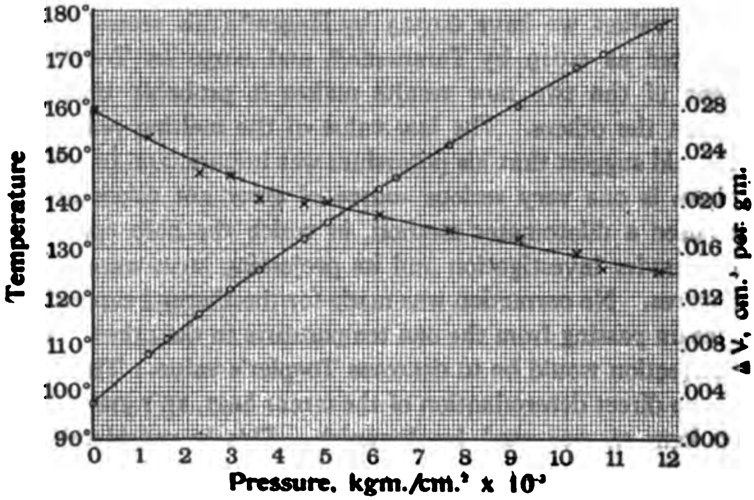
Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	62°.5	0.02680	5.51	5.51
1,000	78 .7	2368	5.81	5.58
2,000	92 .4	2105	6.02	5.60
3,000	104 .7	1877	6.15	5.59
4,000	115 .8	1676	6.22	5.54
5,000	126 .0	1504	6.21	5.44
6,000	135 .4	1347	6.12	5.31
7,000	144 .1	1205	6.00	5.15
8,000	152 .5	1073	5.85	4.98
9,000	160 .1	950	5.67	4.80
10,000	167 .0	838	5.43	4.58
11,000	173 .6	738	5.16	4.34
12,000	179 .6	642	4.83	4.09

These results may first be compared with others at atmospheric pressure. For the freezing point we have: 62.1° by Hagen[19], 62.5° by Holt and Sims[20], and 62.5° by Kurnakow and Puschin[21]. The two present experiments at low pressures gave by an extrapolation 63.3° and 62.8°. As already stated this method does not give accurate results, but the high value is at least evidence of the purity of the metal. The two measurements of the change of volume at atmospheric pressure gave 0.0266 and 0.0262 cm.^{3} per gm. This is considerably lower than the only other values we have 0.0313 by Hagen[19] (this seems to be incorrectly quoted as 0.029 by Tammann[22], and 0.030 by Toepler[23]. The agreement of the two new results makes it probable that they are better than the others. The low value of the melting point given by Hagen would suggest that his potassium was impure, and in all Toepler's work there is one very serious source of error not taken account of. Toepler used a dilatometer method, in which the bulb containing the substance under investigation and its projecting stem were at different temperatures. No correction was made for the thermal expansion of the substance on passing from the one temperature to the other. The effect of the correction would be to decrease Toepler's value. There seems to be only one direct determination of the latent heat, 15.7 gm. cal. per gm. (or 7.00 kgm. m. per gm.) by Joannis[24]. This is considerably higher than the value that was computed from the present data (5.51 kgm. m.), but since the initial slope admits of less adjustment here than for many of the other substances, no attempt was made to bring the two values into agreement. The presumptive error in latent heat measurements is so great that 7.00 could not be accepted without corroboration in any event.

The results at high pressure differ markedly from those of Tammann[25], whose specimen must have been very impure, as shown by its low freezing point, 59.5°, and very slow freezing. Tammann says that he found it particularly difficult to obtain sharp settings with this substance, and had to modify somewhat his usual method. Tammann's results run to only 3,000 kgm. At this pressure he finds an equilibrium temperature nearly 8° lower than that found here. Tammann predicts from his data that a maximum melting point will be found at 10,000 kgm. and 130°. Both of these values are considerably exceeded here, with no indication whatever of a maximum.

Tammann's results must also appear low because of error in his pressure measurement. That this error may be considerable is shown by the fact that he has in his recent work[26] used a gauge giving results at 2,000 kgm., about 100 kgm. lower than the gauge of his previous work. Tammann apparently regards the new gauge as the more reliable of the two. It is unfortunate that he himself had no direct means of calibrating these gauges, but had to rely on the word of the manufacturer.

In the search for other solid modifications, pressure was raised to 12,000 kgm. at room temperature, and to 12,500 kgm. at 142°, but none was found. A comparison of the curves for the change of volume and the latent heat with those for other liquids shows that the behavior of potassium is a little unusual. The change of volume has become an unusually small fraction of its initial value, and the latent heat decreases



Sodium

Fig. 4.

Sodium. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

at the high pressures more than is normal. Both of these considerations would seem to suggest that a new modification of the solid may be at hand.

Sodium.—The material was obtained from Eimer and Amend. That used in the first set of experiments was carefully purified by distilling in vacuo, but this precaution proved unnecessary, and in subsequent work the commercial material, freshly cut under oil so as to avoid all oxide, proved entirely satisfactory. Three sets of measurements were made. The first was with the original apparatus up to 6,400 kgm. This series was terminated by an explosion. The second set comprised two measurements at low pressure, and the third nine measurements with the final apparatus over the entire range up to 12,000 kgm. The experimental results are shown in Fig. 4 and the computed latent heat and the change of internal energy in Fig. 5. The numerical values are given in Table II.

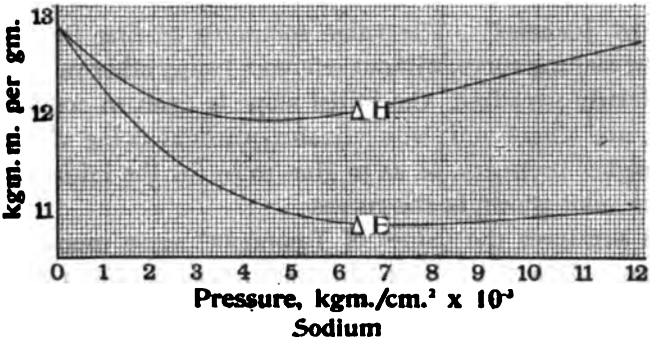


Fig. 5.

Sodium. The computed values for the change of internal energy and the latent heat when the liquid freezes to the solid.

TABLE II.

Sodium.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	97°.6	0.02787	12.90	12.90
1,000	105 .9	2555	12.46	12.22
2,000	114 .2	2362	12.16	11.70
3,000	121 .9	2203	12.00	11.33
4,000	129 .1	2072	11.93	11.08
5,000	135 .8	1968	11.94	10.93
6,000	142 .5	1873	11.99	10.85
7,000	148 .9	1790	12.10	10.83
8,000	154 .8	1711	12.22	10.85
9,000	161 .0	1634	12.35	10.88
10,000	166 .7	1556	12.48	10.92
11,000	172 .2	1476	12.60	10.96
12,000	177 .2	1398	12.72	11.00

There are the following data for comparison at atmospheric pressure. For the melting point, 92.0° (evidently a misprint) by Holt and Sims[20], 96.7° by Hagen[19], 97.5° by Kurnakow and Puschin[21], and 97.8° by Tammann[27], against the values 97.62° and 97.63° found here. This evidence makes still further probable the high purity of the sodium used here. For the change of volume we have 0.0264 cm.^{3} per mm. by Toepler[22], and 0.0256 by Hagen[19]. But here again, the low value of Hagen's melting point makes impurity probable in his specimen, and the error already mentioned runs through all Toepler's work. In view of this uncertainty two measurements were made at 60 kg., giving by extrapolation 0.02785 and 0.02789. The agreement of these two values is very good, but is no better than would be expected from the self-consistency of the two individual experiments. There is only one value for the latent heat at atmospheric pressure, 31.7 gm. cal. per gm. (13.53 kgm. m.) by Joannis.[24] The value computed at first from the initial slope of the melting curve, without reference to any other value, was 12.00. But as already explained, the initial slope is open to considerable uncertainty, and therefore it was adjusted, without doing violence to the slope at higher pressures, so as to give 12.90 for the initial latent heat. This is the value shown in the curves.

At high pressures the values of Tammann[28] agree much better with the present values than did those for potassium. At 3,000 kgm. his melting temperature is about 2° below that found here; this is to be explained in part by error in his high pressure measurement. Tammann also gives very rough values for ΔV, with a probable error of 20 per cent., according to his own estimation. Within this limit his values agree with those found here. But Tammann makes a rather daring linear extrapolation from these rough values for ΔV, and hints at a maximum melting point at 8,000 kgm. These data show no evidence whatever of such a point up to 12,000 kgm.

At 40° pressure was raised to 12,000 kgm. and at 170° to 13,000 kgm. but no new solid modification was found.

Carbon Dioxide.—The carbon dioxide was obtained from one of the commercial drums used to supply soda fountains. It was collected in the well-known way in the form of snow by placing a heavy bag over the open valve. The condensation to the solid in this way from the compressed gas acts as a further purifying process, and the carbon dioxide used gave sharper freezing curves than any of the organic substances, almost as sharp as a metal like mercury. A special form of bulb was necessary in placing the carbon dioxide in the apparatus. It is shown in Fig. 6. In general appearance it is much like the bulbs used for other substances except that it is much heavier. The problem was to provide a means of retaining the carbon dioxide in the bulb initially at considerable pressure. This was accomplished as follows. The lower part of the stem was closed by a lead cone *A*, covered with a disc of steel *B*. The cone was driven with a hammer against the conical seat so as to be gas-tight. The bulb was then filled by putting in the snow at the open end, and tamping it into a solid mass with a steel rod. The cap *D* was then screwed into place. This cap was made tight by a ring of solder at *C*, which was forced tightly into all the crevices. When the filling was complete, the entire bulb was of course at the temperature of solid carbon dioxide at atmospheric pressure, − 79°. As the bulb warmed to room temperature, the carbon dioxide liquefied and exerted a pressure, which under the conditions probably rose to 500 kgm. There was at first a slight leak of gaseous carbon dioxide, but this was soon stopped by expansion of the solder gasket. The quantity of carbon dioxide was now determined by weighing the steel bulb. It was about 7.5 gm. The stem of the bulb was then screwed into the mercury cup, *E*, and then placed in the pressure cylinder. Now when pressure in excess of the internal pressure was applied to the exterior of the bulb, the lead cone was forced into the bulb, and perhaps dissolved by the mercury. The rest of the experiment was exactly the same as for other substances. Of course after the lead cone was once dislodged, the pressure could not be allowed to fall below the initial value of about 500 kgm., but in this form of apparatus the friction of the moving piston automatically provided for this.

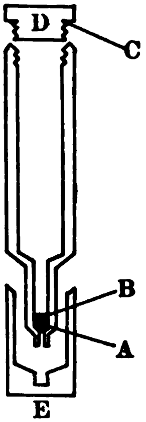


Fig. 6.

The receptacle for containing the carbon dioxide.

In filling the bulb, some care was necessary to prevent condensation of moisture from the air onto the carbon dioxide. This was prevented by placing the closed bulb in a vessel surrounded by solid carbon dioxide, until it came to temperature. The cap was then removed and it was filled from a large funnel fitting the bulb closely. Only the carbon dioxide in the lower part of the funnel passed into the bulb, and there was no chance for condensation on the lower part of the carbon dioxide, since it was protected by the layers above from direct contact with the air.

Only one set of observations was made on carbon dioxide, with the high pressure apparatus, from 3,400 to 12,000 kgm. The results were perfectly regular. It would not have been possible to reach temperatures much below zero without considerable trouble, or even redesigning the apparatus. Since the evidence given by this substance on the main question at issue is perfectly unmistakable, the trouble of reaching lower temperatures did not seem worth while. The experimental results are shown in Fig. 7 and the computed results in Fig. 8. The numerical values are given in Table III.

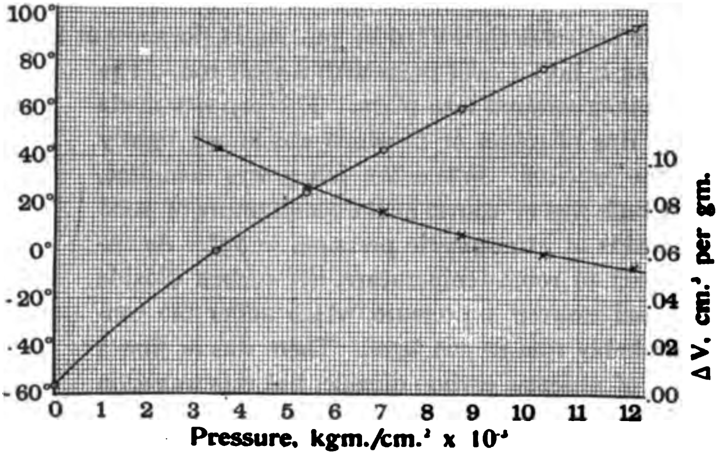


Fig. 7.

Carbon Dioxide. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

There are no results for comparison at low pressures, except a determination of the triple point at 5.2 kgm. and − 56.7° by Villard and Jarry.[29] This value has been used in determining the probable course

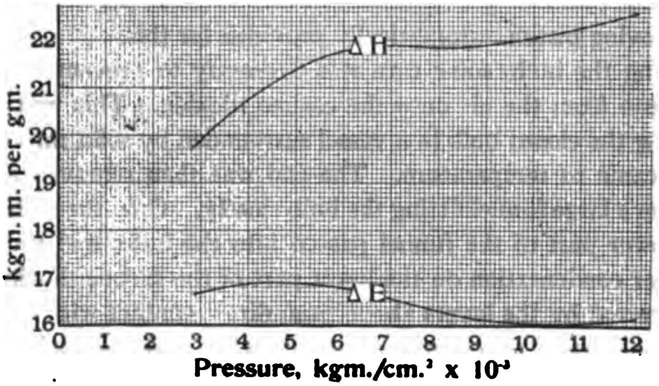


Fig. 8.

Carbon Dioxide. The computed values for the change of internal energy and the latent heat when the solid melts to the liquid.

of the curve below 0°. There are no values at present known for the latent heat or the change of volume at atmospheric pressure, and an extrapolation from the values found here would be too daring. All the indications are, however, that the change of volume at the pressure of the triple point will be found to be unusually high.

Table III.

Carbon Dioxide.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	−56°.6			
1,000	−37 .3			
2,000	−20 .5			
3,000	− 5 .5	.1071	19.92	16.68
4,000	8 .5	.0979	20.77	16.88
5,000	21 .4	896	21.39	16.89
6,000	33 .1	822	21.77	16.79
7,000	44 .2	755	21.90	16.55
8,000	55 .2	697	21.84	16.30
9,000	65 .8	644	21.90	16.10
10,000	75 .4	602	22.06	16.03
11,000	84 .6	564	22.28	16.04
12,000	93 .5	531	22.54	16.12

Comparison with the results of Tammann at high pressures is of little use, because Tammann had no adequate means for keeping the carbon dioxide pure. In his first experiment, described in "Kristallieren und Schmelzen",[30] a solid cylinder of carbon dioxide was wrapped in a piece of parchment paper, and placed directly, with no other protection, in the mixture of glycerine and water serving to transmit pressure. The fact that after release of pressure the paper was found not wet by the glycerine was taken as evidence that there was no contamination of the carbon dioxide. With this apparatus Tammann found irregularities which he accepted as evidence of the existence of another modification of the solid, and carbon dioxide was accordingly listed by him among the polymorphic substances. Later, however, because a recently developed theory of Tammann's indicated that there should be only one solid modification, he repeated his experiment,[31] and came to the conclusion that there was only one solid modification, and that the effects which he had previously explained by two modifications were in reality due to dissolved water or glycerine. His new data are not at all self-consistent, and he represents them within the limits of error between 2,000 and 4,000 kgm. by a straight line. This gives a lower melting point at 2,000 than that found here, and a higher one at 4,000. Tammann did not measure ΔV.

No evidence whatever was found here of the existence of a second solid phase. Search for such a modification was made at 25° to 12,000 kgm. and at 67° to 12,600 kgm.

It is interesting to note in passing that the freezing temperature at pressures above 6,000 kgm. is higher than 31°, that is, higher than the critical temperature between liquid and vapor. It is possible, therefore, by the application of pressure alone to change a gas directly into a crystalline solid. This is the second case for which this has been realized, Tammann[32] having previously shown that such is the case for phosphonium chloride at pressures above 75 kgm.

Chloroform.—This was obtained from Eimer and Amend and purified by fractional distillation just before using. Only one distillation was necessary. The purity was sufficient, as shown by the sharp freezing curve.

Two sets of measurements were made on chloroform. The first set was with the form of high pressure apparatus made entirely of one piece. Three points were obtained with this before the flaw developed that made it necessary to discard the apparatus. The second set was made with the modified high pressure apparatus with connecting tube, and comprises six points between 0° and 107.7°. The quantity of chloroform used was about 25 gm. The experimental results are shown in Fig. 9

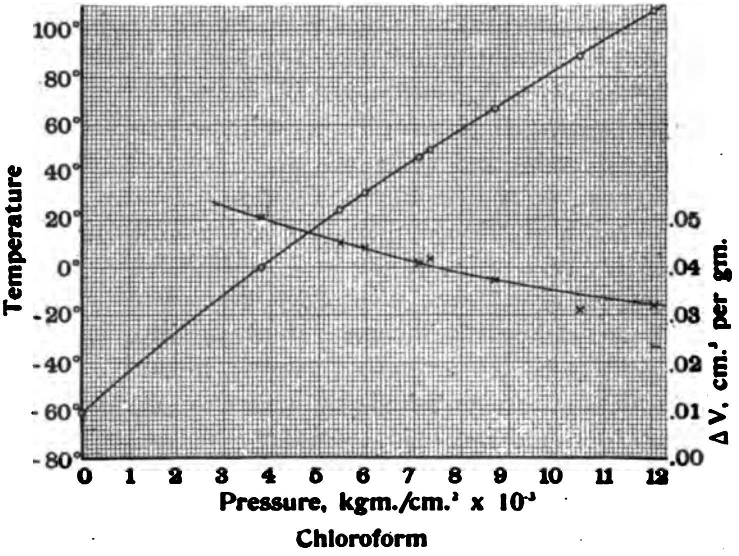
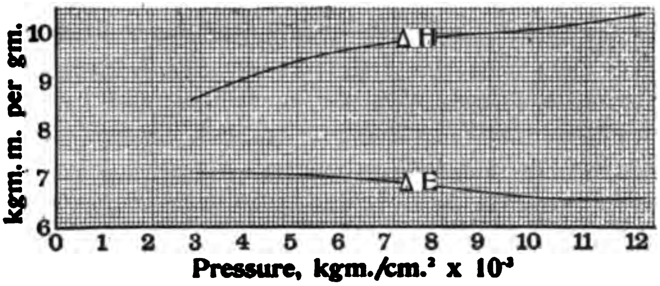


Fig. 9.

Chloroform. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

and the computed values of latent heat and change of volume in Fig. 10. The numerical values are shown in Table IV.



Chloroform

Fig. 10.

Chloroform. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

Table IV.

Chloroform.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	−61°.0	....	....	....
1,000	−45 .7	....	....	....
2,000	−28 .3	....	....	....
3,000	−12 .1	0.0530	8.70	7.11
4,000	3 .4	498	9.10	7.10
5,000	18 .2	467	9.43	7.08
6,000	32 .4	438	9.65	7.01
7,000	45 .6	412	9.81	6.93
8,000	58 .6	389	9.93	6.82
9,000	71 .3	368	10.00	6.70
10,000	83 .7	350	10.08	6.60
11,000	96 .1	334	10.20	6.56
12,000	107 .9	321	10.35	6.59

It had already been shown in another paper that chloroform could be solidified by pressure,[33] and two rough values for the solidifying pressure at 40° and 80° have already been given, which agree rather well with those found here. These two instances, however, seem to be the only previous record we have of the freezing of chloroform under pressure, so there are no other results for comparison at high pressures.

As in the case of carbon dioxide, it was not feasible to make observations below 0°. The freezing of the mercury seal, apart from any other consideration, would demand an essentially different apparatus for readings much below 0°. Over the range investigated, however, the results are just as significant in their bearing on the main question as were the results for carbon dioxide.

There are very few observations on chloroform at atmospheric pressure. For the melting point Beilstein's Handbuch gives − 63.2° and Niescher[34] − 61°. The latter has been accepted for use here as more probably accurate, because higher. For the latent heat at atmospheric pressure we have only the value 19.2 gm. cal. per gm. (8.19 kgm. m.) by Niescher,[34] obtained by indirect means. An examination of the values found here for pressures above 3,000 kgm. shows that they may be extrapolated without great violence to Niescher's value at atmospheric pressure.

Pressure was pushed to 12,000 at 25° and to nearly 13,000 kgm. at 107° in the search for another solid modification, but none was found. Search to 12,000 at a temperature much lower than 25° was not feasible because of the freezing of the mercury. It might be expected by analogy with CCl_4, that chloroform, $CHCl_3$, a substance of much the same chemical constitution, would also show several modifications. It may still be that such is the case, for a glance at the melting curve will show that the explored region is after all comparatively restricted, and that there is room in the unexplored region for several solid modifications of much the same relationship to each other as the modifications of CCl_4. This possibility is still further increased by the rather large subcooling of 2,000–3,000 kgm. that chloroform may support, so that the domain of a new form may have been actually entered, but not far enough to compel its appearance.

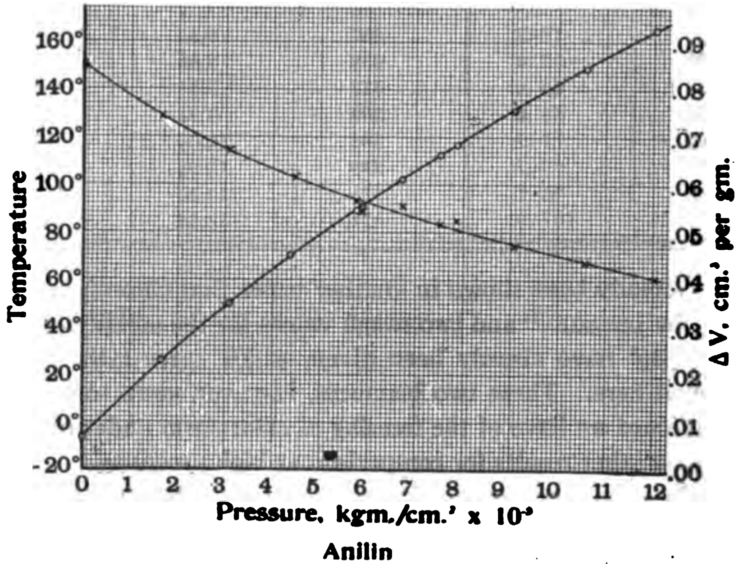


Fig. 11.

Anilin. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

Anilin.—This substance, Kahlbaum's purest, obtained from Eimer and Amend, was purified by distilling, then by crystallization, and then again by a second distillation immediately before making the readings. Measurements on this were made in three series: the first at six temperatures with the first apparatus, the second at approximately atmospheric pressure with the low pressure apparatus, and the third at five pressures up to 12,000 kgm. with the final high pressure apparatus. About 15 gm. of anilin were used. The experimental results are shown in Fig. 11, and the computed latent heat and change of internal energy in Fig. 12. The numerical values are shown in Table V.

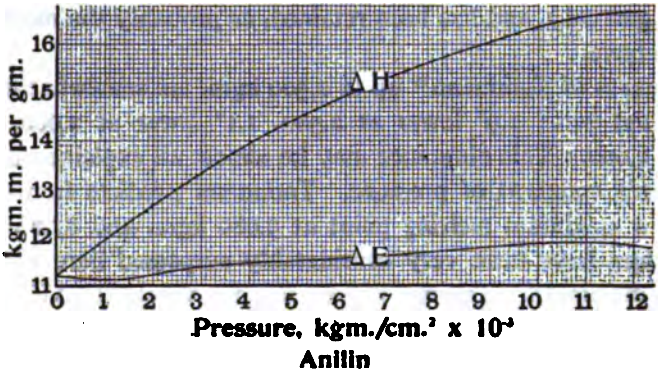


Fig. 12.

Anilin. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

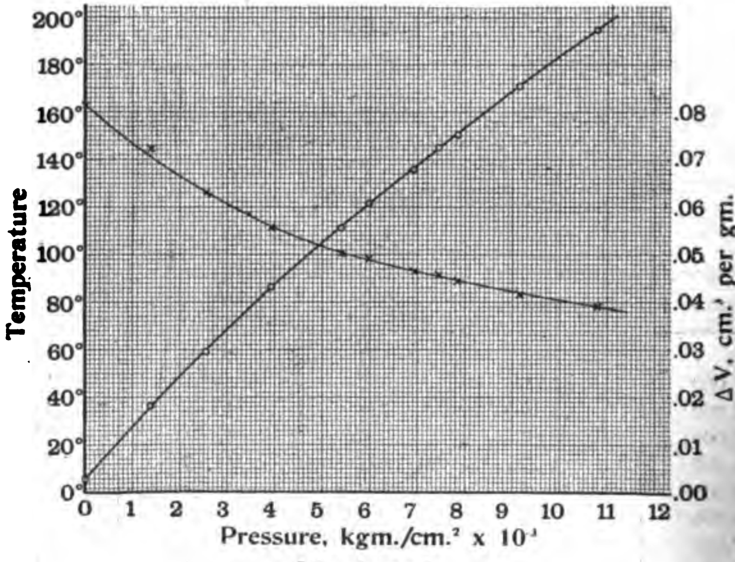
TABLE V.

Anilin.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	− 6°.4	0.0854	11.20	11.20
1,000	13 .1	784	11.94	11.12
2,000	31 .6	724	12.66	11.21
3,000	48 .7	673	13.33	11.38
4,000	64 .5	631	13.95	11.45
5,000	79 .0	594	14.48	11.50
6,000	93 .2	561	14.93	11.55
7,000	106 .5	530	15.36	11.62
8,000	119 .1	502	15.73	11.70
9,000	131 .5	476	16.06	11.80
10,000	143 .2	451	16.38	11.87
11,000	154 .7	427	16.60	11.90
12,000	165 .3	405	16.69	11.83

There are only a few results at atmospheric pressure for comparison. For the melting temperature we have − 8.0° by Lucius,[35] − 6.1° by Tammann,[36] − 6.0° in Beilstein's Handbuch, and − 6.45° found here by an extrapolation over about 1.5°. There is only one determination of the latent heat, 20.9 gm. cal. per gm. (8.91 kgm. m. per gm.) by de Forcrand.[37] But the author himself recognizes that the experiment on which this value was founded is probably in error, as is shown by the fact that a specific heat for the solid was found greater than that for the liquid. De Forcrand, from apparently slightly justified theoretical grounds, prefers to replace the experimental value 20.9 by 39.9, rather a large change. The value found here from the initial slope is 11.20. kgm. m. (26.4 gm. cal.), and has been retained, as probably the most accurate value we have.

The results of Tammann[38] up to 2,500 kgm. are somewhat lower than those found here; 1.9° lower at 2,500, 1.1° lower at 2,000, and 0.1° lower at 1,000. This difference may be almost all explained by error in Tammann's standard of pressure. Tammann predicts from his curve to 2,500 a maximum melting point at 9,080 kgm. and 87.2°. Both of these values have been very considerably surpassed here without any sign of a maximum. Tammann does not give values for ΔV.



Nitrobenzol

Fig. 13.

Nitrobenzol. The freezing curve and the change of volume curve. The o freezing temperatures are shown by the circles, and the observed changes of volum crosses.

In the search for another solid modification the pressure was raised to 12,000 kgm. at 25° without result.

Nitrobenzol.—This was Kahlbaum's purest, further purified by fractional distillation, crystallization, and redistillation immediately before using. Three sets of observations were made; the first set comprises six observations with the first apparatus to 7,840 kgm., the second a single observation at approximately atmospheric pressure, and the third four observations with the high pressure apparatus to 10,780 kgm. About 17 gm. of nitrobenzol were used. The experimental results are shown in Fig. 13, and the computed values of latent heat and change of volume in Fig. 14. The numerical values are shown in Table VI.

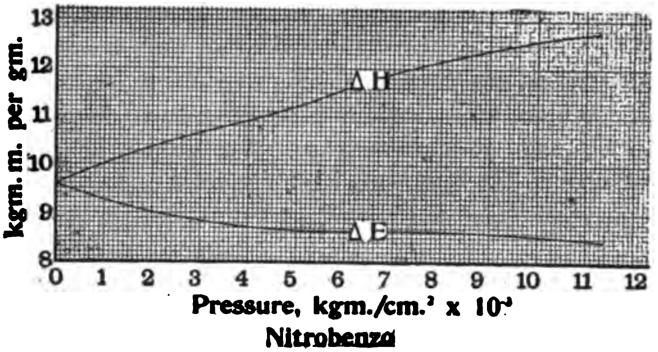


Fig. 14.

Nitrobenzol. The computed values for the latent hent and the change of internal energy when the solid melts to the liquid.

TABLE VI.

Nitrobenzol.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	5°.6	0.08136	9.60	9.60
1,000	27 .2	7326	10.00	9.26
2,000	48 .1	6639	10.36	9.01
3,000	68 .3	6052	10.66	8.84
4,000	87 .6	5552	10.92	8.71
5,000	105 .5	5172	11.21	8.64
6,000	122 .3	4885	11.58	8.63
7,000	138 .1	4641	11.91	8.64
8,000	153 .8	4415	12.16	8.62
9,000	169 .3	4210	12.39	8.60
10,000	184 .5	4028	12.59	8.53
11,000	198 .6	3864	12.73	8.47

There are a number of values for comparison at atmospheric pressure; For the melting point there is 5.82° by Meyer[39], and 5.67°. by Tammann[40]. The directly determined freezing point of the nitrobenzol used in this experiment was 5.67°. For the latent heat we have 30.2 gm. cal. per gm. by de Forcrand[37] (this is certainly greatly in error), 22.30 by Pettersson and Widman[41], and 22.46 by Meyer[39]. The corresponding values in the kgm. m. units of this paper are 12.89; 9.51 and 9.58. The value computed from the present data without any regard to the above values was 10.14. But since, as already explained, the initial slope, and hence the initial latent heat, is open to considerable uncertainty, the slope was corrected so as to give 9.60 for the initial latent heat, which is the value shown in the curves. For the change of volume on freezing there is one value by Meyer[39], 0.0808 cm.^{3} per gm., against 0.0814 found above. The agreement is better than usual.

Tammann's[42] results at higher pressures run a little low, as we have always found them, the greatest discrepancy being between 2,000 and 3,000 kgm. At 3,000 his curve is 2.0° lower than that given here, at 2,000 it is 0.2° lower, and at 1,000, 0.9° higher. Tammann predicts a maximum melting point at 10,100 kgm. and 124°. The curve has been carried in this work to 11,000 kgm. and 197.8°, with no approach to this supposed maximum.

No other modification of the solid was found. The region explored lies between the melting curve, the isothermal at 25°, out to 12,000 kgm., the isothermal at 200° from the melting curve to 12,800 kgm., and the straight line connecting the point (12,000 kgm., 25°) with the point (12,800 kgm., 200°). Analogy with benzol would lead one to expect that possibly another modification is not far away.

Diphenylamine.—The substance used was Kahlbaum's purest, provided by Eimer and Amend. It comes in the form of fine flakes, such as those familiar naphthalene preparations used for moth preventives. It is of a most dazzling whiteness, but there is some impurity present as shown by the yellow color of the melt. The material used here was further purified by slow crystallization at constant temperature in the thermostat. It was found possible in this way to obtain beautiful perfectly colorless and transparent crystalline plates, sometimes 2 or 3 cm. across.

Three series of observations were made. The first comprises six points with the first apparatus up to 200°. An explosion wrecked the apparatus while obtaining the highest point. The second series consists of two observations at low pressure, and the third of two observations at the upper end of the curve with the high pressure apparatus. In addition, several unsuccessful attempts were made in which the diphenylamine became contaminated with kerosene by the collapse of the steel bulb. The manipulation of starting the experiment required some care, as pressure should not be applied while the diphenylamine was solid because of danger of collapse, and the temperature must not be raised so high in the preliminary melting as to allow any of the diphenylamine to escape from the bulb by temperature expansion. The experimental results are shown in Fig. 15, and the computed values of the latent heat and the change of internal energy in Fig. 16. The numerical values are given in Table VII. The rapid rate of rise of temperature with pressure on the melting curve is worth noticing.

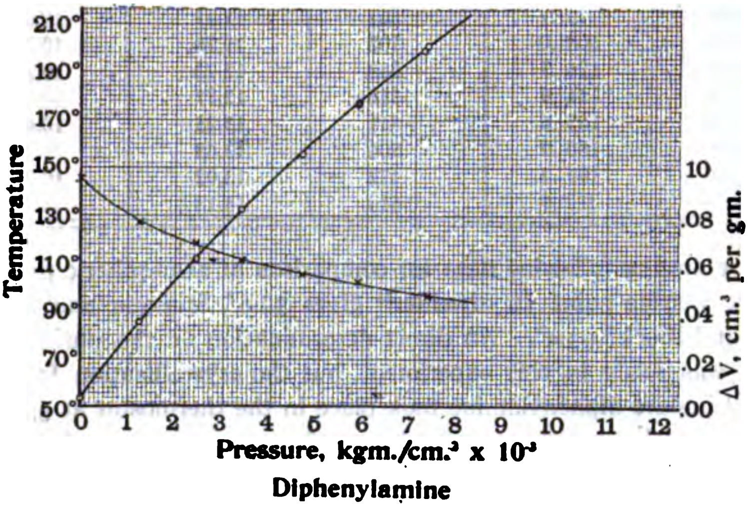


Fig. 15.

Diphenylamine. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

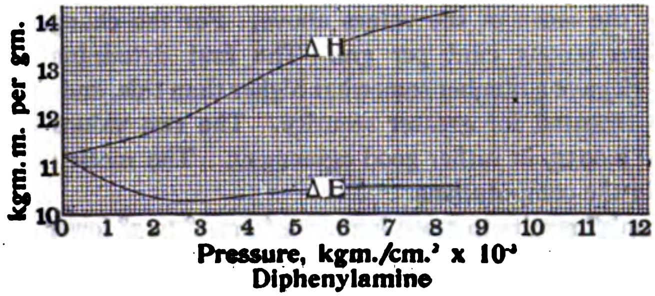


Fig. 16.

Diphenylamine. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

TABLE VII.

Diphenylamine.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	54°.0	0.0958	11.24	11.24
1,000	79 .1	807	11.47	10.67
2,000	103 .0	708	11.78	10.33
3,000	124 .7	638	12.23	10.29
4,000	144 .9	586	12.77	10.40
5,000	163 .6	541	13.25	10.49
6,000	180 .9	504	13.63	10.54
7,000	197 .3	472	13.92	10.55
8,000	212 .9	448	14.18	10.57

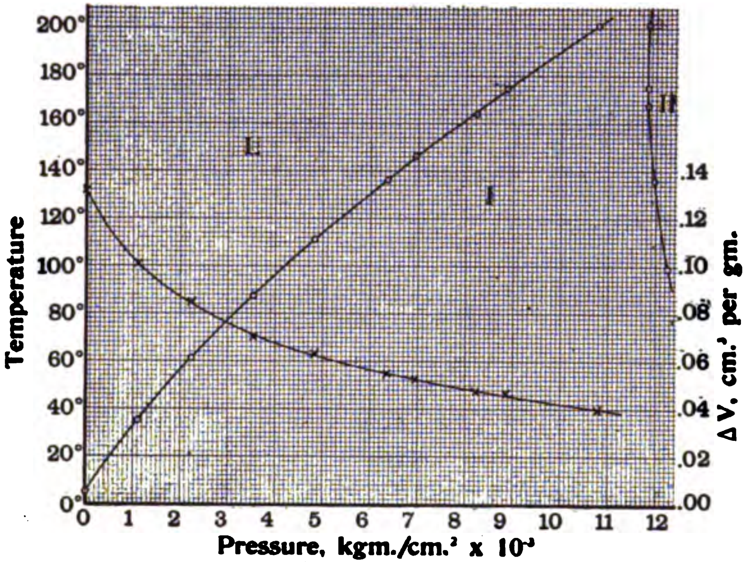
There are the following data for comparison at atmospheric pressure. For the melting point Heydweiller[43] gives 52.6°, Stillman and Swain[44] 54.0°, and Block[45] 53.4°. No direct determination on the purified substance was made in this experiment, but the crystallization from the original impure diphenylamine took place in the thermostat at 53.5°, so that the melting point of the finally purified substance must have been somewhat higher. For the latent heat there are three values. 23.97 gm. cal. per gm. by Stillman and Swain[44], 25.3 by Battelli and Martinetti[46] (because of an obvious misprint this number is quoted in tables of constants as 21.3), and 26.3 by Bogojawlensky[47]. The corresponding values in kgm. m. are: 10.23, 10.79, and 11.18. The number found by computation from the present work was 11.24. Because of the somewhat wide variation of the values by different observers shown above no attempt was made to so adjust the initial slope as to bring this into agreement with the mean of the values above. For the change of volume Block[45] gives 0.0905 cm.^{3} per gm. The first determination of the present work gave a number somewhat higher than this, and the measurement was repeated for greater security. The two values found were 0.0960 and 0.0955, in rather good agreement. The mean of these two was used in the computations.

Tammann's[48] results to 3,000 kgm. are from 2° to 3° lower than those found here; this is probably in part due to impurity, as he himself recognizes that his material was somewhat impure. For the change of volume he gives one value at 455 kgm., 0.0838 cm.^{3} per gm., against 0.0880 found here. As usual Tammann represents his results to 3,000 by a parabolic formula, but in this case does not venture to guess from the constants of the formula what the maximum temperature may be.

At 25° and at 200° the pressure was raised to 12,000 kgm., but no new solid modification was found.

This completes the presentation of data for those substances for which only one solid modification was found.

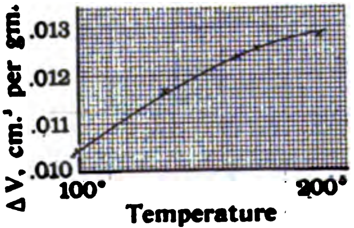
Benzol.—Kahlbaum's purest benzol was purified by distillation, by crystallization, and be redistilling immediately before use. The original benzol, when tested with sulphuric acid, showed no thiophen, the most likely impurity. Four sets of observations were made on benzol. The first two were with the first piece of apparatus and include eight points; these two sets were both terminated by explosions. There was one obser-



Benzol

Fig. 17.

Benzol. The phase diagram, showing the equilibrium curves between the liquid and two varieties of the solid, and the change of volume between the liquid and solid *I*. The observed transition temperatures are shown by the circles, and the observed changes of volume by the crosses.



Benzol

Fig. 18.

Benzol. The change of volume between solid *I* and *II* as a function of the temperature. The curve of transition between these two solids runs so nearly at constant pressure that it would not have been feasible to plot the change of volume as a function of the pressure.

vation at low pressure, and finally eight observations with the new apparatus. The experimental results are shown in Figs. 17 and 18 and the computed values for latent heat and change of internal energy in Figs. 19 and 20. The numerical values are given in Table VIII.

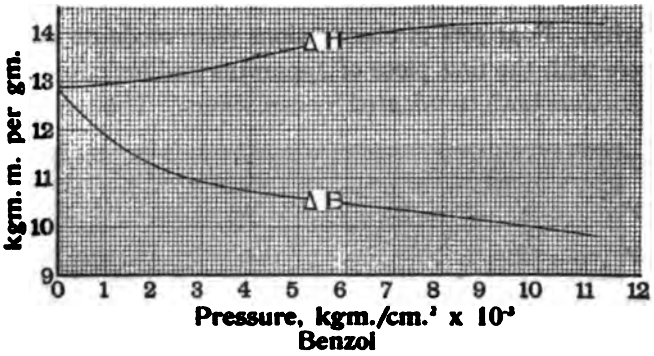


Fig. 19.

Benzol. The computed value of the latent heat and the change of internal energy when the liquid melts to the solid *I*.

TABLE VIII.

Benzol.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	5°.4	0.1317	12.88	12.88
1,000	32 .5	1026	12.94	11.89
2,000	56 .5	872	13.06	11.27
3,000	77 .7	759	13.24	10.93
4,000	96 .6	675	13.47	10.72
5,000	114 .6	614	13.70	10.60
6,000	131 .2	564	13.90	10.47
7,000	147 .2	522	14.05	10.36
8,000	162 .2	485	14.15	10.23
9,000	176 .7	451	14.20	10.10
10,000	190 .5	422	14.21	9.97
11,000	204 .2	394	14.20	9.82
		I-II.		
12,260	100°	0.01048	−3.7	−16.6
12,080	120	1110	−3.4	−16.9
11,950	140	1168	−3.0	−16.8
11,860	160	1219	−2.0	−16.5
11,810	180	1262	−0.5	−15.5
11,840	200	1281	1.4	−13.8

Benzol has a second modification of the solid, stable at the very highest pressures reached here. In fact, the transformation line so nearly marks out the arbitrary limit of pressure that had been set for this work that the discovery of the modification can be regarded only as a piece of good fortune. The transformation curve runs nearly vertically (showing low latent heat), convex toward the temperature axis. This seems to be the first example of a curve of this type; the other nearly vertical transformation curves, such as those between the different varieties of ice or the two kinds of phenol,[49] are concave toward the temperature axis. The fact that a transformation between two solids shows such a distinct curvature at so high a pressure seems a bit surprising. It seems natural to think that the properties of a solid at high pressure would vary nearly linearly with temperature and pressure; under these conditions the transformation line would be nearly straight. In fact, it is in any event rather surprising to find a vertical transformation curve, because this means that one solid changes into another of smaller volume with increase of internal energy, and that almost all the work done by the external pressure is stored up within the substance. The internal forces would seem to have become forces of repulsion instead of forces of attraction. It may be that the increased temperature energy of the molecules, corresponding to a greater number of degrees of freedom in the new modification, may account for the absorption of energy. But this seems unlikely, because the indications are that at atmospheric pressure benzol is entirely normal, that is, entirely dissociated into single molecules. In the later part of this paper a possible explanation is given of this increase of energy.

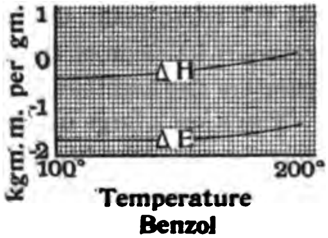


Fig. 20.

Benzol. The computed values of the latent heat and the change of internal energy when the solid *I* changes to the solid *II*, as a function of the temperature of transition. Observe that the internal energy of the form with the smaller volume is greater.

The reaction velocity of the two solid forms shows the same rapid variation with temperature that has been found for the modifications of ice. At the highest temperature, 201.6°, the reaction runs almost immediately, while at the lowest temperature, 99°, the reaction runs so slowly that it was not feasible to wait for complete equilibrium, but the point was approximated to from the two sides. The difference of the two pressures reached from above and below was 100 kgm. The slowness of the reaction increases so rapidly with decreasing temperature that it was not feasible to try for points below 99°, especially since the pressure rises more and more rapidly with falling temperature. Along with the slow reaction velocity at low temperatures goes the possibility of considerably passing over the transformation line without the reaction running. Within the pressure limits set here it was not possible to obtain the second modification at 99°; temperature had to be raised to 135° before it appeared, and the temperature was then lowered to 99° and the readings taken.

At 25°, pressure was raised to 12,500 kgm., but no other modification was found.

The triple point between the two solids and the liquid would apparently lie at about 216° and 12,000 kgm. The temperature was too high above the limit set to make it seem worth while to take the risk of reaching it. At the triple point the transformation line between the two solids has reversed its slope of the lower temperatures, so that pressure and temperature rise together.

There are a large number of data for comparison at atmospheric pressure, inasmuch as benzol has been a favorite substance for investigation because of the comparative ease of obtaining it pure. For the melting temperature we have 5.43° by Demerliac[50], 5.35° by Heydweiller,[43] 5.43° by Ferche,[51] 5.44° by Meyer,[39] and 5.42° by Lachowicz,[52]. The value found here by extrapolation from the determination of ΔV at 60 kgm. was 5.43°. For the latent heat we have 30.38 gm. cal. per gm. by Demerliac,[50] 29.43 by Pickering,[53] 30.18 by Ferche,[51] 29.09 by Pettersson and Widman,[54] 30.39 by Meyer,[39] 30.08 by Fischer,[55] and 30.6 to 31.0 by Bogojawlensky[56]. The corresponding values in kgm. m. are: 12.96, 12.55, 12.87, 12.41, 12.96, 12.83, and 13.05 to 13.22. The value given by these data from the uncorrected initial slope was 12.33. The initial slope was so corrected as to bring the latent heat to 12.88. For the change of volume there are the values 0.1304 cm.^{3} per gm. by Heydweiller,[43] 0.1316 by Ferche,[51] and 0.1333 by Meyer[39]. The result found here was 0.1316, and is in unusually good agreement with the mean of these three.

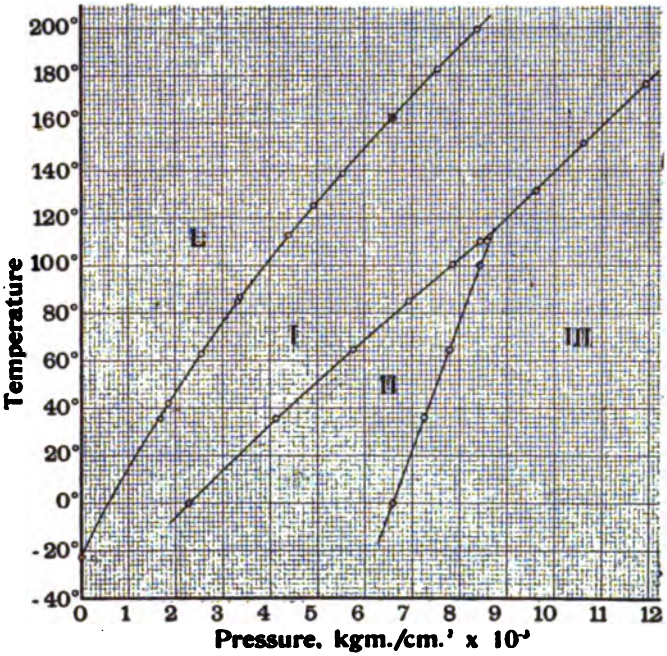
Tammann's,[57] results up to 3,000 kgm. are considerably lower than those found here; 4.5° lower at 3,000 and 3° lower at 2,000. The discrepancy is not to be entirely explained by impurity.

Tammann as usual fits a parabolic curve to his results. The maximum of the parabola would lie at about 7,100 kgm., although Tammann does not explicitly predict this as the pressure of the maximum point. The data here reach to 12,000 with no tendency to a maximum.

Benzol is one of the few substances for which Tammann attempted measurements of the change of volume over his entire pressure range of

3,000 kgm. His results above 1,500 are considerably lower than those found here, doubtless due to leak around the piston, while his results below 1,500, although showing considerable irregularity, agree with the present ones within the limits of error.

Carbon Tetrachloride.—This was obtained from Eimer and Amend, and was purified by a double fractional distillation. The second distillate showed a constant boiling point. Observations were made in three series; the first with the original apparatus to 183° includes seven points, the second, one point at low pressure, and the third nineteen points with the final high pressure apparatus. The experimental points are shown in Figs. 21 and 22, and the computed values of latent heat and internal energy in Fig. 23. The numerical values are given in Table IX.



Carbon Tetrachloride

Fig. 21.

Carbon Tetrachloride. The phase diagram of the liquid and three solid forms. The observed transition temperatures are shown by the circles.

Three solid modifications of CCl_4 were found, two of them not known before. This was the first of the four substances studied here for which more than one solid form was found, and the discovery of this was by accident. At 35°, when the experiment was performed for the third time with the high pressure apparatus, pressure was pushed several thousand kilograms beyond the freezing pressure to ensure complete freezing, because the curve for the change of volume liquid-solid had been showing some irregularities. In this way the second modification was found. The third modification was found while working on the transformation curve *I–II*. The first data in which *III* appeared were puzzling until the existence of the new phase had been made certain, because by chance the first readings were taken at almost exactly the temperature of the triple point.

TABLE IX.

Carbon Tetrachloride.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	−22°.6	0.02580	1.67	1.67
1,000	14 .2	2006	1.72	1.50
2,000	45 .9	1653	1.77	1.41
3,000	75 .8	1401	1.78	1.34
4,000	102 .7	1197	1.76	1.27
5,000	126 .8	1019	1.72	1.20
6,000	149 .5	862	1.65	1.13
7,000	171 .0	730	1.56	1.04
8,000	192 .1	622	1.46	0.95
9,000	211 .9	538	1.37	0.88
		I.–II.		
2,000	− 5°.9	0.02429	3.17	2.68
3,000	13 .8	2343	3.43	2.72
4,000	32 .8	2246	3.68	2.76
5,000	51 .2	2147	3.87	2.78
6,000	68 .6	2042	4.02	2.79
7,000	86 .0	1929	4.12	2.77
8,000	102 .8	1816	4.16	2.71
		I.–III.		
9,000	120°.0	0.02259	4.60	2.55
10,000	139 .4	2229	4.75	2.52
11,000	158 .9	2187	4.87	2.47
12,000	178 .4	2132	4.94	2.39
		II.–III.		
6,500	− 4°.9	0.00555	0.27	−0.09
7,000	21 .8	562	0.30	−0.09
7,500	48 .5	562	0.33	−0.08
8,000	75 .2	555	0.36	−0.08
8,500	101 .9	543	0.38	−0.08

There are no special peculiarities shown by the reactions between the different solid forms. CCl_4 proved itself throughout a particularly pleasant substance to work with because of the sharpness of freezing, and of the speed of reaction, both between solid and liquid and between the two solid phases. We are by this time accustomed to high reaction velocity at high pressure between two solid forms, but in all previous cases the high velocity has been associated with very small latent heat, and the transformation curve has been nearly vertical. In the case

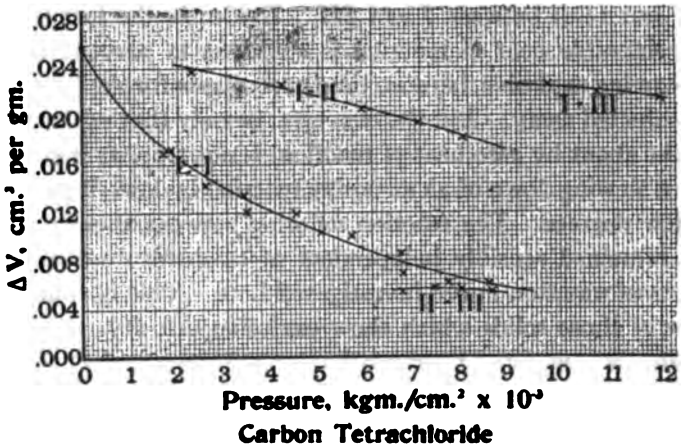


Fig. 22.

Carbon Tetrachloride. The change of volume curves for the liquid and the three solid modifications. The observed values are shown by the crosses.

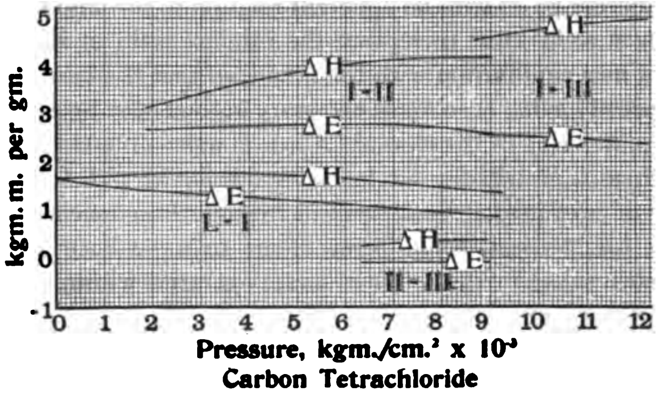


Fig. 23.

Carbon Tetrachloride. The computed values for the latent heat and the change of internal energy for the various transitions between the liquid and the three solid forms.

of these new modifications of CCl_4 the reaction between solids is noticeably rapid, much more rapid than between solid and liquid, but nevertheless does not approach the explosive rapidity that we have found previously. The reaction velocity between *II* and *III* is notably less than that between *I* and *II* or between *I* and *III*. Evidently the fact that there is here considerable heat of reaction is sufficient to prevent the reaction from becoming explosive, because time must elapse for the heat of reaction to be conducted away. But the converse, namely that explosive rapidity is brought about by zero heat of reaction, is not true, as is shown by the enormous slowing down of an explosive reaction by lowering the temperature a few degrees. The reaction velocity between these modifications of CCl_4 remained sensibly independent of temperature over the extent of the transformation curve investigated here. This is contrary to the behavior of those solids which show explosive velocity. This suggests, as will also be suggested by the behavior of o-kresol, that the explosive rapidity of reaction between two solids is something that is essentially brought about by the nearness of the liquid phase; we never find it except in the neighborhood of a triple point with a liquid.

It was found possible to superheat *III* with respect to *II*; in this respect, therefore, two crystalline phases are essentially different from a liquid and a solid. Previous examples of this are not common. But no case was found of the superheating of either *II* or *III* with respect to *I*.

The phase diagram of CCl_4 is different from that of most other substances with which we are familiar in that the various reactions from one solid to another go on with no apparent relation to the liquid. It is usual for the new solid form to replace the original solid at high pressures, forming a new equilibrium with the liquid, so that the new solid has the appearance of having been made necessary in some way by new conditions in the liquid. But in the case of CCl_4 it is quite different; it is evident that if there is a triple point between the liquid and *I* and *III* it is probably at pressures at least twice as high as those reached here. The necessity for the new solid forms seems to have been here brought about almost solely by the action of forces operative within the crystalline phase, independent of the liquid.

It should be possible to realize the phase *II* at atmospheric pressure at low enough temperatures. Such an attempt was made by cooling CCl_4 in carbon dioxide snow to − 80°, but the depression of temperature was not sufficient to overcome the viscous resistance to the reaction.

The two forms found here at high pressures seem to be entirely new, but there are hints by Tammann and Amagat, who have both worked with CCl_4 under pressure that there are other solid forms. Amagat[58] used an apparatus with glass windows, and was able to obtain photographs of the CCl_4 crystallizing under pressure. He found crystals of different shapes, and assumed the existence of allotropic forms. But such an inference, without careful measurements of the crystalline angles, is dangerous, as shown by the varied appearance of snow flakes, for example. Amagat certainly did not obtain a modification of CCl_4 with a freezing point different from that of the ordinary variety, which makes it exceedingly probable that his crystals of different shapes were only crystals of the same crystalline system, but of different crystalline habit from the common form. Tammann's[59] evidence for other forms is also by no means convincing, being chiefly certain inconsistencies that he found in his determinations of ΔV. He was not able to find two distinct melting temperatures at the same pressure, as would be expected if he really had two distinct forms of the solid, but apparently he found exactly the same equilibrium temperature and pressure for two supposedly different forms. Tammann's inclination to explain these discrepancies by new allotropic modifications apparently is a bias left from his interpretation of some erroneous results that he had obtained in 1898.[60] His original experiment was performed on a very impure specimen of CCl_4 with a melting point 3° below that used here. An error in recording the temperature had led Tammann to think that his specimen was unusually pure. Irregular results were obtained with this impure liquid that were explained by the existence of three polymorphic forms. But the properties of these supposed modifications were so remarkable, such as ability to exist indefinitely in contact with the liquid without the reaction running, that Tammann reëxamined the question, and in "Kristallieren und Schmelzen" retracted his former results. He still explained the outstanding irregularities, however, by the existence of two polymorphic forms. But there now seems to be some doubt in Tammann's own mind as to the reality of the existence of his second modification, for in a recent paper[61] he marks it with an interrogation point.

There are few other data for comparison at atmospheric pressure. For the melting point there is a value $-24°$ by Niescher,[34] and $-22.6°$ by Bugarszky.[62] Tammann's specimen melted at $-22.96°$. The specimen used in this work melted at $-22.6°$, determined by extrapolation from data at 60 kgm. There seems to be only one value for the latent heat, 4.2 gm. cal. per gm. or 1.79 kgm. m., determined by Niescher[34] by an indirect method. The value computed from these data is 1.67, in close enough agreement with Niescher's somewhat doubtful value to make unnecessary any adjustment of the initial slope of the melting curve. The exceptionally small value of the latent heat should be noticed. No other values of ΔV at atmospheric pressure are known; 0.0258 cm.^{3} per gm. was found here.

As might be expected from the probable impurity of Tammann's[63] sample, his results up to 3,000 kgm. are considerably lower than those found here, 6.6° lower at 3,000, 5.4° lower at 2,000, and 3.5° lower at 1,000. The change of volume was measured by Tammann at three points. The change found at 700 and at 2,000 for his supposedly second modification is not in violent disagreement with the values found here, but his value at 700 for the so-called first modification is much too high.

O-Kresol.—This substance was Kahlbaum's purest, supplied by Eimer and Amend. It was further purified by twice crystallizing at constant temperature in the thermostat. The crystals were obtained in the form of large transparent needles. The original substance came in the form of a powder of about the same coarseness as granulated sugar, and was somewhat impure, as shown by the yellow color of the melt. Three series of observations were made; the first with the original apparatus comprises 15 points up to 7,500 kgm., the second one point at low pressures with the low pressure apparatus, and the third nine points with the final apparatus. The experimental results are shown in Fig. 24, and the computed latent heat and change of internal energy in Fig. 25. The numerical values are given in Table X.

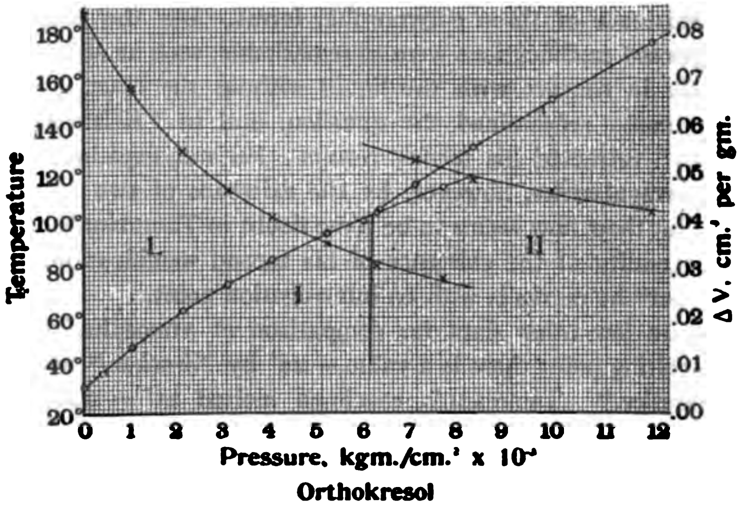


Fig. 24.

Orthokresol. The phase diagram for the liquid and two forms of the solid, and the change of volume curves between the liquid and the two solid forms. It was not possible to find experimentally values for the change of volume between the two solids, because of the extreme slowness of the reaction. The observed transition temperatures are shown by the circles and the observed changes of volume by the crosses.

Table X.

Orthokresol.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	30°.8	0.0838	14.38	14.38
1,000	47 .4	678	14.10	13.41
2,000	61 .9	557	14.10	13.00
3,000	74 .2	471	14.28	12.94
4,000	81 .8	406	14.50	12.88
5,000	94 .5	359	14.61	12.80
6,000	102 .9	319	14.60	12.70
7,000	110 .8	288	14.61	12.61
8,000	118 .1	264	14.72	12.59
Liquid—II.				
6,000	102°.7	0.0559	14.88	11.50
7,000	116 .4	529	15.57	11.85
8,000	129 .3	499	16.08	12.07
9,000	141 .4	475	16.43	12.12
10,000	153 .7	454	16.73	12.14
11,000	164 .6	436	17.05	12.22
12,000	175 .9	422	17.42	12.33

O-kresol has two solid modifications. The second modification was not found during the first set of experiments, although two equilibrium points between the liquid and solid *I* were found in the domain of stability of solid *II*. The new modification requires a good deal of urging to appear. At 80°, pressure on solid *I* was raised to 12,500 kgm., 6,500

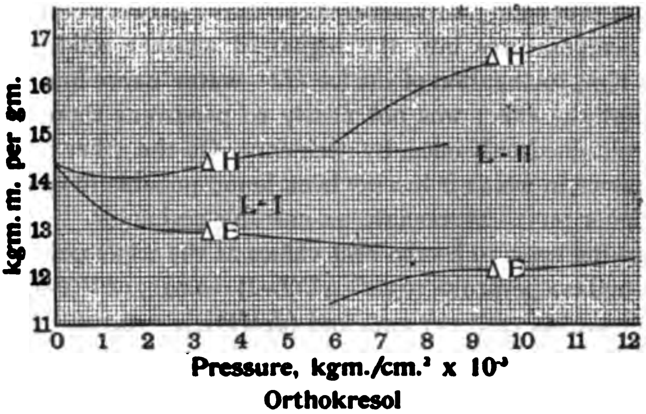


Fig. 25.

Orthokresol. The computed values for the latent heat and the change of internal energy when the liquid melts to one or the other of the two solid forms.

kgm. beyond the transformation point, without the appearance of *II*, which was obtained only by raising the temperature at 12,500 kgm. to 165° and waiting for some little time. All of the reactions with o-kresol were abnormally slow, both between the liquid and either modification of the solid or between the two solids. A high degree of subcooling of the liquid was also possible. On one occasion pressure on the liquid at 130° was raised to 12,500 kgm., 4,500 kgm. beyond the freezing pressure, and 50° below the freezing temperature, without solidification. The temperature had to be lowered at this pressure to induce solidification. The sluggishness of the reaction between the two solids was so great that only one point could be found on the transformation curve *I–II*. At 95.4°, 7.8° below the triple point, the reaction was so slow that absolutely no progress of the reaction within a region 500 kgm. wide could be detected in four hours, while 5.4° higher, 2.4° below the triple point, the reaction velocity had become great enough so that it was possible to shut the equilibrium point in between two values differing by only 70 kgm. in the course of an hour. This is the most striking example yet found of the enormous variation of reaction velocity between two solids as the triple point with the liquid is approached. The sluggishness of the solid reaction is not to be explained by the heat of reaction, because the transformation line between the two solids is almost vertical and the latent heat abnormally low.

During the experiment, pressure was raised to 12,500 at 25° without the appearance of any other solid form.

The two points found in the first series of observations in the domain of stability of *II* are interesting as the second example we have of the possibility of prolonging a transformation curve between solid and liquid to higher temperatures into the region of another solid. The other example is the prolongation of the ice *III*—water curve into the domain of ice *V*, but the effect was not nearly so persistent there as here; in fact it was obtained only once, by accident. On the other hand, several cases are known in which it has not been found possible to so prolong the curve to higher temperatures into an unstable region.

The following seem to be the best values at the triple point: pressure, 6,100 kgm. and temperature, 103.2°; $\Delta V_{L-I} = 0.0317$; $\Delta V_{I-II} = 0.0238$, $\Delta V_{L-II} = 0.0555$ cm.³ per gm., and $(d\tau/dp)_{I-II} = 0.700$. That is, the transformation curve *I–II* rises 700° for an increase of pressure of 1,000 kgm.

O-kresol is a substance for which Tammann claims two solid modifications. His solid form has no relation with that found here, but entirely disappears beyond 640 kgm. and 38.8°, and at atmospheric pressure at temperatures below 22.5°. (See Fig. 26 for the domain of existence of this supposed modification.) This means that if liquid o-kresol is cooled at atmosheric pressure, it solidifies at about 30° to a solid which has a very limited region of stability, passing over at 22.5° to the form stable throughout the most of the phase diagram. Tammann gives the coördinates of five points on the transformation curve between the two solid forms. However, he apparently did not measure the magnitude of the change of volume between the two phases, and gives no hint as to what order of magnitude to expect, as he might if the reaction had been clean cut. Most careful search was made during this present investigation for such another modification, but none was found. Two different methods were employed in the search. First, the equilibrium pressure and temperature was determined at eight points at pressures both above and below the supposed triple point, but no discontinuity in the curve could be found. These points are shown in Fig. 26 together with the points of Tammann. Secondly, measurements were made on the solid at 60 kgm. from 15° to the melting point at about 31°. Absolutely no discontinuity was found on passing over the supposed transformation point at 22.5°. The evidence seems unquestionable that at least in the present work there was only one low pressure variety present. If there are really two low pressure varieties, then the measurements given here must have been on the second of Tammann's varieties (that is, the low temperature variety). But this possibility is ruled out by the high melting point of the modification used here. The melting point of Tammann's variety should be about 26°.

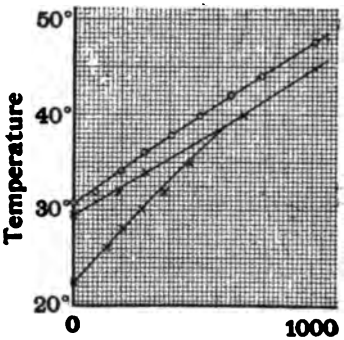


Fig. 26.

Orthokresol. Equilibrium temperatures at low pessures (circles), together with Tammann's points (crosses). It will be noticed that in this work no trace could be found of a second solid form at low pressures.

There seems little room for doubt that Tammann's two varieties are only the apparent effect of impurities. The melting point of his o-kresol was about 1.2° lower than that used here. One is the more inclined to accept this explanation since Tammann has himself retracted announcements of new modifications which he later found to be due to impurities. Examples of this are CCl_4, carbon dioxide, æthylendibromid, p-xylol, and trimethylcarbinol. At the same time, it must be admitted that the evidence against there being two varieties is not so absolutely conclusive as it has been in other instances. If there are two modifications at low pressures, they must be very much indeed alike.

There are practically no measurements at atmospheric pressure for comparison. The melting point has been determined to be 30° by Béhal and Valeur.[65] The directly measured melting point of the substance used here was 30.75° to 30.78°, showing that this sample was probably purer than any on which measurements have been previoulsy made. There seem to be no measurements of the change of volume or of the latent heat.

In view of the impurity of Tammann's sample we should expect his values to be considerably lower than those found here. His results are about 3.5° low at 2,500 kgm. He predicts from his data a maximum melting point at 4,700 kgm. The data here show that this temperature may be considerably exceeded with no suggestion of a maximum before the second phase appears.

Phosphorus.—The purest commercial stick phosphorus (yellow) from Eimer and Amend was used. For the first experiment this was further purified by slow crystallization in the thermostat, giving colorless and transparant crystalline plates 2 cm. across and perhaps 8 mm. thick. Subsequent work, however, showed that this careful purification is not

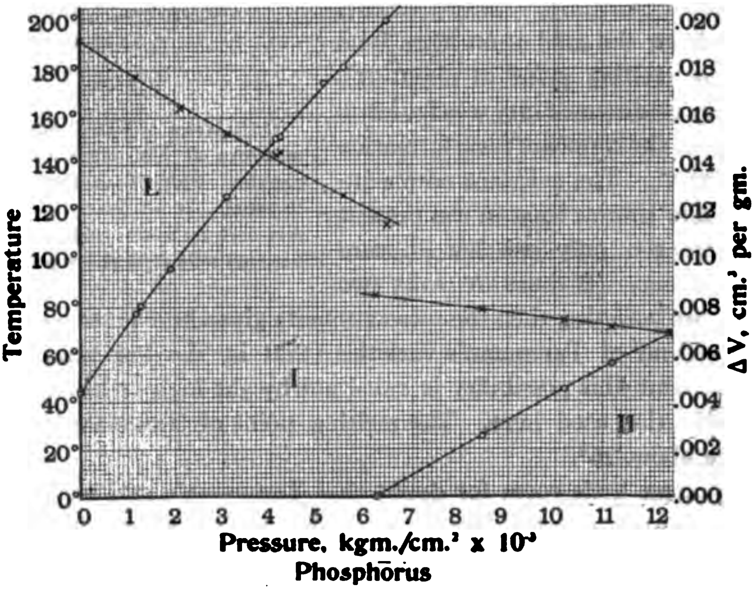


Fig. 27.

Phosphorus. The phase diagram and the change of volume curves for the liquid and ordinary solid yellow phosphorus, and for the yellow and another variety of the solid. The observed transition temperatures are shown by circles, and the observed changes of volume by crosses.

necessary; the commercial material without further treatment is good enough. Four sets of readings were made; the first comprises six observations with the original apparatus, the second one observation at low pressure, the third eight observations with the final apparatus, and the fourth was a redetermination of one slightly doubtful point of the previous work. The experimental results are shown in Fig. 27 and the computed latent heat and the change of internal energy in Fig. 28. The numerical values are given in Table XI.

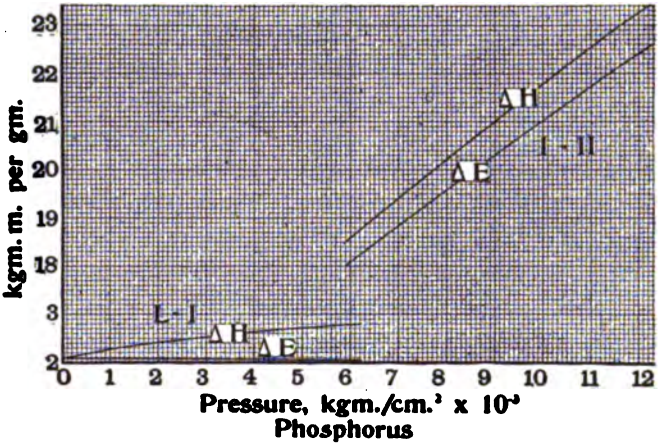


Fig. 28.

Phosphorus. The computed values for the latent heat and the change of internal energy between the liquid and the two forms of the solid.

During the third series of observations the second modification of the solid was found, and the equilibrium curve and the changes of volume determined. This second form is of interest because yellow phosphorus is itself unstable with respect to red, so that we have here a reversible reaction between two unstable varieties. There is no possibility of the new modification being the ordinary red phosphorus, because the change of volume is not nearly great enough, and all indications point to the reversible change between yellow and red taking place only at high temperatures, if indeed it takes place at all. The reaction velocity between these two solid forms was slower than that between any other two solid forms studied, except between the two varieties of o-kresol. The reaction is unlike that of o-kresol, however, in that it will run to completion if enough time is allowed, so that it was possible to reach the same equilibrium pressures from above and below. But this takes many hours. To expedite matters, the equilibrium pressure was found here by observing the progress of the reaction with time from above and below during melting or freezing, and extrapolating for the equilibrium pressure. In very few cases did the possible error of such a proceeding amount to as much as 10 kgm. There is no marked change in reaction velocity from one end to the other of the equilibrium curve.

TABLE XI.

Phosphorus.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	44°.2	0.01927	2.09	2.09
1,000	72 .7	1792	2.27	2.08
2,000	99 .3	1667	2.41	2.07
3,000	124 .4	1549	2.52	2.07
4,000	148 .2	1436	2.63	2.06
5,000	170 .5	1326	2.72	2.05
6,000	191 .9	1218	2.78	2.04
		I.–II.		
6,000	−2°.4	0.00851	18.61	18.10
7,000	9 .6	825	19.43	18.86
8,000	21 .4	799	20.24	19.61
9,000	32 .7	772	21.04	20.34
10,000	43 .7	746	21.82	21.06
11,000	54 .4	720	22.58	21.77
12,000	64 .4	694	23.29	22.44

Interesting effects were also found at the higher temperatures of the equilibrium curve between solid and liquid, particularly during the first series of readings. Perfectly satisfactory readings had been made up to 150°, the freezing being as sharp as for metals, and some preliminary work had been done at 175° with every promise of sharp freezing here also, when suddenly the character of the melting changed completely to that of an impure liquid, the freezing taking place over a long interval of pressure, and varying with the quantity of liquid present. When the apparatus was taken apart, the phosphorus was found to be of a brilliant scarlet color, which has survived the melting of the phosphorus and been stable for six months since. The explanation that suggested itself was that at the high temperature some of the yellow phosphorus had been transformed into red, which is presumably the stable form, and had dissolved in the yellow. For some unknown reason the reaction did not run further. The amount transformed to red, if this is the explanation, must have been slight, because the change of volume was too small to be detected with certainty. Of course it was natural to fear that the same effect would make it impossible to reach the higher temperatures on the repetition of the experiment. However, the effect did not show itself again, and it was found possible to make satisfactory readings of the change of volume up to 200° with only slightly greater rounding of the corners than found at the lower temperature.

Nevertheless, it was felt that the transformation to red phosphorus might be possible, and in searching for this the most interesting fact of all connected with phosphorus was discovered. At 150° the pressure was raised to 12,000 without effect, and again at 200° to 12,000 without immediate effect. Some irregularity in the working of the apparatus made it desirable to keep the pressure at the maximum longer than would have been done naturally. After about fifteen minutes there was a sudden drop of pressure to about 4,000 kgm., a truly remarkable drop, for which the only explanation seemed to be a leak. But no leak could be found. 4,000 kgm., it will be observed, is considerably below the melting pressure of yellow phosphorus at 200°, so that if there were a leak the phosphorus must have melted. Pressure was now raised to 9,500 kgm. (the limit set by the stroke of the piston), with no sign of the liquid freezing to the solid again, as it almost certainly would under a super-pressure of 3,000 kgm., and then the pressure was lowered again to about 1,000 kgm. without any transformation taking place. The only apparent explanation was that red phosphorus had been formed.

On taking the apparatus apart the next morning it was found that the phosphorus had been transformed indeed, but not to the familiar red form, but to another modification that is apparently quite new. The new form is grayish black like graphite, breaks with a similar greasy looking fracture, and will mark on paper. It is stable in the air although slightly deliquescent, is ignited with difficulty by a match, and cannot be exploded by a blow from a hammer, as red phosphorus can. It is a conductor of electricity and a rectifier. The most definite characteristic is its high density, 2.69 against 2.34 for the red variety, and 1.9 for the yellow. The experiment was repeated twice, successfully each time. Once it was necessary to go to nearly 13,000 kgm. to start the transformation. The time necessary to force the reaction to start may also vary considerably. An attempt to similarly transform the commercial powdered red phosphorus into the new variety by subjecting it to 200° and 13,000 kgm. for over half an hour was without result. If the gray phosphorus is sealed into a heavy glass capillary and heated, it sublimes and condenses to yellow and red phosphorus in the colder parts of the tube, exactly as red phosphorus powder does under the same circumstances.

The discovery of this new modification reopens the whole puzzling question of the relationship of the various phosphorus modifications. It makes very improbable the correctness of Roozeboom's suggestions as to the relationship of the red and yellow forms. Probably, judging from the greater density, gray phosphorus is more stable than either red or yellow at atmospheric temperatures. The problem is one that requires further experimental investigation, but it is not necessary to investigate it further for the purposes of this paper, since we are here concerned only with reversible reactions. We may emphasize, however, that this is apparently the first instance of a permanent transformation for which a high pressure is essential. For at low pressures this new modification is not produced by the action of high temperatures alone, even up to a red heat.

Returning now to the ordinary yellow phosphorus, there are a number of data for comparison at atmospheric pressure. For the melting point we have 44.10° by Hulett,[66] 44.2° by Person,[67] 44.4° by Pisati and de Franchis,[68] and 44.27° by Lussana.[69] The melting point of the phosphorus used in this experiment was not directly determined. The rough value found by extrapolation from the determination of ΔV at 60 kgm. was 43.8°. For the latent heat there are apparently only two determinations: 5.05 gm. cal. per gm. by Pettersson,[70] and 4.71 by Person[67] (these values in kgm. m. are 2.15 and 2.01). Tammann[71] quotes Person's value as 5.03; the authority for this other number is not clear. The value computed from the present observations was 2.09, almost exactly the mean of Pettersson and Person. Hence no adjustment of the initial slope was necessary. For ΔV we have 0.0190 cm.^{3} per gm. by Hess,[72] 0.01894 by Kopp,[73] 0.0179 by Damien,[74] 0.01939 by Pisati and de Franchis,[68] and 0.0191 by Leduc.[75] The value found here was 0.01926.

Tammann's[76] results are about 6° lower than the present ones at 3,000 kgm. and about 2.5° lower at 2,000. His results show a sudden change in the direction of the melting curve above 2,000; below 2,000 his curve is nearly linear. The explanation is doubtless to be found in an error in Tammann's high pressure measurements, which we have seen on other grounds to be probably the case.

Besides the data already given, the attempt was made to find the melting curve of two other substances, which, however, proved to be too impure. Nevertheless, some fragmentary data were obtained which may be worth giving.

Monochloracetic Acid.—This was purified by slow crystallization, and was apparently in a state of sufficient purity initially. No trouble was found in making the low pressure measurement, for which it was enclosed in a glass bulb. At the high pressures it was necessary to enclose it in a steel bulb; and under pressure the acid attacks the steel slowly, becoming after several hours' use too impure to give results worth while. The results that were obtained are shown in Table XII. The corners were very much rounded by the impurity in obtaining the value at 139°. There is no reason, however, why the value at atmospheric pressure should not be as good as the values found for any of the other substances.

Table XII.

Approximate Values for Monochloracetic Acid.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.
1	62°.53	.1070
7,540	151°.7	.0414
9,320	164°.8	.0281
6,350	139°.4 ±	.....

Acetone.—Another attempt was made with this, the purest acetone "from Bisulfite" of Kahlbaum being twice distilled. But it was still too impure, and no better results could be obtained than were obtained previously in the work on the thermal properties of twelve liquids.[17] At 40°, the freezing pressure is in the neighborhood of 10,000 kgm.

Discussion.

Shape of Experimental Curves.—Before proceeding to the main question as to the probable character of the melting curve, it will pay us to examine the results for the different substances to find what characteristics they have in common.

The melting curve itself first concerns us. One universal feature strikes us: that the concave side is always toward the pressure axis. This is true for the liquid-vapor transition as well as for liquid-solid. We should not expect, therefore, that the direction of curvature of the melting curve would of itself give us much information about the particular mechanics of the change from the liquid to the solid.

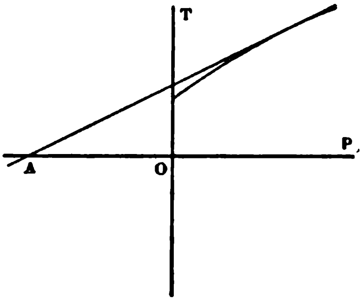


Fig. 29.

Diagram to show the significance of a freezing curve concave toward the pressure axis.

A geometrical interpretation of the thermodynamic quantities involved throws some light on the question, and suggests the reason for the universal direction of curvature. From Fig. 29 it is obvious that the intercept of the tangent on the negative pressure axis (AO) will increase with increasing pressure if the curve is concave downwards. And conversely, if the curve is convex downwards, the intercept AO will decrease with increasing pressure. Now AO has a simple thermodynamic interpretation. It is at once obvious that

$$AO = \tau\frac{dp}{d\tau} - p.$$

But

$$\Delta E = \Delta V\left(\tau\frac{dp}{d\tau} - p.\right).$$

That is, AO is the factor by which ΔV is multiplied to give the difference of energy between the two states. Now ΔE may be thought of as due to two things. In the first place, the internal forces do work as the molecules come closer together during change of state. And in the second place, the temperature energy of a liquid molecule may be different from that of a solid molecule, so that there may be an absorption or liberation of energy when change of state occurs. Let us for the moment consider the effect of only the first factor. As the molecules are brought closer together with increasing pressure, we should expect the intensity of the force of attraction between them to increase, so that the change of energy for a given decrease of volume would increase. That is, the factor by which we multiply the change of volume to obtain the change of energy would increase as the volume decreases, or as the pressure increases. Now we have just seen that this is equivalent to the melting curve being concave downwards, and this is actually what happens. The argument is not altered by considering the change of temperature energy, if we suppose, as does not seem unlikely, that passage from solid to liquid means an increase in the number of degrees of freedom per unit volume. If the change in the number of degrees of freedom does not decrease too rapidly with increasing temperature on the melting curve, then the temperature change of energy will increase with increasing temperature (increasing pressure) and the factor by which ΔV is to be multiplied to give the part of ΔE due to temperature effects will also increase, and the curve will be concave downwards for this reason also.

The direction of curvature of all the curves is just what we should expect on general reasoning, therefore, and cannot be used as evidence in support of any particular hypothesis.

The melting curves also all show a decreasing curvature with increasing pressure; at the higher pressures many of the curves have become nearly straight lines. This is also what we would be inclined to expect, since in general at high pressures physical properties vary more nearly linearly with pressure than at low pressures. But the curves given here do not reach to high enough pressures to justify speculation as to whether they would ultimately become asymptotic to a straight line either inclined or horizontal, or whether the curvature would continue, as in a logarithmic curve.

The curves for the change of volume also all have a common curvature, convexity toward the pressure axis. This is opposite to the curvature of the melting curves. The fact that all these curves are convex to the pressure axis constitutes the most important new evidence of this paper. Tammann's data were not accurate enough to justify him in assuming anything else than a linear relation, and there is little other experimental evidence on the point. The only other measurements are those previously made by the author[15] on water and mercury with apparatus like that used here. The evidence of water is not of much value at low pressures, because of abnormalities, but at high pressures, where all the evidence points to water becoming as normal as other liquids, there is a reversal in the direction of the ΔV curve, and it becomes convex to the pressure axis. The universal direction of curvature found here verifies most gratifyingly a prediction that was ventured in the paper on water; that the convex curvature would be found to be the normal curvature for all liquids. The only exception found so far is for mercury, which is concave up to 12,000 kgm. But the variation of ΔV for mercury over this range is very small (about 8 per cent.) in comparison with the variation found for other substances. The apparently abnormal behavior of mercury need not disturb us, therefore; there is chance enough for the curve to reverse its curvature at higher pressures. But the fact that mercury is exceptional makes it hazardous to extrapolate to find the point where ΔV might become zero, as van Laar[16] has done. He finds this pressure to be about 35,000 kgm.

It is not by any means impossible that the curvature shown by mercury is the normal curvature for all liquids at low pressures. The variation of ΔV with pressure is unusually slow for mercury; for most of the substances investigated here ΔV has decreased by more than 8 per cent. in less than the first thousand kilograms, that is, in the region not reached here by direct measurement. It is therefore possible that there may be a point of inflection on all the ΔV curves below 1,000 kgm. Special experiment would be necessary to show it.

The curves for latent heat and change of internal energy do not show a common curvature for all substances, but there are individual variations. But the fact is striking, as shown in Fig. 30, that there is on the whole comparatively little change with pressure. It would perhaps be fair to say that the general tendency is for the latent heat to increase with rising pressure, and for the change of energy to decrease. This agrees with Tammann, who found that the latent heat showed little tendency to change along the melting curve.

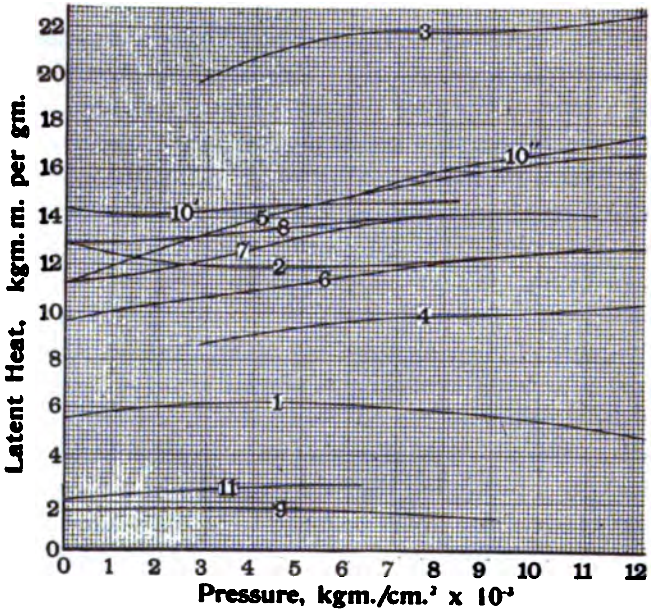


Fig. 30.

Collected curves for the latent heat between the liquid and the solid for the various substances experimented on in this paper.

The substances referred to by the numbers on the curves are as follows: *1*, potassium; *2*, sodium; *3*, carbon dioxide; *4*, chloroform; *5*, anilin; *6*, nitrobenzol; *7*, diphenylamine; *8*, benzol; *9*, carbon tetrachloride; *10′*, orthokresol (liquid to the first variety of the solid), *10″*, orthokresol (liquid to the second variety of the solid); *11*, phosphorus (the ordinary liquid to the ordinary yellow solid phosphorus).

Thermodynamics Cannot Determine Shape of Melting Curve.—Before applying the evidence of these results to discussing the shape of the melting curve, it will pay us to emphasize again that there is no purely thermodynamic evidence as to the probable shape of this curve; this must be entirely determined by the special mechanism involved in the change from a liquid to a crystal. It is easy to prove that no particular shape of the melting curve is made impossible by either the first or second laws of thermodynamics. It may also be proved that no restriction is placed by one fact of experience, which we have come to regard as a law, although it does not seem to be thermodynamically necessary. This is the more worth mentioning because Tammann's thermodynamics on this point seems to be faulty. It is our experience that in a great many cases when a change in a system is produced by an external agency there is an automatic reaction in the direction opposite to that of the applied force. Thus if we compress a substance by raising the pressure, and thus raise the temperature, as time passes the pressure will drop slightly as the substance regains the temperature of the surroundings. Or, if we suddenly stretch a wire and hold it stretched by a fixed amount, the force necessary will gradually become less in virtue of elastic after-effects. In the same way, if we suddenly compress a mixture of a solid and a liquid in equilibrium, and keep the mass as a whole adiabatic, we expect the increment of pressure will gradually drop as equilibrium is reëstablished between liquid and solid. Tammann[77] discusses this question, and concludes that if the adiabatic lines of solid and liquid are steeper than the melting curve, then the secondary pressure reaction will be a still further increase, instead of the decrease that we have come to expect. But this would be the case in the neighborhood of a maximum, where the curve is nearly horizontal. Tammann expected both of the following phenomena to be shown at high pressures; a maximum in the melting curve, and a secondary pressure increase following a primary increase, instead of the secondary decrease with which we are familiar. He states, however, that up to 3,000 kgm. he was never able to find such an increase. It may also be stated that such an effect was never found in the present work up to 12,000 kgm.

If Tammann's analysis were correct, we should have here a small piece of presumptive evidence from thermodynamic grounds alone making the maximum melting point improbable. But detailed analysis will show that Tammann's thermodynamics was much too off-hand and simple. The problem may be rigorously formulated as follows. Given a mixture of liquid and solid in equilibrium on the melting curve. Pressure is suddenly applied adiabatically. The temperature of both solid and liquid changes because of the compression, the change in the liquid being in general different from that in the solid. The mass as a whole is now kept adiabatic and at constant volume until internal equilibrium is restored. The process of restoration of equilibrium is irreversible. We require that during this process the entropy of the system shall increase (the second law), and that the pressure shall drop, but not below its initial value. The analysis is complicated, and will not be given in detail; merely the results will be stated. The second law will be satisfied if the condition

$$\left\{\frac{c_p}{\tau}\left(\frac{\partial v}{\partial p}\right)_\tau+\left(\frac{\partial v}{\partial \tau}\right)_p^2\right\}\left\{\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2-2\left(\frac{\partial v}{\partial \tau}\right)_p\frac{d\tau}{dp}-\left(\frac{\partial v}{\partial p}\right)_\tau\right\}<0$$

is satisfied by the liquid and the solid separately, where $d\tau/dp$ is the slope of the melting curve. Now the first factor is equal to $(\tau/c_p)(\partial v/\partial p)_s$ and is always negative, because c_p and τ must be positive, and $(\partial v/\partial p)_s$ is negative if the substance is stable. The condition requires, therefore, that the second factor shall be always positive. But this is true, for it may be shown by a differentiation that the minimum value of the factor is $-(\partial v/\partial p)_s$, which is intrinsically positive. This shows, therefore, that a mixture of a solid and a liquid together in equilibrium will always satisfy the second law, no matter what the shape of the melting curve, provided that both liquid and solid separately satisfy the conditions of internal stability.

Now the condition that the mixture of liquid and solid shall together be stable, that is, that the final pressure after the above operation shall be greater than the initial pressure, is:

$$\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\left(\frac{\partial v}{\partial \tau}\right)_p \frac{d\tau}{dp} - \left(\frac{\partial v}{\partial p}\right)_\tau > 0 \qquad \text{(A)}$$

which must hold for liquid and solid separately. But this is exactly the second factor above, which we have just proved to be always positive. The mixture of liquid and solid is stable, therefore, if the liquid and solid are stable separately.

Finally, the condition that the secondary pressure reaction shall be a decrease, and not an increase is that

$$\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\left(\frac{\partial v}{\partial \tau}\right)_p \frac{d\tau}{dp} + \frac{\tau}{c_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2 > 0 \qquad \text{(B)}$$

shall hold for liquid and solid separately. Now the difference between (A) and (B) is $-(\partial v/\partial p)_\tau - (\tau/c_p)(\partial v/\partial \tau)_p^2$, which we have just seen is precisely the minimum value of (A). That is, in the most unfavorable case the value of (B) is zero, and in all other cases positive. The secondary pressure reaction, therefore, is never an increase, no matter what the shape of the melting curve, provided only that liquid and solid are each separately stable, as of course they must be. The condition, therefore, that our ordinary experience continue to be valid at high pressures imposes no condition of shape whatever on the melting curve.

Although we might find it difficult to give a rigorous proof, we conclude that the presumption at present is very great that thermodynamics alone cannot determine the shape of the melting curve. The question must be settled by experimental evidence in addition to pure thermodynamics.

We proceed to examine the bearing of the new experimental evidence presented above on the two theories in possession of the field.

As to a Critical Point.—It must be emphasized at the outset that our present knowledge of the atomic structure of liquids and solids is not sufficient to enable us to decide in the light of pure reason whether a critical point exists or not. Tammann has made this mistake. His argument against a critical point consists in saying that our conception of the atomic structure of crystals makes unthinkable a continuous transition from the chaos of the liquid to the orderly array of the solid. The answer to this is that many men have not found such a continuous passage unthinkable, men like Poynting, Planck, Ostwald, Weimarn, and van Laar. Van Laar in particular indicates a possible mechanism for such a continuous passage, and the author[78] has also made another suggestion to the same end. In our present state of ignorance we must be content, therefore, to find from experiment whether a critical point exists, and from this to reason back to a probable mechanism of solid and liquid.

The evidence of these experiments may be stated almost immediately. If there is to be a critical point, thermodynamics demands that the latent heat and the change of volume vanish together. But an examination of the curves shows no tendency toward any such effect; the change of volume decreases while the latent heat remains sensibly constant. What is more, the change of volume decreases in such a way that there is no necessity that it should ever vanish, and we have not even the first condition for a critical point satisfied, quite apart from any possible change in the behavior of the latent heat at pressures very much higher than those reached here. The hope left to van Laar by the previous data on mercury is taken away by these new data.

One must have been struck on reading the history of the subject to notice how the pressure at which a critical point was looked for was pushed higher and higher into the region of as yet unreached pressures by each new experiment. It is hoped that these experiments will give the final push to this supposed critical pressure, so that it will disappear in the limbo of the infinite.

As to a Maximum.—The argument as to a maximum will be concerned almost entirely with Tammann's work, because this is essentially his theory; the only other evidence for it by Damien resting entirely on fallacious experiments. Tammann seeks by two lines of reasoning to make a maximum plausible. The first is from the shape of the melting curve. The melting curves are universally concave toward the pressure axis, as they would be if there were a maximum. Furthermore, Tammann found that within his limits of accuracy the curves could be represented by a second degree equation $(t - t_0 = ap + bp^2)$, as might be expected for any curve of slight curvature. But now Tammann, firm in his belief of a maximum, assumed that the position of the maximum given by the equation must be near the actual maximum, and he computed the probable maximum for many of his substances in this way. But it should be noticed that this is properly not an argument for a maximum, but merely an argument for the probable position of the maximum, granting that it exists. Tammann himself recognizes that the maximum as predicted by the second degree equation would probably be too low. This was indicated by a few rough experiments which he performed at pressures higher than he could measure. Nevertheless, he thought the maximum given by the formula sufficiently good to make it worth while tabulating in a good many cases.

As regards the effect of Tammann's experimental error on the shape of his melting curves, it will be found on plotting his points that there are numerous irregularities. Furthermore, there is in all probability a constant source of error in the high pressure measurements which makes the temperature appear too low at the higher pressures, thereby increasing the curvature of the melting curves, and bringing the maximum too low.

Tammann's second line of argument is from measurements of the change of volume during freezing. His experimental means of measuring this quantity were not very good, as he could never entirely avoid leak, and for many of his substances he did not attempt it. On plotting the values of ΔV it will be seen that they are much more irregular than the points on the melting curve.[1] The data do show without question, however, that ΔV decreases with increasing pressure, and Tammann assumed that the relation was linear with the temperature (or the pressure), which he was justified in doing in view of the rather large experimental error. But just here is the crux of the whole matter. Shall we regard the relation between ΔV and p as actually linear, or is the linear relation merely an approximation within the region of the experiments? Tammann chose to think that the relation would actually be a linear one. The rest is easy. By extrapolation, the pressure may be found at which ΔV vanishes; this is the maximum point, unless it should happen that the latent heat should vanish also. But computation by Clapeyron's equation from the slope of the melting curve and the observed values of ΔV shows that the change in the latent heat is relatively slight, the tendency being toward an increase. Hence the existence of a maximum.

It is significant that Tammann has been able to give no "atomistic"

---

[1] See "Kristallisieren und Schmelzen," p. 66.

argument in favor of the maximum melting point, especially since he invokes such an argument in making the critical point seem improbable. This is a matter of no small difficulty, and is doubtless responsible for much of the intuitive mistrust with which Tammann's theory is viewed. Whether we find it easy or difficult to conceive a mechanism making continuous passage from the solid to the liquid probable, we find it much more difficult to conceive a mechanism by which the usual volume relations of liquid and solid are reversed at high pressures, so that the orderly arrangement of the solid comes to occupy more space than the haphazard disorder of the liquid. No one seems to have succeeded in forming a molecular picture of how this might occur.

In answer to Tammann's first argument from the shape of the melting curve, the data here show that the curvature of all the curves decreases rapidly with increasing pressure, and that there is no tendency to turn over toward a maximum. The curves found here almost invariably lie above those of Tammann and show less curvature than his, even in his own range of pressure. The differences, which become accentuated toward 3,000, are doubtless to be explained by impurities and by the error in his pressure measurements. The details of the disagreement have been given under the discussion of the separate liquids. For almost every substance investigated the pressure and temperature assigned by Tammann as the probable maximum have been exceeded with no sign whatever of a maximum.

Tammann's second argument, from the variation of ΔV, is fully answered by an inspection of the curves given here. The curves present the results of complete measurements over the entire range for all the substances (except for carbon dioxide and chloroform at low pressures). The experimental error is very much less than Tammann's, because a means was found of avoiding Tammann's most fruitful source of error, leak past the piston. The ΔV curve is not linear with pressure, but is convex toward the pressure axis. This universal convexity is sufficient to invalidate Tammann's entire argument, for up to at least 12,000 kgm. there is no tendency for ΔV to become zero, and the direction of curvature is such that ΔV need never become zero. Certainly an unprejudiced observer, examining the curves on their own merits, would not be justified in predicting that the curves would ever cross the axis.

The conclusion to be drawn is that there is at present no evidence for either a maximum or a critical point, that the melting curve rises indefinitely, and that along this curve the change of volume becomes less but does not become zero for any finite pressure, while the latent heat changes only slightly and usually increases.

Possible Mechanism.—The facts we have just seen to be very simple. It may perhaps be permitted to indicate a very simple conception of the mechanism of crystallization which would lead us to expect just these simple facts. The fundamental idea is the same as that which was strongly suggested by the previous work on the thermodynamic properties of liquids,[79] namely that at high pressures we must begin to take account of the intrinsic shapes of the molecules. Now it seems almost axiomatic to suppose that the arrangement of a large number of similar objects which will occupy the least possible space is in general an order in which the same grouping of the fundamental units will constantly recur at regular intervals, that is, an order which repeats itself in space. But a crystal is just such an aggregate of similar elements arranged in a repeating order in space. (It is not *universally* true that the smallest possible volume is that occupied by a repeating order, for it is possible to set up examples for which this is not true.) We would expect in general, therefore, that at any temperature, no matter how high, a pressure so high could be applied that the molecules would be forced to take up the smallest possible space (that is, to crystallize) in spite of the deorienting forces of temperature agitation. Also as pressure increases the unoccupied space left by the uncoördinated motion of the molecules of the liquid would be expected to become smaller, so that the change of volume on freezing would become less as pressure increases. On the other hand, at low pressures, there are probably orienting forces tending to produce crystallization quite apart from the tendency to crystallize in virtue of the effort to assume the smallest possible volume. It may well be that the crystalline shape that would be demanded by these two sets of forces is not the same; that at low pressures the orienting forces of the molecules build up the molecules in their own characteristic shape, but that at high pressures the molecules are constrained to take up quite another crystalline form, the one occupying the minimum volume. In this way we may account for allotropic forms. It may be that there are several symmetrical arrangements possible, corresponding to the degree to which the natural orienting forces are compelled to yield to the demands of external pressure. Furthermore, it seems natural that the crystalline form assumed under the free action of the orienting forces is one in which the potential energy of the attractive forces is a minimum, that is, that the local centers of attraction within the molecule have approached as close as possible to each other. If the molecules are forced to assume a different arrangement, even one occupying less volume, these centers of attraction must be pulled apart, and work done against the attractive forces while decreasing the volume. That is, the internal energy of the form with the smaller volume will be the greater. This may well be the case with the two modifications of benzol, for example.

This hypothesis assumes that any particular crystalline phase, thermodynamically considered, is characterized by the same grouping of the molecules throughout its region of existence; in other words, that a given crystalline phase belongs to the same crystalline system throughout its region of stability, no matter how pressure and temperature vary. It is perhaps worth while to make an explicit statement of the question at issue, because the result seems to have often been assumed (correctly) without clearly formulating the question. The question is this: is it possible by subjecting a crystal to hydrostatic pressure or to changes of temperature to so change the type symmetry that it no longer belongs to the same crystalline system? The question is not utterly foolish; a cubic crystal, for instance, when subjected to a tensile pull no longer has the symmetry of the cubic system, and nearly every crystal when subjected to hydrostatic pressure undergoes changes of angle as well as change of absolute size. May the change of shape be such as to alter the type of symmetry of the original crystal, and so change the crystalline system? The answer is provided by examining, in the light of the theory of elasticity, the effect of hydrostatic pressure when applied to each of the nine elastically different types of crystal. It will be found that in general the effect of hydrostatic pressure (so long as Hooke's law holds) is to alter unequally the length of unequal crystallographic axes, but to leave the angle between the *axes* unchanged. That is, hydrostatic pressure may change the numerical values of the index numbers of a crystal, but cannot change the crystalline system. The only apparent exception is the triclinic system, in which hydrostatic pressure does alter the angle between the axes, but this evidently does not mean in this case a change of crystalline system, since the triclinic system is merely the class of left-overs, which have no symmetry at all. The analysis for the effect of changing temperature is much simpler than for the effect of hydrostatic pressure, and leads to the same result. The crystalline system cannot be changed, therefore by variations of temperature or of hydrostatic pressure (within the domain of Hooke's law), and we are justified in thinking of a single crystalline phase as being characterized by the crystalline system to which it belongs.

The Existence of New Polymorphic Forms.—A discussion of the several new allotropic forms may well be left to a future paper, when more data have been collected. One point may be mentioned, however, because the data are sufficient to definitely settle the question. Tammann[80] has recently developed a theory of the prediction of new allotropic forms.

volume has become reduced to half its initial value must be corresponding coördinates. This means that the temperatures at the normal freezing point and at the point at which the change of volume has become one half of its initial value are corresponding temperatures. The ratio of the absolute value of these temperatures should be a constant for all substances if the law of corresponding states holds. Table XIII. shows the results. It will be seen that the ratio of the two temperatures is not constant, and that therefore the law of corresponding states does not hold for these substances. The ratio is nearly the same for sodium and potassium, but this one would expect, quite apart from any law of corresponding states, from the close chemical similarity of the two elements. This suggests the same result that some writers on the quantum hypothesis have already reached from other grounds; namely, that although the law of corresponding states may hold for solids, it does not hold for liquids, and therefore does not hold for the transition curve solid-liquid.

TABLE XIII.

Law of Corresponding States.

Substance.	ΔV_0.	T_0. Abs. temp. of normal mpt.	T. Abs. temp. at which $\Delta V = \frac{1}{2}\Delta V_0$.	$\frac{T}{T_0}$.
Potassium	.0268	335.6	409	1.218
Sodium	.02785	370.7	451.6	1.218
Anilin	.0854	267	427	1.60
Diphenylamine	.0956	326	467	1.44
Nitrobenzol	.0813	278.7	454	1.64
Benzol	.1316	278.5	375	1.35
Carbon tetrachloride	.0258	251	363	1.45
Orthokresol	.0839	304	355	1.17
Phosphorus	.0193	317	509	1.61

SUMMARY.

The melting curves and the change of volume curves have been found for eleven substances between 0° and 200° and up to 12,000 kgm. Four of the substances have been found to have new allotropic forms of the solid: CCl_4 two new forms, o-kresol one new form, benzol one new form, and phosphorus two new forms, one of which transforms itself into yellow phosphorus reversibly under the proper conditions, while the other is a form (grayish-black) stable under atmospheric conditions, obtained from yellow phosphorus irreversibly at 200° and 12,000 kgm.

The results have been used in discussing the most probable shape of the melting curve. There is no evidence for either a critical point or a maximum melting point, the two hypotheses which have been hitherto considered most probable. The results suggest strongly, so far as such a conclusion can be suggested by results over a limited range, that the melting curve continues to rise indefinitely to higher pressures and temperatures.

Acknowledgment.—It is a pleasure to acknowledge assistance in purchasing the chemicals used in this investigation from a generous grant from the Bache Fund of the National Academy of Sciences.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

REFERENCES.

1. J. H. Poynting, Phil. Mag., 12, 32 and 232 (1881).
2. M. Planck, Wied. Ann., 15, 446 (1882).
3. W. Peddie, Proc. Roy. Soc. Edin., 13, 155 (1885).
4. E. H. Amagat, C. R., 105, 165 (1887).
5. B. C. Damien, C. R., 108, 1159 (1889), and C. R., 112, 785 (1891).
6. C. Barus, Bull. U. S. Geol. Sur., No. 96 (1892).
7. E. H. Amagat, C. R., 117, 507 (1894).
8. R. Demerliac, C. R., 122, 1117 (1896), and C. R., 124, 75 (1897).
9. A. Heydweiller, Wied. Ann., 64, 725 (1898).
10. E. Mack, C. R., 127, 361 (1898).
11. G. A. Hulett, Zs. f. phys. Chem., 28, 629 (1899).
12. G. Tammann, The following is only a partial reference to Tammann's papers. Wied. Ann., 62, 280 (1897); 66, 473 (1898); 68, 553 and 629 (1899). Ann. Phys., 2, 1 (1900); 3, 161 (1900); and his book "Kristallisieren und Schmelzen," E. Barth, Leipzig.
13. P. P. von Weimarn, Zs. Chem. u. Ind. Koll., 6, 307 (1910).
14. J. J. van Laar, Arch. Néerl. (3A), 1, 51 (1911).
15. P. W. Bridgman, these Proceedings, 47, 347 (1911), and 47, 441 (1912).
16. J. J. van Laar, Chem. Zentralbl., 2, 1798 (1912).
17. P. W. Bridgman, Proc. Amer. Acad., 49, 1 (1913).
18. P. W. Bridgman, Proc. Amer. Acad., 47, 441 (1912).
19. E. B. Hagen, Wied. Ann., 19, 436 (1883).
20. W. Holt and W. E. Sims, Trans. Chem. Soc., 65, 432 (1894).
21. N. S. Kurnakow and N. A. Puschin, Zs. anorg. Chem., 30, 109 (1902).
22. G. Tammann, "Kristallisieren und Schmelzen," p. 248. (In the future reference to Tammann's book will be abbreviated by "K. S.")
23. M. Toepler, Wied. Ann., 53, 343 (1894).
24. A. Joannis, Ann. Chim. et Phys. (6), 12, 358 (1887).
25. G. Tammann, "K. S.," p. 247.
26. G. Tammann, Zs. phys. Chem., 72, 609 (1910).
27. G. Tammann, "K. S.," p. 245.
28. G. Tammann, "K. S.," p. 245.
29. P. Villard and R. Jarry, C. R. 120, 1413 (1895).
30. G. Tammann, "K. S.," p. 294.
31. G. Tammann, Zs. f. phys. Chem., 80, 737 (1912).
32. G. Tammann, "K. S.," p. 282.
33. P. W. Bridgman, Proc. Amer. Acad., 49, 18 (1913).
34. Niescher (1909), quoted in the Collection of Constants of the Soc. Franc. de Phys.
35. E. Lucius, Ber. Chem. Ges., 5, 154 (1872).

36. G. Tammann, "K. S.," p. 228.
37. De Forcrand, C. R., 136, 945 (1903).
38. G. Tammann, "K. S.," p. 282.
39. L. Meyer, Zs. phys. Chem., 72, 225 (1910).
40. G. Tammann, "K. S.," p. 227.
41. O. Pettersson and O. Widman, Vet. Akad. Förh. Stock., 36, 75 (1879).
42. G. Tammann, "K. S.," p. 227.
43. A. Heydweiller, Ann. Phys., 64, 725 (1898).
44. J. M. Stillman and R. E. Swain, Zs. phys. Chem., 29, 705 (1899).
45. H. Block, Zs. phys. Chem., 87, 385 (1912).
46. A. Battelli and M. Martinetti, Att. Lin. Rend., 1, 621 (1884).
47. A. Bogojawlensky, quoted by Tammann, "K. S.," p. 238.
48. G. Tammann, "K. S.," p. 236.
49. G. Tammann, Zs. phys. Chem., 75, 75 (1910).
50. R. Demerliac, Jour. de Phys. (3), 7, 591 (1898).
51. J. Ferche, Ann. Phys., 44, 265 (1891).
52. Br. Lachowicz, Ber. Chem. Ges., 21, 2206 (1888).
53. S. W. Pickering, Proc. Roy. Soc., 49, 11 (1891).
54. O. Pettersson and O. Widman, Jour. prak. Chem., 24, 163 (1881).
55. W. Fischer, Wied. Ann., 28, 400 (1886).
56. A. Bogojawlensky, quoted by Tammann, "K. S.," p. 213.
57. G. Tammann," K. S.," p. 207.
58. E. H. Amagat, C. R., 105, 165 (1887).
59. G. Tammann, "K. S.," p. 222.
60. G. Tammann, Wied. Ann., 66, 490 (1898).
61. G. Tammann, Ber. Chem. Ges., 44, 3624 (1911).
62. S. Bugarszky, Zs. phys. Chem., 71, 705 (1910).
63. G. Tammann, "K. S.," p. 222.
64. G. Tammann, "K. S.," p. 268.
65. Béhal and Valeur, quoted in the Collection of Constants of the Soc. Franc. de Phys., p. 265.
66. G. A. Hulett, Zs. phys. Chem., 28, 629 (1899).
67. C. C. Person, C. R., 23, 163, 336 (1846).
68. G. Pisati and G. De Frenchis, Gazz. Chim. Ital., 4, 497 (1874).
69. S. Lussana, Nuov. Cim., 5, 153 (1903).
70. O. Pettersson, Jour. Prak. Chem., 24, 296 (1881).
71. G. Tammann, "K. S.," p. 250.
72. A. Hess, Phys. Zs., 6, 185 (1905).
73. H. Kopp, Lieb. Ann., 93, 129 (1885).
74. B. C. Damien, Jour de Phys., 10, 394 (1881).
75. A. Leduc, quoted by Tammann, "K. S.," p. 250.
76. G. Tammann, "K. S.," p. 250.
77. G. Tammann, "K. S.," p. 87.
78. P. W. Bridgman, Proc. Amer. Acad., 47, 437 (1911).
79. P. W. Bridgman, Proc. Amer. Acad., 49, 86 (1913).
80. G. Tammann, Ber. Chem. Ges., 44, 3618 (1911).
81. F. A. Lindemann, Phys. Zs., 11, 609 (1910).

THERMAL ELECTROMOTIVE FORCES IN OXIDES.

By Charles C. Bidwell.

THERMAL electromotive forces across junctions composed of oxides, sulphides, silicates and other compounds as well as across metallic junctions were noted by Seebeck[1] as early as 1826. Seebeck made observations on certain naturally occurring minerals and arranged a series like the series for the metals. Later Stefan[2] measured some of these electromotive forces at high temperatures by clamping different minerals together and heating one contact with an alcohol flame. The largest E.M.F. he observed was that of an element composed of galenite and a cuprous oxide ore. Five of these in series were about equal to a Daniell cell. Bunsen[3] compared the E.M.F. of a circuit of copper and an ore of copper with that of a Daniell cell. The temperature of the hot junction was raised to about 230° C. and he obtained an E.M.F. equal to 1/10 Daniell cell. He found an E.M.F. of about the same size with an element of platinum and pyrolusite heated with a Bunsen flame.

Abt[4] measured thermal electromotive forces between a number of minerals, mostly oxides, and sulphides, keeping one junction in ice, the other in steam. The junction contacts were made through mercury. The largest electromotive forces he observed were those of galenite against pyrite, which gave an E.M.F. 13.4 times that of an antimony-bismuth junction for the same temperature difference, and chalcopyrite against pyrite which gave an E.M.F. 10.8 times an antimony-bismuth junction.

Bädeker,[5] keeping the lower end of a specimen in paraffin oil and the upper end in air, measured electromotive forces against copper for CuS and CdO, and against platinum for Cu_2O. With cold junctions at 20° C. and hot junctions at 100° C., he found for Cu-CuS 7.33 microvolts per degree, for Cu-CdO 30.0 microvolts per degree and for Pt-Cu_2O 480.0 microvolts per degree.

Weiss and Königsberger[6] made measurements on electromotive forces

---

[1] Pogg. Ann., 6, 1 pp. 1 and 253, 1826.

[2] Pogg. Ann., 124, p. 632, 1865.

[3] Pogg. Ann., 123, p. 505, 1864.

[4] Wied. Ann., 2.2, pp. 266–279.

[5] Wied. Ann., 22, 4, pp. 749–766.

[6] Phys. Zeitschr., 10, pp. 956–957

of certain metallic ores against copper for temperatures between 20° and 80°. Among their results is that of an E.M.F. between magnetite and copper of which the thermo-electric power in volts per degree for the mean temperature is 5.5×10^{-5}. Magnetite is likely to be pure Fe_3O_4. Their other observations are mostly for sulphides, silicates, etc.

There is considerable lack of agreement in the results reported by various observers. This is to be expected, for naturally occurring minerals certainly vary in their composition and slight changes in composition greatly alter thermal electromotive forces. Apparently no attempt has been made to study prepared specimens of oxides or other compounds of known chemical purity. It seemed to the author that such observations would be reproducible and probably significant. No attempt has apparently been made to plot E.M.F.-temperature relations or to determine the thermo-electric lines for oxides and other compounds. This report may be considered as a preliminary attempt in that direction. The report is not complete, as some data (as noted later) require further checking and verification.

Pure oxides were fused where possible in the oxy-hydrogen flame or baked into hard rods. At first, attempts were made to maintain one end of the specimen at zero degrees and raise the temperature of the other end. Because of the high resistance of most of the oxides extremely short rods were required in order that there might be sufficient current to operate a potentiometer. Attempts to keep one end at constant temperature were soon given up and, following a suggestion made by Prof. J. S. Shearer that a constant temperature at the cold junction was not required as long as we knew both temperatures, the following method was devised and found satisfactory.

A small vertical resistance furnace was made by winding a quartz ring or cylinder with nickel wire. The windings were longitudinal, passing through the cylinder, in and out. The furnace was about 6 cm. high and 1.5 cm. inside diameter. The inside of the furnace was really a tube lined with the vertically wound nickel heating wire. The outside windings constituted an outer heater. With this furnace it was possible to heat a specimen to 1350° C. without melting the nickel. The specimen, which was usually an oxide, fused or baked into the form of a small rod, one cm. long by 0.2 cm. thick, was suspended in this furnace by means of platinum, platinum-rhodium thermo-junction wires, a junction being fused or threaded into each end of the specimen with the corresponding cold junction in melting ice. The temperature of each end of the specimen could thus be determined and if the circuit composed of the two platinum leads and the specimen were closed through the potentiometer one could observe the thermal E.M.F. between platinum and the specimen for the known junction temperatures. The specimen was adjusted so that the upper end was about at the middle of the furnace, the lower end thus being considerably cooler. The difference of temperature thus obtained was from 50° to 100°, depending upon the average temperature of the furnace and the exact position of the specimen. Steady thermal conditions were insured by covering the top with a piece of asbestos paper with small holes for the junction wires and by surrounding the lower end of the specimen with a short quartz tube as a protection against air currents.

After making a set of observations the temperature of the furnace was raised usually so that the temperature of the lower end of the specimen was still below the previous temperature of the upper end. New observations were then taken. This procedure was repeated until the maximum temperature of the furnace was reached, usually then temperatures were decreased to the starting point. Sometimes it was advantageous to begin observations at a fairly high temperature and decrease the temperatures to as low a point as possible and then increase to the maximum.

A glance at Fig. 1 will show the procedure. When the junction leads *A* and *A′* are connected to the potentiometer, the temperature at the hot junction is given; the leads *B* and *B′* give the temperature at the cold junction; while the leads *A* and *B* give the thermal E.M.F. across the junctions between the oxide and platinum.

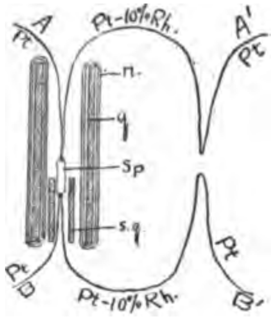


Fig. 1.

Vertical Section of Furnace. *n*, nickel heating wires; *q*, quartz cylinder; *sp*, ▮ specimen; *sq*, small quartz tube.

If electromotive forces are plotted as ordinates and temperatures of the hot and cold ends as abscissa, and for the first set a straight line assumed to connect the two points (which would be a first approximation), then the lower point for the next set must lie on this line and the point for the higher temperature serves to extend the curve. The location of the first point is entirely at random as far as its ordinate is concerned but from this point the curve may be extended in both directions and later the horizontal axis shifted so as to bring the origin to zero. In other words, we have the slopes of overlapping portions of the temperature-E.M.F. curve and from these we build up the entire curve.

As an illustration of the method of plotting, let us consult the curve for CuO, Fig. 4. The four lowest sets of observations are

170°, temp. at cold junction; 250°, temp. at hot junction;—0.043 volt (E.M.F.)
190°, temp. at cold junction; 295°, temp. at hot junction;—0.0586 volt (E.M.F.)
195°, temp. at cold junction; 330°, temp. at hot junction;—0.0652 volt (E.M.F.)
215°, temp. at cold junction; 375°, temp. at hot junction;—0.0751 volt (E.M.F.)

Some point on the 250 degree line is taken purely at random as a starting point. Corresponding to the 250 degree point is the cold junction point on the 170 degree line, a distance of 0.0430 volts up. The first placed point is marked with a cross, the other point, which is determined by the position of the first point, is marked with a circle and dot. A straight line is drawn to join these two points. The point on the 190 degree line must lie on the line joining the first two points since it is intermediate between them. The point for 295 degrees is determined by the position of the 190 degree point, and extends the curve downward. The other points are plotted in the same way. The first placed points are marked with crosses, the points dependent upon these are marked with circles and dots. The deviations of the circles and dots from the smooth curve indicate the degree of accuracy of the work.

As regards the sign of the E.M.F. the following should be noted. If the current flows from the oxide to platinum across the hot junction, the oxide is said to be negative to platinum and the E.M.F. is taken as negative. With the following oxides, current flows across the hot junction from the oxide to platinum. The E.M.F. is therefore negative.

SnO_2, Fe_3O_4, Cr_2O_3, WO_3,
CdO, ZnO, CuO (below 600° C.), PbO.

The E.M.F. is positive with the following:

Bi_2O_3, Mn_2O_3, U_3O_8 (below 700° C.),
$Co_3\,O_4$, NiO, CuO (above 600° C.).

E.M.F.-temperature curves were obtained for the above mentioned oxides against platinum (see Figs. 3, 4, 5 and 6). The curves were plotted to a very large scale and the slopes were measured graphically for each curve for points every 50 degrees or, in some cases, every 100 degrees apart. These slopes were corrected so as to refer to an oxide-against-lead junction instead of the oxide-against-platinum junction, actually used. They were then plotted against the temperatures and gave straight lines, the thermo-electric lines for the oxides (see Fig. 7).

The correction above mentioned consists in subtracting from each slope, for any particular temperature, the slope of the platinum-lead curve for that temperature. The following consideration will show this.

π (Fig. 2) represents the Peltier E.M.F. per degree; σ_{pt} and σ_{ox} the Thompson E.M.F. per degree for platinum and the oxide respectively; dT is the temperature difference between the two junctions. The E.M.F. for the circuit is given by equation (1)

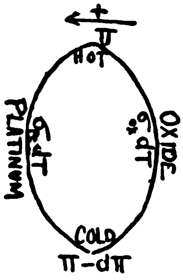


Fig. 2.

$$d\pi + (\sigma_{pt} + \sigma_{ox})dT = de. \tag{1}$$

σ_{pt} and σ_{ox} may be positive or negative. By the second law of thermo-dynamics

$$\frac{\pi}{T} - \frac{\pi - d\pi}{T - dT} + \frac{(\sigma_{pt} + \sigma_{ox})dT}{T} = 0. \tag{2}$$

From these two equations it maybe shown that

$$\left(\frac{d^2e}{dt^2}\right)_{ox-pt} = \frac{\sigma_{pt} + \sigma_{ox}}{T},$$

whence

$$\left(\frac{de}{dt}\right)_{ox-pt} = \int \frac{\sigma_{pt}}{T} dT + \int \frac{\sigma_{ox}}{T} dT.$$

If the oxide is referred to lead instead of platinum

$$\left(\frac{de}{dT}\right)_{ox-pb} = \int \frac{\sigma_{ox}}{T} dT,$$

since for lead

$$\int \frac{\sigma_{pb}}{T} dT = 0.$$

Likewise if platinum is referred to lead

$$\left(\frac{de}{dT}\right)_{pt-pb} = \int \frac{\sigma_{pt}}{T} dT.$$

That is, $\int (\sigma_{pt}/T)dT$ is the slope of the platinum-to-lead curve and if this be subtracted from the slope of the oxide-to-platinum curve we get the slope of the oxide-to-lead curve.

The fact that the curves of slopes, the thermo-electric lines, are straight, shows that the E.M.F.-temperature curves are parabolas. Therefore we may write as an equation for these curves

$$e = aT + bT^2 \tag{3}$$

e is the thermal E.M.F.; T is the temperature difference, or the actual Centigrade temperature of the hot junction if the cold junction is at zero Centigrade; a and b are constants. a and b may be determined from the thermo-electric lines and the E.M.F.-temperature curves replotted by means of this equation. The curves originally plotted, may now be shifted along the y axis to coincide with these computed curves. The original and computed curves (see Figs. 3, 4 and 5) are strictly parallel, indicating that the observations will accurately fit the computed curves.

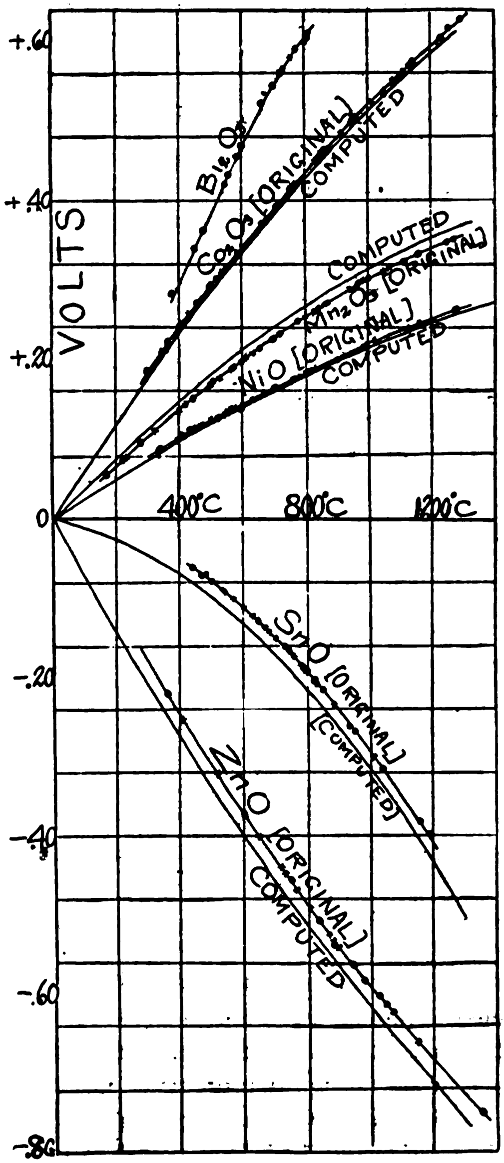


Fig. 3.

E.M.F.-Temperature Curves for Various Oxides against Platinum.

The thermo-electric lines may be plotted directly without determining the E.M.F.-temperature curves and going to the trouble of measuring their slopes. If we divide the E.M.F. found in any particular case by the particular temperature difference we have the thermo-electric power (*de*/*dT*) for the mean temperature. We may then plot this thermo-electric power directly. The thermo-electric lines for CuO and Fe_3O_4 were determined directly in this way, as well as by the other method. The points thus directly determined are plotted as heavy black dots (see Fig. 7). CuO and Fe_3O_4 were selected for trying the direct method because the points on the E.M.F.-temperature curves for these two show the greatest deviations from the smooth curves. The direct method checks the lines previously determined in a very satisfactory manner.

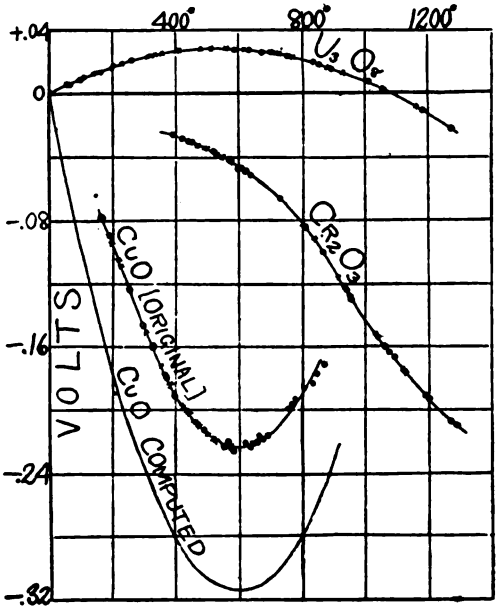


Fig. 4.
E.M.F.-Temperature Curves for Various Oxides against Platinum.

As to the chemical composition of the oxides investigated the following facts may be called to mind. Fusion in the oxy-hydrogen flame in some cases produces higher oxides. For instance, FeO and Fe_2O_3 both go over to magnetic Fe_3O_4 on strong ignition or fusion in air. MnO_2 goes over to Mn_2O_3 on strong ignition. Cu_2O on heating to a dull red in air goes over to CuO. The oxides studied were therefore only the very stable combinations capable of withstanding strong ignition or fusion in an oxidizing atmosphere. ZnO, CuO, and CdO were packed in cylinders of asbestos paper and baked for several hours at a temperature of about 850° C. From the resulting solid sticks specimens were cut or ground to the desired dimensions. Near the ends of the baked specimens small holes were bored, through which the thermo-junctions wires were threaded. With the fusible specimens the junctions were fused in at the ends.

A number of interesting facts are brought out on the thermo-electric diagram (Fig. 7). First, the Tait diagram may be extended to include

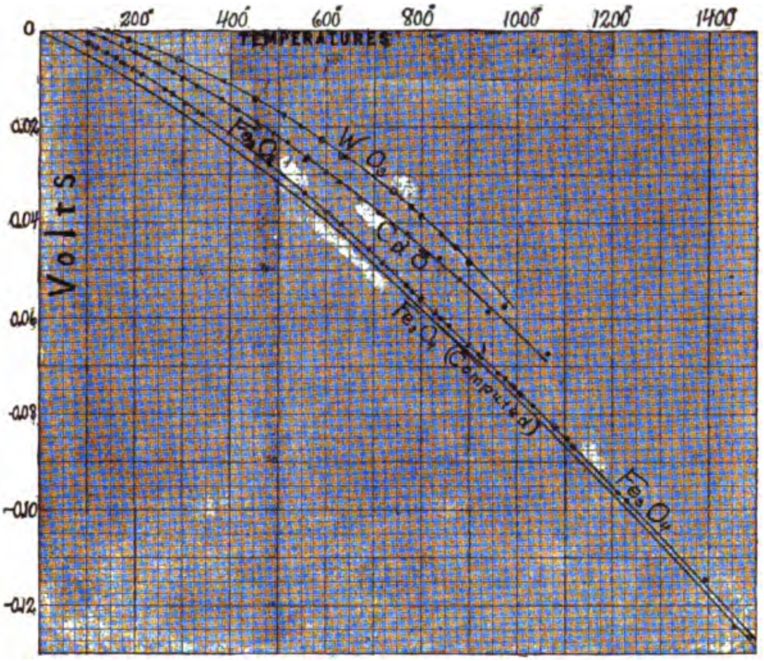


Fig. 5.

E.M.F.-Temperature Curves for Various Oxides against Platinum.

the oxides. Second, the thermo-electric powers for the oxides are of far greater magnitude than for the metals. Above 1,000 microvolts per degree are recorded for some oxides, while for the metals 100 microvolts per degree is extreme. It may or may not be significant but as a general rule both on this diagram and on the Tait diagram for the metals thermo-electric powers are high where resistances are high.

Iron oxide (Fe_3O_4) which is magnetic shows a break in the line at about 875° C. which probably is the recalescence point. Satisfactory observations on this oxide were extended to 1450° C. by means of a carbon resistance furnace.

Lead oxide (PbO) shows a break in the thermo-electric line at about 400° C., suggesting possibly a change in crystalline structure there.

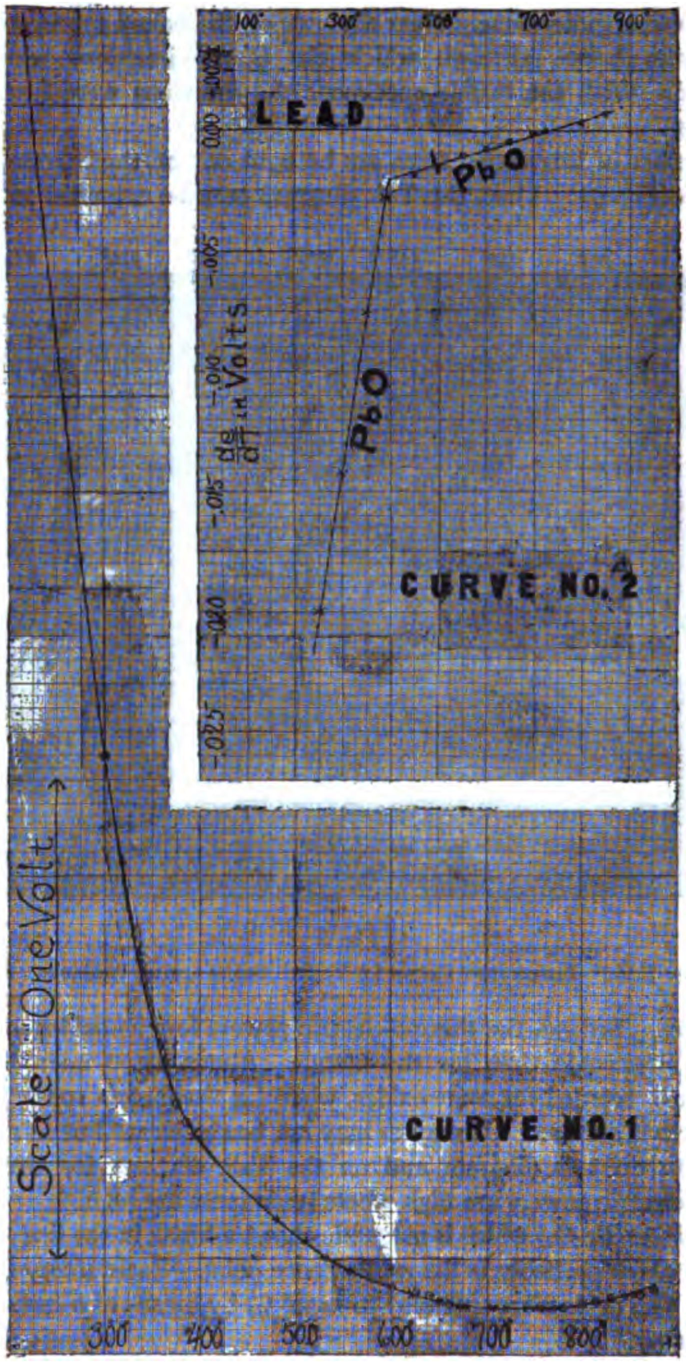


Fig. 6.

Curve 1. E.M.F.-Temperature Curve for Lead Oxide (PbO) against Platinum.
Curve 2. Thermo-electric Power Line for Lead Oxide (PbO).

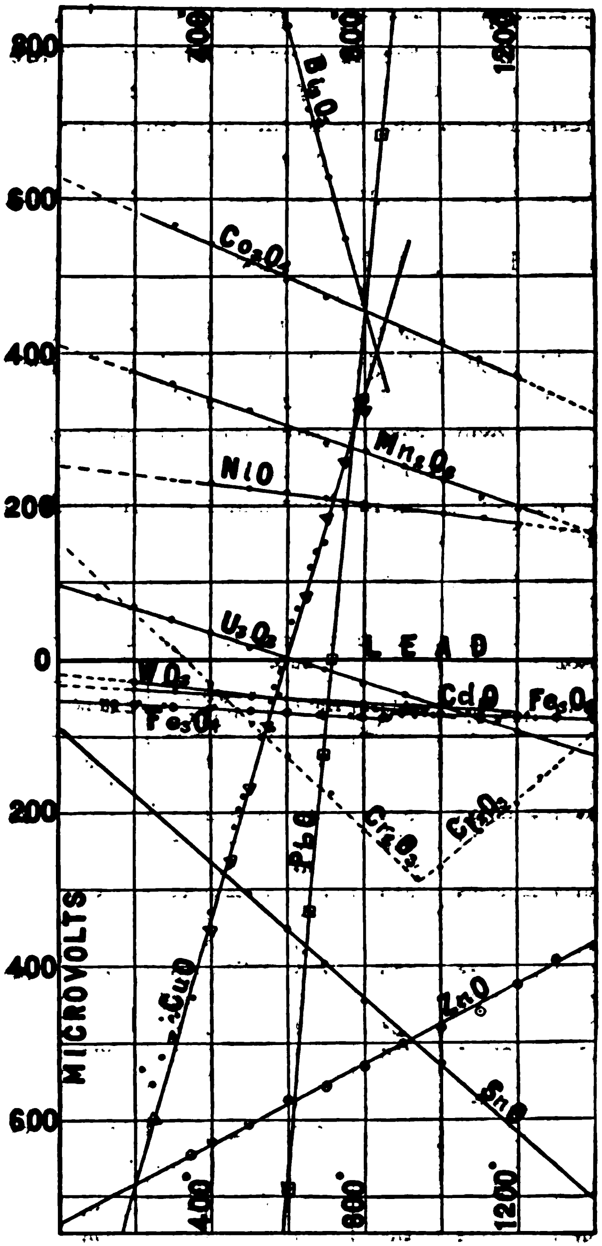


Fig. 7.

Thermo-electric Power Diagram for Various Oxides.

Only the line for temperatures above 600° C. is shown on the general diagram. The other part of the line is shown on a special diagram, Fig. 6, Curve 2. The thermo-electric power is here given in volts per degree instead of microvolts per degree. Definite conclusions should not be drawn from this line as the data for PbO below 400° are insufficient. Difficulty was experienced in getting potentiometer settings owing to the very high resistance of the specimen. Measurements of this E.M.F. by means of an electrometer are now in progress. Further work at low temperatures is also in progress on some of the other high resistance oxides.

Chromium oxide (Cr_2O_3) shows a break in the thermo-electric line. There is some doubt about this line also, as a chemically pure sample was not at hand. This oxide also is being further investigated.

The data which follows is given in the order in which the observations were actually taken in making a run on a given oxide. A number of specimens of each oxide were prepared and each table comprises in most cases observations on several of these.

The work was carried on in the summer of 1913 under a grant from the Carnegie Institution.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY

Fe_3O_4.			CuO.			U_3O_8.		
Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.
170	260	−.00600	515	850	+.0418	165	320	+.0100
175	280	−.00645	520	880	+.0455	150	310	+.0095
195	305	−.00715	515	840	+.0324	100	200	+.0080
215	340	−.00817	455	710	−.0065	70	140	+.0066
100	140	−.00214	440	690	−.0122	65	150	+.0063
110	160	−.00285	440	680	−.0158	80	185	+.0075
120	175	−.00330	385	575	−.0400	110	240	+.0091
330	480	−.00140	420	640	−.0257	205	415	+.0087
395	555	−.01255	420	650	−.0240	260	515	+.0060
600	770	−.01530	460	750	+.0089	335	640	+.0015
630	800	−.01525	465	760	+.0118	360	675	−.0010
690	845	−.01385	470	770	+.0161	405	750	−.0063
720	860	−.01330	425	655	−.0162	405	755	−.0073
780	910	−.01270	420	650	−.0230	885	1010	−.0073
800	925	−.01245	370	555	−.0421	710	840	−.0044
900	1015	−.01175	330	550	−.0616	480	590	−.0011
920	1035	−.01140	355	615	−.0500	565	700	−.0030
990	1105	−.01110	310	490	−.0617	620	750	−.0041
1010	1120	−.01115	500	630	−.0092	720	850	−.0063
1115	1210	−.01025	250	450	−.0910	770	890	−.0070
1130	1230	−.01000	220	395	−.0825	930	1050	−.0095
780	1080	−.0288	215	375	−.0751	1065	1180	−.0106
975	1395	−.0420	195	320	−.0652	1155	1265	−.0110
995	1455	−.0490	190	295	−.0586			
1015	1485	−.0520	170	250	−.0430			

WO_3.			ZnO.			CdO.		
Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.
545	630	−.00650	520	600	−.0550	560	720	−.0123
640	740	−.00700	355	405	−.0300	600	775	−.0141
510	590	−.00530	650	750	−.0544	628	810	−.0151
385	450	−.00395	720	835	−.0670	565	710	−.0123
230	290	−.00243	805	940	−.0724	455	555	−.0080
140	185	−.00250	845	970	−.0740	410	520	−.0073
780	875	−.00875	870	1020	−.0792	330	415	−.0050
800	900	−.00900	880	1040	−.0810	300	380	−.0043
840	970	−.01500	730	870	−.0640	210	250	−.0023
			770	885	−.0700	200	245	−.0024
			900	1060	−.0790	230	280	−.0028
			1155	1350	−.0900	110	135	−.00085
						100	110	−.00065
						140	180	−.00125
						170	200	−.0018
						190	220	−.0019
						490	620	−.0106
						625	800	−.0144
						770	945	−.0170
						865	1065	−.0172
						880	1065	−.0154
						670	840	−.0125
						490	610	−.0077

Cr_2O_3.			Co_3O_4.			SnO.		
Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.
390	515	−.0110	460	550	+.0413	470	530	−.014
450	570	−.0150	420	500	+.0365	485	570	−.025
500	600	−.0148	365	430	+.0321	570	640	−.022
510	625	−.0151	423	500	+.0330	665	730	−.027
530	640	−.0152	500	590	+.0447	620	725	−.040
510	605	−.0110	660	760	+.0453	750	820	−.037
480	570	−.0082	760	868	+.0420	800	950	−.072
470	555	−.0088	840	950	+.0443	670	820	−.064
435	520	−.0075	755	860	+.0440	500	600	−.035
415	490	−.0065	830	948	+.0440	440	535	−.025
730	855	−.0320	920	1055	+.0466	680	815	−.063
750	875	−.0330	1010	1145	+.0524	785	930	−.074
690	805	−.0242	1080	1235	+.0578	880	1035	−.078
625	730	−.0160	1100	1250	+.0583	1000	1160	−.081
800	925	−.0375	1110	1255	+.0585	1035	1195	−.080
820	940	−.0375	1130	1290	+.0600	700	790	−.040
830	945	−.0372	960	1100	+.0526	755	845	−.043
915	1055	−.0435	830	950	+.0470			
925	1075	−.0430	755	850	+.0440			
945	1090	−.0415	620	705	+.0470			
1033	1190	−.0410	610	700	+.0475			
1040	1195	−.0400	525	600	+.0445			
1120	1270	−.0338	470	535	+.0413			
1125	1285	−.0330	368	430	+.0327			
			360	405	+.0320			
			300	350	+.0275			

NiO.			Bi_2O_3.			Mn_3O_4.		
Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.
405	550	+.0250	550	660	+.105	165	230	+.020
430	575	+.0270	580	700	+.090	220	325	+.036
415	555	+.0280	450	555	+.092	285	400	+.040
470	640	+.0355	380	480	+.080	440	575	+.040
560	802	+.0437	630	730	+.070	500	640	+.039
600	825	+.0440	600	660	+.052	565	710	+.041
700	990	+.0490	700	770	+.045	640	780	+.041
810	1130	+.0546	720	800	+.039	710	870	+.0425
900	1170	+.0450	735	815	+.035	800	970	+.0445
995	1285	+.0485	750	820	+.032	825	1000	+.0430
770	1020	+.0490				960	1155	+.0390
595	785	+.0410				1045	1250	+.0332
520	675	+.0352				1065	1270	+.0332
450	575	+.0300				935	1115	+.0335
395	500	+.0265				840	990	+.0360
340	435	+.0230				725	855	+.0360
						600	710	+.0325
						500	615	+.0296
						415	525	+.0300
						660	820	+.0450

PbO.								
Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.	Cold Jc.	Hot Jc.	Volts E.M.F.
220	300	−1.50	600	710	−.041	680	800	+.0115
385	510	−0.24	625	750	−.030	705	815	+.0160
375	480	−0.23	640	755	−.025	720	830	+.0200
300	390	−0.80	650	770	−.0116	740	845	+.0260
500	620	−0.124	660	775	−.0060	760	855	+.0275
530	650	−0.095	670	780	−.0026	768	860	+.0260
555	675	−0.073	670	785	−.0000	800	875	+.0270

ON THE VIBRATIONS OF A LECHER SYSTEM USING A LECHER OSCILLATOR, III.[1]

By F. C. Blake and Charles Sheard.

In our last paper[2] we stated that when the Lecher system was in exact tune with the oscillator and receiver circuits Abraham's theory ought to apply, provided the various harmonics were damped out proportionately. We proposed at that time to try this. The present paper contains some of the results of our experiments in this direction.

Some of the results of the last paper were taken with a receiver which had an effective length one and one half times the length of the Lecher system. The results here reported were taken with the receiver length just one half of the Lecher system length. Fig. 1 shows the arrangement of the circuits. New apparatus was built which permitted quick adjustment of (*a*) the distance between the two parallel wires in each of the three circuits, (*b*) of the distance between the end capacity plates *MN* and *RS* and (*c*) of the distance *MM'*, etc., between the plates of each circuit. The essential data for all the curves here shown are collected together in Table I. The oscillator length, *AB*, is expressed as the distance measured from the axis *A* of the cylindrical steel rods forming the oil-gap to the first bend *B* in the copper wire leading to the end capacity plate *M*. A similar measurement expresses the length *CD* of the Lecher circuit and the length *EF* of the receiver circuit. The end capacity systems *MM' NN'* and *RR' SS'* were exact counterparts of each other except for very slight errors. The plates were made to screw into a small rod 3.5 cm. long and 4.6 mm. in diameter. In this way plates of different diameters could be readily used. All plates used

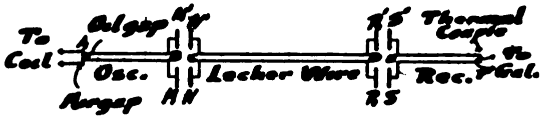


Fig. 1.

---

[1] Read in part before the American Physical Society and Section B, A. A. A. S., Cleveland, December, 1912, and in part before the Ohio Academy of Science, Oberlin, November, 1913. We gratefully acknowledge our thanks to the Trustees of the Elizabeth Thompson Fund for financial aid in carrying on the work here reported.

[2] Phys. Rev., Vol. XXXV., 1912, p. 13.

TABLE I.

1	2	3	4	5	6	7	8	9	10
No. Figure.	Curve No.	Length of Oscillator (Cm.).	Length of Lecher Wires (Cm.).	Length of Receiver (Cm.).	Oscillator Coupling (Cm.).	Receiver Coupling (Cm.).	Distance between Lecher Wires (Cm.).	Diameter Capacity Plates (Cm.).	Distance between Plates Center to Center. (Cm.).
2	I	79.15	158.3	79.15	6	6	5	5	20.0
	II	79.0	158.0	79.0	12	12	5	5	20.0
	III	78.0	156.0	78.0	17	17	5	5	22.4
3	I	77.7	154.8	77.8	3	13	2	7	16.5
	II	77.2	154.4	77.2	13	3	2	7	16.5
3*a*	I	77.2	154.4	77.2	13	10	2	7	16.5
	II	77.2	154.4	77.2	13	7	2	7	16.5
	III	77.2	154.4	77.2	13	5	2	7	16.5
	IV	77.2	154.4	77.2	13	3	2	7	16.5
4	I	85.6	155.0	77.45	13	13	2	7	16.5
	II	81.3	155.0	77.45	13	13	2	7	16.5
	III	77.4	155.0	77.45	13	13	2	7	16.5
5	I	77.5	155.0	80.3	10	12	2	7	16.5
	II	77.5	155.0	77.7	10	12	2	7	16.5
	III	77.5	155.0	75.4	10	12	2	7	16.5
	IV	77.5	155.0	73.2	10	12	2	7	16.5
6	I	77.6	155.0	77.45	8	13	2	5	16.5
	II	79.8	155.0	77.45	8	13	2	5	16.5
	III	82.2	155.0	77.45	8	13	2	5	16.5
	IV	84.5	155.0	77.45	8	13	2	5	16.5
	V	89.8	155.0	77.45	8	13	2	5	16.5
7	I	69.4	↓	↓	↓	↓	↓	↓	↓
	II	66.9							
	III	62.6							
	IV	55.8							
	V	48.2							
	VI	40.5							
	VII	38.0							
	VIII	35.7							
8	I	19.2							
	II	21.2	155.0	77.45	8	13	2	5	16.5
	III	23.1							
	IV	27.8							
9	I	16.8							
	II	14.6							
	III	12.4							
	IV	10.8							
	V	8.2							
	VI	6.1							
	VII	1.5	↑	↑	↑	↑	↑	↑	↑

were made of brass 4.3 mm. thick and turned down in a lathe until they were quite plane. In the table, the distance *MM′* is expressed as the distance between the plates, center to center, while the distance *MN*, *i. e.*, the oscillator coupling, and *RS*, the receiver coupling, are expressed as the thickness of the dielectric (air) between the plates.

The Lecher system was explored in the usual manner by the use of a single sliding bridge.

Some investigations were carried out with capacity plates ranging from 5 to 10 cm. in diameter. The results of this work will form a part of our next paper. Suffice it to say at this point that it was impossible, using the largest sized plates, to get the free thirds entirely on the straight-away portion of the Lecher system. Plates 5 cm. in diameter were accordingly used in order to examine fully the wave system on the Lecher wires. The effect of changing the coupling an equal amount at both ends of the Lecher system was determined. The results are shown in Fig. 2. Three couplings were chosen; 17 cm., 12 cm. and 6 cm. The curves of this figure are not directly comparable as to the energy recorded by the receiver. In none of the curves are the two thirds of equal intensity, the third near the oscillator being the stronger. For the 6 cm. coupling the fundamental is broad and rounding and the third near the receiver has already split into two maxima, though not of equal intensity. It is rather interesting to note that for the loose coupling, 17 cm., the free fifths are higher than the free thirds.

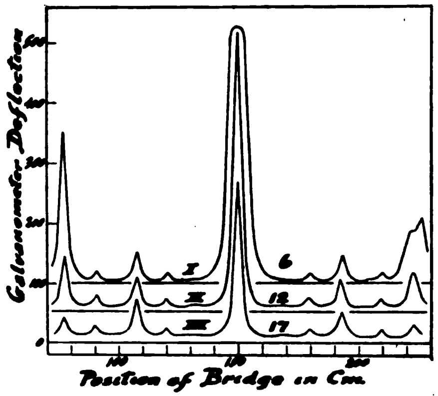


Fig. 2.

That the receiver responded much more quickly to changes of coupling at the receiver end of the Lecher system than it did to changes at the oscillator end is shown by the curves of Fig. 3. In this case plates 7 cm. in diameter were used. Curve I. of this figure was taken with the oscillator coupling 3 cm., receiver coupling 13 cm.; Curve II., the reverse. The two curves are not directly comparable so far as the energy at the receiver is concerned, for the galvanometer shunt for Curve I. was 0.5 ohm and for Curve II., 50 ohms. The latter is a much more complicated curve. Fig. 3*a* shows the central portion of the Lecher circuit for various receiver couplings, the oscillator coupling being held constant at 13 cm. One sees at once how closing the coupling at the receiver end begins to change the simplicity of the wave system. Curve IV., Fig. 3*a*, is the central portion of Curve II., Fig. 3. A study of Curve II., Fig. 3, reveals the following points worthy of mention. The third near the oscillator is beginning to split up into two maxima, one at 76 cm. and the other at 78 cm., the second being weaker than the first. The third in the center of the system is split still further, one of the maxima being considerably stronger than the other. In between these two maxima lies the maximum due to the fifth, while on either side lies the fundamental split in two. For the fundamental likewise the peak nearer the receiver is the weaker. The third near the receiver end is split the most completely of all the thirds on the system, only one of its peaks being obtainable. The fifth near the receiver is weaker and broader than that near the oscillator and shows a tendency to split. It is not surprising, under these conditions, that the internodal spaces are not entirely equal for a given harmonic. If this interpretation is correct, one can then say that any further increase of the closeness of the receiver coupling, after a certain degree of closeness has been reached, causes the harmonics to split up readily, the ease with which they do so being more or less directly proportional to their proximity to the receiver and their intensity at the same time being proportionately lowered.

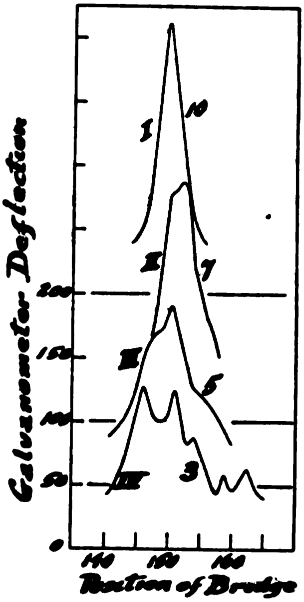


Fig. 3.

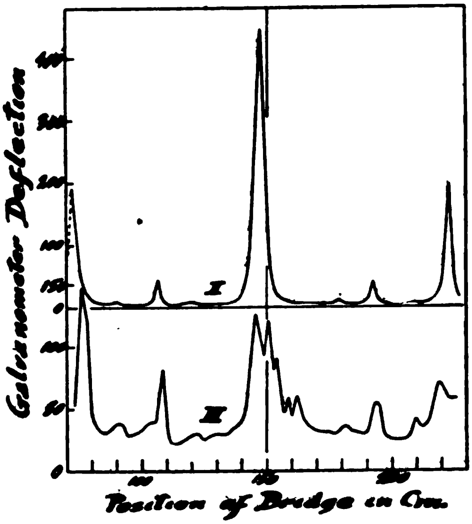


Fig. 3a.

Again using 5 cm. plates we tried the effect of changing the length of the oscillator, leaving the receiver length exactly half of the Lecher system, the couplings at the two ends of the Lecher system being each

13 cm. Fig. 4 shows the results; the numerals marked on the curves are the oscillator lengths. Plainly the relative intensity of the various harmonics is dependent to a marked degree upon the length of the oscillator. Curve II. shows how strong the fifths are for an oscillator somewhat longer than half the Lecher system length. For an oscillator still longer the thirds are much stronger and the fifths very weak, while the sevenths are scarcely in evidence (Curve I.). These results confirmed a suspicion, which we had had for some time, that we would not be able to verify Abraham's theory to any close degree of accuracy, since it would be impossible experimentally to get the various tones to give their maximum strength under identical conditions.

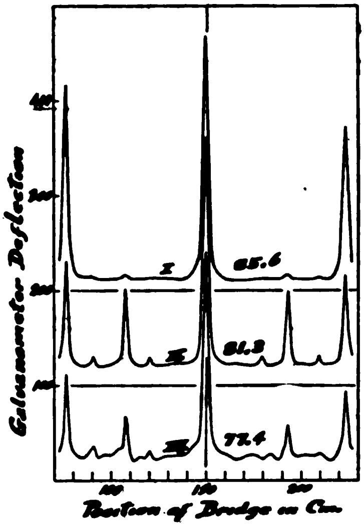


Fig. 4.

It became apparent from the work reported above that an extended research would be necessary to find out the full effect of the oscillator length upon the wave system present in the Lecher wires. Before doing this, however, it seemed desirable to make sure that the optimum length of the receiver was that practically equal to half the length of the Lecher system. Accordingly, with the oscillator length exactly equal to one half of the Lecher system, with the oscillator coupling 10 cm. and the receiver coupling 12 cm., the curves of Fig. 5 were taken as the receiver length was changed. A study of these curves will readily convince the reader that the optimum length of receiver is practically half of the Lecher length. A close measurement of the wave-length for the thirds for the various receiver lengths gave the results plotted in the small curve at the top of Fig. 14 (q. v.). It will be shown farther along in this paper that the *optimum length of the oscillator* for maximum resonance of the thirds is obtainable from the *maximum* wave-length for these thirds (see uppermost of the three curves of Fig. 14). Although the receiver length was changed through a range of 7 cm. only, if the same line of reasoning is used for the receiver, the *optimum length of receiver* for maximum resonance of the thirds, obtained by taking the *minimum* in the small curve of Fig. 14, is found to be a length but slightly less than half the Lecher length, viz., 76.6 cm. On the other hand, if one takes the average ratio of the thirds in Fig. 5 divided by the minimum at 130 cm. one obtains the small curve given at the top of Fig. 10. Here again the optimum length of receiver as determined by the thirds is practically half of the Lecher length, the curve showing it slightly more than half.

It having been satisfactorily established that the receiver length should be half the Lecher length, we began a more complete investigation of the effect of the variation of the oscillator length upon the wave system present in the Lecher wires. The results are shown in Figs. 6 to 9 inclusive. They were all taken with the oscillator coupling 8 cm., the receiver coupling 13 cm. and the receiver length just half of the Lecher length. Considerable care was taken to have the oscillator adjusted so as to make the fundamental tone of maximum strength before taking each curve. The curves need no special discussion other than to have their salient points summarized. Such a summary is made in the curves of Figs. 10, 11 and 12. In Figs. 10 and 11 the minimum at the bridge position 130 cm. was chosen as the denominator for the ratios expressed as ordinates in the curves. Curve I. of Fig. 10 shows four main maxima at 9.0, 15.0, 85.5 and 90.5 cm. respectively. Subtracting 15.0 from 85.5 gives 70.5 cm. as the half wave-length for the free thirds, in good agreement with the mean half wave-length for the free thirds obtained by inspection of the curves of Figs. 6 to 9, viz., 70.7 cm. Curve II. of Fig.

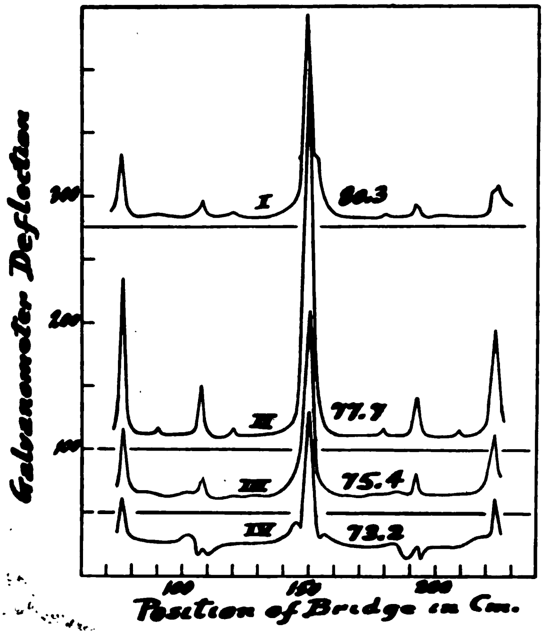


Fig. 5.

10 clearly supports this interpretation of these two maxima of Curve I. The maximum at 90.5 is plainly due to the fundamental tone but the one for the oscillator length 9.0 cm. seems spurious. A special investigation proved its existence, however. It reveals itself in Curve II. for the free third, though not so strongly. A survey of Curve III. of Fig. 6 shows why in Curve I. of Fig. 10 secondary maxima appear at 28 and 60 cm. When the free fifths and sevenths are absent there is a good opportunity for the minimum to be lowered, hence the ratio of the fundamental to the minimum would be increased. Curve II., Fig. 10, was summarized for the free third near the receiver. The curve for the free third near the oscillator differs from it in no essential feature however. It is clear from the curves of Figs. 6 and 9 that the free third at the bridge position 220 (roughly) is sometimes greater and sometimes less in intensity than the third at 79. Their relative magnitudes are summarized in Fig. 11. The two peaks are displaced 2.0 cm. with respect to Curve II., Fig. 10, but the half wave-length remains unaltered. It should be noted that the variation from unity of this ratio between the intensities

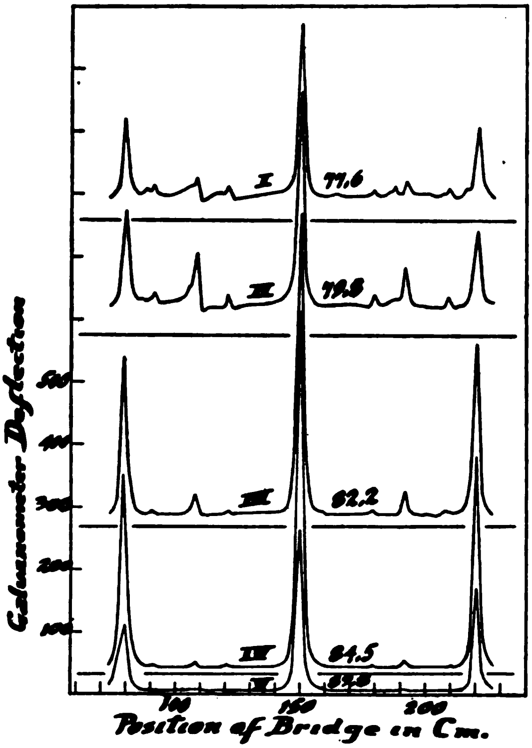


Fig. 6.

of the two thirds is decidedly in favor of the third near the receiver. It would seem as if a real bridge at position 220 and a virtual bridge at 79

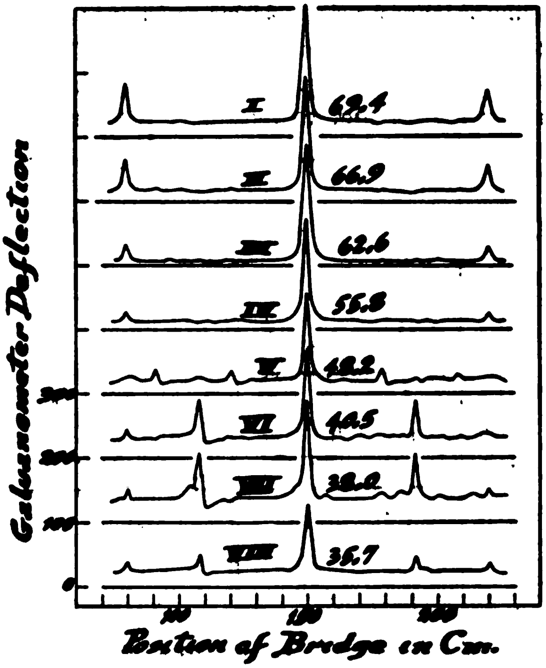


Fig. 7.

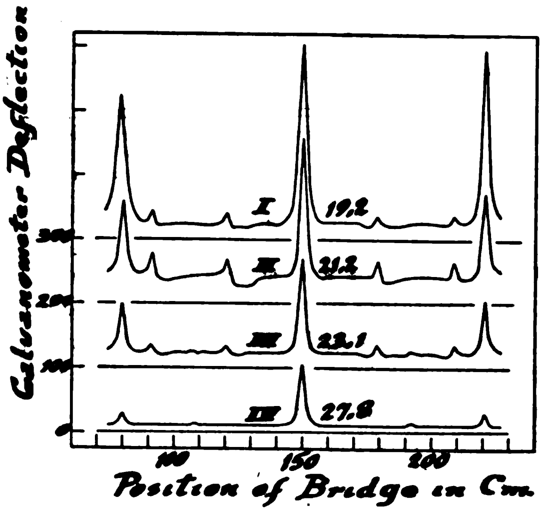


Fig. 8.

makes for a greater resonance at the receiver than the reverse does. Naturally, the use of two real bridges holds the ratio at unity. It was very difficult to determine the true existence of the two secondary maxima for oscillator lengths 75 and 101 cm. Although several attempts were made to make sure of them, we are not disposed to insist on them at present, for slight changes of the oscillator spark-gap in oil exerts a rather

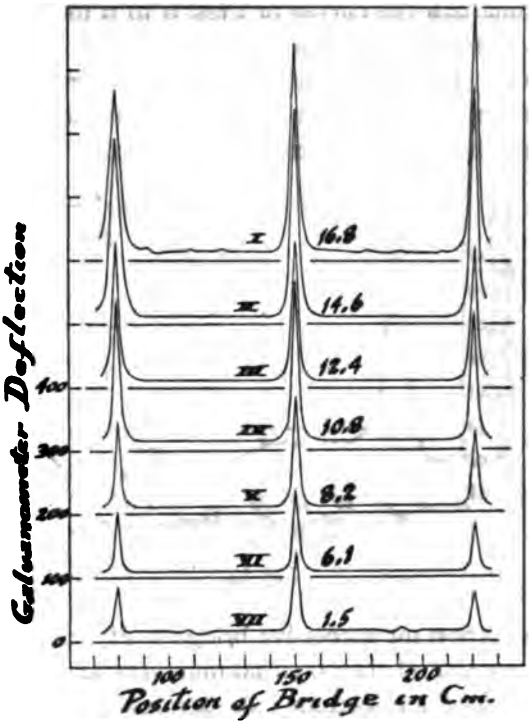


Fig. 9.

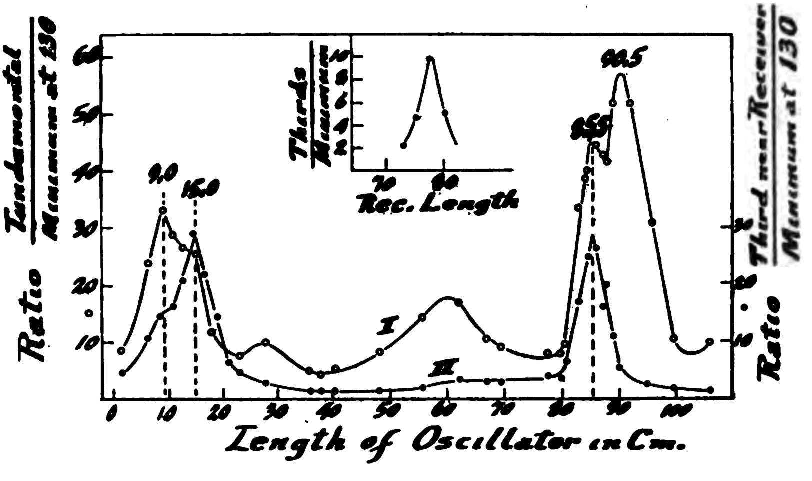


Fig. 10.

large influence upon the relative intensities of the various tones, especially for certain oscillator lengths.

Fig. 12 summarizes the curves of Figs. 6 to 9 for the free fifths and sevenths. In these curves there are many points not lying upon the curves as drawn. This is to be attributed to two things. First, oscillator variation would materially affect such small ratios as are shown in Fig. 12. It is always hard to tell when a small variation in the reading is due to oscillator variation for successive bridge positions and when it is due to a genuine variation of the potential difference along the wires. Such slight variations naturally become more serious for the higher harmonics with their relatively low intensities. It should be borne in mind also that the curves in Figs. 6 to 9 were taken with only a single reading at any bridge position and hence the minimum at 130 could readily be somewhat in error. In the second place, although before taking a curve the oscillator was adjusted to a maximum reading for the fundamental tone, our control of the oscillator was not good enough to prevent entirely changes in the relative intensities of the various tones. Certain it is that for various lengths of the oscillator the relative intensity of the free thirds as against the fundamental is markedly affected by lengthening or shortening the oil-gap 0.05 mm., while for other lengths of the oscillator one can change the oil-gap length over a much larger range without materially affecting the relative intensity of the various tones. This matter requires a special investigation before a wholly satisfactory report can be made upon it.

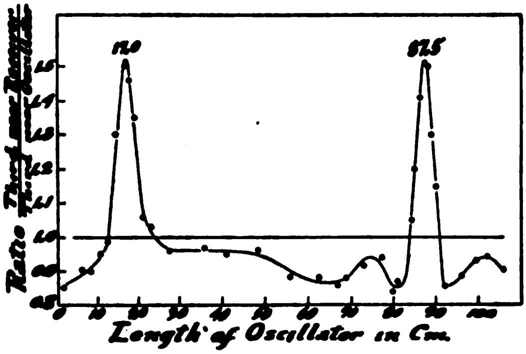


Fig. 11.

The reader will agree, we believe, that the location of the main peaks shown in Fig. 12 cannot be much in error. They give for the half wavelength for the fifths 41.1 cm. and for the sevenths 29.0 cm., in fair agreement with the values obtained from the curves of Figs. 6 to 8; viz., 41.8

cm. and 29.3 cm. The fact that one of the curves of Fig. 12 goes below the axis is not surprising. For Curves I., II. and IV. of Fig. 7 show clearly that at the positions where the free fifths ought to be, phase relations between the two sets of waves, the incident and the reflected, present in the Lecher system are such as to make slight depressions at these points. In Curve III. of Fig. 7, on the other hand, the fifths show slightly. It is possible that a slight readjustment of the oscillator might have put the fifths below the axis for this oscillator length, 62.6 cm., as well. (See dotted portion of curve, Fig. 12.)

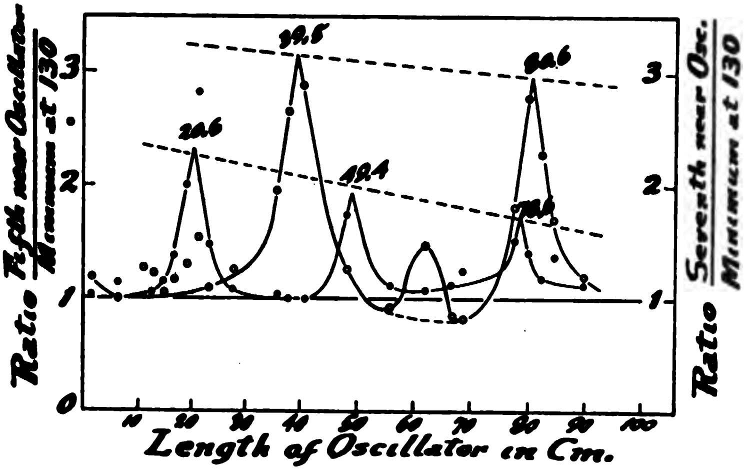


Fig. 12.

A close inspection of the curves in Figs. 6 to 9 shows that there is a slight displacement of the maxima as the oscillator length is changed. To get any satisfactory clue, however, as to the true relationship between these two things a special investigation was required. For, as we have so often found in this work, the exact position of any maximum, as well as its intensity and the degree of verticality of its center of gravity line, is controlled to a measurable degree by the length of the spark-gap in oil.

The results of such an investigation are shown in the curves of Figs. 13 and 14. Here the receiver length was 77.9 cm., or 4.5 mm. longer than the receiver used in obtaining the curves in Figs. 6 to 9. The Lecher system was correspondingly greater than before. The points plotted in Figs. 13 and 14 are the average of several sets of readings varying more or less by reason of our inability to hold the oscillator always in adjustment. That the center of gravity line is not always vertical is illustrated clearly in the upper two curves of Fig. 13, which indicate the two free thirds, plotted to a large scale, for an oscillator length 88.1 cm., Lecher wire length 155.0 cm. and receiver length 77.7 cm. The two lower curves represent the inclination of the center of gravity line for the free thirds near the oscillator and receiver respectively. When the center of gravity line had its upper end pointing away from the oscillator the inclination was called positive; when, on the other hand, toward the oscillator, negative. We were not able, in general, to get the two peaks to incline the same amount. Roughly speaking, the two lower curves may be said to be the mirror images of each other, though this is not true in all strictness. For instance, for oscillator lengths 12.7 and 84.4 cm., when the third near the receiver is quite vertical the third near the oscillator slants slightly toward the oscillator. But at best in work of this sort, by reason of oscillator variation, one is working not very far outside the range of experimental error. In taking the curves here shown, the center of gravity line was always located by getting the readings for any peak by moving the bridge forward by steps and then retracing. We think, therefore, that the difference in the character of the two lower curves of Fig. 13, occurring as it does in the region of maximum resonance for the free thirds, is to be attributed to the essential difference, so far as the effect at the receiver is concerned, between a *virtual* bridge and a *real* bridge. Perhaps, if there were no such difference, the lowest curve of Fig. 13 would be more nearly a counterpart of the one above it, as indicated by the dotted lines.

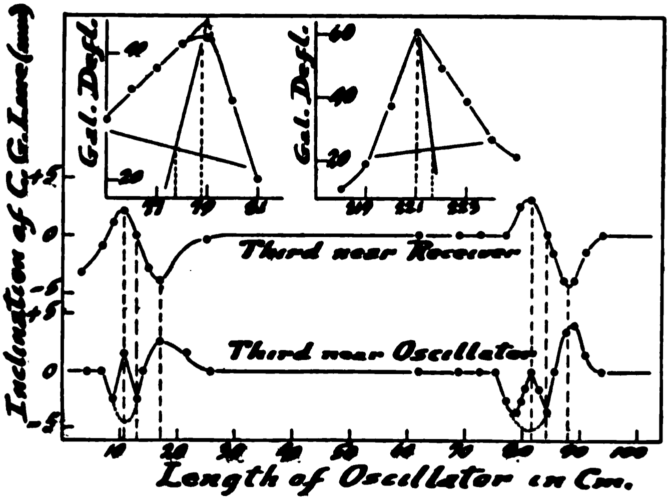


Fig. 13.

Fig. 14 gives the influence of the displacements of these maxima at the two ends of the Lecher system upon the wave-length for the free thirds. The data obtained in the special investigation needed for Fig. 13 was used here. The middle curve shows that the third near the receiver is scarcely affected by a change in the oscillator length, since it is displaced only a few millimeters away from the oscillator when the oscillator length is such as to produce maximum resonance for the thirds. The lowest curve shows a much stronger influence of the oscillator length upon the position of the free third near the oscillator. Naturally this influence ought to be about five times as great for this third as for the third near the receiver, since the third near the oscillator is the fifth and the third near the receiver the first quarter-wave away from the receiver.

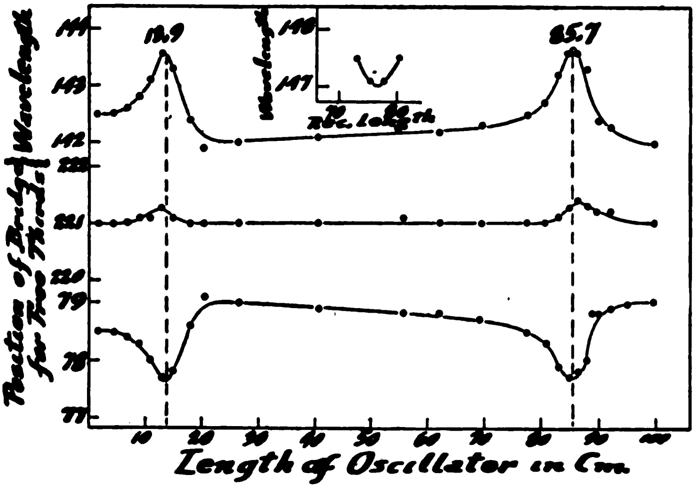


Fig. 14.

This is roughly true. The displacement, however, is toward the oscillator as the length for maximum resonance of the free thirds is approached. The top curve, obtained by subtracting the ordinates for the other two, shows that as the oscillator length increases the wave-length increases up to the point of maximum resonance for this tone and then decreases again. Subtracting 13.9 from 85.7 gives 71.8. This, multiplied by 2, gives 143.6 cm., which is the wave-length indicated by the curve. When the receiver was 77.4 cm. long the wave-length was 142.2 cm. for the free thirds, or about what it should be for Curves IV. of Fig. 6 and Curves I. to III. of Fig. 9.

There is no doubt but that the oscillator length, in an entirely similar manner, influences the location of the free fifths and hence their wave-lengths. Our data point to a length of 84 cm. for oscillator lengths such as to give the maximum resonance for the fifths, whereas the average value obtained from the curves of Figs. 6 to 9 is 83.7 cm. For the sevenths the wave-length for maximum resonance was 59.0, while the average was 58.7 cm.

If the values for the wave-lengths obtained in the manner indicated for maximum resonance for the various tones are multiplied by their frequency numbers and are then plotted against their respective frequency numbers, Curve I. in Fig. 15 is obtained. The curve is a straight line.

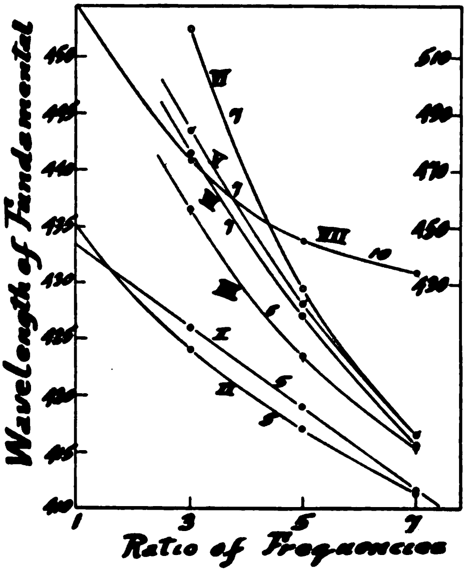


Fig. 15.

If on the other hand we use the values obtained from such a curve as Curve II. of Fig. 6 we get Curve II. of Fig. 15. This curve is similar in type to the curves of Fig. 11 of our preceding paper.[1] It would appear from this work that while the overtones are not only not exactly harmonic—a condition we have always found—yet the variation is strictly linear if proper care be taken to get maximum resonance for each tone. This statement implies practical verticality for the center of gravity lines of the various tones.

Curve III. of Fig. 15 was obtained using 5 cm. plates, with the Lecher and receiver circuits slightly longer than before, but with the distance between the parallel wires 5 cm. instead of 2 cm. A comparison of Curve II. with Curve III. as to slope shows that an increase in the distance between the parallel wires increases the degree to which the wave-lengths for the various tones are inharmonic. It would seem that the tones become strictly harmonic only when the distance between the

---

[1] Phys. Rev., Vol. XXXV., 1912, p. 16.

parallel wires approaches zero, *i. e.*, when the bridge length approaches zero.

Curves IV., V. and VI. were taken with 7 cm. plates. Specifications for all the curves of Fig. 15 are found in Table II. Comparing Curves IV. and V. we see that decreasing the coupling at both ends of the Lecher wires does not affect appreciably the degree of harmony of the tones. On the other hand, Curve VI. proves that increasing the coupling at the oscillator end only *does* decrease the harmony of the tones. Curve VII. was taken with 10 cm. plates with the Lecher wires 5 cm. apart. It is plotted to the larger numerical scale shown to the right of the figure. Comparing this curve with Curve III. shows at once that an increase in the end capacity decreases the harmony of the several tones. This is a necessary consequence of the theory, of course.

TABLE II.

1	2	3	4	5	6	7	8	9	10
No. of Curve.	Diameter Plates (Cm.).	Length of Oscillator (Cm.).	Length of Lecher Wires (Cm.).	Length of Receiver (Cm.).	Oscillator Coupling (Cm.).	Receiver Coupling (Cm.).	Distance Between Lecher Wires (Cm.).	Distance Between Plates Center to Center (Cm.).	See Curve No.
I	5	various	155.0	77.45	8	13	2	16.5	
II	5	79.8	155.0	77.45	8	13	2	16.5	II, Fig. 6.
III	5	79.0	158.0	79.0	12	12	5	20.0	
IV	7	77.4 or 81.3	155.0	77.45	13	13	2	16.5	II or III, Fig. 4.
V	7	82.1	155.0	77.45	9	9	2	16.5	
VI	7	77.7	155.0	77.45	3	13	2	16.5	I, Fig. 3.
VII	10	79.0	157.8	78.8	4	4	5	18.5	

It would seem that three conditions need to be fulfilled if the various tones are to be strictly harmonic, viz.: (1) the distance between the Lecher wires must approach zero; (2) the end capacity must approach zero; and (3) the coupling must be loose at both ends of the Lecher system.

(To be continued.)

PHYSICAL LABORATORY, OHIO STATE UNIVERSITY,
December, 1913

AN EXTENSION OF PROFESSOR MAYER'S EXPERIMENT WITH FLOATING MAGNETS.

By E. R. Lyon.

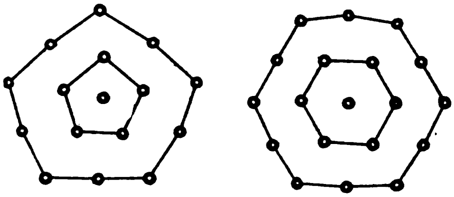
THE experiment with floating magnetic needles and an attracting bar magnet, known as Professor Mayer's experiment, has been frequently cited, as demonstrating the periodic grouping of a number of mutually repelling bodies, restrained by a central force. This experiment is often shown as an illustration of Sir J. J. Thomson's theory of the atom,[1] according to which the negative electrons are arranged in concentric rings in a positive sphere. The floating magnets take the place of the electrons and a bar magnet above them takes the place of the positive sphere. Reference may be made here to a paper by A. C. Crehore, PHYSICAL REVIEW, April, 1912, page 241. The hope of observing an even more complete analogy led the author in the winter and spring of 1911 to attempt an extension, in size and number, of the groups in the Mayer's experiment.

In the initial experiments a glass battery jar was employed for a container, and it was observed that, if the attracting bar magnet were removed, the floating magnetized needles would mutually repel one another to the wall of the jar, where they remained, partly held by their repulsion, and partly by the surface tension of the water. It was further observed that nearly a solid ring of magnets could thus be formed, and that the inward directed repulsion from this ring was, especially with respect to symmetry, even more efficacious in the formation of the Mayer's groups than was a centrally attracting bar magnet. Following this lead, a coil of wire of the same depth and position, and wound upon the outside of the jar, was substituted for the ring of magnets. This coil had forty turns of No. 18 enamelled wire, and a current of from one fourth to one half ampere was passed through it, in such manner that the magnetic field should repel the floating magnets towards the center of the jar. With this device it was observed that still more symmetrical groups could be obtained, and that, furthermore, groups of as high as thirty and forty needles could be easily studied, without any of the inconvenient over concentration at the group center, and sticking together of pairs of needles, such as had been observed when using the suspended bar magnet to produce the central force.

---

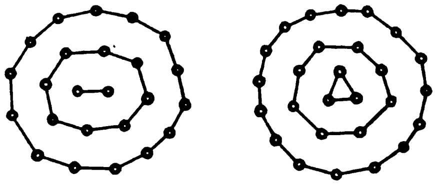
[1] Corpuscular Theory of Matter.

This suggested that any sized group might be obtained by simply constructing a sufficiently large containing tank and repelling coil. Accordingly, a circular zinc tank three feet in diameter and six inches deep was obtained, and wound with a coil of No. 18 enamelled wire. This coil had two layers of forty turns each, with separate leads brought out from each, so that one, or both combined, might be used at pleasure.



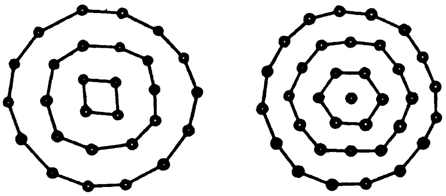
O = 16 = 1-5-10 F = 19 = 1-6-12.

Fig. 1.



Mg = 24 = 2-8-14 Al = 27 = 3-8-16

Fig. 2.



Si = 28 = 4-10-14 Cl = 35 = 1-6-12-16

Fig. 3.

The width, or depth, of the coil was 3.8 centimeters, which was the same as the length of the needles employed. Moreover, care was taken that the tank should be filled to the level of the top of the coil, in order that the magnetic needles, suspended from corks, should float in the plane of the coil. A single layer of the coil, actuated by about one half ampere, was generally found to yield sufficient field intensity, and, as before, the direction of the current was such as to repel the magnets towards the center of the tank.

This tank was never tested to its full capacity, as the interval of one to seventy-five magnets, inclusive, soon proved to be of greatest interest.

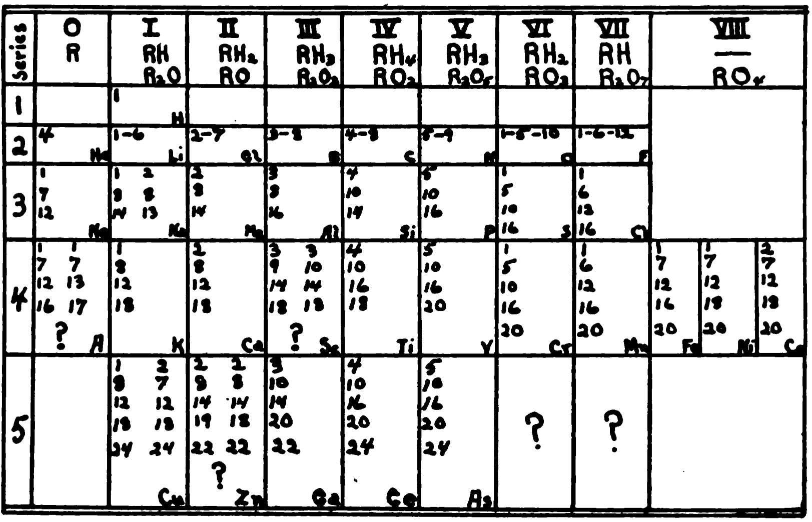
group, the corresponding place in the zero group is unoccupied, and vice-versa. The eighth and zero groups may accordingly be thought of as divergent members of the same family, which have become differentiated on the apportionment of the maximum and minimum valencies. The members of the eighth group are characterized by the maximum valency of the family, eight. The members of the zero group, on the contrary, have taken the minimum valency, zero, or eight minus eight. The eighth and zero groups, when thus united into a single family, conform to our provisional explanation. Besides these, there are, of course, a number of minor valencies, which we can not now consider, except, in passing, to observe that some of the experimental groups also exhibit several arrangements, having instead of one, several possible configurations, but usually only one of a high order of stability.

The following is a list of the experimentally obtained groups from one to seventy-five, inclusive.

1	1	
2	2	
3	3	
4	4	
5	5	
6	1–5	
7	1–6	
8	1–7	
9	2–7	(1–8)
10	2–8	
11	3–8	(2–9)
12	4–8[1]	(3–9)
13	4–9	
14	5–9	(4–10)
15	1–5–9	
16	1–5–10	
17	1–5–11	
18	1–6–11	
19	1–6–12	
20	1–7–12	
21	1–7–13	
22	1–8–13	
23	1–8–14[1]	(2–8–13)
24	2–8–14	
25	2–8–15	
26	3–8–15	
27	3–8–16	(3–9–15)
28	4–10–14	
29	4–10–15	
30	5–10–15	
31	5–10–16	
32	1–5–10–16	
33	1–6–11–15	
39	1–8–12–18	
40	2–8–12–18	
41	2–8–13–18	
42	3–8–13–18	
43	3–9–13–18	
44	3–9–14–18	
45	3–10–14–18	
46	4–10–15–17	
47	4–9–15–19[1]	
48	4–10–16–18	(4–10–15–19)
49	4–10–16–19	
50	5–10–15–20	
51	5–10–16–20	
52	1–5–10–16–20	
53	1–5–10–16–21	
54	1–6–12–16–19	
55	1–6–12–16–20	
56	1–7–12–16–20	
57	1–6–12–17–21	
58	1–7–12–18–20	(2–6–12–18–20)
59	1–7–13–18–20	(2–7–12–18–20)
60	1–7–13–18–21	
61	1–7–13–18–22	
62	2–7–13–18–22	(1–8–13–18–22) (2–8–14–19–20)
63	1–8–12–18–24	(2–7–12–18–24)
64	2–8–13–18–23	(2–8–14–18–22)[1]
65	2–7–14–20–22	(2–8–14–19–22)
66	3–8–14–19–22	
67	3–8–14–19–23	(3–9–14–19–22)
68	3–10–14–19–22	(4–9–14–19–22)
69	3–10–14–20–22	
70	4–9–15–20–22	

34	1-6-12-15	71	4-10-15-20-22	
35	1-6-12-16	72	4-10-16-20-22	
36	1-7-12-16[1]	73	4-10-16-20-23	(5-10-16-20-22)[1]
37	1-7-13-16	74	4-11-16-21-22	(4-10-16-20-24)[1]
38	1-7-13-17	75	5-10-16-20-24	

The table in Fig. 5 contains the first five series of Mendeléeff's table, showing the experimental groups corresponding to each element.



Series	O R	I RH R_2O	II RH_2 RO	III RH_3 R_2O_3	IV RH_4 RO_2	V RH_3 R_2O_5	VI RH_2 RO_3	VII RH R_2O_7	VIII — RO_4		
1		1 H									
2	4 He	1-6 Li	2-7 Gl	3-8 B	4-8 C	5-9 N	1-5-10 O	1-6-12 F			
3	1 7 12 Ne	1 2 8 8 14 13 Na	2 8 14 Mg	3 8 16 Al	4 10 14 Si	5 10 16 P	1 5 10 16 S	1 6 12 16 Cl			
4	1 1 7 7 12 13 16 17 ? A	1 8 12 18 K	2 8 12 18 Ca	3 3 9 10 14 14 18 18 ? Sc	4 10 16 18 Ti	5 10 16 20 V	1 5 10 16 20 Cr	1 6 12 16 20 Mn	1 7 12 16 20 Fe	1 7 12 18 20 Ni	2 7 12 18 20 Co
5		1 2 8 7 12 12 18 18 24 24 Cu	2 2 8 8 14 14 19 18 22 22 ? Zn	3 10 14 20 22 Ga	4 10 16 20 24 Ge	5 10 16 20 24 As	?	?			

Fig. 5.
Mendeléeff's Table with Group Substitutions.

It will at once be noticed that the above are only a chosen few out of all the groups indicated in the experimental list. Let the reader compare the above groups with those which have no corresponding atoms and he will observe that, in the majority of cases, the latter groups are unsymmetrical, and have odd-numbered rings; while a majority of the former groups are symmetrical, and have even numbers of magnets in every ring, except the center group, which we do not consider in either case. For example, there is 5–10–16, which should have a maximum valency of five, and a weight of thirty-one. Every ring, except that of the valency determining center group, is an even number. The element phosphorus, corresponds. A group, 5–10–15, should have a valency of five, and weight thirty. Fifteen is an odd number, and no element corresponds. However, there are several exceptions.

The group which we prefer for argon is 1–7–12–16. This would give an atomic weight of thirty-six, instead of thirty-nine. It is possible that the thirty-eight group, 1–7–13–17, may stand for argon. These

[1] Groups so marked are of weak stability and formed with difficulty in the experiment.

experiments therefore suggest that the atomic weight of argon may be less than thirty-nine.

A further point of interest is, that the group for chlorine, 1–6–12–16, simply adds a ring of 16 to the group of fluorine, which is 1–6–12. This is very suggestive in view of the strong family resemblance of these elements, and seems to experimentally confirm a suggestion first made by Sir J. J. Thomson. The reader may find for himself other such instances by comparing the groups given in the Mendeléeff's table.

In carrying out these experiments, a small jar of eight or ten inches diameter will be found most suitable for the small groups, one to twenty; while the large tank, described, is most suitable for the larger groups. The field strength should be made such that the average distance between needles is nearly equal to their lengths, which may be one and one half to two inches. Care should be taken to avoid drafts of air on the surface, or currents within the body of the liquid. Much patience is required with some of the larger groups. The author has waited as long as three hours for a single group to establish its permanent equilibrium.

These experiments were done in the physical laboratory of Phillip's University (Enid, Oklahoma), through the permission of Professor A. F. Reiter, of that institution. For this and for other assistance and inspiration which he has rendered to me I wish to thank him. I am now engaged, in the physical laboratory of the Rice Institute (Houston, Texas), in the continuation of this work towards the clearance of some exceptional cases, and the investigation of larger groups.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THERMAL ELECTROMOTIVE FORCE AT THE JUNCTIONS OF METALS AND METALLIC OXIDES.[1]

BY S. L. BROWN.

THIS work suggested itself when it was noticed that considerable electromotive force is generated when a cold wire is brought in contact with a similar or dissimilar hot wire. If two iron wires are fastened to the terminals of a galvanometer, one wire heated in a flame and the heated portion is touched with the cool wire, the electromotive force is many times sufficient to throw the galvanometer deflection off the scale. If two similar wires are left in the flame, the electromotive force will reduce to zero or nearly zero; and, if they are dissimilar, the electromotive force will reduce to the value that is characteristic of the two metals at the particular temperature.

These large electromotive forces were found to be due to the oxides which formed on the heated metals and experiments were planned to investigate the thermal electromotive force at a junction of the oxide and the metal. The high resistance of the metallic oxides caused some difficulties, but if the oxides are obtained by completely oxidizing no. 12 or no. 16 wires of the metals, an inch length of the oxide can be inserted in the unknown electromotive force arm of the potentiometer and still permit the electromotive force to be measured to millivolts when a reasonably sensitive galvanometer is used to detect a balance.

The following data gives the electromotive forces of the copper copper-oxide couple and the corresponding temperatures of the hot junction while the cool

Temp. of Cold Junction.	Temp. of Hot Junction.	E.M.F. in Millivolts.
°	°	
20 C.	50 C.	14.7
"	139	58.8
"	270	152.
"	393	294.2
"	455	411.
"	500	491.
"	530	556.

---

[1] Abstract of a paper presented at the Atlanta meeting of the Physical Society, December 31, 1913.

junction was maintained at about 20° centigrade. Examination of the data indicates that the thermo-electric equation of such a couple would be fairly accurately expressed by the parabola,

$$E = .105t + .00175t^2$$

where E is expressed in millivolts and t is expressed in degrees centigrade.

The iron copper-oxide couple and the iron iron-oxide couple have been examined but not sufficiently accurately to determine the exact form of their electromotive force temperature curve. The electromotive forces of the iron copper-oxide couple are of about the same magnitude as those of the copper copper-oxide couple. The electromotive forces of the iron iron-oxide couple are only about half as large as those of the copper copper-oxide couple. These couples as well as couples formed with other metallic oxides are going to be investigated with the hope of soon being able to thermo-electrically classify these oxides.

The electromotive force produced when a cool wire is brought in contact with the hot wire is, therefore, explained as due to the oxide on the wire or wires. The temperature of the oxide at the point of contact with the cool wire is much lower than the temperature of the oxide at the point of contact with the hot wire and consequently a metal metal-oxide thermo-couple is formed.

These results emphasize the necessity of close contact between the metals of any thermo-couple since a very small difference between the temperatures of the wires would produce erroneous results if an oxide separated the wires. There also seems to be sufficient reason for discarding the method that is sometimes used to test thermo-couple wires for homogeneity. This method is to bring two wires in contact in a flame and by moving from point to point along one wire non-homogeneity would result in a thermo-electromotive force if the wires were of the same material or a change in the electromotive force if the wires were of different materials. A small difference between the temperatures of the wires and an oxide between them would produce electromotive forces much larger and much more variable than the electromotive force due to non-homogeneity.

An electromotive force of half a volt or more can easily be maintained between two copper rods by heating one in a flame to redness and holding the rather sharp point of another large rod in contact with the oxide on the hot rod. Since only a small surface of the cooler rod is in contact with the oxide and since the high conductivity of the copper permits the heat to be rapidly conducted away from the point, the one rod remains comparatively cool and the electromotive force is maintained.

Second Series. *April, 1914* *Vol. III., No. 4.*

THE

PHYSICAL REVIEW.

SOME NEW DIFFRACTION PHOTOGRAPHS.

By Mason E. Hufford.

IT is well known that if monochromatic light from a point source is made to pass through a circular opening and fall upon a screen and if the size of the opening is chosen so that the difference in optical paths by way of the boundary and by way of the center of the opening is some whole number of half wave-lengths of the light used, then in the illuminated area where the paths end there will be interference. At the center of the area the interference will be constructive or destructive depending upon whether the path difference is an odd or an even number of half wave-lengths of the light. Openings of this sort may be considered as being made up of a series of annular rings or half period elements—due to a point source of light at a finite distance—similar to the Huyghens half period elements in the case of a plane wave. When the number of half period elements is even they destroy the effect of one another in pairs and the center of the area is black. When the number is odd the effect of one ring is not destroyed and the center is white.

Photograph *b* shows how this theory is verified by a photograph of the diffraction patterns from a series of openings varying consecutively from one to twenty-five half period elements in size. The light chosen to obtain Photograph *b* was the intense fluting beginning at wave-length $3{,}880 \times 10^{-8}$ cm. in the spectrum of the carbon arc. This region appeared most effective on the photographic plate used. It was isolated by means of a spectrometer as shown in Fig. 1.

Light from an arc *A* was focused on the slit of a spectrometer *Sp* from which the eyepiece was removed. The desired spectral region was focused on an opening .3 mm. in diameter through which the light passed along the axis of a light tight box 12.3 meters long and 20 cm. by 20 cm. in cross section. At the center of the length of the box and at right angles to the light rays was placed a brass plate .8 mm. thick through which had been drilled twenty-five circular holes ranging from 2.185 mm. to 10.927 mm. in diameter. Since it is difficult to drill accurately circular openings in a plate so thin, the plate was first bolted securely at the corners and soldered at the edges to another plate of equal thickness. Thus burring of the drills was prevented. The desired diameters were indicated on long accurately gauged tapering reamers and these used to finish the drilling. The diameters of the holes were measured by means of a dividing engine. It is probable that the calculated and actual diameters did not differ by more than .0005 cm. Photograph *a*, reduced to one half, shows the arrangement of these holes. Photograph *b* (actual size) shows the resultant diffraction patterns. The alternate light and dark centers show clearly the constructive and destructive interference depending upon an odd or even number of half period elements in the openings.

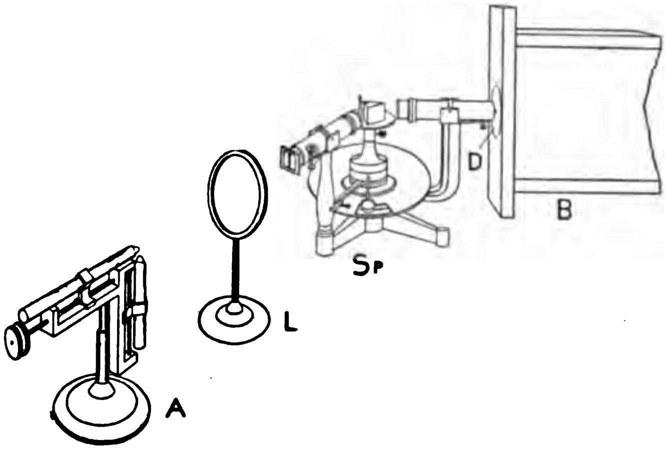


Fig. 1.

In order to photograph the Arago white spot at the center of the geometric shadow of large discs and spheres, apparatus was arranged as shown in Fig. 2.

Here *S* represents the disc or sphere suspended by fine wires in the box previously mentioned. Reflection from the walls was prevented by diaphragms *Sc*. The discs ranged from 2.55 cm. to 6 cm. in diameter and the spheres from .382 cm. to 6.35 cm. in diameter. The bright spot was obtained using any one of the discs or spheres and varied in diameter from .3 mm. to 1 cm. depending upon the size of the aperture which admitted light to the box.

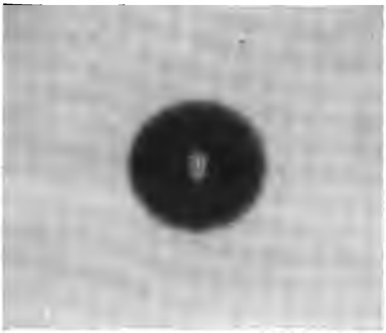
The very large bright spots thus obtained show that each point in the aperture produces a corresponding effect in the shadow. This suggests therefore, that the aperture may be any sort of figure and in the shadow of the disc or sphere there should be an inverted image of it.

To test this conclusion an aperture 1.4 cm. high by .8 cm. wide, of the form of a monogram of the letters *I* and *U* was made in a thin aluminium e. This aperture was mounted over the opening in the box and the

PHYSICAL REVIEW, VOL. III., SECOND SERIES.
April, 1914.

PLATE I.
To face page 242.

a



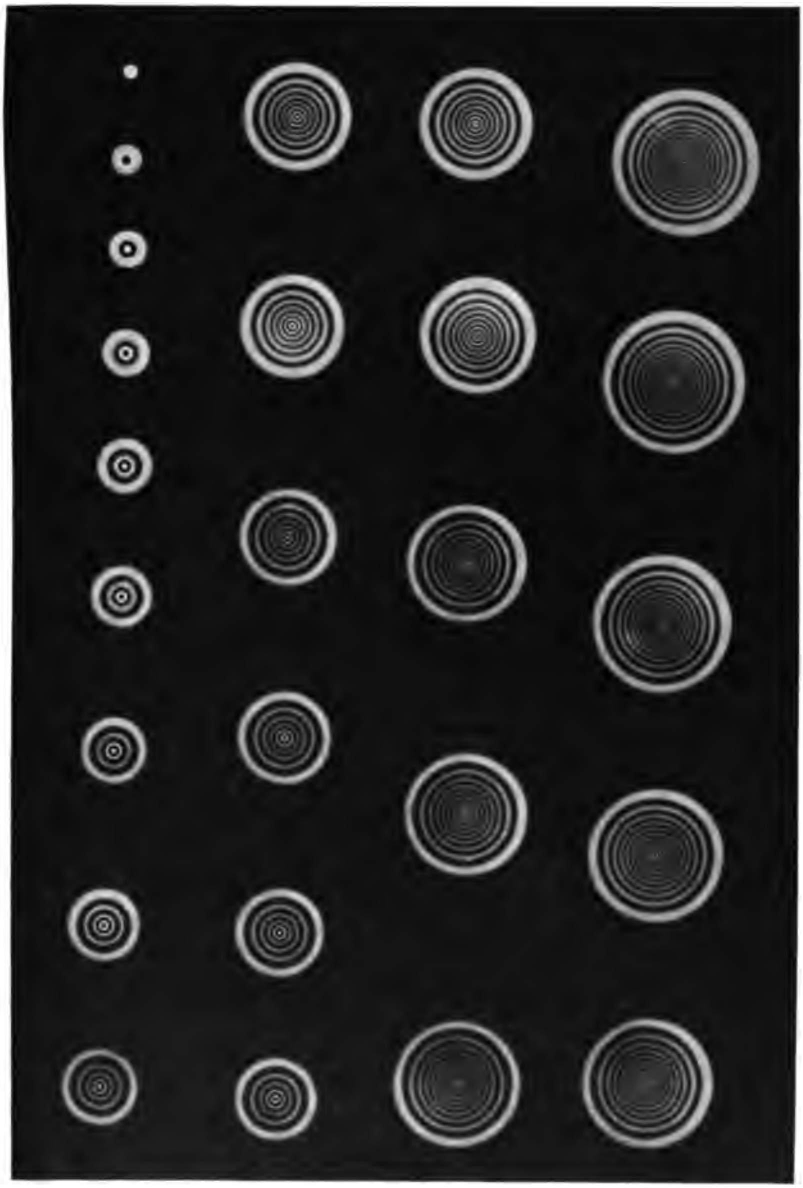
c

d

e

f

MASON E. HUFFORD.



b

MASON E. HUFFORD.

arc focused upon it as shown in Fig. 2. Photographs *c* and *d* show the diffraction images obtained.

It is easily seen that moving the disc or sphere nearer the aperture produces an enlarged image while moving it farther away produces a smaller one. For Photograph *c* (reduced to two-thirds) the sphere was 3.5 cm. in diameter, the distance from the sphere to aperture was 8.2 meters and from sphere to photographic plate was 4.1 meters. For Photograph *d* (reduced to two-thirds) using the same sphere, the distances from sphere to aperture and from sphere to photographic plate were reversed.

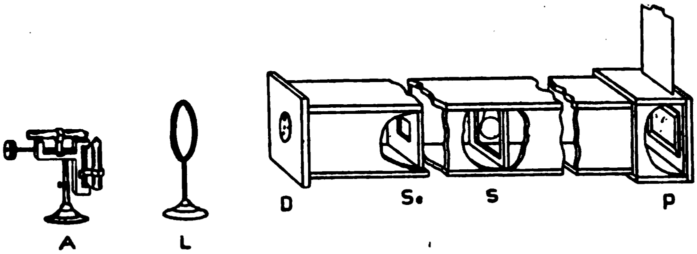


Fig. 2.

From these photographs it is seen that with sufficient contrast on a photographic transparency an actual picture may be made, in which a disc or sphere replaces a lens.

Photograph *e* (actual size) represents a transparency 3.4 cm. high by 2.7 cm. wide which was used for this purpose. In this case the box was 23 meters long and 35 cm. by 35 cm. in cross section. The sphere was suspended 13.5 meters from the aperture over which the transparency was mounted. Photograph *f* (actual size) was obtained by using the transparency described above and a steel sphere 4.5 cm. in diameter as a diffraction object. The positive carbon of the arc was focused on the aperture (in this case the transparency) and the photographic plate exposed for ten seconds.

All of the results here described are in complete accord with diffraction theory. Photographs *c*, *d* and *f* show that by using a disc or sphere, diffraction images may be obtained which in size and position are analogous to those obtained from lenses and with a definition that is surprisingly good. In none of the photographs shown was the negative intensified or retouched.

It gives me great pleasure to acknowledge here my indebtedness to Professor A. L. Foley, whose suggestions and interest in this work have been most helpful.

Laboratory of Physics, Indiana University,
December, 1913.

THE PRINCIPLE OF SIMILITUDE.

By Richard C. Tolman.

THE purpose of the following article is to present some considerations which appear to have validity throughout the field of physical science. Our conclusions will all be drawn from a single postulate which we shall call the principle of similitude. This new principle may be stated as follows: *The fundamental entities out of which the physical universe is constructed are of such a nature that from them a miniature universe could be constructed exactly similar in every respect to the present universe.*

For particular kinds of dynamical systems a somewhat similar hypothesis was advanced by Newton[1] but we shall see that any complete development of the consequences of our postulate is dependent both on a knowledge of the electron theory and the theory of relativity.

We shall find that our principle provides a very simple and general method for obtaining conclusions as to the form of functional relations connecting physical magnitudes. As examples of the method we shall first deduce a number of relations in various branches of physics which will be found in agreement with those that can be obtained by more specific methods of attack. We shall then use the principle for obtaining a conclusion as to the nature of gravitational action. In a later article we shall use the principle of similitude in deriving a formula for the specific beat of homogeneous isotropic elastic solids. In the future we may regard the principle of similitude at least as a temporary criterion for the correctness of physical theories which may be advanced.

In order to derive the desired conclusions from our postulate let us consider two observers, O and O', provided with instruments for making physical measurements. O is provided with ordinary metker stics, clocks and other measuring apparatus of the kind and size which we now possess, and makes measurements in our present physical universe. O', however, is provided with a shorter meter stick, and correspondingly altered clocks and other apparatus so that he could make measurements in the miniature universe of which we have spoken, and in accordance with our postulate obtain exactly the same numerical results in all his experiments as does O in the analogous measurements made in the real universe.

---

[1] Principia, lib. II., prop. 32.

UNITS OF LENGTH.

Let the meter stick used by O' be shorter than that used by O in the ratio $1 : x$. Hence if O and O' should both measure the *same* given distance they would find for it respectively the lengths l and l' connected by the relation

$$l' = xl. \tag{1}$$

UNITS OF TIME.

We may next inquire as to the units of time employed by the two observers. Since by our postulate we could construct for O' a universe which would appear to him exactly the same as the actual universe does to O, it is obvious that the velocity of light in free space must measure the same both for O and O'. The *only way*[1] in which this can be possible is for O' to use a shorter unit of time than does O, shorter in the ratio of $1 : x$. This shorter unit of time will then exactly compensate for the shorter meter stick, and O' will thus obtain the same numerical value for the velocity of light as does O. If now O and O' should both measure the *same* interval of time they would find for it respectively the number of seconds t and t' connected by the relation

$$t' = xt. \tag{2}$$

UNITS OF VELOCITY AND ACCELERATION.

Since we have seen that O' uses units of length and time both of which are shorter than those of O in the ratio $1 : x$, it is evident that any *given* velocity will appear the same both to O and to O' giving us the relation,

$$v' = v. \tag{3}$$

Furthermore, since acceleration has the dimensions $[l]\ [t]^{-2}$ it is evident that their measurements of a *given* acceleration will be connected by the relation

$$a' = \frac{(1)}{x} a. \tag{4}$$

UNITS OF ELECTRICITY.

We must next inquire as to the relation between measurements of a given electrical charge as made by the two observers. In accordance with the electron theory we may accept the general principle that electricity is not a continuum but exists in definite amounts, each elementary charge being that of the electron. From this fundamental point of view

---

[1] The possibility of making the velocity of light appear the same to O' as to O by filling O''s space with an ether having different properties from that of O is excluded, since in accordance with the theory of relativity free space contains no ether.

the proper way to measure an electrical charge is to count the number of electrons which it contains, the fundamental unit of electricity will be the charge of the electron, and the magnitude of a charge will be expressed as an integral number. Now it is evident that if O and O' should examine the *same* electrical charge and count the number of electrons which it contains they would necessarily arrive at the same result, and hence if e and e' are their values for the magnitude of a *given* charge, we shall have the relation

$$e' = e. \tag{5}$$

UNITS OF MASS.

In order to obtain a relation between the units of mass employed by O and O' we may consider how a simple electrostatic experiment would appear to the two observers. Consider two charges of electricity e_1 and e_2 placed on suitable bodies and separated by a considerable distance l. From Coulomb's law the force between the charges is e_1e_2/l^2, and hence if we release one of the bodies which has the mass m it will obtain the acceleration a as given by the following equation:

$$ma = \frac{e_1e_2}{l^2}. \tag{6}$$

We may suppose the quantities in this equation to have been measured by observer O. If O', however, should also observe the same experiment, it is evident from the principle of similitude that he too would have to find Coulomb's law obeyed and would obtain the relation

$$m'a' = \frac{e_1'e_2'}{l'^2}. \tag{7}$$

We have, however, transformation equations for all the quantities in this equation except m'. These equations, Nos. (1), (4) and (5), give us on substitution the relation

$$m'\frac{a}{x} = \frac{e_1e_2}{x^2l^2}. \tag{8}$$

Combining with equation (6) we obtain the desired relation between the measurements of a given mass as made by the two observers, namely:

$$m' = \frac{(1)}{x}m. \tag{9}$$

FURTHER TRANSFORMATION EQUATIONS.

We have now obtained transformation equations for the fundamental magnitudes, length, time and mass, and can hence obtain a whole series of further equations for force, temperature, etc., by merely considering the dimensions of the quantity in question.

Since force has the dimensions $[m]\,[l]\,[t]^{-2}$ we shall obtain the transformation equation

$$f' = \frac{(1)}{x^2} f. \tag{10}$$

Energy and *absolute* temperature both have the dimensions of $[m]\,[l]^2\,[t]^{-2}$, leading to the transformation equations

$$E' = \frac{(1)}{x} E \tag{11}$$

and

$$T' = \frac{(1)}{x} T. \tag{12}$$

It should be pointed out that the transformation equation for energy has the same form as for mass, which agrees with the requirements of the theory of relativity, which has made mass and energy identical.

For area we shall evidently obtain the transformation equation,

$$S' = x^2 S. \tag{13}$$

For volume,

$$V' = x^3 V. \tag{14}$$

For pressure,

$$P' = \frac{(1)}{x^4} P. \tag{15}$$

For density of mass or energy,

$$u' = \frac{(1)}{x^4} u. \tag{16}$$

For frequency,

$$\nu' = \frac{(1)}{x} \nu. \tag{17}$$

DETERMINATION OF THE FORM OF FUNCTIONAL RELATIONS FROM THE THEORY OF SIMILITUDE.

Having obtained the above transformation equations for physical measurements made by the two observers O and O', we may make use of them for finding the necessary form of a number of relations between physical magnitudes. Our general method of procedure will be to consider some construct which could exist either in the actual universe or in the miniature universe which to observer O' appears the same as the actual universe. It is evident from the principal of similitude that the properties of this construct will have to obey the same general laws, whether measured by observer O or by observer O', while a further condition will be imposed upon the magnitude of these measurable properties by the transformation equations which we have just developed. These two sets of conditions will permit the attainment of definite information as to the necessary form of the functional relation connecting the measurements of different properties of the construct.

THE PROPERTIES OF AN IDEAL GAS.

Let us first consider an ideal gas made up of rigid, elastic, material particles. It is obvious that such a construct would appear to be an ideal gas both to observer O and to observer O', although in accordance with equation (9) the mass of each particle would appear to O' to be $m' = \frac{(1)}{x}m$, where m is the mass as it appears to O.

The Law of Charles.—Suppose now we are interested in the way in which the pressure volume product of such a gas would vary with the temperature, we have,

$$PV = F(T), \tag{18}$$

where $F(T)$ is the unknown function whose form we wish to determine. If there is a general law connecting the pressure volume product and the temperature of an ideal gas, it is evident from the principle of similitude that this law must also apply to measurements made by observer O', and hence we shall also have

$$P'V' = F(T'),$$

where F is the same function as in the previous equation. Substituting for the accented letters their values as given by transformation equations, Nos. (15), (14) and (12), we obtain

$$\frac{PV}{x} = F\left(\frac{T}{x}\right)$$

and combining with equation (18) we have

$$PV = xF\left(\frac{T}{x}\right) = F(T).$$

Since x may be any number the only solution of this functional equation is $F(T) = kT$, where k is some constant which leads to the relation

$$PV = kT.$$

In other words, we have derived from the principle of similitude the law of Charles for an ideal gas.

The Specific Heat of an Ideal Gas.—Let us suppose that the energy of such an ideal gas is dependent merely on the temperature. We have,

$$E = F(T) \tag{19}$$

and from the principle of similitude

$$E' = F(T').$$

Substituting transformation equations (11) and (12) we have,

$$\frac{E}{x} = F\left(\frac{T}{x}\right)$$

and combining with (19) we have,

$$E = xF\left(\frac{T}{x}\right) = F(T),$$

a functional equation for which the only solution is,—

$$E = kT,$$

where k is some constant.

This proves that the energy content of such an ideal gas is proportional to its temperature, or that the specific heat is independent of the temperature, a relation which is known to hold for gases which can be considered as composed of elastic, rigid, material particles.

THE PROPERTIES OF THE HOHLRAUM.

A hohlraum is another construct which would obviously appear as such both to observer O and observer O', although in accordance with our transformation equations its temperature and the frequency of the radiation which it contains would appear different to the two observers.

The Energy Density in Thermodynamic Equilibrium.—Consider for example a hohlraum which is in thermodynamic equilibrium; we may determine the law connecting the energy density and the temperature. We have,

$$u = F(T), \tag{20}$$

where F is the unknown function whose form we wish to determine. And from the principle of similitude we also have,

$$u' = F(T').$$

But from the transformation equations (16) and (12) we obtain,

$$\frac{u}{x^4} = F\left(\frac{T}{x}\right).$$

Combining with (21) we have,

$$u = x^4 F\left(\frac{T}{x}\right) = F(T),$$

and the only solution for this functional equation is

$$u = aT^4,$$

where a is some constant. Hence we see that the principle of similitude has led to Stefan's law for the energy density of a hohlraum.

Distribution of Radiation.—It is also possible to obtain from the principle of similitude some information concerning the distribution of energy among the different wave-lengths. Let $u_\nu = \dfrac{du}{d\nu}$ be the rate of change of of the energy density with the frequency.

We have,

$$u_\nu = \frac{du}{d\nu} = F(\nu, T) \tag{21}$$

and from the principle of similitude,

$$u' = \frac{du'}{d\nu'} = F(\nu', T').$$

Substituting transformation equations (16), (17) and (12) we obtain,

$$\frac{u_\nu}{x^3} = F\left(\frac{\nu}{x}, \frac{T}{x}\right),$$

$$u_\nu = F(\nu, T) = x^3 F\left(\frac{\nu}{x}, \frac{T}{x}\right).$$

Unfortunately, this functional equation has no unique solution; it is important to point out, however, that a particular solution of our equation is the functional relation

$$u_\nu = F(\nu, T) = \nu^3 F^1\left(\frac{T}{\nu}\right)$$

which Wien has shown to be a necessary condition for any radiation equation.

THE PROPERTIES OF THE ELECTROMAGNETIC FIELD.

The principle of similitude leads to simple proofs of a number of important relations in the theory of electromagnetism.

Energy Density of an Electrostatic Field.—Suppose, for example, we wish to determine how the density of the energy u in an electrostatic field depends upon the field strength E. We have,

$$u = F(E), \tag{22}$$

and from the principle of similitude,

$$u' = F(E').$$

Now the field strength E has the dimensions of force per unit charge so that by applying transformation equations (16), (10) and (5) we obtain

$$\frac{(1)}{x^4}u = F\left(\frac{E}{x^2}\right),$$

and by combining with equation (22) we have,

$$u = F(E) = x^4F\left(\frac{E}{x^2}\right),$$

for which the only solution is

$$u = kE^2,$$

where k is a constant. In other words, the energy density of an electrostatic field is proportional to the square of the field strength. By similar methods we could show that the energy density of a magnetic field is proportional to the square of the magnetic field strength.

There are many other electromagnetic relations upon which light is thrown by the theory of similitude. We shall content ourselves, however, by pointing out that the five fundamental equations of electromagnetic theory

$$\text{Curl }\mathbf{H} = 4\pi\mathbf{k} + \frac{(1)}{c}\frac{d\mathbf{E}}{dt},$$

$$\text{Curl }\mathbf{E} = -\frac{(1)}{c}\frac{d\mathbf{H}}{dt},$$

$$\text{div }\mathbf{E} = 4\pi\sigma,$$

$$\text{div }\mathbf{H} = 0,$$

$$\mathbf{F} = \mathbf{E} + \frac{(1)}{c}\mathbf{v}\times\mathbf{H},$$

are in complete accord with the principle of similitude as will be seen by the application of the transformation equations which we have presented.[1]

Properties of the Electron.

The principle of similitude permits us to draw two interesting conclusions as to the properties of the electron. We may consider an electron as a sphere of radius r containing the unit quantum of electricity.

Relation between Mass and Radius of an Electron.—We may now deter-

---

[1] For example, consider the first of these equations, curl $H = 4\pi K + (1/c)(dE/dt)$. If the principle of similitude is correct we must also have as a true equation, curl $H' = 4\pi K' + (1/c')(dE'/dt')$. Now the curl operation is essentially a differentiation with respect to length, and the transformation equation for magnetic field strength is the same as for force, so that we could put curl $H' = (1/x)$ curl $(H/x^2) = (1/x^3)$ curl H. For current density our transformation equations would evidently give us $k' = (1/x^3)k$, and for $(1/c')(dE'/dt')$ we can evidently write $(1/x^3c)(dE/dt)$. Substituting above, we obtain $(1/x^3)$ curl $H = (4\pi/x^3)k + (1/x^3c)(dE/dt)$, but this equation evidently reduces to the one we started with, thus showing no conflict with the requirements of the theory of similitude.

mine how the mass of an electron would depend on its radius. We have,

$$m = F(r),$$

and from the principle of similitude,

$$m' = F(r'). \tag{23}$$

Applying transformation equations (9) and (1) we have,

$$\frac{m}{x} = F(xr).$$

Combining with (23) we obtain

$$m = xF(xr) = F(r),$$

for which the only solution is

$$m = \frac{k}{r},$$

where *k* is a constant. Hence, according to the principle of similitude, the mass of the electron would be inversely proportional to the radius, a relation which can also be obtained by the more elaborate calculations of electromagnetic theory.

Radiation from an Electron.—We may also determine with considerable ease the relation between the energy radiation from an electron and its acceleration. We have

$$\frac{dE}{dt} = F(a) \tag{24}$$

and from the principle of similitude,

$$\frac{dE'}{dt'} = F(a').$$

Substituting transformation equations (11), (2) and (4) we have

$$\frac{dE}{x^2dt} = F(a),$$

and combining with (24) we obtain

$$\frac{dE}{dt} = x^2F\left(\frac{a}{x}\right) = F(a),$$

for which the only solution is

$$\frac{dE}{dt} = ka^2,$$

where *k* is a constant. We thus see that the rate of emission of energy from an accelerated electron is proportional to the square of the acceleration.

The Theory of Gravitation.

In what has preceded we have shown that the principle of similitude provides a simple method for obtaining relations in the most diverse fields of physical science. These relations can all be obtained, however, by the more specific methods of attack used in the particular branches of science under consideration. We shall now point out that in the field of gravitation theory an acceptance of the principle of similitude will lead to quite new conclusions.

Science has long been troubled by questions as to the mechanism by which gravitational forces are produced. On the one hand, almost countless hypotheses have been advanced to explain gravitation by the action of moving corpuscles, ether waves, or some electromagnetic influence, while, on the other hand, it has been warmly urged that gravitational attraction is an inherent property of the mass of a body, and that, having found in Newton's law an exact description of the way in which this attraction acts, any search for a mechanism by which the force is produced is meaningless. An acceptance of the principle of similitude, however, will force us to believe that the gravitational attraction between two bodies is not merely a function of the masses of the bodies and the distances between them, but must depend on something else as well, perhaps, for example, on the properties of some intervening medium.

To prove our point let us assume that the gravitational attraction between two bodies does depend *merely* on their masses m_1 and m_2, and the distance l between them. We have from Newton's law

$$f = k\frac{m_1m_2}{l^2}. \tag{25}$$

But if our assumption that gravitation depends *merely* on the physical entities m_1, m_2 and l is correct, it is evident from the principle of similitude that we must have for the same system

$$f' = k\frac{m_1'm_2'}{l'^2}.$$

But substituting transformation equations (10), (9) and (1) we obtain

$$\frac{f}{x^2} = k\frac{\frac{m_1}{x}\frac{m_2}{x}}{x^2l^2},$$

$$f = \frac{l}{x^2}k\frac{m_1m_2}{l^2},$$

an equation which does not agree with the one with which we originally started, No. (25).

Of course this absurd conclusion might merely mean that the principle of similitude is not universally true. If, however, we have accepted the principle, there are two possible solutions of the problem. In the first place gravitational action may really be proportional not to mass but to some quantity which is itself more or less accidentally proportional to mass, and which like electrical charge appears of the same magnitude both to observer O and to observer O'. A second possible solution of the problem is that the attraction of gravitation does not depend merely on the masses of the attracting bodies and the distance between them, but also on the properties of some mechanism by which gravitational action is produced. The search for the true nature of gravitational action will now become an important problem of physics, and the principle of similitude will be a criterion for judging the correctness of proposed solutions.

Let us suppose, for example, that the force of gravitation depends not only on the masses of the gravitating bodies and the distance between them, but on the magnitudes, A, B, C, etc., of some properties of a gravitational mechanism. We shall then have,

$$f = F(A, B, C \cdots) \frac{m_1 m_2}{l^2},$$

and from the principle of similitude,

$$f' = F(A', B', C' \cdots) \frac{m_1' m_2'}{l'^2}.$$

Let us assume that the transformation equations for A, B, C, etc., are of the form $A' = x^a A$, $B' = x^b B$, etc., we may then obtain

$$f = F(A, B, C \cdots) \frac{m_1 m_2}{l^2} = F(x^a A, x^b B, x^c C \cdots) \frac{m_1 m_2}{x^2 l^2}$$

as an equation which must be fulfilled by a successful hypothesis for the explanation of gravitational attraction.[1]

CONCLUSION.

In the preceding article we have seen that the principle of similitude can be used for the derivation of a large number of physical relations. The methods to be applied have the advantage of great simplicity and generality, but the disadvantage of not providing any information as to the magnitude of the numerical constants which enter the equations.

---

[1] The writer first conceived the idea of the principle of the relativity of size eight or nine years ago, and for more than a year has been engaged in a definite attempt to draw useful conclusions from its corollary the principle of similitude. His progress has always been stopped, however, by the apparent failure of the phenomena of gravitation to meet the criterion of similitude. It is now hoped that the above treatment of the gravitational problem successfully removes this difficulty.

We have also seen that the principle of similitude could be of use for testing new physical theories which may be advanced.

In conclusion we may point out that our fundamental postulate is, as a matter of fact, a relativity principle. Indeed it might be called the principle of the relativity of size. Our postulate states that the fundamental physical entities are of such a nature that from them a miniature universe could be constructed exactly similar in every respect to the present universe, and in the transformation equations which we have developed we have shown just what changes would have to be made in lengths, masses, time intervals, energy quantities, etc., in order to construct such a miniature world. If, now, throughout the universe a simultaneous change in all physical magnitudes of just the nature required by these transformation equations should suddenly occur, it is evident that to any observer the universe would appear entirely unchanged. The length of any physical object would still appear to him the same as before, since his meter sticks would all be changed in the same ratio as the dimensions of the object, and similar considerations would apply to intervals of time, etc. From this point of view we see that it is meaningless to speak of the absolute length of an object, all we can talk about are the relative lengths of objects, the relative duration of intervals of time, etc., etc. The principle of similitude is thus identical with the principle of the relativity of size.

Berkeley, Cal.,
January 18, 1914.

CERTAIN EXPERIMENTS IN SOUND DIFFRACTION.

By G. W. Stewart and Harold Stiles.

THE general character of sound diffraction is well understood and there is little likelihood that experimental study in this field will lead to important discoveries. Nevertheless such experimental examination is highly desirable. The selection of experiments recorded in this paper was influenced by apparatus already constructed and immediately available.

The Shadow of a Rigid Sphere.

The theoretical investigation of the acoustic shadow of a rigid sphere was first made by Rayleigh[1] and was later extended by one of the writers[2] to the more general case where the distance from the sphere concerned is not limited. This theory was tested by the writers[3] and it was found that the experimental results varied from theoretical prediction in a manner indicating errors due to the distortional effect of resonance.

Apparatus.—In those experiments the source of sound was located on a hollow cement sphere, circumference 135.9 cm. This sphere was mounted near the edge of the roof of the physics building and the sound issued from it in a 5 cm. pipe opening. The sound-measuring device was a modified form of Rayleigh disc described in a previous article.[4] The sphere was rotated about a vertical axis which permitted the disc to remain stationary. The sound was produced by an electromagnetically operated tuning fork, 256 d. v., mounted on a resonator box which was introduced into a funnel from which the sound was conducted 7 meters to the vertical pipe entering the sphere.

The same sphere was used in the experiments here recorded but the disc was removed to the floor below and a 5 cm. pipe led from the disc to the position desired in the neighborhood of the sphere. The constancy of the source of sound was all that could be desired. The contact terminal attached to the fork was a short helical spring, 0.3 cm. in radius, of platinum wire, No. 29 B. and S. gauge. When the fork was actuated by storage battery voltage, it would operate for an hour without a change in its amplitude of one per cent.

[1] Rayleigh's Theory of Sound, 1896, Vol. II., p. 254.

[2] Stewart, Phys. Rev., Vol. XXXIII., No. 6, Dec., 1911, p. 467.

[3] Stewart and Stiles, Phys. Rev., Vol. I., No. 4, April, 1913, p. 309.

[4] See Stewart and Stiles, loc. cit.

As shown in Fig. 1, the sphere was rotated about a vertical axis. The Rayleigh disc was removed to the inside room below to prevent the disturbance due to air currents and to decrease the absorption due to resonance at the sphere, it having been observed that both of these errors were serious. With the pipe placed as shown in Fig. 1 the intensity produced in it was strictly proportional to the potential energies at the opening. The disc in the room below was attached directly to the pipe. Fortunately, the pipe length was such that there was no tendency for resonance. This statement is verified by the results.

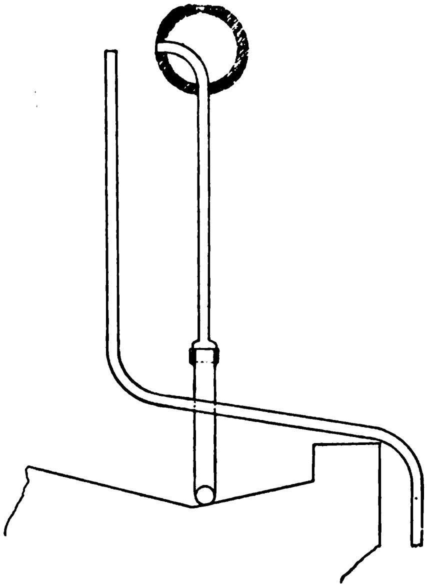


Fig. 1.

The improved apparatus demanded a more sensitive disc and this was obtained by inserting a finer quartz fiber. The period of the disc became 15 seconds.

Theory.—The mean potential energy per unit volume is given by the expression,[1]

$$\tfrac{1}{2}\rho_0(F^2 + G^2)(k/2\pi r\int\int U\,dS)^2.$$

The relative intensities are therefore given by relative values of $F^2 + G^2$. The pipe opening remained at a constant distance r from the sphere center and various values of intensities were obtained by rotating the sphere, this being equivalent to a stationary sphere with the intensities measured at various points in a circumference whose plane includes the diameter of the sphere passing through the source of sound. The relative values of intensities computed as indicated in a previous article[2] for $kr = 2$, are for 0° (the position shown in Fig. 1), 1.00; 30°, 0.560; 60°, 0.187; 90°, 0.065; 120°, 0.034; 150°, 0.033; 180°, 0.033.

Results.—The results obtained for a distance from the center of the sphere equal to twice its radius are shown in Table I. This gives a record of four series of observations. The deviations from the mean can be accounted for by the smallness of the deflection, about 2 cm., and the error due to the setting of the sphere at 30° where the intensity changes

---

[1] For derivation and meaning of symbols see Stewart, loc. cit.

[2] For numerical values see Stewart and Stiles, loc. cit.

rapidly. In order to compare these results with the theoretical values and to show the great improvement over the earlier experimental arrangement, both the present and former results are plotted in Fig. 2, and the theoretical values are shown by the full line curve. The earlier results are represented by crosses and the later ones by small circles. The agreement between theory and experiment is better than could be expected. Our belief is that the errors in the earlier results were due to air currents and to the absorption caused by resonance. The distortion produced by the latter would have the effect of "ironing out" the curve, and the former observations show that that is the case.

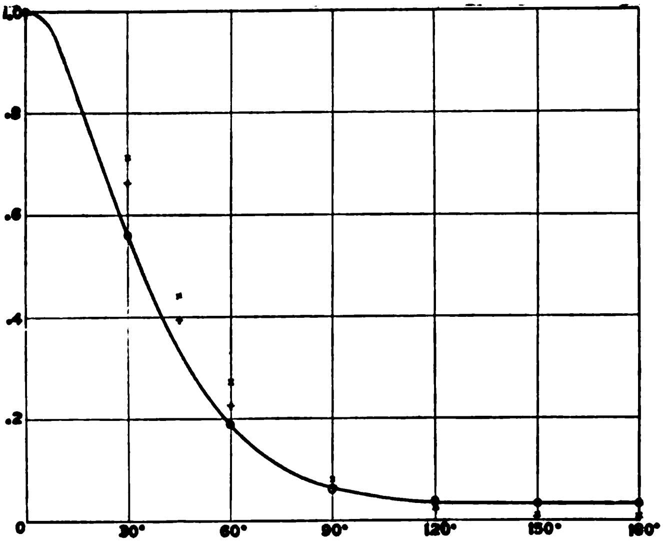


Fig. 2.

TABLE I.

	0°	30°	60°	90°	120°	150°	180°
	1.00	0.580	0.230	0.067	0.035	0.025	0.025
	1.00	0.625	0.175	0.050	0.035	0.035	0.035
	1.00	0.555	0.170	0.050	0.040	0.035	0.030
	1.00	0.475	0.185	0.075	0.045	0.040	0.035
Mean........	1.00	0.558	0.190	0.060	0.039	0.034	0.031

The verification of the theory is very satisfactory. This increases our confidence not only in the theory, but also in the Rayleigh disc. So far as we are aware, there has been no study which has shown that the deflections of the disc are proportional to the potential energy at the opening of the disc tube. It is true that the correctness of the theory of the disc has been experimentally[1] verified so far as the relation between the kinetic energy of the air at the disc and the deflection of the disc are concerned. The writers attempted to show the proportionality of the disc deflection and the potential energy at the disc tube opening by observations of the amplitude of the fork and the deflection of the disc when both were placed in the same room. The dimensions of the room were about 25, 7, and 4 meters. The temperature as measured by wall thermometers was constant to within 1° C. It was found that, if comparisons were made quickly over the range of deflection of the disc, there was a constant proportionality between the square of the fork's amplitude and the deflection of the disc. But the apparent sensibility of the disc measured in this manner changed with time. In other words, the ratio of deflection to the square of the amplitude changed from moment to moment, being quite appreciable in a few minutes. The explanation seemed to be that the maxima and minima intensities shifted their locations with changes in temperature. The changes, however, seemed greater than could be produced by standing waves caused by only one reflection. This might have been anticipated. These tests satisfied our minds of the correctness of the assumption of proportionality of deflection and intensity at the tube opening.

PASSAGE OF SOUND THROUGH NARROW SLITS.

Rayleigh has investigated the passage of sound through narrow slits both theoretically[2] and experimentally.[3] The result of the former can be briefly presented. Consider an aperture in a thin plane screen of infinite extent. Let a plane wave be incident from the left. Its velocity potential, omitting the harmonic time factor and considering the modulus unity, is $\varphi = e^{-\iota\kappa x}$. Consider the conditions without aperture and then the supplementary values of the velocity potential representing the changes produced by the aperture. By addition, the velocity potential on each side of the screen is obtained. The resulting velocity potential at a great distance, r, on the right side is,

$$\varphi = e^{-\iota\kappa r}\frac{M}{r}$$

or

$$\varphi = \frac{M}{r}\cos^{\kappa(at-r)},$$

where k is 2π ÷ *wave-length* and where M is the "capacity." The term

---

[1] Zernov, Annal. d. Phys., No. 26, p. 79, 1908.

[2] Rayleigh, Phil. Mag., XLIII., p. 259 (1897); Scien. Paper IV., p. 291.

[3] Rayleigh, Phil. Mag., XIV., p. 153 (1907).

"capacity" is used because M is the total quantity of electricity which can be distributed over the aperture in a manner to produce a uniform potential of unity over the aperture. It is known that for an ellipse,

$$M = \frac{a}{F(e)},$$

where a is the major axis, and small e the eccentricity, and F is the symbol of the complete elliptic function of the first kind. If the ellipse be very elongated,

$$M = \frac{a}{\log_e\left(\frac{4a}{b}\right)}.$$

Inasmuch as the only variable in the expression for the velocity potential at a fixed great distance, r, is M, the same values of M would determine the same sound intensities. The above formula shows that the intensity is much more sensitive to alterations in a than in b, the minor axis, and Rayleigh attempted to verify this by experiment. The difficulties he encountered were great, and in addition he depended upon ear memory for the reproduction of identical intensities. The arrangement of our Rayleigh disc and the possibility of experimentation practically free from reflection, tempted us to test the above formula.

For the infinite plane a rectangular piece of galvanized iron 33 × 38 cm. was utilized, the dimensions and shape being accidental. This plate was fastened on the horizontal end of an elbow placed upon the end of the pipe shown in Fig. 1. In the center of the vertical plate an opening 0.8 × 4.0 cm. was made, and over the opening was constructed the slit. Four small safety razor blades, 1.8 × 4 cm., beveled on both sides, were used. Three were placed in the same plane and to the fourth was attached an edge made out of a copper strip, whose thickness was the desired width of the slit. Changes in the slit width required different copper strips. Changes in the length could be readily obtained by sliding the fourth blade with its attached copper strip. Vaseline was freely used to stop all openings and was found entirely satisfactory.

The source of sound was the electrically operated tuning fork with the open end of the resonator mounted directly in front of the slit and about 150 cm. distant.

Our first experiments were made with sharpened brass edges but these were found unsatisfactory when the slit became narrow. Experiments with these edges with a width of 1 mm. (b = 0.5 mm.), showed that the variation of intensity with length was practically linear. This fact simplified our experiments with the razor blades. We obtained a deflection with *a* 17.5 mm. and *b* 0.1 mm., then a deflection with *a* 17.5 mm. and *b* 0.5 mm. and finally a deflection with *a* 10.0 mm., and *b* 0.5 mm. The ratio of intensities of the first and second slits were found to be approximately 0.52, the separate values being 0.51, 0.49, 0.55. The ratio of intensities of the third and second was approximately 0.49, the separate values being 0.47, 0.50, and 0.49. By assuming that the linear relation above cited holds, it is readily seen that the value of *a* giving the ratio of 0.52 with *b* 0.5 mm., would be 10.5 mm. We would then have the same value of *M* for the two slits, 35. × 0.2 mm. and 22. × 1.0 mm. Substituting these experimental values, we have

$$M = \frac{a}{\log_e\left(\frac{4a}{b}\right)} = \frac{17.5}{\log_e\left(4\frac{17.5}{0.1}\right)} = 2.66$$

$$= \frac{10.5}{\log_e\left(4\frac{10.5}{0.5}\right)} = 2.37.$$

Thus the formula for *M* is verified as nearly as could be expected with the lack of conformity with theoretical conditions. For it is to be noted that the presence of the pipe behind the slit destroyed the plane of infinite area, and further, that there is resonance in the pipe leading to the disc. This resonance would of course be modified by the size of the aperture. Other experiments cited below would indicate that the error due to resonance is of the same order as the variation between the two values of the *M* given above.

Passage Through Circular Apertures.

Tests were made by varying the area and by varying the number of circular apertures of equal area. The value of *M* for a circle is $2a \div \pi$ where *a* is the radius. If the velocity potential at a great distance is proportional to *M*, then the intensity at a given distance, proportional to $\dot{\varphi}^2$, is proportional to M^2, or to a^2. An experimental test of this relation did not prove satisfactory, for as *M* changed the resonance in the pipe was altered and the conditions of the experiment were thus seriously modified. The values actually obtained are shown in the accompanying table, Table II. The deflections were reduced to the same scale, the aperture *F* giving a deflection of unity. The ratio in the last column is the relation of experimental and theoretical values of *M*. The ratio varies not more than 10 per cent. from the mean for a range of radii from 0.42 cm. to 1.28 cm. These variations, as well as those for the smaller apertures are accounted for by variations in resonance. The indications are, however, that if resonance could be avoided a close agreement between experiment and theory would be found.

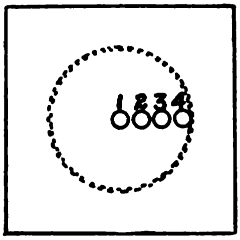


Fig. 3.

The value of M for N circles is $N \times M$, and the corresponding intensity is proportional to N^2M^2. If the M's are not alike, the intensity is proportional to the square of their sum. A test was made as follows. Four circular apertures, each 0.30 cm. in radius were made in a screen, see Fig. 3, and intensities obtained by opening them separately and simultaneously as indicated in the accompanying Table III. The agreement between theory and experiment is indicated by the ratio in the last column. It should be observed that the variation is not great and can readily be interpreted as due to change of resonance in the pipe. The variations of M for the separate apertures is doubtless due to the proximity of the apertures to the pipe. The arrangement is faulty also in that the apertures are close together. The lack of agreement between the experimental and theoretical results is explained by the lack of conformity

TABLE II.

Screen.	Deflection.	$\sqrt{\text{Defl.}} \propto M$.	$2a$.	Ratio.
L	5.45	2.34	2.56	0.91
K	3.67	1.91	1.88	1.02
J	2.00	1.41	1.27	1.11
F	1.00	1.00	1.00	1.00
D	0.56	0.75	0.83	0.90
C	0.20	0.45	0.60	0.75
B	0.06	0.25	0.40	0.62

TABLE III.

Apertures Used.	Relative Observed Values of Intensity.	Relative Values of M $\sqrt{\text{Intensity}} \propto M$.	Relative Computed Values of M $M = M_1 + M_2 + M_3 + M_4$.	Ratio.
1	1.00	1.00		
2	1.00	1.00		
3	0.80	0.90		
4	0.58	0.76		
1 + 2	3.73	1.93	2.00	0.96
1 + 2 + 3	6.23	2.50	2.90	0.86
1 + 2 + 3 + 4	9.66	3.10	3.66	0.83

to theoretical conditions and the variation in resonance in the pipe. The latter seems to produce the greater error. Indeed, all the experiments with apertures indicate that the errors due to changes in resonance are of the same order as the differences between experimental and theoretical results.

The results with both slits and apertures show the difficulty of securing satisfactory experimental conditions. Experiments of this character should be continued with improvements in apparatus that will avoid the errors due to resonance.

Physical Laboratory,
State University of Iowa.

POLARIZATION IN THE ALUMINIUM RECTIFIER.

BY CLARENCE W. GREENE.

THE primary object of this investigation was to make a study of the potential difference between the electrodes of the aluminium rectifier at extremely short intervals after breaking the charging circuit. It was hoped that the investigation might also throw some further light on the action of electrolytic cells. The methods employed and results obtained are new and may be suggestive in the further study of the electrolytic cell.

The aluminium plates, which were used as electrodes, were prepared in the instrument shops of the University of Michigan and were hammered out of 98 per cent. pure aluminium ingots. They were 10 cm. long, 2.7 cm. wide and 0.3 cm. thick. The plates were so insulated with Bank of England sealing wax as to leave a definite area exposed as active electrode to the electrolyte. The cathode was a platinum plate of 20 sq. cm. exposed area, totally immersed in the electrolyte, the platinum wire leading out of the solution being thoroughly insulated from the solution. The insulation thus eliminated any possibility of surface effects, which are found to be present when the electrode surfaces are exposed at the surface of the electrolyte. The active surfaces of the aluminium electrodes were polished with fine sand paper and rinsed with distilled water before each experiment was begun. The electrolytes used were ammonium aluminium sulphate (40 grams per liter of water) and potassium dichromate (26.18 grams per liter of water).

After checking some of the results obtained by former investigators[1] by the ballistic galvanometer-condenser method, a potentiometer method for measuring the counter E.M.F. was devised and the results thereby obtained were compared with those obtained by the former method. The potentiometer method invariably gave larger values for the counter E.M.F. of the rectifier than did the condenser method, the differences being far beyond the range of experimental error. For instance, with a given E.M.F. the difference was consistently about 4.7 per cent. A

---

[1] Theory of the Electrolytic Rectifier, by S. R. Cook, PHYS. REV., 18, pp. 23–29, Jan., 1904; also PHYS. REV., 20, pp. 312–321, May, 1905; H. W. Morse and C. L. B. Shuddemagen, American Acad. Arts and Sciences, *Proc.*, 44, pp. 367–397, 1908–9.

repetition of comparative experiments gave a similar characteristic difference, which indicates that when the charged rectifier is connected to a condenser, a quantity of electricity required to charge the condenser being taken from the rectifier, the electrical condition of the rectifier is thereby disturbed and the difference of potential between the electrodes of the rectifier decreased. The potentiometer method was, therefore, used throughout the remainder of the experimental work.

The arrangement of apparatus for the measurement of the counter E.M.F. of the rectifier after the expiration of definite periods of open circuit is indicated in Fig. 1. *R* is the aluminium rectifier, in which *A* is

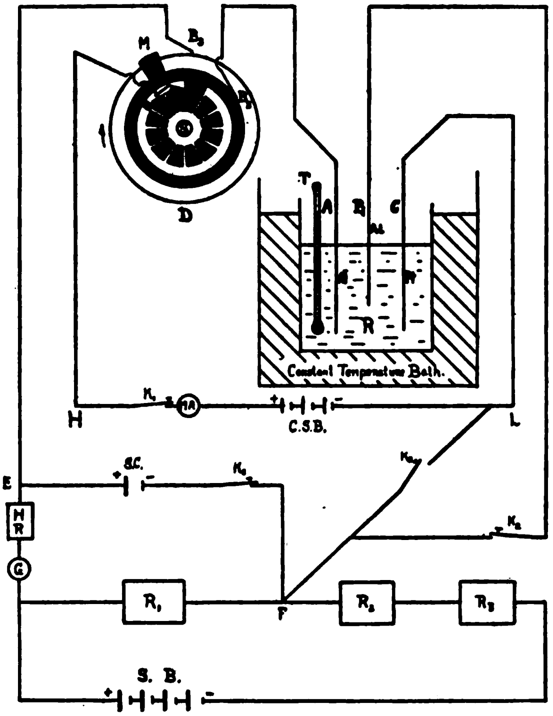


Fig. 1.

the aluminium anode; *C*, the platinum cathode; and *B*, an aluminium test electrode placed at one side and somewhat in the rear of the anode so as not to be in the path of the current between anode and cathode; *C.S.B.*, the charging storage battery; *MA*, a milliammeter; R_1 and R_2, two high grade Leeds and Northrup resistance boxes; R_3, a high grade Leeds and Northrup resistance box with travelling plug; *H.R.*, a 250,000 ohm resistance box; *S.C.* a cadmium standard cell; *G.*, a Leeds and, Northrup high sensibility galvanometer having a resistance of 1,600 ohms; *S.B.*, a storage battery; and *D*, a disc especially designed for this experimental work. The disc consisted of a single piece of hard rubber, 13.5 cm. in diameter and 1 cm. thick, to which were firmly riveted two concentric brass rings, 2 mm. thick and 1.5 cm. wide, the outside diameters being 7.5 cm. and 13 cm., respectively. The inner ring was divided into 30° sectors, one of which was subdivided into two 15° sectors; one of these 15° sectors was later soldered to the adjoining 30° sector, as indicated in the figure. These sectors could be connected, when desired, by inserting a brass plug between them. One of these sectors was electrically connected, as shown in the diagram, to the outer ring. The outer ring was in turn connected to the brass contact maker, *M*, which fitted closely over the rim of the rubber disc. The contact maker could be shifted along the rim by 15° intervals and was firmly held in place by a plug inserted through the contact maker and into the disc from the rear. The disc was rotated by a motor running at an approximately constant speed of 2,000 R.P.M. B_1, B_2, B_3 are spring brass brushes so adjusted as to make good electrical contact with the inner ring, outer ring and contact maker, respectively.

The division of the inner ring into sectors makes it possible to regulate the portion of the period of rotation during which the impressed E.M.F. is applied to the rectifier; the portion of the period finally adopted was the time required for the brush to sweep over a 45° sector. Regulation of the contact maker made it possible to vary the period of decay of the counter E.M.F. of the rectifier before this E.M.F. was balanced against the fall of potential over R_1. The sum of R_1 and R_2 was kept constant and the resistance in R_2 adjusted until the current flowing through R_1 was 0.001 ampere, as was shown, on closing K_4, by balancing the fall of potential over R_1 against the E.M.F. of the standard cell. This made it possible to read the counter E.M.F., on obtaining a balance, directly from the resistance in R_1. On closing K_1, *C.S.B.* charges the rectifier through the disc; on closing K_2 the counter E.M.F. of the rectifier is balanced against the fall of potential over R_1, while B_3 sweeps over *M*.

The arrangement of apparatus indicated in Fig. 1 is such, on closing K_2, as to give the data for the curve of decay between the aluminium anode and the aluminium test electrode, thus giving the effect at the anode only, due to the impressed E.M.F. By closing K_3 instead of K_2 the data for the curve of decay of E.M.F. between anode and cathode were obtained, thus giving the total effect of polarization. To obtain the effect of polarization at the cathode only the positive terminal of *C.S.B.* was disconnected from the disc and connected directly to the anode, while the negative terminal of *C.S.B.* was connected to the cathode through the disc.

It was ascertained that in order to obtain the maximum counter E.M.F. of the rectifier by charging it through the disc while revolving, it was necessary that the motor run for a period of from 10 to 15 minutes before the polarization was measured and 15 minutes was the interval accordingly adopted before any measurements were taken. One of the greatest difficulties met with in experimental work with the rectifier is the slow change in the character of the film with time; and it is therefore necessary (1) that the series of results be taken as rapidly as possible, (2) that the period of open circuit between the determinations of the balance for successive intervals of decay be kept constant, (3) that the points on the decay curve be determined in the same order. A cyclic order of performing the operations was followed, thus rendering it feasible for each series of results obtained to be checked. Yet the author believes that the curves obtained are characteristic of the general behavior of the anode film.

Table I. gives the mean corrected values obtained from a number of experiments and Fig. 2 gives the curves plotted therefrom for the decay of the counter E.M.F. between the anode and the aluminium test electrode (*A*–3), between the anode and cathode (*AC*) and between the cathode and aluminium test electrode (*C*–3), for an applied E.M.F. of 6.16 volts. Table II. gives the corresponding data and Fig. 3 gives the curves for an applied E.M.F. of 12.25 volts. Table III. and Fig. 4 give the corresponding results for an applied E.M.F. of 18.13 volts.

Table I.

Electrolyte: Ammonium Aluminium Sulphate.
Applied E.M.F.: 6.16 volts.
Temperature: 23° C.
Current: 0.00025 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC}, Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	6.43	6.15	....	....	....
0.0013	6.20	5.90	0.31	6.21	−0.01
0.0025	6.02	5.66	0.36	6.02	0.00
0.0038	5.91	5.50	0.39	5.89	+0.02
0.0050	5.78	5.36	0.35	5.71	0.07
0.0075	5.57	5.17	0.36	5.53	0.04
0.0100	5.43	5.01	0.35	5.36	0.07
0.0150	5.24	4.80	0.38	5.18	0.06
0.0200	5.08	4.64	0.38	5.02	0.06
0.0250	4.90	4.51	0.40	4.91	−0.01

TABLE II.

Electrolyte: Ammonium Aluminium Sulphate.
Applied E.M.F.: 12.25 volts.
Temperature: 23.°2 C.
Current: 0.00035 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC}, Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	12.52	12.31	....	.....	....
0.00083	11.92	11.72	0.31	12.03	−0.11
0.0021	11.32	11.07	0.31	11.38	−0.06
0.0033	11.00	10.69	0.31	11.00	0.00
0.0046	10.69	10.42	0.32	10.74	−0.05
0.0071	10.37	10.02	0.33	10.35	+0.02
0.0096	10.14	9.71	0.35	10.06	0.08
0.0146	9.60	9.28	0.36	9.64	−0.04
0.0196	9.37	8.89	0.37	9.26	+0.11
0.0246	9.23	8.75	0.36	9.11	0.12

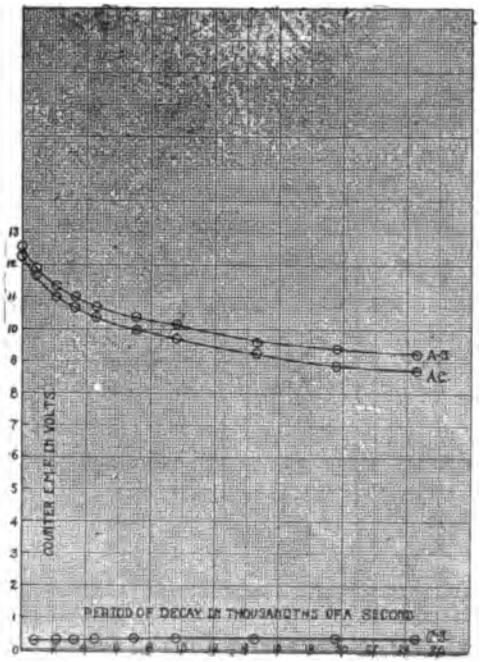


Fig. 2.

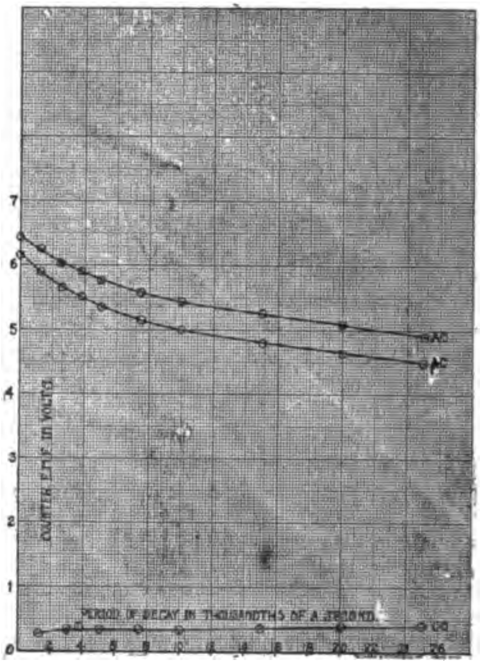


Fig. 3.

It is worthy of note that the polarization E.M.F. between the anode and the aluminium test electrode exceeds the applied E.M.F. by about 0.3 of a volt. The excess voltage is due to the fact that the electrolytic cell, acting as a primary cell, furnished an effective voltage of about 0.3

Table III.

Electrolyte: Ammonium Aluminium Sulphate
Applied E.M.F.: 18.13 volts.
Temperature: 23° C.
Current: 0.0005 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC} Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	18.43	18.02	....	....	.....
0.0013	17.01	16.59	0.34	16.93	+0.08
0.0025	16.11	15.68	0.32	16.00	0.11
0.0038	15.57	15.12	0.31	15.43	0.14
0.0050	15.29	14.70	0.31	15.01	0.28
0.0075	14.63	14.09	0.32	14.41	0.22
0.0100	14.00	13.67	0.31	13.98	0.02
0.0150	13.33	12.91	0.34	13.24	0.09
0.0200	12.98	12.53	0.36	12.89	0.09
0.0250	12.75	12.34	0.37	12.71	0.04

volt in series with the charging storage battery to assist in the process of polarization. The difference between E_{A3} and $E_{AC}+E_{C3}$ for corresponding decay intervals is also seen to be negligible, the error rarely exceeding 1 per cent., which demonstrates that the method used renders possible the attainment of a high degree of accuracy. The results show conclusively that the E.M.F. of polarization, at the instant when the charging circuit is opened, is equal to the polarizing E.M.F., and that there has been no considerable *IR* component in the surface film during the charging period.

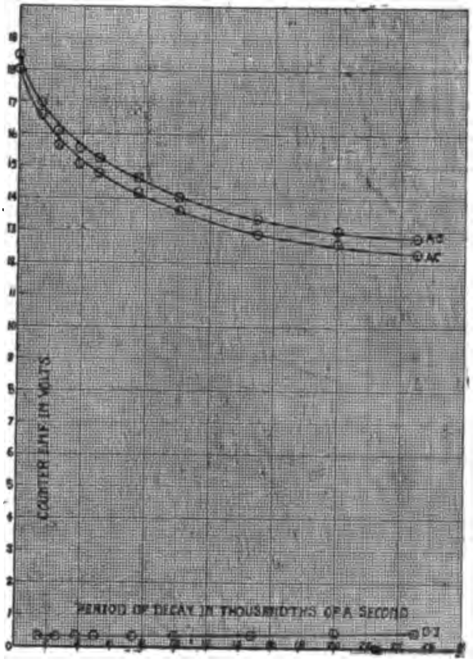


Fig. 4.

It has been proved by Schulze,[1] in an extensive series of experiments, that the effective anodic layer, in conformity with the suggestion of

---

[1] Ann. d. Physik, 21, 5, pp. 929–954, December 14, 1906; also 22, 3, pp. 543–558, March 5, 1907.

Guthe,[1] consists of oxygen gas. An extension of the gas film theory accounts for the slight residual current that flows through the electrolytic cell. The negative ions accumulate in the electrolyte next to the gas layer and electrons are forced from some of the carriers by the high potential gradient. These free electrons pass through the gas layer, thus causing the observed small residual current. The higher the value of the impressed voltage, under the experimental conditions maintained by the writer, the higher is the potential gradient through the gas film, and the larger should be the number of detached electrons and the resulting current. The results are seen to conform to this theory, since, for example, the residual current for an applied voltage of 6.16 volts was 0.00025 ampere; for 12.25 volts, 0.00035 ampere; for 18.13 volts, 0.00050 ampere.

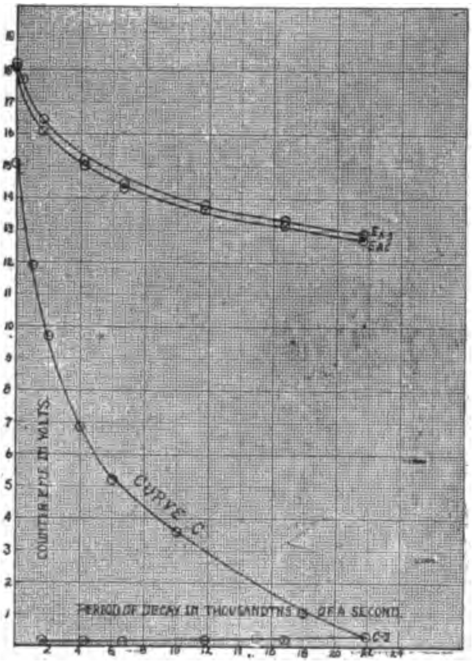


Fig. 5.

The above way of looking at the counter E.M.F. of the aluminium cell very closely corresponds to our ideas of the process of charging a condenser and by many experimenters the aluminium anode is spoken of as a condenser. This comparison should, however, not be carried too far. When the two plates of a charged condenser are connected by a conductor of very high resistance, the potential difference between the plates decreases in accord with the well-known law: $V = V_0 e^{-t/RC}$. Passing to logarithms, $\text{Log } V = \text{Log } V_0 - t/RC$. If the action of the rectifier were that of an ordinary condenser, a straight line should be obtained by plotting the logarithms of V as ordinates and the corresponding periods as abscissæ. Applying this test to the data of Table IV., for instance, curve C, of Fig. 5, is obtained. It shows that the rate of decrease of counter E.M.F. is not such as to indicate that the rectifier conforms to the law of the ordinary condenser. The explana-

---

[1] Theory of Electrolytic Rectifier, PHYS. REV., 15, pp. 327–334, 1902.

tion of this discrepancy may lie in the fact that the decrease of potential in the rectifier is due to the diffusion of the ions back into the solution rather than to ordinary metallic conduction.

Table IV.

Electrolyte: Potassium Dichromate Solution.
Temperature: 23.1° C.
Applied E.M.F.: 18.16 volts.
Current: 0.0005 ampere.

Period of Decay, Second.	E_{A3} Volts.
0.0000	18.22
0.0004	17.70
0.0017	16.31
0.0042	15.17
0.0067	14.44

When the impressed voltage causing the polarization of the rectifier is increased the ionic concentration near the film is increased and with it the rate of change in the concentration passing from the film to the body of the electrolyte is increased. Therefore, when the impressed voltage is removed, the ions should disappear from the boundary of the gas layer the more rapidly the higher the impressed voltage. A comparison of the curves of Fig. 6 confirms this view. If the assumption that the rate of diffusion of the ions from the gas layer back into the solution is a function of the difference between the ionic concentration near the anode and that in the remainder of the electrolyte, is correct, — then as the process of diffusion proceeds and the difference in ionic concentration decreases, the rate of diffusion (or the rate of decay of the counter E.M.F. of polarization) should decrease. This is seen to be true of each of the curves of decay.

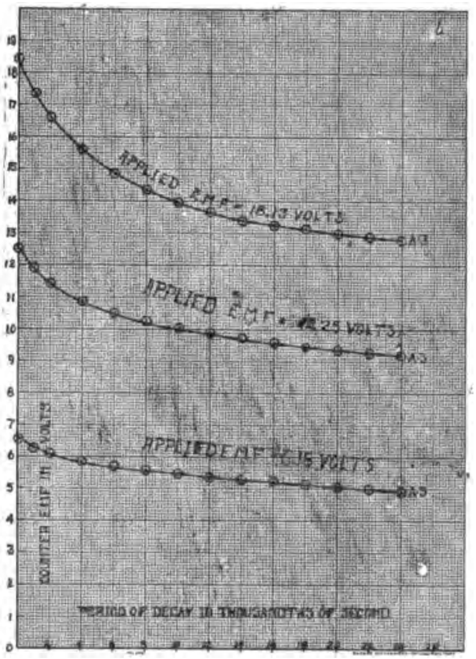


Fig. 6.

It is believed that the curves of decay obtained represent with a fair degree of accuracy no other effects than those of ionic diffusion, since during the extremely short intervals of decay used the effect of any disintegration of the film may be assumed to be negligible.

The results of this investigation may be summarized as follows:

1. The condenser method of measuring the counter E.M.F. introduces an error due to the taking of a charge from the rectifier.

2. The rectifier does not behave as an ordinary condenser.

3. When aluminium is used as the anode, the counter E.M.F. alone accounts for the reduction of the current to its exceedingly small value.

4. The results obtained in this investigation are apparently in accord with the gas film theory and the theory of ionic diffusion.

The writer is indebted to the University of Michigan for the special apparatus provided for the work and to Professor K. E. Guthe, of the University of Michigan, for many helpful suggestions received.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

A COMPLETE COLLECTION OF THERMODYNAMIC FORMULAS.

By P. W. Bridgman.

IN this paper is presented a complete and systematic collection of thermodynamic formulas involving the first and second derivatives of the ordinary thermodynamic quantities. It has been possible to compress such a collection into a reasonable compass by a short-hand method of expression. The fundamental quantities whose various relations are treated in the tables are ten in number; namely p, v, τ, E, s, Q, W, H, Z, and Ψ. It will be remarked that the specific heats are not included in the fundamental ten quantities. This is because the specific heats are properly first derivatives, $C_p = \left(\frac{\partial Q}{\partial \tau}\right)_p$, and $C_v = \left(\frac{\partial Q}{\partial \tau}\right)_v$. These ten quantities, with their first and second derivatives, are connected by various relations. The relations between the quantities themselves are simple, and mostly of the nature of definitions. But the relations between the first and second derivatives are more complicated, and it is these which are of special interest.

We consider first the first derivatives. The conditions imposed by the first and second laws of thermodynamics and the particular properties of the substance under consideration are such that every derivative of the type $\left(\frac{\partial W}{\partial \tau}\right)_Q$ has a definite meaning. This derivative means that the particular body in question is allowed to change so that Q remains constant, that is, no heat is absorbed, and the ratio of the change of W to the change of τ found during this change.[1] Every first derivative involves, therefore, three different variables, and it is at once seen that the total number of such derivatives is 720 ($= 10 \times 9 \times 8$). These 720 derivatives are connected by various relations, and in general there is an equation connecting any four of them and certain of the fundamental ten quantities. There are, therefore,

$$\frac{720 \times 719 \times 718 \times 717}{1 \times 2 \times 3 \times 4} = 11{,}104{,}365{,}420$$

such relations between the first derivatives.

---

[1] It should be noted that although the derivatives always have a meaning in the sense indicated, the functions which are being differentiated need not be expressible as functions of the position coördinates. W and Q are such functions; it is impossible to assign any meaning to them as functions of p and τ for example, but still the variations of W and Q in definite directions are entirely determined.

A complete collection of first derivatives would involve the tabulation, therefore, of these 11,104,365,420 relations. This of course is absolutely out of the question; the best we can do is to tabulate some of the derivatives in such a form that any of the derivatives may be obtained by slight and obvious effort. We evidently shall attain this object if every one of the 720 first derivatives is tabulated in terms of the same three fundamental derivatives. To obtain any desired one of the numerous relations between any four derivatives, therefore, we merely have to eliminate the three fundamental derivatives between the four equations for the four derivatives.

The three fundamental derivatives may be chosen in a great variety of ways. The three chosen here are the three which are perhaps given most directly by experiment; the isothermal compressibility $\left(\frac{\partial v}{\partial p}\right)_\tau$, the isopiestic dilatation $\left(\frac{\partial v}{\partial \tau}\right)_p$, and the specific heat at constant pressure C_p. The first two of these may be obtained from the characteristic equation of the substance, that is, the relation connecting p, τ, and v. To determine C_p, calorimetric measurements must be made in addition to the measurements for the characteristic equation. It may be proved that C_p is completely determined, if in addition to our knowledge of the characteristic equation, C_p is known along some line not at constant temperature. Such information, for instance, would be given by a determination of C_p as a function of temperature at atmospheric pressure.

It should be remarked that the method used here of tabulating the 720 derivatives in terms of the same fundamental three will largely do away with the necessity for determining the other relations by an elimination, as suggested above. For if in any special problem every quantity of interest is kept in terms of the same fundamental three, which are independent, one may be sure that at the end of the discussion there are no essential relations not brought to light.

It is now possible to still further reduce the number of expressions needed. To do this, the 720 derivatives may be divided into groups, the variable kept constant during differentiation being kept constant in each group. There are, therefore, ten of these groups, 72 to a group. Let us suppose, for example, that the group is that in which p is the constant element. Any one of the 72 derivatives of this group is of the type $\left(\frac{\partial x}{\partial y}\right)_p$, where x and y are any two of the nine remaining of the ten fundamental quantities. Now let us write, merely as a matter of notation, $\left(\frac{\partial x}{\partial y}\right)_p \equiv \frac{(\partial x)_p}{(\partial y)_p}$. The abridgement in the number of required formulas is suggested by noticing that we may tabulate $(\partial x)_p$ and $(\partial y)_p$ separately as appropriate functions of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p, and always get the right value for the derivative by replacing $(\partial x)_p$ and $(\partial y)_p$ by these functions and taking the ratio. But there are only nine such expressions in any group, so that we have reduced the number of expressions needed from 720 to 90.

To prove the possibility of splitting up a derivative in the way above is simple. We have the mathematical identity $\left(\frac{\partial x}{\partial y}\right)_p = \left(\frac{\partial x}{\partial \alpha}\right)_p \Big/ \left(\frac{\partial y}{\partial \alpha}\right)_p$ where α is any variable, not even necessarily one of the fundamental ten, which remains the same throughout the group of 72. If therefore, we replace $(\partial x)_p$ by $\left(\frac{\partial x}{\partial \alpha}\right)_p$, and similarly $(\partial y)_p$ by $\left(\frac{\partial y}{\partial \alpha}\right)_p$, we shall always obtain the right answer when we take the ratio of any two such functions to find the derivative. It is especially to be noticed that $(\partial x)_p$ is not equal to $\left(\frac{\partial x}{\partial \alpha}\right)_p$; in fact, $(\partial x)_p$ in general does not have the same dimensions as $\left(\frac{\partial x}{\partial \alpha}\right)_p$. The finite functions replacing the differentials have meaning only when the *ratio* of two is taken.

Finally it is possible to further reduce the number of expressions from 90 to 45. We notice that α, of the paragraph above, is not subject to any essential restriction—any function will do. There are ten of these α's. We may now impose a restriction, making $(\partial x)_p = -(\partial p)_x$, thus reducing to one half the number of fundamental functions. The proof of this will not be given here, but it may be readily seen on writing out the derivatives of the various groups that if an α is chosen so that the relation is satisfied for one derivative of a group, then it will be satisfied by all the others also. The α's so restricted are not completely determined by any means, but the derivatives, which only we are interested in, are now nearly determined. There is still a certain amount of arbitrariness left, in that the entire collection of functions replacing the partial differentials may be modified by the addition of any factor, but otherwise the functions are determined. This arbitrary factor will be so chosen as to make the functions as simple as possible.

In the actual derivation of the formulas, the α's play no part; they are simply the mathematical scaffolding used in proving the possibility of replacing the differentials by finite functions, and may now be completely discarded. The method actually used in deriving the formulas was to find a sufficient number of derivatives by well established methods, and then to split them up, by inspection, into the functions replacing numerator and denominator.

We turn now to a consideration of the second derivatives. The number of combinations of second derivatives is so great that it cannot be reduced to a reasonable number, as could the number of combinations of first derivatives. All that we can do here is to tabulate a sufficient number of the fundamental second derivatives so that any relation existing between them may be found readily by such purely formal mathematical operations of differentiation or elimination as are in the mathematical equipment of every one.

The problem in the case of the second derivatives is analogous to that for the first derivatives; namely to express everything in terms of the same fundamental second derivatives. It may be shown that in general there are four such second derivatives, and for use here we choose the four most directly given by experiment, $\left(\frac{\partial^2 v}{\partial p^2}\right)_\tau$, $\frac{\partial^2 v}{\partial p \partial \tau}$, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, and $\left(\frac{\partial C_p}{\partial \tau}\right)_p$.

Suppose now that we wish to find any second derivative. The general second derivative is of the type $\left[\frac{\partial}{\partial x_1}\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5}$. This is mathematically equivalent to $\left[\frac{\partial}{\partial p}\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5} \cdot \left(\frac{\partial p}{\partial x_1}\right)_{x_5}$. But $\left(\frac{\partial p}{\partial x_1}\right)_{x_5}$ is a function of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p, which is already known from the tables for the first derivatives. Furthermore, $\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}$ is also a known function of the same three fundamental derivatives, so that $\left[\frac{\partial}{\partial p}\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5}$ may be found by a purely formal differentiation, if we know $\left(\frac{\partial}{\partial p}\right)_{x_5}$ of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p. There are 27 such second derivatives. The only exception to this scheme of treatment is when $p \equiv x_5$, in which case we have an indeterminate form to evaluate. This may be avoided by taking τ instead of p as our auxiliary variable of differentiation. The differentiation in this case is so simple that it may be performed by inspection.

From these 27 second derivatives we may obtain by a simple formal differentiation any of the 64,800 second derivatives. Each of these second derivatives involves, besides certain of the ten original quantities and the three fundamental first derivatives, only four independent second derivatives. Hence by eliminating these four second derivatives between the equations for any five second derivatives, we may obtain the relation between any combination of five second derivatives. There are approximately 9.5×10^{21} such relations.

The tables follow. These are given in three parts. First are the fundamental ten quantities with their equations of definition; second the tables in abbreviated form for the first derivatives; and lastly the 27 second derivatives necessary in obtaining any of the 64,800 second derivatives.

TABLE I.

The Fundamental Ten Quantities.

In this table are given the notation and the definition of the fundamental ten thermodynamic quantities. It is to be understood that all the quantities refer to unit amount of the substance. This unit is usually chosen either as 1 gm., or as the quantity that at 0° C. and atmospheric pressure occupies a volume of 1 c.c.

p = pressure per unit area.

τ = temperature on the absolute thermodynamic scale.

v = volume of the unit quantity of the substance.

s = entropy, defined by the integral, $\int dQ/\tau$.

Q = heat absorbed, measured in the mechanical units appropriate to p and v. A physical meaning can be given only to dQ, the heat absorbed during a given change.

W = work done by the substance, in the appropriate mechanical units. Here again, only dW has a physical meaning.

E = the internal energy of the substance in mechanical units. E may be changed by an additive constant without changing its physical meaning. E is one of the thermodynamic potential functions.

$H = E + pv$, the "total heat," also one of the potential functions.

$Z = E + pv - \tau s$, the Gibbs thermodynamic potential.

$\Psi = E - \tau s$, also a thermodynamic potential, the "free energy" of Helmholtz.

TABLE II.

The First Derivatives.

This contains the abbreviated notation by which any of the 720 first derivatives may be found in terms of $\left(\frac{\partial v}{\partial p}\right)_\tau$, $\left(\frac{\partial v}{\partial \tau}\right)_p$, and C_p. For instance, if $\left(\frac{\partial E}{\partial \tau}\right)_p$ is desired, write this in the equivalent form $\frac{(\partial E)_p}{(\partial \tau)_p}$, and take the ratio of the functions given in the table for $(\partial E)_p$ and $(\partial \tau)_p$. Notice in general that $(\partial x)_y = -(\partial y)_x$.

$$
\begin{aligned}
(p)\qquad (\partial \tau)_p &= -(\partial p)_\tau = 1,\\
(\partial v)_p &= -(\partial p)_v = (\partial v/\partial \tau)_p,\\
(\partial s)_p &= -(\partial p)_s = C_p/\tau,\\
(\partial Q)_p &= -(\partial p)_Q = C_p,\\
(\partial W)_p &= -(\partial p)_W = p(\partial v/\partial \tau)_p,\\
(\partial E)_p &= -(\partial p)_E = C_p - p(\partial v/\partial \tau)_p,\\
(\partial H)_p &= -(\partial p)_H = C_p,\\
(\partial Z)_p &= -(\partial p)_Z = -s,\\
(\partial \Psi)_p &= -(\partial p)_\Psi = -[s + p(\partial v/\partial \tau)_p].
\end{aligned}
$$

. . . .

$$
\begin{aligned}
(\tau)\qquad (\partial v)_\tau &= -(\partial \tau)_v = -(\partial v/\partial p)_\tau,\\
(\partial s)_\tau &= -(\partial \tau)_s = (\partial v/\partial \tau)_p,\\
(\partial Q)_\tau &= -(\partial \tau)_Q = \tau(\partial v/\partial \tau)_p,\\
(\partial W)_\tau &= -(\partial \tau)_W = -p(\partial v/\partial p)_\tau,\\
(\partial E)_\tau &= -(\partial \tau)_E = \tau(\partial v/\partial \tau)_p + p(\partial v/\partial p)_\tau,\\
(\partial H)_\tau &= -(\partial \tau)_H = -v + \tau(\partial v/\partial \tau)_p,\\
(\partial Z)_\tau &= -(\partial \tau)_Z = -v,\\
(\partial \Psi)_\tau &= -(\partial \tau)_\Psi = p(\partial v/\partial p)_\tau.
\end{aligned}
$$

. . . .

$$
\begin{aligned}
(v)\qquad (\partial s)_v &= -(\partial v)_s = 1/\tau\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\\
(\partial Q)_v &= -(\partial v)_Q = C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p,\\
(\partial W)_v &= -(\partial v)_W = 0\\
(\partial E)_v &= -(\partial v)_E = C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p,\\
(\partial H)_v &= -(\partial v)_H = C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p - v(\partial v/\partial \tau)_p,\\
(\partial Z)_v &= -(\partial v)_Z = -\{v(\partial v/\partial \tau)_p + s(\partial v/\partial p)_\tau\},\\
(\partial \Psi)_v &= -(\partial v)_\Psi = -s(\partial v/\partial p)_\tau.
\end{aligned}
$$

. . . .

$$
\begin{aligned}
(s)\qquad (\partial Q)_s &= -(\partial s)_Q = 0,\\
(\partial W)_s &= -(\partial s)_W = -(p/\tau)\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\\
(\partial E)_s &= -(\partial s)_E = (p/\tau)\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\\
(\partial H)_s &= -(\partial s)_H = -vC_p/\tau,\\
(\partial Z)_s &= -(\partial s)_Z = -(1/\tau)\{vC_p - s\tau(\partial v/\partial \tau)_p\},\\
(\partial \Psi)_s &= -(\partial s)_\Psi = (1/\tau)\{p[C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p]\\
&\qquad\qquad + s\tau(\partial v/\partial \tau)_p\}.
\end{aligned}
$$

. . . .

$$
\begin{aligned}
(Q)\qquad (\partial W)_Q &= -(\partial Q)_W = -p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\\
(\partial E)_Q &= -(\partial Q)_E = p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\\
(\partial H)_Q &= -(\partial Q)_H = -vC_p,
\end{aligned}
$$

$$(\partial Z)_Q = -(\partial Q)_Z = -\{s\tau(\partial v/\partial \tau)_p - vC_p\},$$
$$(\partial \Psi)_Q = -(\partial Q)_\Psi = p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\} + s\tau(\partial v/\partial \tau)_p.$$

. . . .

(*W*)
$$(\partial E)_W = -(\partial W)_E = p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},$$
$$(\partial H)_W = -(\partial W)_H = p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p - v(\partial v/\partial \tau)_p\},$$
$$(\partial Z)_W = -(\partial W)_Z = -p\{v(\partial v/\partial \tau)_p + s(\partial v/\partial p)_\tau\},$$
$$(\partial \Psi)_W = -(\partial W)_\Psi = -ps(\partial v/\partial p)_\tau.$$

. . . .

(*E*)
$$\begin{aligned}(\partial H)_E = -(\partial E)_H = {} & -v\{C_p - p(\partial v/\partial \tau)_p\} \\ & - p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\},\end{aligned}$$
$$\begin{aligned}(\partial Z)_E = -(\partial E)_Z = {} & -v\{C_p - p(\partial v/\partial \tau)_p\} \\ & + s\{\tau(\partial v/\partial \tau)_p + p(\partial v/\partial p)_\tau\},\end{aligned}$$
$$(\partial \Psi)_E = -(\partial E)_\Psi = p\{C_p(\partial v/\partial p)_\tau + \tau(\partial v/\partial \tau)^2{}_p\}.$$

. . . .

(*H*)
$$(\partial Z)_H = -(\partial H)_Z = -v(C_p + s) + \tau s(\partial v/\partial \tau)_p,$$
$$\begin{aligned}(\partial \Psi)_H = -(\partial H)_\Psi = {} & -[s + p(\partial v/\partial \tau)_p][v - \tau(\partial v/\partial \tau)_p] \\ & + p(\partial v/\partial p)_\tau.\end{aligned}$$

. . . .

(*Z*)
$$(\partial \Psi)_Z = -(\partial Z)_\Psi = -s[v + p(\partial v/\partial p)_\tau] - pv(\partial v/\partial \tau)_p.$$

. . . .

TABLE III.

The Second Derivatives.

In this table auxiliary formulas are given which simplify the computation of any second derivative in terms of the four following fundamental second derivatives; $\left(\frac{\partial^2 v}{\partial p^2}\right)_\tau$, $\frac{\partial^2 v}{\partial p \partial \tau}$, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, and $\left(\frac{\partial C_p}{\partial \tau}\right)_p$. In general, if we desire to compute $\left[\frac{\partial}{\partial x_1}\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5}$, we write this in the form $\left[\frac{\partial}{\partial p}\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}\right]_{x_5} \times \left(\frac{\partial p}{\partial x_1}\right)_{x_5}$. But $\left(\frac{\partial p}{\partial x_1}\right)_{x_5}$ is already known, and $\left(\frac{\partial x_2}{\partial x_3}\right)_{x_4}$ is a known function of $\left(\frac{\partial v}{\partial \tau}\right)_p$, $\left(\frac{\partial v}{\partial p}\right)_\tau$, and C_p. Hence the result may be obtained by a purely formal differentiation, provided we know $\left[\frac{\partial}{\partial p}\left(\frac{\partial v}{\partial \tau}\right)_p\right]_{x_5}$, $\left[\frac{\partial}{\partial p}\left(\frac{\partial v}{\partial p}\right)_\tau\right]_{x_5}$, and $\left[\frac{\partial}{\partial p} C_p\right]_{x_5}$. These derivatives are listed in the following tables. If $x_5 \equiv p$, then we may use τ as our auxiliary variable of differentiation, and the entire differentiation may be performed by inspection.

. . . .

[illegible] $\partial v/\partial p)_T$, $(\partial v/\partial T)_p$

[illegible] $\partial v/\partial p)_T$, $(\partial v/\partial T)_p$

[illegible] $\partial v/\partial p)_T$, $(\partial v/\partial T)_p$

[illegible] $\partial T)_p$, C_p

[illegible] $\partial T)_p$, C_p

[illegible] $\partial v/\partial T)_p$, C_p

[illegible] to the corre-

[illegible] corre-

[illegible]

$\Psi \quad [\partial/\partial p\,(\partial v/\partial p)_\tau]_\Psi = (\partial^2 v/\partial p^2)_\tau - \{\partial^2 v/\partial \tau \partial p\} \cdot \{p(\partial v/\partial p)_\tau\}/\{s + p(\partial v/\partial \tau)_{p,}\}$
constant:

$$[\partial/\partial p\,(\partial v/\partial \tau)_p]_\Psi = \partial^2 v/\partial p \partial \tau - \{(\partial^2 v/\partial \tau^2)_p\} \times \{p(\partial v/\partial p)_\tau\}/\{s + p(\partial v/\partial \tau)_p\},$$

$$(\partial C_p/\partial p)_\Psi = -\tau(\partial^2 v/\partial \tau^2)_p - \{(\partial C_p/\partial \tau)_p\} \times \{p(\partial v/\partial p)_\tau\}/\{s + p(\partial v/\partial \tau)_p\}.$$

. . . .

The Jefferson Physical Laboratory,
Harvard University,
Cambridge, Mass.

A STUDY OF THE PROPAGATION AND INTERCEPTION OF ENERGY IN WIRELESS TELEGRAPHY.[1]

By Charles A. Culver.

Part II.

KIEBITZ and others have shown that it is possible to utilize horizontal antenna placed close to the earth's surface in practical radio-telegraphy.

The purpose of this investigation is to compare the absorbing and radiating efficiency of a simple vertical antenna with certain horizontal types.

As a standard of comparison, an antenna was erected on the college campus consisting of a single vertical wire 21 m. in length. Number 14 aluminum wire was used for this and the other antennæ in these experiments. A standard earth connection was also established. This consisted of four holes located on the cardinal points and one meter deep. The holes were placed two meters apart and were 25 cm. in diameter. A cylindrical piece of galvanized iron netting enclosing charcoal was placed in each hole. This filled the holes to within 40 cm. of the top. Earth completed the filling. All four earths were connected together by a heavy copper wire. The soil in this vicinity consists largely of sand and gravel.

The horizontal aerials referred to later were supported by small porcelain insulators attached to wooden stakes, these stakes being just high enough to prevent the wire from touching the grass.

A thoroughly equipped private station belonging to Mr. Hiram Morgan and located approximately 5 km. from the Beloit campus was utilized as a coöperating station. The Morgan transmitting equipment consists of a *T* aerial, the horizontal portion consisting of six wires 21 m. in length spaced 60 cm. apart. A single wire 12 m. in length constituted the vertical part. The horizontal portion is approximately parallel to the direction of *B*. Energy from a 1-kw., 60-cycle transformer and non-synchronous rotary gap was supplied to the above aerial through a loose coupling. The wave emitted by this station is 220 m., with an antenna current of 250 milliamperes.

---

[1] For Part I., see Phys. Rev., Vol. XXV., p. 200, Series I., September, 1907.

The plan of the tests consisted in having the Morgan station send long dashes for a period of a half hour daily from 9:00 to 9:30 A.M. The various horizontal aerials were then compared with the standard and with one another by means of the shunted telephone method. While more or less large variations occurred in the data, it was possible to obtain concordant results by repeating given tests on different days. These experiments were carried out between August 1 and September 15. Fig. 1 shows the form and dimensions of the various antennæ which were compared. The first series of tests consisted of a comparison between systems *D* and *C*. The standard earth connection was utilized in this experiment. Type *C* gave the higher efficiency, the ratio of the resistances shunted about the receivers being 8/3. System *E* gave approximately the same efficiency as *C*. Using system *D* and the standard earth, the effect of grounding the free end of the aerial directly and through a condenser (.0015 m.f.) was tried. The signals were barely audible with both of these arrangements.

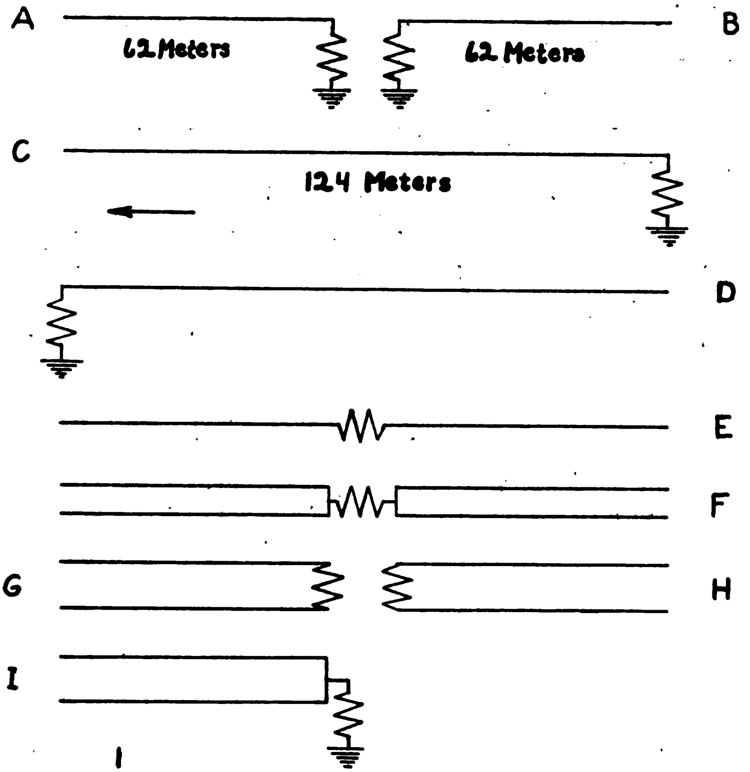


Fig. 1.

In the above diagrams the arrow indicates the direction of the Morgan station. The inductance shown is the primary of the receiving transformer.

On another date a comparison was made between system *C* and the standard vertical aerial. The efficiency of these two systems proved to be practically the same. System *D* showed a lower efficiency than the standard, the ratio of the shunt resistances being approximately 1/5. During the tests just mentioned the ground was very wet.

A test was next made of the effect of grounding the free end of system *A*, both directly and through a condenser (.0015 m.f.). Little if any difference in the efficiency was found to exist whether the system was free or grounded by either method. This test was made while a light rain was falling.

A comparison was next made between systems *C* and *E*. System *C* proved to be more efficient than *E*, the shunt resistances being 185 ohms and 340 ohms respectively.

Comparisons between systems *F* and *E* appeared to indicate that the single wire of the latter system was practically as efficient as the double wire system *F*. At times *F* gave a slightly higher efficiency.

Upon testing systems *G* and *H* it was found that the signals were just audible, but too weak to permit measurements being taken. Comparisons between *E* and *A* and *B* showed that *A* and *E* gave practically the same efficiency, while *B* fell somewhat below *E*, the ratio of the shunt resistances being 5/3.

Repeated comparisons between *E* and the standard showed that while at times the standard gave a slightly higher efficiency than *E*, yet on other days the efficiency was practically the same.

System *G* was so arranged that one of the two wires lay directly on the ground while the other was insulated in the usual manner. No signals could be detected with this arrangement. However, when system *E* was so arranged that the wire lay directly on the grass, readable signals were secured.

The next tests consisted in an effort to utilize a capacity area as a receiving system. The capacity area consisted of a galvanized iron screen one by two meters and supported by suitable insulation two meters above the earth. No signals could be heard with this arrangement. The screen was then placed in a vertical position with the upper edge two meters from the earth, the plane of the screen being at right angles to the line joining the stations. The result was nil in this case also.

In the following described tests the Beloit station operated as a transmitting equipment and the Morgan station received the signals. When receiving the Beloit signals, the Morgan station utilized a T aerial consisting of six horizontal wires 91 m. in length spaced 60 cm. apart, and vertical leads 12 m. in length. The horizontal section is parallel to the direction of Beloit. This aerial was connected to the usual loosely coupled receiving equipment in series with the primary of which was inserted a Duddell thermo-galvanometer for the purpose of measuring the intercepted energy. The Beloit transmitting equipment consisted of a 1 kw. transformer operated through a fixed gap, a typical set of connections being indicated in Fig. 2. A series of tests was made in an effort to determine the relative efficiencies of the above mentioned horizontal aerials as radiating systems. A wave length of 300 meters was used in these latter tests, except with types *C* and *D*, this being the shortest wave which could be advantageously employed with this particular transformer. In order to strongly excite systems *C* and *D* it was necessary to employ at least a 780 m. wave. The results of the radiation experiments are shown in the following table.

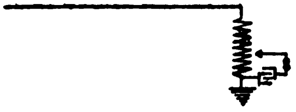


Fig. 2.

Test Number.	Type of Aerial.	Conditions.	Current in Aerial (Approximate.)	Current at *M.* Scale Units.
I	Std.	Std. earth		2.0
	A	Std. earth	0.65 amp.	2.2
	B	Std. earth	0.6	1.2
II	Std.	Std. earth	0.25	0.8
	C	Std. earth	0.6	7.5
	E	No earth	0.4	4.5
III	*I*	Std. earth	0.3	1.0
	G	No earth	0.5	0 0
	A	Std. earth	0.3	1.2
	E	No earth	0.3	3.5
	D	Std. earth	0.35	2.5
IV	*A*	Std. earth and free end grounded through condenser	0.25	1.0

Recently we have received signals at this laboratory when utilizing a pair of number 12 galvanized iron wires in parallel extending between the college observatory and Pearson's Science Hall. This local telephone line is approximately 250 m. in length and about 4 m. above the ground. The line, while somewhat curved, has in general a southerly direction. Several stations at different points along the Atlantic coast have been identified when using this line as a receiving aerial, among which might be mentioned Key West and Cape Cod. Further long distance tests of this character are in progress at the present writing, the results of which will be reported shortly.

DISCUSSION.

The data secured from experiments carried out in a particular geographical locality do not warrant general conclusions. However, certain of the above results are at least significant. The experiments of the author confirm and extend the tests made by Kiebitz and others, and would appear to indicate that horizontal antennæ placed very near the earth's surface exhibit efficiencies both as receiving and radiating systems which are comparable with a simple vertical aerial.

The data would also appear to indicate that when utilizing such low horizontal antennæ either as absorbing or radiating systems, the free end of the aerial should point in the direction of the second station. This appears not to conform to Marconi's law of horizontal antennæ and may be due to local topographical conditions.

The fact that energy was intercepted and radiated when both ends of the horizontal systems were grounded would appear to indicate that we are dealing in such cases with what Sommerfeld calls a surface wave, as more or less distinct from a space wave. This would also appear to be borne out by the results obtained with system *G*, and by the fact mentioned above, namely, that the receiving and exciting equipment operated most effectively when located at the remote end of the aerial. The amplitude of the surface wave, which acts to develop a difference of potential between the ends of the horizontal wire, would be greatest at the remote end when that end pointed toward the second station. These conditions would result in a maximum effect on a potential operated device such as the crystal detector used in the first part of the above experiment when connected as in systems *A* and *C*. An examination of the above data will show that the empirical results are in conformity with this explanation.

In conclusion the writer has to thank Professor Goodspeed, of the University of Pennsylvania, for the loan of valuable apparatus used in certain of the above experiments. We are also deeply indebted to Mr. Hiram Morgan, of this city, for his careful and faithful coöperation in carrying out these experiments.

BELOIT COLLEGE,
January 1, 1914.

ON THE CONTINUED APPEARANCE OF GASES IN VACUUM TUBES.

By George Winchester.

IN undertaking any investigation where a high vacuum is necessary the phenomenon of "occluded gases" is encountered, that is, when a high potential is applied to the electrodes, hydrogen, helium and neon are freed and apparently keep coming out of the electrodes for a considerable length of time. Some discussion has arisen concerning the origin of these gases. One idea suggested is that the gases are simply occluded and that the impact of the cathode rays against the anode frees them and they escape into the tube; another is that they are occluded, but instead of being freed at the anode by the bombardment of cathode rays, they are freed at the cathode by reason of the high potential placed upon the electrodes; still another notion is that the material of which the anode or cathode is made disintegrates in somewhat the same manner as uranium does and that these gases are the product of the disintegration process. E. Cohnsteadt,[1] working with a differential method, aims to eliminate the gases which may emanate from the glass walls of the tube and to measure only the gases evolved from the electrodes. A close relation between the amounts of gases given off and the amount of water vapor present is established. He then concludes that the gases are not evolved from the metal electrodes but are due entirely to water vapor on their surfaces and that the amounts of gases produced do not depend upon the volume of the electrodes but upon their area. He uses P_2O_5 to free his tubes from moisture.

Sir William Ramsay, Professor Collie and Mr. Patterson[2] described some experiments which they believe to prove the transmutation of other elements into helium and neon. These experiments consist simply in applying high potentials to the electrodes in vacuum tubes; they further suggest that helium (4) and oxygen (16) may combine to form neon.

Sir J. J. Thomson, using the positive ray method, has shown the presence in vacuum tubes of hydrogen, helium and neon, and another gas, which he calls X_3. He concludes that these gases are given out by

---

[1] The Water-Film on Glass and Aluminium, and its Influence on the Pressure in Vacuum Tubes, Ann. d. Physik, 38, 1, pp. 223–238, May 7, 1912.

[2] Report in Nature, Vol. 90, p. 653, February 13, 1913.

the different materials which were subjected to the bombardment of cathode rays.[1] Professor Skinner[2] in a series of experiments on the evolution of hydrogen in gases shows that gases may be absorbed by the metal in a vacuum tube as well as given out; he also describes experiments to show that the cathode itself is the sole source of the supply of hydrogen.

My attention was first directed to this evolution of gas about ten years ago while preparing tubes for work in ultra-violet light. Several years ago the attempt was made to find out whether or not the electrodes could be entirely denuded of gases. At that time, not knowing the large quantity of gases contained in metals nor the length of time consumed in getting it out, I used electrodes of aluminium 2 mm. in diameter and 7 cm. in length with the free ends formed into rings facing each other coaxially at 1 mm. distance. I found this method of placing the electrodes most fertile in the production of gas, for at extremely low pressures I could place very large potentials on the electrodes when they were close together and force the gas out at a more rapid rate. Using this method the experiment must be watched or the electrodes will bridge.

One thing noticeable in tubes of this kind is that, whereas some yield only comparatively small amounts of helium, others are very rich in this gas. One tube which at first gave only a small amount of helium in comparison with hydrogen, suddenly after running for fifteen days gave out an enormous amount of helium for a few days and then just as suddenly became normal again. The pump was worked on this tube so that the pressure never rose much above .3 mm. Since then I have found two tubes that showed the same phenomenon. Some electrodes seem to be very rich in helium and some very poor. All of the aluminium electrodes mentioned in this paper were made of c.p. aluminium unless otherwise stated.

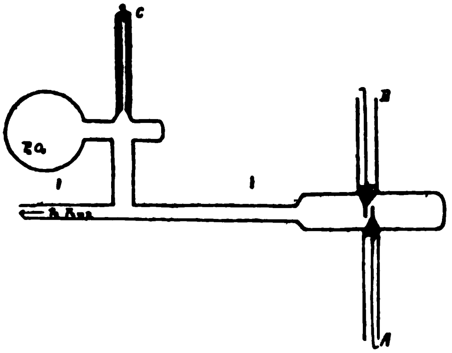


Fig. 1.

During the last year I have again attempted to denude electrodes of their gases by using very small electrodes, placing them close together, and applying high potentials. In these experiments as well as in the

---

[1] Some Further Applications of the Method of Positive Rays, Nature, Vol. 91, p. 333, May 29, 1913.

[2] The Evolution of Hydrogen from the Cathode and its Absorption by the Anode in gases, PHYS. REV., Vol. XXI., p. 1, July, 1905.

first ones, the pumps used were cleaned thoroughly with a hot saturated solution of potassium bichromate in concentrated sulphuric acid, rinsed with distilled water and then with c.p. alcohol; the tubes were cleaned in the same manner and sealed directly to the pump; a small bulb containing P_2O_5 was also directly sealed to the pump. Fig. 1 shows the arrangement in diagram. Usually before any account was taken of the gases given off the tube was heated for three or four hours with a bunsen flame and the coil run from ten to twenty hours. The tube was heated to the highest temperature before the pump was started so that if softening of the glass took place the tube would not collapse.

The presence of stop-cock grease has apparently nothing to do with either the amounts or kinds of gases that are given off. For example, in one experiment especial care was taken in cleaning the pump and tube to eliminate hydrocarbons; the bulb was heated almost to melting to drive off water vapor, leaving as nearly as possible nothing but glass and the c.p. aluminium electrodes. This tube was run for several months during which time the gases were measured and examined with the spectroscope and photographic plate. The tube was then cut off, a stop-cock sealed on to the pump and to this a tube containing commercial aluminium electrodes of the same size as the chemically pure electrodes. No attempt was made to clean this tube more than to heat it while the process of exhaustion was going on. The gases were measured and examined by the photographic plate; exactly the same gases were given off from the two sets of electrodes in approximately equal amounts.

Analysis, by means of the spectroscope, of the gases produced shows the presence of hydrogen, helium and neon. If the gases which are given off first are pumped out into an examination tube the helium and neon spectra are quite prominent. If the gases given off are examined in the same manner, after running the tube for a month, these two spectra have entirely disappeared. Seven different tubes were thus denuded of all traces of either helium and neon, as determined by photographic methods. This supports the theory that the helium and neon are simply occluded and not transmuted from some other element. For if these gases are produced by the disintegration of some element because of the application of a large voltage, we should be able to produce them so long as conditions are kept constant within the tube; that is, as long as there is any electrode, the continuous application of a high potential should produce helium and neon. Thomson[1] describes an experiment in which he sparked iron electrodes in an atmosphere of 3 cm. of hydrogen for an hour or so each day for four days; at the end of that time not a trace of helium or

---

[1] Loc. cit., p. 6.

neon could be found, even by the positive ray method. In my experiments I have never been able to eliminate these gases so quickly from aluminium electrodes; using one aluminium electrode of 10 mg. weight as cathode with a platinum electrode of about 5 mg. weight as anode, helium has been discovered after several weeks of sparking almost constantly, *i. e.*, say, in the neighborhood of eight hours a day. I have noted that when the pressure within the apparatus becomes at all appreciable the gases are very slow in coming out; and it may be that in the presence of 3 cm. of hydrogen the gases refuse to come out except from the surface layer. The case of hydrogen is different; I have sparked tubes until the electrodes were entirely wasted away and this gas can be obtained as long as any metal remains.

Skinner's[1] experiments show that after the current has flowed for a short time "the pressure appears to have reached a constant maximum value." This seems to be true unless the coil is run for a considerable length of time, since the ordinary McLeod gage does not show very small differences in pressure. Fig. 2 shows this phenomenon when the potential applied is approximately 100,000 volts. Here the current is continued for two hours after the apparent maximum has been reached and the curve shows a slight rise in pressure. The gage used in determining these pressures magnified them about 150 times. That there is not a maximum pressure, but merely an elbow, and that the gas is evolved at a very slow but constant rate, is shown when the gage used is more sensitive. Figure 3 shows the increase in pressure with the time when the pressures within the tube have been magnified about three thousand times. Of

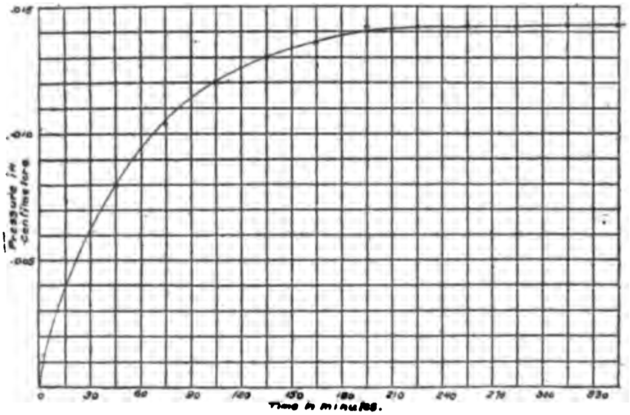


Fig. 2.

---

[1] Loc cit., p. 6.

course the position of this elbow depends upon the value of the potential applied to the electrodes as will be shown farther on. Undoubtedly this apparent discrepancy in the value of the pressure is explained by the unreliability of Boyle's law for very small pressures as determined by the McLeod gage. Since the curves shown by Professor Skinner represent experiments upon the evolution of gas in helium at 3 mm. pressure, while Fig. 2 represents the increase in pressure starting at a pressure of perhaps one-millionth of a millimeter, the position of the elbow seems not to be determined by the actual pressure within the tube but perhaps by some function of the relation between the amount of gas evolved and the amount still remaining within the surface layer.

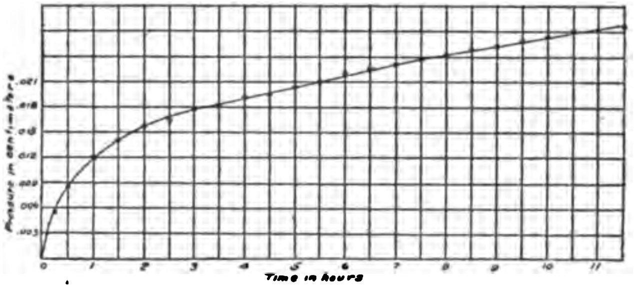


Fig. 3.

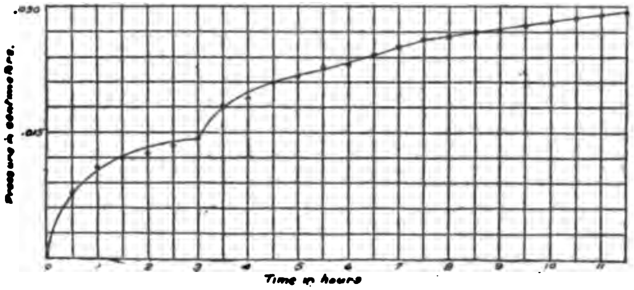


Fig. 4.

It may be observed under different conditions; for example, Figure 4 shows the increase in pressure taking place in the usual manner for three hours; then the tube was rested for eighteen hours and the coil started again. Here again the gas flows very readily at the start and the curve rises very rapidly for a time and then settles down to a constant slope. Fig. 5 is an analogous curve showing what happens when the potential on the electrodes is suddenly increased. The gas is evolved copiously for a short time when the increase in potential is made. Fig. 6 represents the increase in gas pressure which takes place under the following conditions: on the first part of the curve the coil is run steadily for fifteen hours showing a very steady flow of gas; at the end of this time all the gas is quickly pumped out (requiring forty-six minutes, in this instance) and the coil started again. This is apparently equivalent to resting the electrode or raising the potential. The gas is evolved in the same manner as at the beginning of the experiment, only not so profusely.

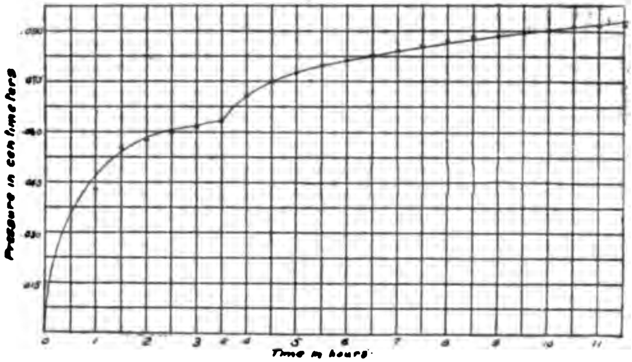


Fig. 5.

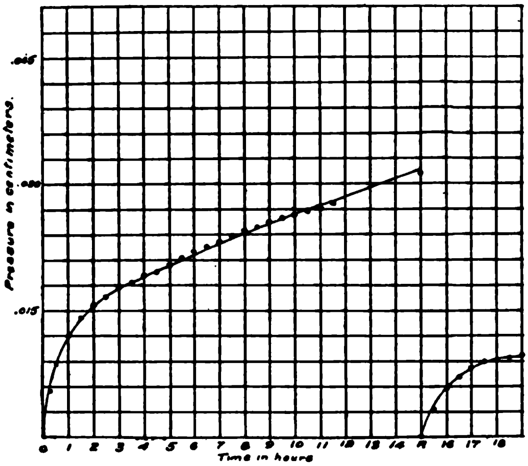


Fig. 6.

CONCLUSIONS.

1. Chemically pure electrodes give off gases in different proportions; for example, of two cathodes of the same weight one may be rich in helium and the other give off comparatively little; or one may give off

more hydrogen than the other. Thus, there is apparently no relation existing between the size of the cathode and the amounts of gases which may be thrown off in a high vacuum when large potentials are applied to the electrodes by means of an induction coil. The explanation of this fact may depend upon the manner in which the gases are occluded in the metal. It seems probable that they are not a part of the metallic molecule in the same sense that the α particle is a part of the molecule of radium. Suppose, for instance, that the gaseous atom is simply held in contact with the aluminium atom or molecule by some force of adhesion, and that it is freed by repulsion on account of the very large number of negative electrons applied to the cathode. Then if one cathode should disintegrate more thoroughly than the other before it was consumed, it would give off the more gas.

2. The presence or absence of hydrocarbons within the experiment tube has no influence upon the amounts or kinds of gases evolved. Thus, after having used all precautions in removing hydrocarbons from the tube the experimental results are similar to those obtained when a stopcock is used close up to the experiment tube. If, as some believe, the hydrogen comes from the moisture within the tube, there should be some indication of the liberated oxygen, for in such a dry atmosphere there should be absolutely no reaction between either oxygen and hydrogen and the phosphorous pentoxide.

3. So far as these experiments have gone there has been no instance when hydrogen could not be obtained if any metal of the cathode remained; with this exception: a cathode of 10 mg. of aluminium when about three-fourths disintegrated suddenly stopped giving out gas and remained thus for fourteen hours. That is, the pressure did not increase during the last fourteen hours the coil was running. At that time it was discovered that the coil was acting very poorly and upon testing gave a comparatively low potential. Before the coil could be repaired and the experiment continued the tube cracked. It seems very improbable, though, that this tube should behave differently from the others. Apparently, then, hydrogen is evolved as long as any metal remains in the tube.

4. The fact that helium and neon may be entirely eliminated from the tube shows that they are not disintegration products; if they were we should be able to generate them as long as we apply high potentials to the electrodes. The fact that these two gases may be eliminated from the metal before a very appreciable part of it has disintegrated might indicate that they were occluded at or near the surface. If this is true, it may be that the helium and the neon are absorbed from the atmosphere.

This would account for the presence of more helium or neon in one electrode than in another because the previous history of the metal would somewhat determine how much of a certain gas had been absorbed.

But the case of hydrogen is different. There is the possibility of its being a disintegration product of the metal in somewhat the same manner as the α particle is disintegrated from radium. But while radium disintegrates spontaneously, the hydrogen requires the assistance of a large electric force before it is able to leave the metal.

PHYSICAL LABORATORY OF WASHINGTON AND JEFFERSON COLLEGE,
February 20, 1914.

THE MAGNETIC SUSCEPTIBILITY OF WATER.

By H. C. Hayes.

The magnetic susceptibility of water has been a subject of investigation by many physicists among whom, excepting Townsend who used a method of induction, three methods have been employed, each based on the fact that a substance is acted on by a force when it is placed in a non-uniform magnetic field. I shall speak of these methods as the method of Faraday, the method of Quincke, and the method of Wills.

The Method of Faraday.—This method is based on the well-known law,

$$F_s = XMH\frac{dH}{dS},$$

where F_s is the force which the specimen experiences in the direction S, X is the specific susceptibility, M is the mass of the specimen, H is the value of the field in the space occupied by the specimen, and dH/dS is the space derivative of the field in the direction S. The method is useful for comparing the susceptibility of different substances, but has been discarded as a means of getting absolute values, because of the difficulty in measuring the factor dH/dS and also because of the error that may arise from the assumption that this derivative is constant through the space occupied by the specimen.

The Method of Quincke.—If a liquid has two free surfaces one of which is in a magnetic field of strength H and the other in a null field, a difference in level, d, will exist between the two surfaces such that

$$d = X\frac{H^2}{2g},$$

where g is the acceleration due to gravity. This method requires the measurement of but two factors and lends itself to exact experimentation.

The Method of Wills.—If a uniform cylinder of a substance has one end placed in a magnetic field of strength H_1 and the other end in a weaker part of the field H_2, the cylinder will experience a force, F, in the direction H_2H_1 such that

$$F = {}^1/_2XDS[H_1^2 - H_2^2],$$

D and S being the density and cross-section respectively of the cylinder. This method also admits of exact experimentation, but the factor, F, like the factor *d* in Quincke's method, is very small when a substance as weakly magnetic as water is used. As a result some experimenters have determined the value of X for a para-magnetic substance by one of the last two methods and then found the value for water in terms of this by Faraday's method.

The following table gives the results obtained by various investigators and the method employed.

Date.	Experimenter.	Method.	Temperature.	$-X \times 10.^7$
1855	Faraday	Faraday	—	6.7
1880	Becquerel	Faraday	—	6.4
1881	Schumeister	Faraday	—	4.19–5.25
1885	Quincke	Quincke	20	8.1
1888	Wahner	Quincke	15	5.3
1888	Du bois	Various	—	8.3
1892	Henrichsen	Wills, Faraday	—	7.24
1895	Curie	Faraday	15–159	7.87
1896	Townsend	Induction	10	7.4
1898	Fleming, Dewar	Faraday	20	7.4
1898	Konigsberger	Quincke, Faraday	20	6.7
1899	Jager, Meyer	Quincke Wills, Faraday	13–30	6.4
1902	Piaggesi	Quincke	23–86	7.8
1903	Stearns	Wills	22	7.06
1904	Wills	Wills	22	6.95
1912	Sève	Quincke	24	7.2
1912	de Haas, Draper	Quincke	24	7.3
1912	Weiss, Piccard	Quincke, Faraday	20	7.193
1913	Hayes	Faraday	24	7.26

The present investigation was begun in 1911 for the purpose of obtaining an accurate standard to be used in an investigation of the magnetic properties of some weakly magnetic alloys. The work was well under way when the papers by Sève, de Haas and Draper, and Weiss and Piccard came out in succession. As the table shows, their results are in good agreement, so this paper which offers results in excellent agreement with theirs is valuable only as a piece of corroborative evidence.

Method.—The present work has made use of Faraday's method. As shown above, this method is based on the law

$$F_s = XMH\frac{dH}{dS}$$

and the experimental difficulties, so far as making absolute determinations is concerned, lie in making accurate measurements of the factor dH/dS. Much of the error in the work that has been done by this method has been due to the fact that the specimen was not located at the position where the value of $H(dH/dS)$ was determined. The author has devised an accurate method for determining the factor, dH/dS, and the design of the apparatus eliminates any error due to misplacing the specimen, so the method has been made suitable for determining absolute values.

Apparatus.—The field H was furnished by an electro-magnet MM (Fig. 1), which was suspended from a turn-table provided with ball bearings.

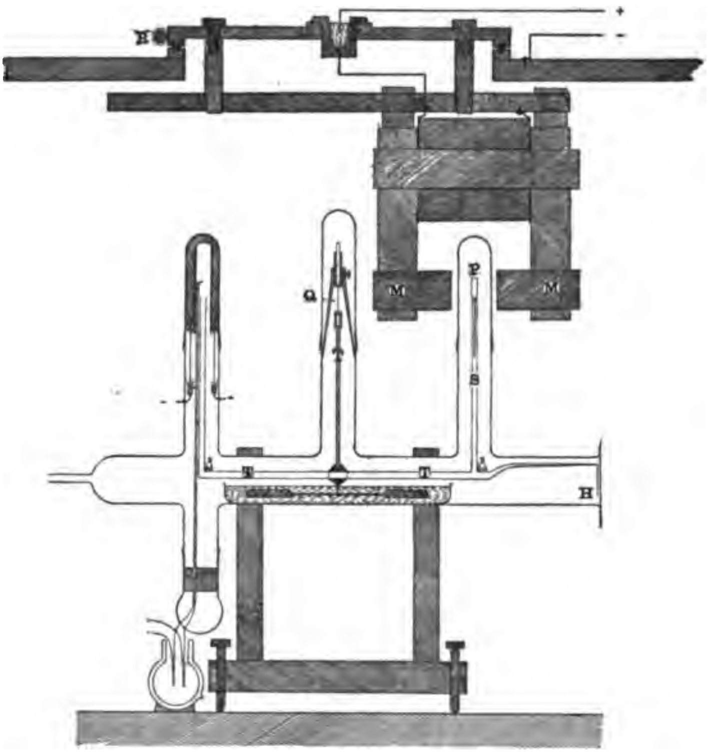


Fig. 1.

Arrangement of apparatus. *MM*, electro-magnet; *R*, worm gear, *TTT*, torsion balance; *S*, standard for supporting specimen; *P*, specimen; *B*, mercury-cup for counterbalance; *Q*, quartz fiber, *H*, cross-hair.

A worm gear R, attached to the rim of the turn-table, made it possible to rotate the magnet to any desired position about a vertical axis, one complete turn of the magnet requiring 793 turns of the worm. To avoid waste of time in moving the magnet, an arrangement was made whereby the worm could be turned either by a motor or by hand. This arrangement is not shown in the figure.

The magnet was made of wrought iron and carefully annealed. It was excited by a current of five amperes taken from a storage battery of twenty cells. The current was controlled by means of a slide-wire resistance.

The specimen P was placed on the standard S erected on one arm of a torsion balance TTT, and counter-balanced by means of the mercury cups BB. The torsion fiber Q, the torsion arm, and the standards were made of quartz. The balance was damped by a pair of vanes submerged in mercury.

The standard from the left arm of the balance enters a small electric furnace provided with a thermo-junction for measuring the temperature. This part of the apparatus plays no part in the present investigation but is used for making alloys and testing their magnetic properties. When the apparatus is used for this purpose the right-hand arm carries the standardizing specimen.

The whole balance is suspended in glass, and all measurements were made in a vacuum varying from 0.002 to 0.003 of a centimeter of mercury. This method has some advantages over the usual one of surrounding the specimen with a so-called magnetically indifferent gas.

Measurements.—The force F_s was determined through the relation

$$F_s = \frac{T}{L \times l} \times d,$$

where L is the length of the cross-hair arm, l is the length of the torsion arm, T is the coefficient of torsion of the quartz fiber, and d is the deflection of the cross-hair H. The values of L and l, as determined by a cathetometer, were 29.66 and 21.64 centimeters respectively. T was determined experimentally by observing the time in which a bar of known moment of inertia made one complete oscillation when it was suspended by the fiber Q at the central point. The value of T proved to be 1,208 so the relation between F_s and d was

$$F_s = 1.882d.$$

The deflection, d, measured with a microscope and micrometer eyepiece, was taken as the maximum value given by moving the magnetic field slowly across the specimen. It follows that the corresponding values of H and dH/dS must be such as to make their product a maximum. This method eliminates any error that might arise from misplacing the specimen, and avoids disturbing the specimen by turning the torsion head.

The Maximum Value of *dH*/*dS*.

First Method.—The value of H was determined at various points across the field corresponding to equal increments of S, and from this data the curve H^2 vs. S was carefully plotted. The slope of this curve is equal to twice the product of H and dH/dS, so the maximum value of this product is half the maximum value of the slope of this curve. As shown is Fig. 2, this particular value of the slope can be determined with considerable accuracy, for it occurs at a point of flection.

The increments in S were taken as 0.172 cm., the distance the field moves across the exploring-coil when the worm is given one complete turn. H was determined by means of a ballistic galvanometer through the relation,

$$\frac{AH}{MI} = \frac{\theta}{\theta_s},$$

where A is the area of cross-section of the exploring-coil, H is the field strength in gausses, M is the mutual induction of the standard in gausses per ampere of current, θ is the deflection of the galvanometer caused by suddenly turning the exploring-coil through 180°, and θ_s is the deflection caused by reversing a current of I amperes in the primary of the standard.

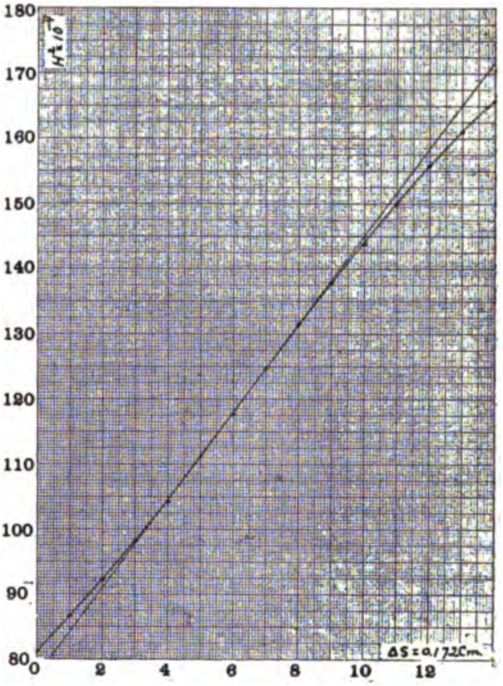


Fig. 2.

Portion of H^2 vs. S curve showing tangent drawn at point of deflection.

By varying the standardizing current I, the value of θ_s was always made nearly equal to θ; and the deflection θ was held to about 10 cm. by varying the resistance of the galvanometer circuit.

The exploring-coil was 2.5 cm. long and 0.35 cm. in diameter, being cylindrical in form and of the same cross-section as the specimen. This coil was made of No. 40 double silk-covered wire wound on a thin strip of mica and covered with bees-wax. It was mounted vertically on a standard that could be rotated through 180° about a vertical axis, and value of $H \cdot dH\ dS$. It should be stated that the ordinates in Curve 3 are only proportional to dH/dS for the factor R/r was omitted in order to simplify the computation. Therefore, the maximum ordinate in Curve 5 must be multiplied by this factor.

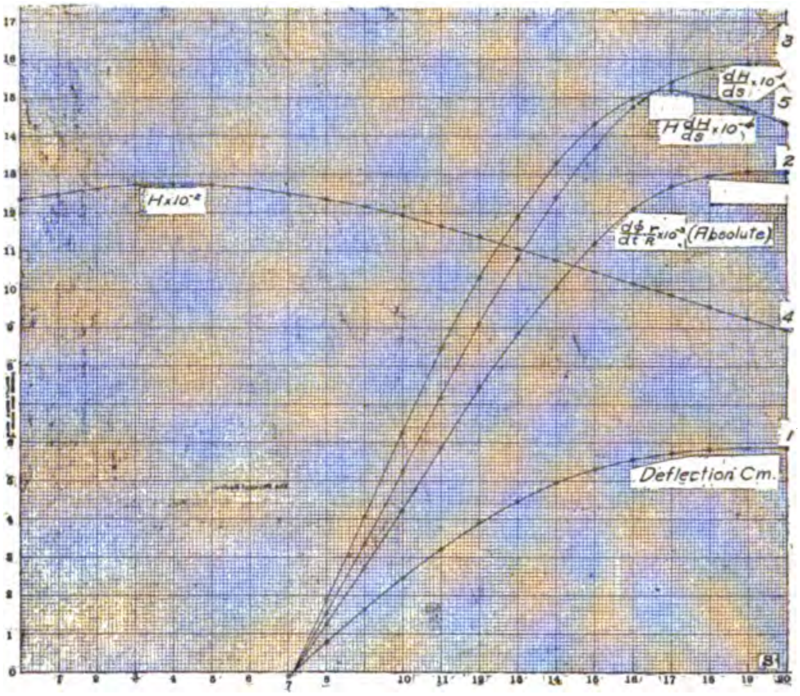
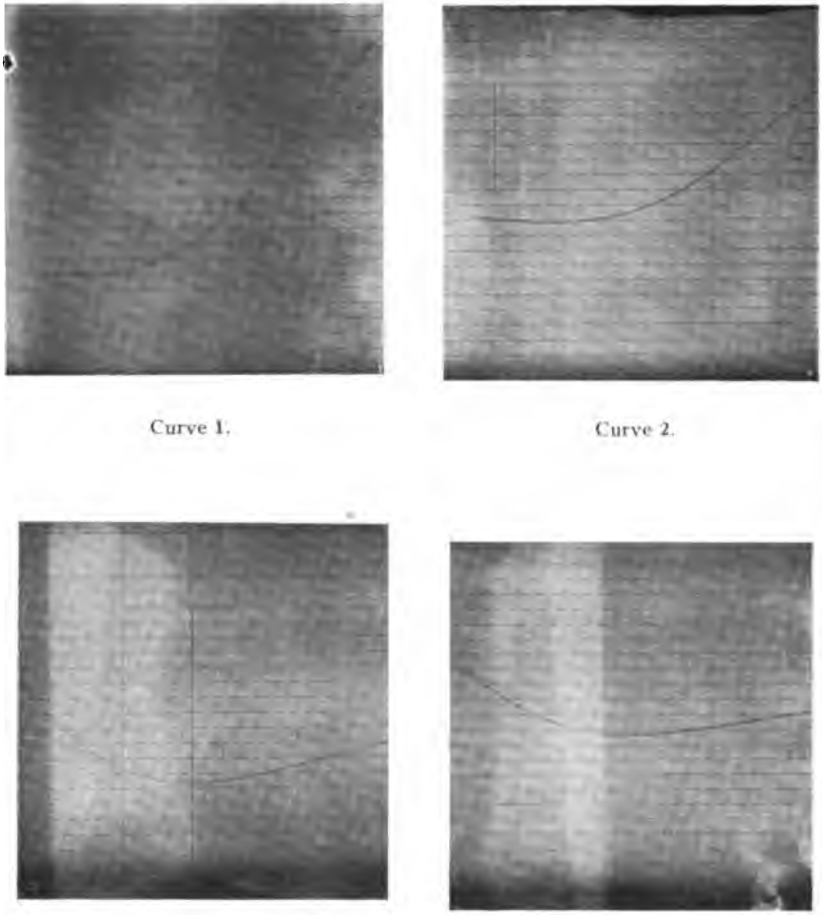


Fig. 3.

Curves showing the method of finding the maximum value of $H(dH/ds)$.

It is to be noticed in Fig. 3 that Curve 1, the deflection curve, and all the curves derived from this, do not cut the axis of abscissæ at the point where H is a maximum, although dH/dS is zero at this point. This displacement is due to lag in the galvanometer and takes place in the opposite direction when the motion of the magnetic field across the exploring-coil is reversed. This lag not only displaces the E.M.F. curve along the axis of abscissæ, but it distorts the curve as well. The lag in this curve, at any particular point, depends upon the rate at which the E.M.F. has been changing before this point is reached. As a result, the galvanometer curve given by a clockwise rotation of the magnet (see Fig. 4) will differ both in shape and position from the curve given by an anti-clockwise motion. Therefore, the error due to galvanometer lag cannot be overcome by shifting the curve so that it will cut the axis of abscissæ at the point where H is a maximum.



Curve 1. Curve 2.

Curve 3. Curve 4.

Fig. 4.

Specimens of the E.M.F. curves given by the Einthoven galvanonometer. Curves 1 and 2 were taken as the coil moved from stronger to weaker fields; Curves 3 and 4 refer to motion of the field in the opposite direction.

H. C. HAYES.

This difficulty was overcome as follows: Electromotive force curves were taken for various velocities of the magnetic field, and the maximum value of $H \cdot dH/dS$ determined for each velocity in the manner described. Fig. 3 shows that the value of $H \cdot dH/dS$ will be too small if the motion of the magnet is such as to carry the E.M.F. curve away from the point where H is a maximum and too large if the shift is in the other direction. It is also clear that the lag, and hence the resulting error, will become less as the velocity of the magnet is decreased, approaching zero as the velocity of the magnet approaches zero. If, therefore, the various values of $H \cdot dH/dS$ are plotted as ordinates against the corresponding velocity of the magnetic field as abscissæ, a curve passed through these points will, if extended, intercept the axis of ordinates at the true maximum value of $H \cdot dH/dS$.

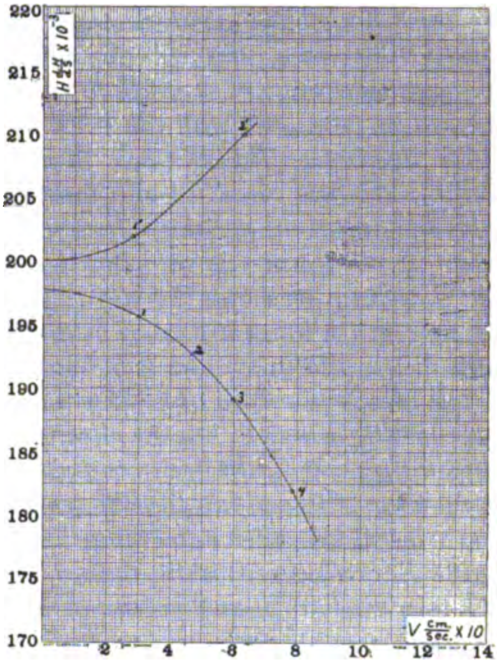


Fig. 5.

Curves showing the variation of $H\ dH/ds$, as determined by the second method, and V, the velocity of the field across the exploring-coil. The true value of $H(dH/ds)$ is given when the lag is zero, hence when V is zero.

The fact that this curve cuts the axis of ordinates perpendicularly aids greatly in the extrapolation. An excellent check on the work is furnished by determining such a curve for motion of the magnet in both clockwise and anticlockwise directions. These curves are shown in Fig. 5. The data for the lower curve was taken with the magnet rotating in a direction such that the E.M.F. curve was shifted away from the point where H is a maximum, and the upper curve refers to motion of the magnet in the opposite direction. The lines were drawn with the aid of a French curve. The intercepts give for the maximum value of $H \cdot dH/dS$ 1.98×10^5 and 2.00×10^5 respectively.

A third degree equation passed through points 1, 2, and 3, with the imposed condition that it cut the axis of ordinates perpendicularly, intercepts the axis of ordinates at 1.99×10^5, while a second degree equation through points 1 and 2, and through points 1 and 3, with the same condition imposed, gives for the maximum values of $H \cdot dH/dS$ 1.99×10^5 and 1.98×10^5 respectively. A second degree equation passed through points 1′ and 2′ gives the value 1.98×10^5. The average value 1.985×10^5 is probably correct to within a small fraction of one per cent.

These values were obtained by using for the E.M.F. the drop across the terminals of the galvanometer, so they must be multiplied by the ratio R/r. The resistance of the whole circuit, R, was 2,854 ohms and the resistance of the galvanometer, r, was 2,784 ohms, giving for the ratio R/r the value 1.025, and this multiplied into 1.985×10^5 gives for the maximum value of $H \cdot dH/dS$ 2.03×10^5. The results obtained by the first method agree with this value to within 0.5 per cent.

The Specimen.—The specimen M consisted of 0.150 gr. of distilled water. This was contained in a small cylindrical capsule made of thin glass and drawn out at one end to a very fine capillary tube about 6 cm. long. By means of this tube the capsule could be filled and centered on the balance, as shown in Fig. 1. The deflection due to the action of the field on the water was taken as the difference between the deflection with the capsule empty and then filled.

The capsule was filled by first heating the glass and placing the end of the capillary in water. As the glass cooled some water was forced in to replace the air that had been expelled. This water was then driven out in the form of steam, carrying the remaining air with it. The open end was then placed under water while the steam was escaping, and as soon as the vapor condensed water entered and filled the tube. The capillary was then carefully heated and the water driven out in the form of steam. At the instant the flame was removed from the stem the capillary was sealed thus leaving a more or less perfect vacuum in the stem. The glass correction was not materially changed by this process.

The Force F, was determined four separate times through the relation,

$$F = 1.882d,$$

where d is the deflection of the cross hair. The average value for d was -0.01175 cm., which gave for F, the value -0.0221 dynes. The equation for X now becomes

$$-0.0221 = 0.150 \times 2.03 \times 10^5 \times X.$$

This gives for X the value -7.26×10^7 with the last figure doubtful.

Conclusion:—The value of the magnetic susceptibility of water at temperature 24° F. has been determined by Faraday's method, the difficulties of the method having been sufficiently overcome to make it capable of giving accurate absolute results. The value of X as found by this method is in excellent agreement with the recent results obtained by Quincke's method, and seems to prove that this value is now known to within one per cent. Moreover, we may feel sure that this value is independent of the field, for the strength of the field used in this work was only 1,180 gausses while Sève, de Haas and Draper, and Weiss and Piccard used fields varying from 15,700 to over 21,500 gausses.

The excellent Einthoven galvanometer, which made possible the work presented in this paper, was obtained through a grant from The Rumford Fund.

Jefferson Physical Laboratory,
Harvard University.

THE EFFECT OF MAGNETIZATION ON THE OPACITY OF IRON TO RÖNTGEN RAYS.

By A. H. Forman.

IN a general way it would seem natural to expect that a change in the molecular arrangement of iron by magnetization, which produces the phenomenon of magneto-striction, should to some extent also affect the opacity of the iron to Röntgen rays. The investigations along this line have all given negative results. Experiments[1] in which the polarized secondary rays were used instead of the ordinary Röntgen rays have been tried with negative results.

In the winter of 1909, the author found indications of a positive character using a rough photographic method. The photographs indicated a slight increase in the opacity when the iron was magnetized in a direction parallel to the axis of the X-ray tube and perpendicular to the Röntgen rays. Because of their magnitude and the possibility that they were due to secondary causes, these results were not conclusive. It was therefore decided to see if they could be duplicated with an apparatus utilizing the ionizing power of the Röntgen rays. A method was devised which was much more sensitive than any used before and capable of detecting a change in the opacity of one part in ten thousand under the most favorable conditions.

Tests using this method, in which the iron was magnetized in a plane perpendicular to the Röntgen rays, with its direction of magnetization parallel to the axis of the X-ray tube, and also with its direction of magnetization perpendicular to this axis, gave negative results. The following is a description of the apparatus and the method of making the tests.

The apparatus finally adopted is shown in Fig. 1. The ionizing chambers consist of upright lead pipes (*CC*) soldered to a horizontal sheet of lead (*MM*). In the axis of each pipe is an insulated bare wire. The two wires are also connected to a grounding switch as shown. The ionizing chambers are both insulated and one maintained at a potential of + 220 volts and the other at a potential of − 220 volts. Two screens, one of lead and the other of a mixture of white-lead and putty, were used to stop rays other than those passing through the iron and entering the

---

[1] J. C. Chapman, Phil. Mag., Vol. 25, p. 792.

ionizing chambers. There is a possibility that very hard rays might even pass through these screens into the space below the charged plates and there ionize the air. This would cause a leakage to the wires and thus mask the effect of the charge which leaks to them in the ionizing chambers. To prevent this a grounded guard plate (*G*) was put below the lead sheets (*MM*). The potential of the wires is very small so that the leakage from the wires to the guard plate is quite small and negligible, while the ionization which results under the charged plates is taken care of by leakage to the grounded guard plate. If the Röntgen rays do get below the lead plates (*MM*) their effect is therefore inappreciable.

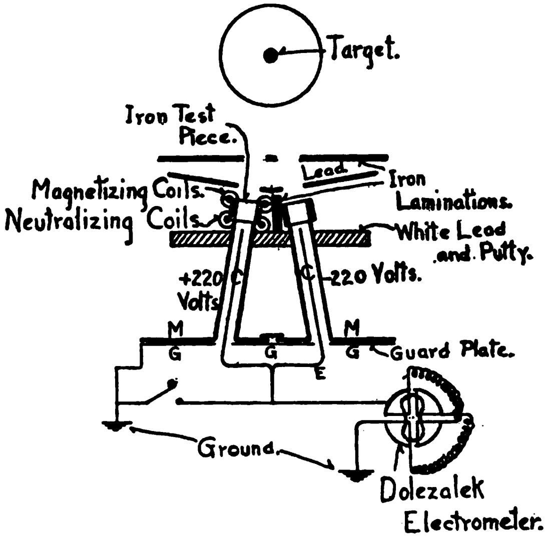


Fig. 1.

The piece of iron to be magnetized is fastened to the yoke of an electromagnet so that it completes the magnetic circuit as shown in Fig. 2. In the course of the experimental work, it was found that the stray field from the magnetizing coils disturbed the balance between the two chambers by deflecting the cathode ray in the X-ray tube. To prevent this two similar coils were placed under the magnetizing coils and connected in series with them so that they set up an opposing flux. This neutralized the effect of the stray field in the vicinity of the cathode ray. A screen of two sheets of iron was placed between the coils and the X-ray tube as an additional precaution. The magnetic effect was screened from the other piece of iron by iron laminations placed between the two pieces as shown in Fig. 1.

Perfect electrostatic screening of the electrometer system was obtained by use of a solid screening of tin-plate, except where the light was reflected from the electrometer mirror. This opening was screened by using a glass cell filled with a solution of NH_4Cl and grounded. The balance between the two ionizing chambers was made by sliding a narrow wedge of lead foil in and out across the top of one of the chambers, using a micrometer screw to adjust the position of the wedge. The electrometer which was used gave a deflection of 84 cm. at a distance of 1 meter, with its needle charged to 62 volts, and a difference in potential of 1 volt across the quadrants.

With the two chambers charged oppositely as indicated, ionization in each tends to neutralize the charge that leaks to the wire from the other, and when there is a perfect balance no charge accumulates on the wire. A very slight change in ionization of either chamber causes a piling up of a charge on the wire, and the deflection of the electrometer is proportional to the change in ionization and the time that the grounding switch is open.

The sensibility of this system is so great that difficulty was experienced at first in getting a balance between the chambers because of disturbances due to a change in the hardness of the X-ray tube. A very slight change in the potential difference across the X-ray tube would destroy the balance. It was therefore necessary to connect a high tension electrostatic voltmeter across the X-ray tube, and take observations for definite potential differences. In taking the readings the following method was used. With the grounding switch closed, a current was sent through the X-ray tube and as soon as this tube had reached the desired condition, the grounding switch was opened. After the switch had been open for five seconds the current through the X-ray tube was stopped and the electrometer deflection observed. The deflection thus obtained is proportional to the charge which accumulates in five seconds, due to the difference in ionization in the chambers.

The effect of the magnetization of the iron on the change of the balance was tried with rays of three degrees of penetrability. Measured by the equivalent spark between sharp points, the potential difference across the X-ray tube was respectively 4.2, 7 and 10.5 cm. The iron used was 0.08 mm. thick and had the following chemical analysis: 0.093 per cent. silicon, 0.06 per cent. sulphur, 0.008 per cent. phosphorus, 0.24 per cent. manganese, 0.1 per cent. carbon and 99.47 per cent iron.

It was magnetized to saturation by sending a large current through the magnetizing coils and it was demagnetized by sending 60-cycle alternating current through the coils and reducing the current by steps to zero.

Tests were made in which the iron was turned with its direction of magnetization parallel to the axis of the X-ray tube, and also with its direction of magnetization perpendicular to this axis. Since the tube varied in hardness even during an observation, it was necessary to take a number of readings with the iron first magnetized and then demagnetized. To guard against any shift due to secondary causes, observations were made in pairs, first with the iron demagnetized and then with the iron magnetized.

The sensibility of the apparatus was tested by finding the smallest change in the area of the iron, penetrated by the rays entering the chamber, which produced a change of balance appreciably greater than any effect noticed in the magnetization tests. The area of the iron penetrated by the rays entering the ionizing chamber was slightly less than the area of the ionizing chamber opening, since the iron was a little distance above the chamber (see Fig. 2). The diameter of the effective area was found experimentally by sliding a lead strip (edge on) across the top of the iron and parallel to a diameter of the opening of the chamber, and finding the first point where a change of balance was produced. It was then moved across the entire opening and another point found where a change of balance was produced. The distance between these points is the diameter of the circle penetrated by the rays entering the ionizing chamber. To get the smallest change in area which could be detected, the lead strip which extended about one fourth of the diameter inside the circle, was moved through the smallest distance that would appreciably disturb the balance. This distance multiplied by the thickness of the lead strip gives the increment in area. - The total area is found by subtracting the area covered by the lead strip from the area of the effective circle, and the sensibility is expressed as the ratio of the change in area to the total area. In one of the tests the values were as follows: Diameter of effective circle 19 mm. Thickness of strip 0.86 mm. Area covered by the strip 3.44 sq. mm. Distance strip was moved to change balance 0.05 mm. Hence the sensibility was 0.043 divided by 280, or 0.00015.

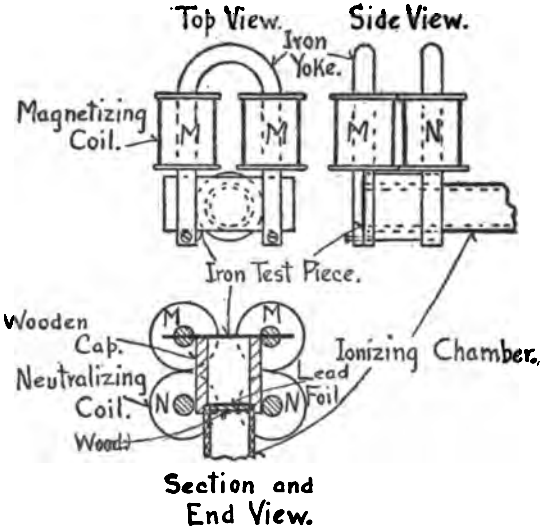


Fig. 2.

The sensibility depends upon the total number of rays passing through the iron into the ionizing chamber, and this depends on the degree of penetrability of the rays and the current passing through the X-ray tube. The sensibility was therefore determined for each degree of penetra-

TABLE I.

Magnetic Field Perpendicular to Axis of X-ray Tube.				Magnetic Field Parallel to Axis of X-ray Tube.				Sensibility Test. Proportional Change of Area = 0.0015.			
X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflection.	
Miliamps.	Equivalent Spark-gap.	Iron Demagnetised.	Iron Magnetised.	Miliamps.	Equivalent Spark-gap.	Iron Demagnetised.	Iron Magnetised.	Miliamps.	Equivalent Spark-gap.	Zero Setting of Lead Strip.	Setting Changed 0.5 mm.
5	4.2 cm.	57		5	4.2 cm.	64.5		5	4.21 cm.	64	
5	4.2	71.5		5	4.2	61.5		5	4.21	64	
5	4.2		49.5	5	4.21		64.5	5	4.2	69.5	
5	4.23		48	5	4.2	63		5	4.22	58.5	
5	4.23	57.5		5	4.21	66		5	4.23		43
5	4.2	51.5		5	4.22		62	5	4.23		42.5
5	4.25		39.5	5	4.23		70	5	4.23	52.5	
5	4.24		50	5	4.23	66		5	4.25	52.5	
5	4.2	25						5	4.25		32
5	4.25	40						5	4.26		21
5	4.25		46					5	4.28	27.5	
5	4.25		41.5					5	4.25	28.5	
5	4.25	35.5						5	4.26	24.5	
5	4.25	24						5	4.27		−5
								5	4.26		−7.5
Mean deflection Difference = 0.45		45.25	45.7	Mean deflection Difference = 1.3		64.2	65.5	Mean deflection Difference = 27.9		48.9	21

Table II.

Magnetic Field Perpendicular to Axis of X-ray Tube.				Magnetic Field Parallel to Axis of X-ray Tube.				Sensibility Test. Proportional Change of Area=0.00015.			
X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflect.	
Miliamps.	Equivalent Spark-gap.	Iron Demagnetized.	Iron Magnetized.	Miliamps.	Equivalent Spark-gap.	Iron Demagnetized	Iron Magnetized.	Miliamps.	Equivalent Spark-gap.	Zero Setting of Lead Strip.	Setting Changed 0.05 mm.
3	7.3 cm.	55.5		4	6.95 cm.	37.5		4.7	7 cm.	−55	
3.2	7.1	−65		4	6.8	−21.5			7.07	−66	
3.2	7.1		−180	4	6.9		19.5	5	7	−68	
3.15	7.2		−180	4	6.95		180	5	7		170
3.3	7.35	89		4	6.95	105		5	7.03		140
3.5	7.1	46		4.2	6.75	−12		4.5	6.85		90
3.6	7.2		−54	4.2	6.75		−31	4.8	6.95	−180	
3.7	7.25		−42	4.1	6.8		−14.5				
4	7.1	−91.5		4	6.8	56.5					
4	7.1		35.5	4.1	6.75	21					
3.9	7.1		40	4.15	6.75		21				
3.9	7.1	−180		4.15	6.75		−31				
3.6	7.1		−33.5								
3.5	7.1		−110								
3.5	7.1	−180									
3.7	7.1	−108									
Mean deflection. Difference = 11.		−54.5	−65.5	Mean deflection. Difference = 8.1		32.1	24	Mean deflection. Difference = 225.		−92	133

Table III.

Magnetic Field Perpendicular to Axis of X-ray Tube.				Magnetic Field Parallel to Axis of X-ray Tube.				Sensibility Test. Proportional Change of Area = 0.00018.			
X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflect.		X-ray Tube.		Electrometer Deflect.	
Miliamps.	Equivalent Spark-gap.	Iron Demagnetized.	Iron Magnetized.	Miliamps.	Equivalent Spark-gap.	Iron Demagnetized.	Iron Magnetized.	Miliamps.	Equivalent Spark-gap.	Zero Setting of Lead Strip.	Setting Changed 0.06 mm.
1.5	10.55 cm.	59		1.9	10.5 cm.	23		—	9.65 cm.	77	
1.6	10.5	35		1.9	10.6	88.5		—	9.55	80	
1.55	10.53	26		1.95	10.6	84.5		1.5	9.45	2.1	
1.85	10.53		20	1.8	10.6	100		1.5	9.45		−23
1.85	10.53		22	1.8	10.6	180		1.4	9.55		19
1.85	10.53		65	—	10.55		17	1.5	9.45		−27
1.8	10.5	−2		1.9	10.6		170	1.5	9.35		23
1.8	10.42	−2.5		2	10.6		18	1.2	9.35		−180
1.7	10.5	27.5		1.9	10.45	−180		1.4	9.4		−175
1.7	10.53	37		1.95	10.6	89.5					
1.7	10.53		31	1.9	10.55		75				
1.5	10.53		42.5	1.95	10.5		30				
1.6	10.53	38.5		1.95	10.45	−170					
1.5	10.53	54.5		1.8	10.55	33					
1.5	10.62		77.5	1.8	10.6		87				
1.65	10.55		24	1.85	10.6		64				
1.8	10.5		33	1.8	10.55	26					
1.55	10.53	52		1.8	10.55	18					
1.5	10.5	50		1.85	10.5		−31.5				
1.5	10.53		63	1.9	10.45		−180				
1.5	10.53		53	1.85	10.5	−47					
1.5	10.53	57									
Mean deflection. Difference = 1.1		38.3	37.2	Mean deflection. Difference = 8.6		20.4	31	Mean deflection. Difference = 120.1		59.6	−60.5

bility. For the softer rays the sensibility was 0.0015, for the medium rays it was 0.00015 and for the hardest rays it was 0.00018. The reason that the sensibility for the run with the hard rays was less than that of the medium rays is that the X-ray tube used for the hard rays was smaller and a smaller current was sent through it.

The preceding tables give the results of the tests.

In some of the tests the values differ considerably. This is because of the high sensibility of the apparatus and the fact that the condition of the X-ray tube varied. It will be noticed that in the magnetization tests the mean values agree closely, thus showing that as a whole there is no change in the balance. In the sensibility tests the change in ionization is evident from the mean values of the deflections and their differences. We therefore conclude that there is no effect due to the magnetization of the iron, with the magnetization in a plane perpendicular to the Röntgen rays and either parallel or perpendicular to the axis of the X-ray tube, unless it is less than the effect produced by shifting the lead strip. In the case of the soft rays it must be less than 0.0015, medium rays less than 0.00015, and hard rays less than 0.00018. In the earlier tests an effect was observed when the magnetizing current was on, but this was found to be due to the deflection of the cathode ray of the X-ray tube, which is probably the cause of the positive results obtained at first photographically. Investigations have been started using a field of 3,500 gauss parallel to the Röntgen rays and perpendicular to the plane of the iron.

As is evident, the method which has been used in this work has the great advantage that even though the ionization in each chamber is quite large, the electrometer measures only the small difference in the ionization. And since this method gave such a high degree of sensibility, it seems to the author that it would be quite useful in other fields of investigation where the changes sought for are likely to be quite small.

Physics Laboratory,
Cornell University,
Ithaca, N. Y.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SEVENTY-FIRST MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall of Columbia University on Saturday, February 28, 1914.

The following papers were presented:

A Method of Rapidly Extracting, Purifying and Compressing Radium Emanation. WILLIAM DUANE.

On the Density of Radiant Action. WILLIAM DUANE.

Secondary Electron Emission from a Hot Cathode Caused by Positive Ion Bombardment. IRVING LANGMUIR.

Additional Data on the Illumination-Photoelectric Relation. H. E. IVES.

An Improved Mercury Pump. A. H. PFUND. (By title.)

Note on the Photoelectric Cell as an Analyzer for Polarized Light. By E. MERRITT.

A Thermoelectric Method of Determining the Purity of Platinum Ware. G. K. BURGESS and P. D. SALE.

The Electric Resistance and Critical Ranges of Pure Iron. G. K. BURGESS and I. W. KELLBERG.

Radiation Constants of a Nitrogen-Filled Tungsten Lamp. W. W. COBLENTZ. (By title.)

The Villari Critical Point in Ferromagnetic Substances. S. R. WILLIAMS. (By title.)

Motion of a Radiating Oscillator. E. B. WILSON. (By title.)

On the Asymmetric Distribution of Velocities of Photo-Electrons from Platinum Cathode Films. OTTO STUHLMANN, JR. (By title.)

A. D. COLE,
Secretary.

AN IMPROVED MERCURY LAMP.[1]

BY A. H. PFUND.

SEVERAL years ago[2] the writer described a convenient type of mercury lamp which served as a source of visible as well as ultra-violet radiations of mercury vapor. Much experience with this lamp has shown that, while it

---

[1] Abstract of a paper presented at New York meeting of Physical Society, February 28, 1914.

[2] Astrophysical Jnl., 27, p. 299, 1908; Ztschr. Für. Wiss. Phot., 4, p. 329, 1908.

has its good features, it also possesses the defect that the iron electrode used gives rise to a yellow coating on the glass—thus limiting the life and usefulness of the lamp to an unnecessarily short period. Recently the lamp has been redesigned and the objectionable features have been eliminated while the good ones have been retained.

The process of making the lamp is as follows: a glass tube 2.5 cm. in diameter is drawn down at one end to a diameter of 1 cm. and is closed; a bulb is then blown and, while the glass is still soft, the lower end of the tube is pushed up, thus creating the annular trough shown in the dotted lines of Fig. 1. Next a side tube *B*, Fig. 2, is attached; a small bulb is blown in the tube *A* and the platinum electrodes are sealed in. The inner end of the wire in *A* is preferably bent as indicated to avoid any possible arcing between this wire and the mercury when the lamp is started subsequently by tilting. The lamp as such is finished after the side tube *C* has been introduced and a lip (ground flat with carborundum powder) has been turned on the upper end of the tube. After the lamp has been cleaned and dried thoroughly, distilled mercury is introduced to the indicated amount and a quartz plate is attached to the open end of the tube by means of sealing-wax.

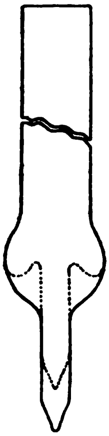


Fig. 1.

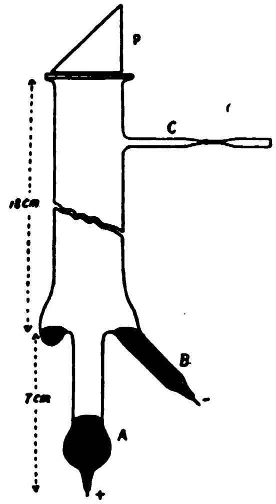


Fig. 2.

After having drawn down the tube *C*, the lamp is attached to a mercury pump and the usual process of exhaustion and boiling of mercury is carried out. The lamp is then connected to a source of direct current (110 volts) through an auxiliary resistance of 5–6 incandescent lamps in parallel, thus reducing the current to about 2 amperes. The discharge is started, either by a high-potential discharge or by boiling the mercury in tube *A* so violently that it rushes up to short-circuit the lamp for an instant. While the lamp is still on the pump, the discharge is continued for an hour or more to drive off gases and vapors. After sealing off from the pump, the lamp is ready for use.

Whenever it is desired to start the lamp subsequently, the tubes *A* and *B* are heated cautiously by means of a bunsen burner and the lamp is tilted so that the mercury from *A* flows *directly* into the top of the tube *B*. Upon returning the lamp to its vertical position, a brilliant discharge sets in. By connecting the lower electrode *A* to the positive end of the source of current, the discharge in the tube *A* becomes very steady, while a brilliant spot dances about on the surface of the mercury in the annular trough. This annoying feature is eliminated by covering the outside of the trough with black paint.

The mercury which condenses in the upper part of the lamp gradually runs down into the trough which overflows periodically into the tube *A*. By constricting, suitably, the larger tube above the trough, it is possible to cause a portion of the falling mercury droplets to reach *A* directly—thus eliminating the sudden overflow previously mentioned. In the great majority of cases, however, the lamp as described, will meet all requirements. In order to avoid the condensation of mercury on the quartz window, the lamp is sealed off from the pump at a pressure of about 1 mm. (thus avoiding the luminous flame which shoots up the tube at high vacua). If, in spite of these precautions droplets persist in forming on the window, this difficulty is overcome by wrapping strips of wet cloth about the upper part of the lamp. If it be desired to utilize the ultra-violet radiations, a totally reflecting quartz prism is introduced at *P*.

While lamps of the type described have been tested for only several months, no defects of design have become apparent.

Johns Hopkins University,
February, 1914.

Contributions to the Thermodynamics of Saturated Vapors.[1]

By J. E. Siebel.

The author finds that the expansion line in indicator diagrams of first class Corliss engines follows an isothermal curve, an outcome which he shows is also theoretically quite in harmony with Gibb's phase rule and which permits the correct calculation of the theoretical work of such engines after the familiar formula of isothermal expansion. The results of these calculations, it further appears, when adapted to the concepts of a theoretically perfect reversible cycle, are amenable to the compound rate of conversion expressive of the second law given by Clausius as

$$W = \frac{Q(t - t_0)}{T} + \frac{Q_1(t - t_0)}{T},$$

in which formula W represents the maximal theoretical work obtainable in an ideal reversible steam engine cycle, between the temperatures t and t_0 when Q signifies the initial heat of vaporization at t degrees and Q_1 the heat becoming free in the expansion stage by the condensation of water; T representing the absolute temperature of the boiler equal to t degrees common temperature.

---

[1] Abstract of a paper presented at the Atlanta meeting of the Physical Society, December 31, 1913.

Second Series. *May, 1914* *Vol. III., No. 5.*

THE

PHYSICAL REVIEW.

A MODIFIED METHOD OF MEASURING e/m AND v FOR CATHODE RAYS.

BY L. T. JONES.

THIS determination of e/m and v is a modification of the usual method employing the simultaneous electrostatic and magnetic deflections. The modification is the result of an attempt to eliminate as nearly as possible the errors of measurement of the deflections and the correction due to the field distribution at the ends of the electrostatic plates. This is brought about chiefly by the position in which the photographic plate was placed.

THE APPARATUS.

A glass cylinder 10 cm. in diameter and 27 cm. long (Fig. 1) was closed at each end by a glass plate. Two holes were made in one of the plates to admit the glass tubes carrying the anode, *A*, and the cathode, *C*. The cathode, an aluminum disc .6 cm. in diameter, was carried on an aluminum rod. This rod was encased in a small glass tube which in turn was supported by a larger glass tube waxed to the glass plate where it entered the discharge chamber. The anode was mounted in a similar manner. Both aluminum rods were connected with the outside by platinum wires sealed in glass.

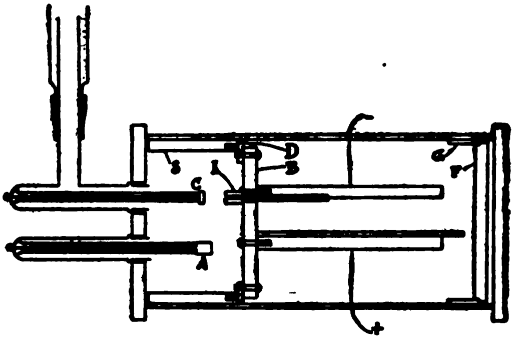


Fig. 1.

A brass ring, *D*, was fastened by sealing wax to the inside of the glass cylinder, and to this were fastened the soft iron shield, *S*, and the ebonite disc, *B*, the latter supporting the electrostatic plates. The electrostatic plates were held to the disc *B* by brass screws. The potential of the electrostatic plates was supplied through two wires that passed through small holes in the walls of the cylinder. The holes were sealed with wax.

By loosening the screws holding the ebonite disc, *B*, to the brass ring, *D*, the disc and electrostatic plates could be taken as a whole from the cylinder.

At the opposite end a short length of brass cylinder, *G*, was waxed to the inside of the glass cylinder and a hard rubber disc, *F*, turned to fit it, darkened the tube. The glass cylinder was coated on the outside with lamp black and the coating connected to earth. All the metal parts inside the tube, except the electrostatic plates and the discharge terminals, were connected to earth.

THE ELECTROSTATIC PLATES.

Two electrostatic plates were mounted exactly 1 cm. apart, as shown in Fig. 2. The beam of cathode rays was made to pass along the upper of the two plates at grazing incidence. The photographic plate was placed flat on the lower of the two electrostatic plates. The beam was bent downward, by adjusting the electric field, to strike the photographic plate well within the geometrical limits of the field plates.

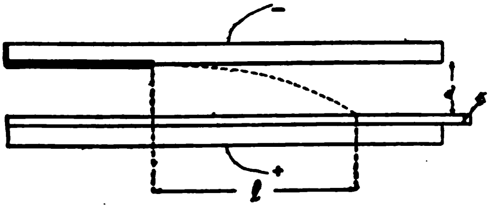


Fig. 2.

The cathode beam emerged from the Thomson plate-tube at a distance of several centimeters from the left end of the electrostatic plates and was then bent downward. Since the plates were plane and parallel the electrostatic deflection was the distance from the upper electrostatic plate to the upper side of the photographic plate.

THE FORMULA.

Let the two electrostatic plates be separated by a distance $d + t$, d being the air place and t the thickness of the photographic plate, which is of dielectric constant K. The two electrostatic plates are kept at constant potentials V' and V''.

If the plates are separated by an air space of thickness $d + t$ there is a given electric surface density of charge on the plates and, consequently, a given electric force, E, in the space between them. If, now, the dielectric of thickness t is introduced, whose equivalent air thickness is t/K, the effective air space will then be reduced from $d + t$ to $d + t/K$. The effective air space has thereby been reduced an air-equivalent amount of $t - t/K$, causing a change in the capacity. Since the potentials of the two plates have remained constant the surface density and hence the electric force have changed. If, now, the air gap between the two electrostatic plates is increased by an amount $t - t/K$, then the capacity, the surface density and the electric force will resume their former values. If, then, while an electric force, E, exists between the two plates of potentials V' and V'', a dielectric slab of thickness t is introduced and at the same time the plates are further separated by an amount $t - t/K$, making $d + 2t - t/K$ in all, the surface density on the plates and hence the electric force, E, will remain constant. The electric force is then given by the equation

$$V' - V'' = E(d + 2t - t/k),$$

or

$$E = \frac{PD \times 10^8}{d + 2t - t/k}, \tag{1}$$

where PD is the potential difference of the two electrostatic plates in volts.

The cathode beam in passing through the uniform electric field, E, is accelerated by a constant force and hence follows Newton's second law. The force on the charge e will be

$$Ee = ma, \tag{2}$$

where a is the acceleration toward the positive plate and m is the mass of the electron. Since the electron falls through a distance d in time t we have the distance of fall expressed by the equation

$$d = {}^1\!/_2 at^2,$$

or

$$a = \frac{2d}{t^2}. \tag{3}$$

If the velocity in the horizontal direction is v and the length of horizontal travel is l we have

$$l = vt,$$

whence

$$\frac{1}{t^2} = \frac{v^2}{l^2}.$$

Substituting this value in equation (3) gives

$$a = \frac{2dv^2}{l^2}.$$

If this value is placed in equation (2) we have

$$Ee = \frac{2dmv^2}{l^2},$$

whence

$$\frac{e}{mv^2} = \frac{2d}{El^2}. \tag{4}$$

If at the same time the moving electron is subjected to the action of a uniform magnetic field of intensity H and its velocity v is perpendicular to the lines of magnetic force, urging the particle in the path of a circle, in the plane of the photographic plate, then the force is given by

$$Hev = \frac{mv^2}{r} \tag{5}$$

where r is the radius of the circle. If the dotted line, Fig. 3, indicates the path of the particle undeflected by the magnetic field, and the circle of radius r the curvature experienced under the influence of the magnetic field of strength H we may represent the horizontal distance traveled by the length l and the magnetic deflection (measured at right angles to the undeflected path) by z, since z is small compared with l. Then, from Fig. 3,

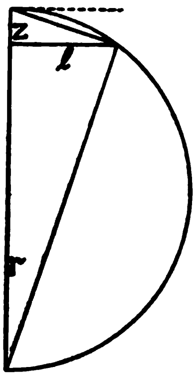


Fig. 3.

$$\frac{z}{\sqrt{z^2+l^2}} = \frac{\sqrt{z^2+l^2}}{2r}$$

and

$$\frac{1}{r} = \frac{2z}{l^2},$$

since z^2, being small in comparison with l^2, may be neglected. Placing this value of $1/r$ in equation (5) we have

$$\frac{e}{mv} = \frac{1}{Hr} = \frac{2z}{Hl^2}. \tag{6}$$

Elimination of e/m between (4) and (6) gives

$$v = \frac{zE}{Hd}.$$

Replacing E by its value given in (1) we get, after simplification,

$$v = \frac{zPD \times 10^8}{Hd(d + 2t - t/K)}. \tag{7}$$

Again, multiplying equations (6) and (7) gives

$$\frac{e}{m} = \frac{z^2PD \times 2 \times 10^8}{H^2l^2d(d + 2t - t/K)}. \tag{8}$$

The Electrostatic Field.

The two electrostatic plates were rectangular brass plates 7.5×15×1 cm. Considerable difficulty was experienced in getting the two plates sufficiently plane. The plates were first planed and then finished by "spotting" on a master plate. A slip of soft iron 5 × 1.5 × .15 cm. was inlaid in the upper plate, as shown in Fig. 2, and the plate again surfaced. Several days were required to surface the plates but they were finally finished sufficiently plane that one would raise the other from the table.

A second slip of soft iron was cut out 5 × 1.5 × .1 cm. and one side made plane. A scratch .005 cm. in width and of about the same depth was drawn full length on this surfaced side. This scratch formed the tube through which the cathode rays passed. The iron slip with the scratch was held against the iron slip inlaid in the upper electrostatic plate by ten brass screws. On account of the small diameter of the scratch and its relatively large length it was subsequently found to be easier to make a scratch of about .05 cm. in diameter, close each end with a small bit of solder, cut off the solder flush with the iron surface and then make a small scratch in the bit of solder at each end. A scratch .1 cm. long at each end was found to give perfect satisfaction, and not nearly so much difficulty was experienced in getting the beam to pass through this tube. In adjusting the cathode to send a beam through the tube the electrostatic plates were first mounted in position with the scratch the full .05 cm. diameter. The vessel was exhausted and a potential difference of about 20 volts applied to the electrostatic plates. The wax joint where the glass tube supporting the cathode entered the plate glass end was then softened by heating and the cathode moved about until a phosphorescent spot on the willemite screen, deposited on the opposite glass end plate, showed the presence of the beam. The wax was allowed to cool while the cathode was in the position giving this spot its maximum brightness. The electrostatic plates were then removed by taking out the screws holding the ebonite disc, *B*, to the brass ring, *D*, and the tube made smaller by the bits of solder mentioned above. The plates were then replaced in position and the vessel exhausted. If the spot failed to show on the willemite screen the process was repeated until finally the beam was made to pass through the small tube.

An iron tube, *I*, .5 cm. diameter and 2 cm. long, was screwed into the disc, *B*, to shield the rays from any magnetic effect before entering the confining tube. The cathode was within 1 cm. of the tube *I*.

The electrostatic plates were spaced by four hollow ebonite cylinders, one placed at each corner, and clamped in position by ebonite bolts passing through the cylinders. The length of these cylinders was measured by a micrometer caliper reading to .001 cm. The cylinder was placed between two thin glass plates and the length of the whole measured. The thickness of the plates was then subtracted. Each cylinder was measured on several successive days and the mean of these measurements was taken as the length. When the cylinders were again measured, after having been in the apparatus under pressure for four months, they were found to have shortened by about 1 per cent. All data was taken during the first fifteen days, however, so no correction was made for this change in length. The potential difference of the electrostatic plates was determined as follows: A high potential storage battery, *T*, was used in sending a small current through the two high resistances, *M* and *R*, as shown in Fig. 4. *M* was a resistance of about 2×10^6 ohms while *R* was an adjustable resistance of about 10,000 ohms. The electrostatic plates were connected directly to the terminals of *M* as shown. By adjusting the value of *R* the potential difference of the terminals of *M* could be kept constant. The potential drop through a small part of *M* was measured by a potentiometer, *P*, against a Weston standard cell of 1.0185 volts at 24° C. The potential difference of the electrostatic plates was thus easily measured to .1 per cent. and by means of *R* the value was kept constant to within .1 volt.

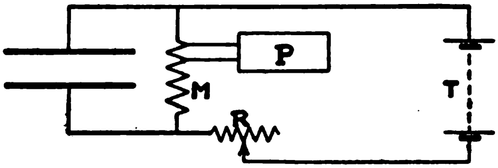


Fig. 4.

The Magnetic Field.

The magnetic field was furnished by a solenoid of 648 turns and 160.2 cm. length. The solenoid was built in two parts and made to join closely at the middle so as to enclose the whole tube. The length of the solenoid was such that the field could be considered uniform and calculated. From the dimensions of the solenoid the strength of the magnetic field at its center was given by

$$H = 5.083\, I,$$

where *I* is the strength of the current in amperes. The current for the magnetic field was supplied by storage cells of 40 amperes capacity. The current, which varied between .5 and 1.5 amperes, was measured by a Siemens & Halske ammeter reading to .005 amperes.

Results.

In placing the photographic plate in the apparatus for exposure the plate was placed solidly against the ebonite disc, *B*. The iron confining tube for the cathode beam was 5.08 cm. long and hence a line drawn

PHYSICAL REVIEW, VOL. III., SECOND SERIES.
May, 1914.

PLATE I.
To face page 322.

No. 18.

No. 6.

No. 3.

Fig. 5.

L. T. JONES.

across the plate 5.08 cm. from the end that touched the ebonite disc established the zero. This line, marked *O* in the photographs, was then directly under the opening of the tube. The length of horizontal travel, *l*, was measured from this line. In photograph 6 two calculations of e/m were made, where the distance l was 4 and 5 cm. respectively. In each photograph the long streamer, second from the top, is the central one, given by zero magnetic field. The two spots immediately on either side are for the magnetic deflection, direct and reversed. The additional spots seen have no significance relative to the value of e/m. The magnetic deflections were accurately measured along the lines drawn parallel to the line marked *O*. The reproductions in Fig. 5 are full size. Twenty photographs were taken in succession. Table I. gives the data relative to all these.

Table I.

Plate No.	I.	PD.	x.	l.	d.	t.	$d+2t-\frac{t}{K}$.	$v\times10^{-9}$.	$\frac{e}{m}\times10^{-7}$.
1	.460	524.0	.138	4.0	.835	.165	1.292	2.866	2.114
2	.450	564.4	.127	4.0	.820	.180	1.210	3.158	2.192
3	.890	498.1	.245	4.0	.825	.175	1.204	2.715	1.838
4	.8902	639.7	.220	4.0	.830	.160	1.177	3.183	1.935
6	.885	425.0	.251	4.0	.811	.179	1.199	2.438	1.701
6*a*	.885	425.0	.3116	5.0	.811	.179	1.199	3.027	1.678
7*a*	.850	323.5	.325	5.0	.805	.185	1.206	2.506	1.508
7*b*	.850	323.5	.371	5.5	.805	.185	1.206	2.861	1.624
7*c*	.850	323.5	.397	6.0	.805	.185	1.206	3.061	1.563
8*a*	.8725	323.0	.314	4.5	.805	.185	1.206	2.355	1.647
8*b*	.8725	323.0	.372	5.5	.805	.185	1.206	2.790	1.547
9	.879	320.3	.335	5.0	.810	.180	1.200	2.470	1.482
10*a*	.864	301.0	.389	5.0	.825	.165	1.182	2.734	1.937
10*b*	.864	301.0	.423	6.0	.825	.165	1.182	2.973	1.591
11	.867	299.0	.377	5.0	.826	.164	1.181	2.622	1.807
12*a*	.873	298.0	.405	5.0	.826	.164	1.181	2.788	2.036
12*b*	.873	298.0	.461	6.0	.826	.164	1.181	3.173	1.832
13	.872	298.0	.382	5.0	.824	.166	1.184	2.632	1.815
14*a*	.874	284.2	.4335	5.5	.819	.171	1.189	2.947	1.837
14*b*	.874	284.2	.499	6.5	.819	.171	1.189	3.278	1.735
15	.881	247.2	.467	6.0	.817	.173	1.192	2.647	1.533
17	.450	248.6							
18	.453	246.6							
19	.4515	245.3							
20	1.289	296.7	.558	5.3	.850	.140	1.153	2.578	1.563
Average									1.748

The value of the dielectric constant of the glass plate was that given by Landolt and Börnstein for "spiegel glas." If the value of K was taken as either 5 or 7 instead of 6 the resulting value of e/m is changed by only about .5 per cent. The probable error of the final result, calculated in the usual way from the data in Table I., is 1.5 per cent.

SUMMARY

The method devised for the determination of e/m and v for cathode rays from a cold cathode is a modification of the usual electrostatic and magnetic deflection photographic method. It has two distinct advantages.

1. Both the electrostatic and magnetic fields are uniform over the entire path of the deflected cathode beam.

2. The electrostatic deflection is kept constant for all strengths of fields employed and thus the inaccuracy in its measurement is eliminated.

The mean of twenty successive photographs gave

$$e/m = 1.75 \pm .03 \times 10^7.$$

I wish to express my appreciation to Dr. C. T. Knipp for his kindly suggestions and to Professor A. P. Carman, Director of the Laboratory, for the facilities offered.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
January 20, 1914.

THE NATURE AND THE VELOCITY OF MIGRATION OF THE POSITIVE IONS IN FLAMES.[1]

By A. H. Saxer.

THE velocity of migration in an electric field, of the positive ions introduced into a colorless bunsen flame by the volatilization of an alkali salt in it, has been determined from time to time by different investigators with widely differing results.

The one extreme is well represented by the work of Lenard[2] who obtained a value of 0.08 cm./sec. for the positive ions produced by lithium. On the other hand we have the value 350 cm./sec. obtained by Lusby[3] for the positive ions of all alkali salts at about 1950° abs. The preceding velocities as well as those which follow are expressed for unit potential gradient.

To account for the facts as observed by himself and others, that the positive ions of all alkali salts give the same velocity in the flame although differing widely in their atomic weights, Wilson[4] offers the theory that the positive ions exist as such only during a fraction of the time—he makes the assumption that they are alternately positive and neutral—and that this fraction increases with increase of atomic weight in such a manner as to give the same velocity for the positive ions of the various alkali metals.

The foregoing explanation offered by Wilson was probably first proposed by Lenard (*loc. cit.*) together with the idea that there exists in the colorless vapor two kinds of positive ions. The first kind were associated with the production of the visible color of the vapor and had a velocity of the order of magnitude determined by himself. The second kind produced no visible coloration and had a velocity of the order of magnitude observed by other investigators. These two kinds of ions were supposed to differ from each other in the fraction of the time during which they were positively charged.

Lusby (*loc. cit.*) offers the idea that the positive carriers are not metallic

---

[1] Accepted by the University of California in partial satisfaction of the requirements for the degree of Doctor of Philosophy.

[2] P. Lenard, Annalen der Physik, 4. 9, 1902.

[3] S. G. Lusby, Philos. Magazine, 22, 1911.

[4] H. A. Wilson, Philos. Magazine, June, 1911.

at all but are atoms of hydrogen and therefore their velocity would be independent of the alkali salt used in their production.

It is the purpose of the writer in the present article to try to show by reasonably direct evidence that the positive carriers of electricity added to a colorless flame when the vapor of an alkali salt is added to it, consist of metallic molecular aggregates about the positive ions as nuclei. It will be shown that they give the spectrum of the metal used in their production and that they have velocities not exceeding 1.8 cm./sec. and from this value downward to an order even lower than that observed by Lenard, the velocity depending only upon the size of the aggregates formed.

So far as the writer is aware, no measurements have been made of the velocity of the positive ions in the pure flame itself. Measurements here made indicate a maximum value of 2.5 cm./sec. under the conditions existing in these experiments.

To investigate this problem, two special burners were made of slate. The larger has an opening 1.25 mm. wide and 9 cm. long and the smaller has an opening 1 × 8 mm. Both burners received their supply of gas and of air from the same source. With the aid of an atomizer and a settling chamber the air supplied to either or both burners could be impregnated with the spray from distilled water or solutions of different concentrations of various alkali salts.

The object of the small burner was to introduce the salts of various alkali metals into the larger flame at any desired position and in such a manner as to insure their supply at a uniform rate and to insure their having an upward velocity equal to that of the gases in the large flame.

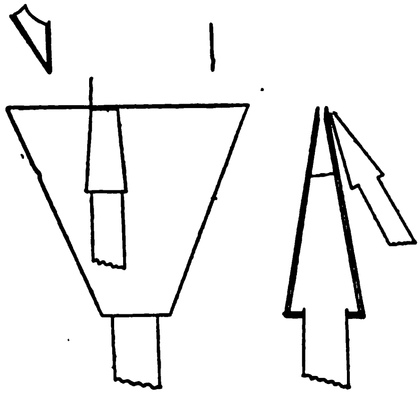


Fig. 1.
Side and Cross Section.

The arrangement of the burners and the electrodes can be seen by reference to Fig. 1.

The burners were placed side by side at the same height and the smaller was so arranged that it could be easily moved back and forth along the larger one and its position accurately read off on a scale attached to their common support. The electrodes used were of platinum and were introduced into the blue cone of the flame at a distance of 1 cm. above the burner and were usually kept at a distance apart of 7 cm.

The anode which was allowed to become incandescent was a thin rectangular piece of platinum 18 × 36 mm. The cathode however was a thin V-shaped piece of platinum 3 cm. long and 18 mm. high on the perpendicular side. It was rigidly fastened in such a position that the side facing the anode was perpendicular. The cathode could be kept continually at a temperature below a red heat by means of a cooler which was simply a large piece of brass made with a "neck" in the center small enough to fit snugly into the V of the cathode and not come in contact with the flame at any point. The large quantity of brass at either end of the neck conducted the heat away rapidly enough to produce the desired effect.

The whole arrangement was placed in a box which served as a support for the electrodes, etc., and to prevent air currents from disturbing the flame.

It was soon found that the colored vapor diffuses very rapidly away from the small burner when introduced in this way although not to such an extent as when it is introduced by means of a bead of salt vaporized in the flame. To prevent this diffusion from taking place in the direction of the cathode before the vapor had arrived at the proper height in the flame, a platinum guard 1 cm. in height and of sufficient length to extend beyond the flame on either side was attached to the small burner on the side next to the cathode.

With this arrangement the small burner would just pass beneath the electrodes and when the guard was properly cleaned it was found that the small burner, when not supplied with gas, could be moved to any position along the larger flame without disturbing either the potential gradient existing in the flame between the electrodes or the current passing between them as measured by a sensitive galvanometer.

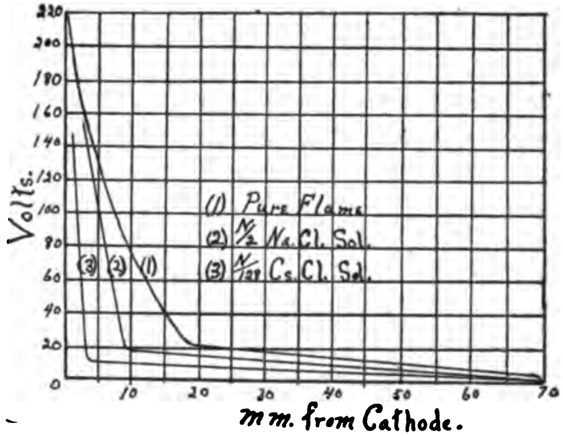


Fig. 2.

The potential gradient was measured by means of small platinum wires placed in the flame, and an electrometer of the Dolezalek type.

The large burner, supplied with gas and air only, was lighted and a potential difference of 220 volts established between the electrodes. The potential gradient was measured and was found to be similar in nature to that found by H. A. Wilson and others for the pure flame with an incandescent cathode (see Fig. 2). In this experiment as well as in all others which follow, unless the contrary is explicitly stated, the cathode is kept cold by means of the device previously described.

The small burner was now supplied with gas and air from the same source as that supplied to the large burner, that is with air free from spray. The additional ionization produced by the small flame caused no change in the current when near the anode, but as it was moved toward the cathode and a point was reached with the guard 18 mm. from the cathode the current began to increase and increased steadily from this point on until the maximum increase was attained with the flame in contact with the cathode.

This increase was assumed (this will be proved later) to be due to the fact that the cathode is now just able to abstract positive ions from the region of increased ionization due to the small flame. The ions in the two flames are in all probability similar and it is only fair to assume that, under the existing conditions, the positive ions that are being supplied to the cathode in the pure flame come from a maximum distance of 18 mm. It is certainly fair to assume that if the positive ions were coming from a greater distance than this there would be an increase of current as soon as the increased ionization due to the small flame reached this point.

It is to be particularly noted that this point —18 mm. from the cathode —is identical with the point in the flame at which the steep part of the potential gradient curve begins (see Fig. 2). This would lead us to suspect that in a uniform flame the steep portion of the potential gradient curve near the cathode marks that portion of the flame from which positive ions are being abstracted and that from beyond this point—along the uniform part—there are no positive ions which reach the cathode. No material change was noted in the potential gradient curves until there was considerable increase in the current.

If in addition to the foregoing we know the upward velocity of the flame gases we have sufficient data to calculate the specific velocity of the ions of the pure flame by means of the relation $u = dv/hx$. In this case u is the specific ionic velocity, d the horizontal distance from guard to cathode, v the upward velocity of the flame gases, h the height of the perpendicular side of the cathode, and x the potential gradient—assumed uniform—along the path.

The upward velocity of the flame gases was determined by the following

method devised by the writer. While this method can la
great accuracy it reccommends itself for its simplicity.
An electric fan was set up one on end of a long table
supply a horizontal current of air across the top of the
burner was then placed in the air current and by varying
the fan and the position of the burner on the table the
deflected to any desired angle from the vertical. The
of the flame was measured by means of a platinum
burner and bent to the desired angle. The upper
having a smaller velocity, was deflected more than the
measurements were therefore made by taking the
cone as this was the part of the flame in which
were made. As soon as the desired deflection
for some time, the gas was turned off and the
air current measured with an anemometer
If θ is the angle of deflection, r the
gases and h the horizontal velocity of the
Six different determinations, using the
were made and none of the calculated
by more than 5 per cent.
Using 200 cm./sec. as the value
positive ions of the pure flame.
region in which these measure
thermocouple and found to
couple were of platinum—
directly in the flame.
The 200-volt drop al
curve has been taken
This is in realit
than the one h
The air
from distill
made no
flame.

to the
nuclei,
ggregates
ter vapor,

pure flame.
the curves ob-
mum value and
(with the excep-
arer the cathode
$3N/1$ it proved no
increase at 18 mm.
ions used. It would
ot present in sufficient
the ions present.
of the apparatus used,
scend together a distance
uld diffuse away from the
That is to say, they were
which, no doubt, had con-
n" of all of the colorless ions

changes as illustrated in Fig. 3
the potential gradient and an
ty of the positive ions from the
soon lead into difficulties. The only
ent safety is that the velocity of the
ed is less than that of the ions of the

er suggested another method for arriving
m various alkali salts. If as suggested in
of the steep portion of the potential grade
dicates the point farthest from the cathode
re abstracted from the flame we should expect
gradient curve in a uniformly colored flame
ep portion should have the same significance.
erefore removed and the air supplied to the
ith the spray from various alkali salt solutions
otential gradient curves determined. The curves
lar in form to those for the pure flame at the same
. There is one essential difference however and that

is that the uniform part of the curve is not so steep and the point where the steep portion begins is shifted toward the cathode. This shift toward the cathode is greater the greater the atomic weight of the metal used. It is to be noted that this is the condition which exists when the electrodes are symmetrically located in the flame and when the flame is uniformly colored for the entire distance between the electrodes. If the colored vapor is introduced only near the anode or in the middle of the flame there is no change in the potential gradient curve. If the colored vapor is introduced near the cathode only then the effect is to cause an anode drop such as is reported in the potential gradient measurements made by Gold.[1]

It was found that the amount of this shift is dependent upon the concentration of the alkali salt vapor in the flame up to a certain concentration when a maximum shift is obtained beyond which it does not go even if the concentration is further increased. The nearest approach to the cathode of the beginning of the steep part of the potential gradient curve and the smallest concentration of the solution used in the sprayer which would produce this shift are given in the following table in the columns headed d and c respectively, the values of d being taken to the nearest millimeter only.

	c	d	d^2	u
Pure Flame	X	18	324	1.80
LiCl	$3N/1$	14	196	1.09
NaCl	$N/2$	8	64	0.35
KCl	$N/8$	6	36	0.20
RbCl	$N/64$	4	16	0.09
CsCl	$N/128$	3	9	0.05

If in the formula $u = dv/hx$, we substitute for x its value e/d where "e" is the fall of potential along the steep part of the potential gradient curve, we get $u = d^2v/he$ and u is seen to vary directly as d^2 provided e remains constant. While the fall along the uniform part of the curve is less for the colored flames, being only half that for the pure flame in the case of CsCl (see Fig. 2), we see that the value of e has been changed from 200 to 210 or only 5 per cent. This lies well within the accuracy of the other measurements and therefore the value of e has been considered constant and equal to 200 volts in calculating the values of u for the positive ions of the various alkali salts. These values of u are given in the last column of the preceding table and are based upon the previously calculated value u = 1.8 cm./sec. for the pure flame. It can be seen that these values are roughly in inverse proportion to the atomic weights of the alkali metals used in their production.

---

[1] E. Gold, Proc. Roy. Soc., 79A, 1907.

A careful study of the current curves (Fig. 3) given by the approach, toward the cathode, of a uniform streak of ionization from either a colored or a colorless flame 8 mm. wide will show that this added vapor contains positive ions of all possible velocities from a maximum of 1.8 cm./sec. as calculated down to velocities which ar very small indeed. If the ions in the streak moved with a uniform velocity, we should have—since the streak is uniform—a gradual increase in the current until the side of the streak farthest from the cathode passed the 1.8 cm. point. The current curve should then be a maximum, or at least should show a decided decrease in its slope, because the whole of the increased ionization is now within the region from which the cathode is abstracting positive ions. Quite the contrary is seen to be the case. The current curve becomes gradually steeper showing that as the streak is approaching the cathode it is furnishing it with a rapidly increasing number of positive ions. This is especially true in the case of the colored vapors. This is not due to any increase in the number of ions present in the streak because the effect is apparent long before it comes in contact with the cathode, and even then we have no increase due to the presence of the cathode because it is continually kept at a temperature below a red heat. This apparent increase in the number of ions present is due to the fact that ions having a smaller specific velocity are continually becoming available to the cathode on account of the smaller distance they are required to travel.

If all the ions moved with the same velocity we should have as a natural consequence that if the anode were brought to within 1.8 cm. of the cathode we would have all the ions abstracted from this region and the current would approach a saturation value. This was tried and found not to be the case even when 400 volts were applied to the electrodes only 1 cm. apart in the flame. It is to be noted that no saturation currents have yet been obtained with both electrodes in the blue cone of the flame. In all cases of so-called saturation currents reported, either one or both of the electrodes was situated in a part of the flame considerably removed from the seat of ionization. There was also no evidence of ionization by impact since the current always increased more slowly than the applied E.M.F. This apparently inexhaustible supply of ions which can be drawn upon more and more as the field strength is increased, is readily accounted for if we assume that ions having continually smaller specific velocities are made available by the increasing electric field.

It has been shown by Tufts[1] that the seat of ionization in the flame is

---

[1] F. L. Tufts, Phys. Rev., Vol. 22, 1906, p. 201.

in the inner blue cone and that as soon as they are formed the ions begin to disappear at an enormous rate due to recombination. He shows that the specific conductivity of the gases 1 cm. above the blue cone is only 1/1,000 as great as the specific conductivity of these same gases in the blue cone. After ascending a distance of only 7 cm., the specific conductivity is only 1/10,000 of what it originally was. This is for a pure flame and Lewis (*loc. cit.*) has shown that the rate of disappearance of the ions in the gases from the pure flame is still very great at a point 20 cm. above the flame where the flame gases lose one-half of their ions in ascending a distance of 5 cm.

Keeping in mind the very small velocities found by Lewis in the gases above the flame, it would appear that it is the faster moving ions that are the first to disappear by recombination, thus leaving the average velocity of the remaining ions very much reduced. It seems perfectly natural to believe that an ion which is the nucleus of a large mass having a small velocity would be less liable to have an opportunity to recombine than would an ion which is the nucleus of a smaller mass having a greater velocity.

The distribution of the velocity in the curves of Fig. 3 shows that the colored streaks possess a relatively larger number of ions having a small velocity than does the colorless one. We should therefore expect to find a much smaller rate of recombination among these larger aggregates. A reference to the work of Lewis previously cited shows this to be the case. It is there shown that the rate of recombination for the colorless ions is three times as great as for the colored ones, at a distance of 20 cm. above the flame.

It has now been shown that the positive ions in the pure flame have their velocity reduced in the presence of colored vapors of sufficient concentration and that larger ionic aggregates are formed in flames containing alkali salt vapors than in pure flames. This is in harmony with the results of modern experiment, which seem to show quite conclusively that positive carriers of molecular size do not become appreciably loaded with air molecules, water vapor, or molecules of carbon dioxide within the range of ordinary temperature and pressure. That is to say, the positive ion, as it is constituted at ordinary temperature and pressure, does not show any abnormal velocity change in the presence of water vapor, etc.—at least not until very low pressures are reached.[1] For this reason the tendency for the positive ions in the pure flame to form aggregates will be much less than in the same flame after the introduction of various salt vapors.

---

[1] G. W. Todd, Philos. Magazine, 22, 1911.

To support this idea it was thought advisable to measure the velocity of the positive flame ion in some medium in which there is less tendency to form aggregates.

The following, which is a modification of the alternating current method first proposed by Rutherford, was used since it has the advantage of taking the ions directly from the flame and measuring their velocity in hot air after an interval of only 1/120 sec. It also eliminates the necessity of measuring the upward velocity of the flame gases.

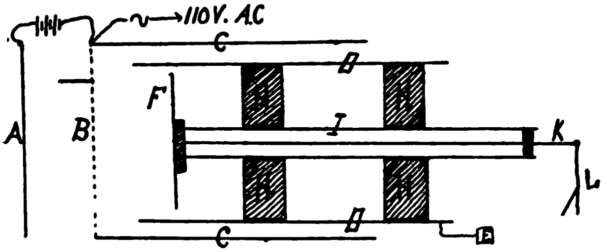


Fig. 4.

Fig. 4 illustrates the arrangement of the apparatus. *C* is a brass tube 7 cm. long and 5 cm. in diameter. One end of this tube is completely closed by a platinum gauze *B*. *D* is another brass tube 4 cm. in diameter, which is kept earthed and is insulated from *C* and *B* by means of an air gap between them. *I* is another tube insulated from *D* at the points *H*, through which it may be moved freely. *F* is a circular aluminum disk 3.5 cm. in diameter insulated from *I* and connected by means of a wire *K* through *I* to a Wilson inclined electroscope at *L*. *A* is a platinum electrode 5 cm. square which can be kept at a constant potential above or below *B* by means of an insulated battery. *B* is connected to an alternating current of 110 volts at 60 cycles. When measurements are being made *B* is placed at the desired position in the flame, and ions are forced into the chamber beyond *B* by properly adjusting the position and the potential of *A*. The specific velocity (u) of the ions is then calculated by means of the formula,

$$u = \frac{\pi d^2 n}{\sqrt{2e}},$$

which is obtained as follows:

u = specific ionic velocity.
d = distance from B to F.
E_0 = maximum potential of B.
E = instantaneous potential of $B = E_0 \sin \frac{2\pi}{T} t$.
t = time from any given instant.

T = period of alternation.
e = voltmeter potential = $E_0/\sqrt{2}$.
v = velocity of ion at time t.

$$v = uE/d = \frac{uE_0 \sin \frac{2\pi}{T} t}{d}$$

When F is brought so near to B that the ions travel the distance d in a time $T/2$ the electroscope will show a deflection. For this to occur we must have

$$d = \frac{uE_0}{d} \int_0^{\frac{T}{2}} \sin \frac{2\pi}{T} t \, dt = \frac{uE_0 T}{\pi d}$$

$$u = \frac{\pi d^2}{E_0 T} \quad \text{but} \quad E_0 = \sqrt{2}\, e \quad \text{and} \quad \frac{1}{T} = n$$

$$\therefore u = \frac{\pi d^2 n}{\sqrt{2} e}.$$

Before being used both B and C were heated in the blowpipe flame to remove as far as possible all surface impurities. Measurements were first made with the secondary field off and the alternating current on. Ions were detected in the chamber due probably to the glowing platinum gauze, but their velocities were considerably less than those due to the pure flame itself. There was therefore no difficulty in keeping the effects separate. When A was made positive with respect to B, thus causing the positive flame ions to drift across the gauze into the chamber beyond B, the electroscope showed a deflection indicating a positive charge on F when it arrived at a point 1.44 cm. from the gauze. When A was made negative with respect to B, the plate F picked up a negative charge when at a distance of 1.9 cm. from the gauze. From these data we get u = 2.535 cm./sec. for the positive ions and u = 4.39 cm./sec. for the negative ions. The measuring chamber was found to be at an average temperature of 475° C. as measured with the thermocouple. From this it would appear that the velocity of the positive ion taken from the pure flame is greater in hot air than when it is measured in the flame itself where the temperature is much higher.

In these two methods of measurement the life of the ion was about the same in each case but the ion, mesaured in the flame itself, existed continually in a medium where the tendency to form aggregates was much greater than in the medium in which the other measurements were made. The alternating current method gives us a true measure of the velocity of the positive ion for the physical state in which it enters the alt
field, since many recent experiments show that under the c

existing in this measurement the positive ion does not show any abnormal velocity changes which would indicate a change in its existing mass. The probability is also very great that here at least the positive ion does not alternate with the positive and the neutral state and remain positively charged during only a fraction of the time.

Measurements were also made when the flame was colored with the vapors of various alkali salts. The rate at which the electroscope received its charge was now much less in the case of the positive ions although approximately the same for the negative ions. The point at which the charge began to be picked up was the same as for the pure flame. The method here used requires very few ions to produce a noticeable deflection in the electroscope—far less than could be detected with the galvanometer—and it would appear that in a flame densely colored with the vapor of an alkali salt there still exist some of the ions of the pure flame which have not had their velocities decreased or rather which enter the alternating current chamber before any of the colored molecules have aggregated with them.

The writer has not attempted to study the negative flame ion in the present series of experiments. In regard to the value 4.4 cm./sec. obtained for the velocity in air of the negative ion of the pure flame, the writer can only say that it seems very small. When we consider, however, that there is considerable experimental evidence to show that negative ions do form aggregates in air at ordinary temperature and pressure and especially when traces of water vapor are present, we can readily conceive of these aggregates reducing the velocity to the observed value. It is also to be noted that according to Lewis (*loc. cit.*) the velocity of the negative ion from the pure flame is only .33 cm./sec. when measured in the flame gases above the flame, where the temperature is 150° C. and the tendency to form aggregates is probably much greater. It seems quite evident however that within the flame itself the negative ion has a velocity much greater than 4.4 cm./sec.

In the foregoing it has been assumed that when the current passing between two electrodes, placed opposite each other in a pure flame, is caused to increase by volatilizing an alkali salt near [illegible] cathode, the increase in current is due to the abstraction of positi[illegible]ic ions from the region of increased ionizatio[illegible]ibed below shows this directly.

When positive i[illegible] th[illegible]om a source considerably re[illegible]ence[illegible]vening space can not be d[illegible]ecau[illegible]latively small number a[illegible]they[illegible]d. When the ions arrive at a hot cathode they have their charge neutralized and are immediately volatilized by the high temperature and there is no accumulation of metal on the hot electrode. When however the cathode is kept cold as in the foregoing experiments the atoms or molecules of the metal that arrive at the electrode are not all volatilized and there is an accumulation of metal on the cathode. If the increased current is maintained for a sufficient length of time, the accumulated metal will readily give its characteristic spectrum when the electrode is allowed to become incandescent.

The small flame densely colored with LiCl was placed near enough to the cathode to produce an increased current. This arrangement was allowed to continue for a period of forty five minutes and there was no evidence of the lithium spectrum about the cathode. When the "cooler" was removed, however, and the electrode allowed to become incandescent the spectrum of lithium was easily visible. Control experiments, with the lithium colored flame in the same position and no current flowing and also with the current flowing as before and the flame placed at such a position as to produce no increase in the current, gave negative results. NaCl and KCl were also used in this manner and gave similar results. In the case of sodium the spectrum is always present even in the so called pure flame, but the change in the intensity of the lines was easily shown by means of a Glan-spectrophotometer which was used for this work.

It is worthy of remark that in the case of the pure flame, in which no salt vapors were being introduced, the sodium lines were decidedly more intense after thirty minutes run with the field on than after the same length of time with the field off. This shows that even in the so called pure flame, a part of the current at least is due to the abstraction of positive sodium ions from it.

BRIEF SUMMARY OF CONCLUSIONS.

The maximum velocity of the positive ions of the colorless bunsen flame is 1.8 cm./sec. when measured in the flame itself where the temperature is 1250° C., and 2.5 cm./sec. when measured in hot air at a temperature of 475° C. These ions have their velocities reduced in the presence of alkali salt vapors.

The velocity of the positive ions of the various alkali salt vapors is less than the velocity of the positive ions of the pure flame. These ions are the nuclei of large molecular aggregates and they carry with them the spectrum of the metal used in their production.

RADIO-ACTIVITY OF SPRINGS NEAR WILLIAMSTOWN, MASSACHUSETTS.

By J. E. Shrader.

THERE is a warm spring near Williamstown called Sand Spring whose waters issue from its sandy bottom at the rate of forty gallons a minute into a large cement basin. From all portions of the bottom bubbles of gas arise. This gas has been analyzed by Professor L. Mears, of Williams College, and has been found to consist of air containing an excess of nitrogen, and a small per cent. of carbon dioxide. Since the spring is thermal, its waters must come from a considerable depth.

It is well known that all springs are more or less radioactive, due to the fact that their waters carry with them radium emanation which is released from the rocks and soil about which they circulate. To determine the amount of radium whose emanation would produce the activity observed in the gas and water of Sand Spring was the purpose of this experiment. Subsequently investigations were extended to other springs in the vicinity.

Apparatus and Method of Procedure.

The diagram (Fig. 1) represents the apparatus used for determining the radio-activity of the water. It consists, essentially, of an emanation electroscope, a gas pipette, and a glass flask for containing the water to be investigated.

The gas chamber of the electroscope was made of a brass cylinder of about eight centimeters inside diameter and fourteen centimeters long. Brass ends were turned and soldered into the ends of the cylinder. Two gas-tight stopcocks were also soldered into the cylinder, one communicating with the gas pipette and the other with a filter pump for exhausting the air. The gold-leaf was mounted on a central electrode with inner insulation of amber, a guard ring, and an outer insulation of hard rubber. The gold-leaf was protected by a second brass cylinder of smaller dimensions. The guard ring was connected by means of a fine wire, *b* (Fig. 1), and a small rod, *d*, to the negative pole of a storage battery, the positive pole being earthed. The battery was of the test tube type of 480 volts, about 240 of which were used. The wire, *b*, was bent so that the spring in the wire always kept it pressed against the rod, *d*. The rod, *d*, also carried a wire, *c*, bent at right angles and carried along parallel with it. By turning *d*, contact could be made with the gold-leaf support so that the electroscope could be easily charged. The wire could then be turned to a definite position when measurements were being made. This arrangement made it easy to keep the central electrode charged for any length of time desired and so concentrate the excited activity of the gas upon it. The various parts of the insulation and guard ring were cemented together and secured in the cylinder with Khotinsky cement. The electroscope was fastened securely to a heavy iron base, *N*.

The gas pipette, *D*, was made of a glass vessel fitted with a three-way stopcock, *e*. Connected to it was a mercury reservoir, *E*, for displacing the gas. The gas was dried by passing it through the U-tube, *C*, filled with calcium chloride. The glass flask, *H*, of about two liters capacity, was connected to the gas pipette by a bent tube and rubber stopper. The glass tube was surrounded by a water jacket, *F*, so that the steam could be condensed when the water in *H* was being boiled.

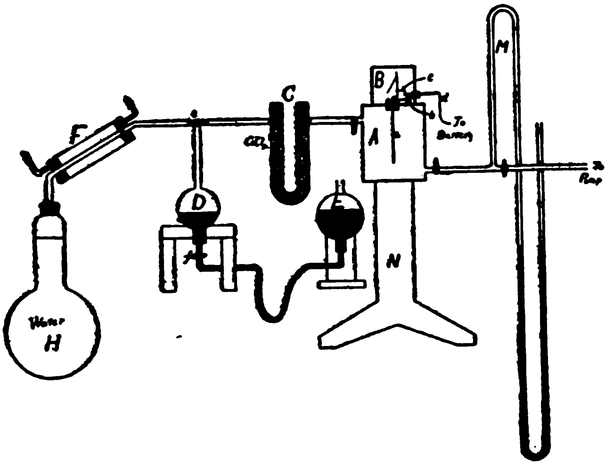


Fig. 1.

When a determination of the activity of the water was to be made, the water was taken from the spring as near the source as possible and carried to the laboratory where it was introduced into the flask, *H*, filling it to a mark previously determined such that the water on being boiled expanded and completely filled the flask. The gas pipette was then filled with mercury and the cock, *f*, closed and the three-way cock, *e*, turned so that connection was made between the flask and the pipette through the bent glass tube which was surrounded by the water jacket. After opening the cock, *f*, a Bunsen flame was applied to the flask and the water heated to boiling. The boiling was continued for fifteen or twenty minutes, the steam being condensed by water flowing through the water jacket. During this time, the air left in the flask and the gas driven off from the water have been carried over into the pipette, displacing the mercury. The mercury reservoir was always placed a little lower than the pipette so that boiling took place under diminished pressure. After sufficient boiling, the mercury reservoir was lowered considerably and the water boiled vigorously so that practically all the gas was drawn into the pipette. The cock, *f*, was now closed and, after two hours from the time the water was taken from the spring (which happened to be a convenient length of time), the collected gases were introduced into the electroscope through the drying tube. This was done by partially exhausting the electroscope chamber with a filter pump to a pressure of three or four centimeters of mercury, as was shown by a manometer, *M*. The stopcock, *e*, was now turned so that the gas could be drawn through the drying tube into the electroscope. The pressure in the gas chamber was equalized by removing the bent tube and allowing the outside air to carry all the gas remaining in the connecting tubes into the electroscope. The capacity of the gas chamber was between 700 c.c. and 800 c.c. and the mixed gases had a volume of about 125 c.c.

Before introducing the gases into the electroscope the central electrode was connected to the negative pole of the battery and kept at a constant potential of −240 volts. Thus the excited activity was concentrated on the electrode, and, after three hours it had come into equilibrium with the radium emanation. After this interval, the rate of deflection of the gold-leaf was taken. The time was taken with a stop-watch and the deflection observed with a telescope fitted with a micrometer eyepiece. The rate of deflection was corrected for the natural ionization of the air. The same part of the scale was always used in taking an observation and the potential of the battery was adjusted so that the gold-leaf was deflected to the point at which the readings began. It was observed that, if the central electrode was kept charged for a considerable time to allow the charge to be evenly distributed over the insulation, the natural ionization was practically constant. Without a guard ring and without the precautions taken, the natural ionization might vary as much as two or three times any observed value.

THE RADIUM STANDARD.

In order to interpret the rate of deflection of the gold-leaf in terms of the activity of a known amount of radium, it is necessary that the electroscope should be calibrated. For this purpose Professor B. B. Boltwood, of Yale University, kindly sent me a small quantity of Joachimsthal uraninite (pitchblende) which he had analyzed. The specimen contained approximately 67 per cent. uranium. Since one gram of uranium by comparison with the New International Radium Standard contains 3.2×10^{-7} grams of radium, one gram of the sample would contain 2.14×10^{-7} grams radium. Since the powdered sample loses 6 per cent. of its emanation, the amount of radium emanation secured on dissolving one gram of the sample would be equal to the amount given off by 2.0×10^{-7} grams radium. From the specimen of uraninite .0099 grams were weighed out and placed in a small flask with a side-tube and water jacket Fig. 2 (*b*). A funnel provided with a stopcock and filled with dilute nitric acid (one part acid to six parts water) was fitted with a rubber stopper into the mouth of the flask. This arrangement was now fitted to the pipette in place of the flask and its water jacket in Fig. 1. The acid was allowed to flow down into the flask to dissolve the sample. Then the flask was heated and the contents boiled and all the gases driven over into the pipette. After two hours as in the case of the water, the gases were introduced into the electroscope and the rate of deflection observed. From this observation, corrected for the natural ionization of the air, the deflection of one scale division could be estimated as that caused by the activity due to the emanation from a certain number of grams of radium. Hence, by comparison, the activity of a liter of the water could be expressed as that due to a certain number of grams of radium.

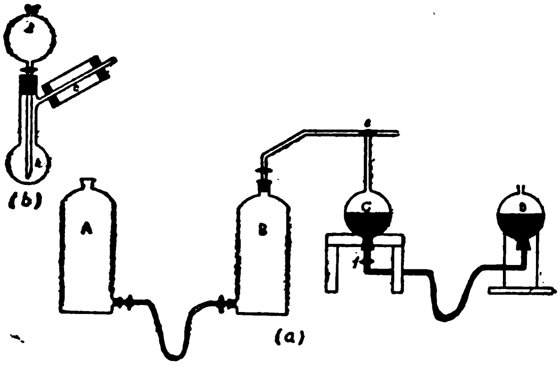


Fig. 2.

ACTIVITY OF THE GASES.

The gases were caught with a funnel which was connected to a bottle filled with water and having an outlet tube extending into the water.

As the gases accumulated, the water was displaced. When the bottle was filled it was made air-tight and taken to the laboratory, and after a period of two hours from the time of its collection, it was introduced into the electroscope. This was done by displacing the gas from *B*, Fig. 2 (*a*), with water from the bottle, *A*, into the pipette, *C*, where its volume under known conditions of temperature and pressure were ascertained. From there it was drawn into the electroscope. After standing three hours the rate of deflection was observed. Hence the activity of the gas could be computed in terms of the standard. The amount of gas used was 145 c.c. This amount of the Sand Spring gas was sufficient to give a deflection of 1.832 divisions per minute. The deflection due to the natural ionization was .007 divisions per minute.

Other Springs Tested.

The second spring tested is located about 200 yards below Sand Spring. It is called Wampanoag Spring. It is of much the same nature as Sand Spring. Its temperature is slightly higher and its flow much less. The activity, as seen from the table below, of both the water and gas is much greater. This might be expected from the fact that the flow is less and the amount of gas given off much smaller.

The third spring, which I will call the "Rich" Spring from the name of its owner, is about one mile distant from the other springs and on the other side of the Hoosac River. It issues from the base of Northwest Hill and is not enclosed. The flow, I should judge, is slightly greater than that of Sand Spring, though I had no ready means of making the determination. The water and gas of this spring are comparatively weak.

The other two springs are Cold Spring and Sherman Spring both of which are used as a part of the water supply for Williamstown. The water from the Sherman Spring was taken as it issued from the earth, but the water from Cold Spring was taken from the reservoir as its source was not easily accessible. For this reason, the latter had lost the greater part of its activity.

The tap-water was taken from the tap of the laboratory after letting the water run for a couple of hours.

Test for Dissolved Salts of Radium.

Eleven liters of the water from Sand Spring were evaporated to two liters and sealed in the flask, *H*, Fig. 1. After standing sixteen days, during which time more emanation would be produced if the salts of radium were present, the water was again boiled and tested for its activity. Not a trace could be detected.

The water and gas were not tested for thorium.

TABLE OF RESULTS.

Name of Spring.	Temperature in Degrees C.		Activity per Liter of Gas, Standard Cond., in Grams Radium.	Activity of Water in Grams Radium.
	Oct.	Jan.		
Sand Spring	20.8	19.8	$653. \times 10^{-11}$	12.16×10^{-11}
Wampanoag	21.9	21.5	$729. \times 10^{-11}$	21.6×10^{-11}
Rich Spring	18.2	18.2	75.9×10^{-11}	$.897 \times 10^{-11}$
Sherman Spring		5.		4.11×10^{-11}
Cold Spring				1.31×10^{-11}
Tap-water				$.25 \times 10^{-11}$

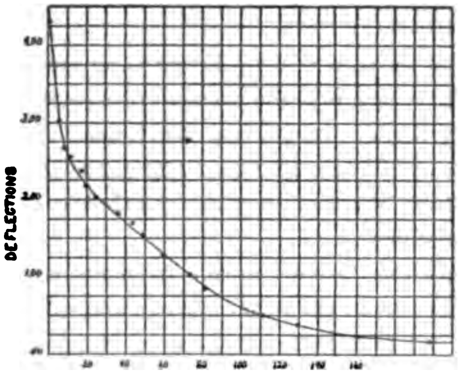


Fig. 3.

THE DECAY OF THE RADIUM EMANATION AND ITS EXCITED ACTIVITY.

Fig. 3 represents the decay of the active deposits radium *A*, *B*, and *C*, concentrated on the central electrode of the electroscope from the emanation in the Sand Spring gas. The electroscope was kept charged and the gas introduced and allowed to stand for three hours. The gas was then drawn off and the measurements of the activity taken at intervals.

Fig. 4 represents the increase of activity due to the active deposits

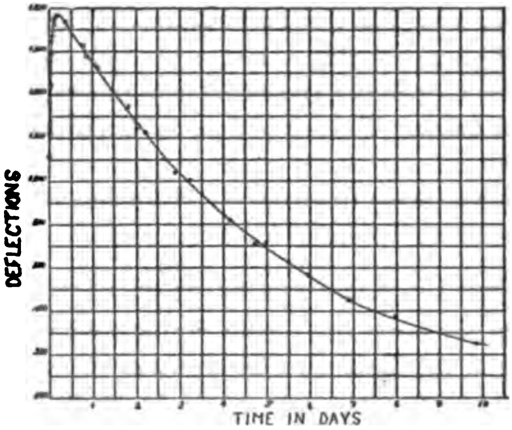


Fig. 4.

after the gas is introduced, and the decay of the radium emanation in equilibrium with its products.

Fig. 5 represents the decay of radium emanation in equilibrium with its products, plotting logarithms of deflections against time in days. The curve is a straight line showing that the gas decays according to an exponential law with a half value period practically the same as that for radium emanation, which is 3.85 days. It was difficult to make the electroscope airtight so that correction was made for diffusion by comparison, under the same conditions, of the decay curve of the radium emanation from the sample of uraninite used for calibration.

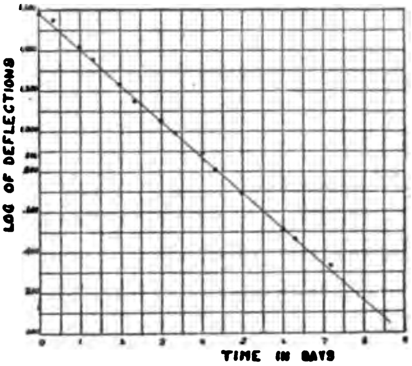


Fig. 5.

In conclusion, I wish to thank Professor B. B. Boltwood for his kindness in furnishing me with the uraninite for the calibration of my electroscope, and also Assistant Professor Brainerd Mears for the loan of apparatus from the Chemical Laboratory and for several valuable suggestions.

Thompson Physical Laboratory,
Williams College,
January 30, 1914.

RADIOTRANSMISSION AND WEATHER.

By A. H. Taylor.

In a previous paper on this subject[1] the writer submitted evidence which seemed to show that unusually good radio transmission across long overland distances at night is preceded the day before by generally cloudy conditions prevailing in the region across which the nocturnal good transmission takes place.

The evidence presented in that paper has been greatly strengthened by subsequent observations. In particular it may be mentioned, that out of some sixty cases of good transmission studied since September 24, 1913, forty-four have followed a generally cloudy condition over the area in case, while of the other sixteen, a majority have occurred during the shortest days of the year, when the hours of sunlight in the latitude of Grand Forks, N. D., are relatively few.

Before discussing the bearing of this evidence on the idea of the reflection and refraction[2] of electric waves by ionized layers of the earth's atmosphere, it will perhaps be well to examine some of the data collected at this station since September 24, 1913, for evidence of a somewhat different character.

In commenting upon the previous paper, the editor of the Electrical World suggested that the effects noted might have been indirectly due to general cloudiness, inasmuch as this would usually bring about some rainfall and would therefore probably reduce the ground absorption which is thought to be much larger in overland than oversea transmission. Fortunately the weather during the fall of 1913, especially during the months of October and November, was of such a nature in this part of the continent as to make it possible to settle this important question. The height of the aerial at this station is but 85 feet, so that the nearest of the Great Lakes stations do not usually make themselves heard until after dark. Nevertheless, during a period of over a month in which no moisture whatever fell in northern Minnesota the stations at Port Arthur, VBA, and Duluth, WDM, were heard as early as 4:30 P. M. on several occasions. Subsequent comparison of weather reports

---

[1] Electrical World, August 30, 1913.

[2] Dr. W. Eccles, in The Electricians, September 27, 1912, and September 19, 1913.

showed that in each instance the intervening region had been very cloudy. In spite of the fact that during this period no rain fell, or even snow until about December 1, there was a great deal of cloudy weather over northern Minnesota, and hence especially close attention was given to the transmissivity from VBA and WDM. In 80 per cent. of the cases of very good transmission from these stations to this one (9YN) the preceding day had been very cloudy in this region. The effect of moisture on ground absorption is here eliminated. I am therefore forced to conclude that the effect of alterations of earth absorption are entirely overshadowed by the larger favorable influence of preceding cloudiness. Incidentally these experiments showed that the normal day absorption on clear days in this region is very large. This is supported by the fact that our own signals sent on a 500 m. wave with 7 amperes aerial current were but fairly received just before dusk in Minneapolis at the North Central High School with a 100 ft. aerial, whereas less than an hour later they were repeatedly picked up by Mr. Keith Russell on a 70 ft. aerial in Toronto. The first distance is 300 and the last 1,000 miles.

It has occurred to the writer to analyze data at hand for the possible influence of barometric pressure on transmission. The weather maps corresponding to the days preceeding the evenings of observation were examined and 24 were found which indicated that rather low barometer readings had prevailed in or near the areas across which transmission had been studied. Of these only two were found to correspond with records of bad transmission, while the others all corresponded to records of good transmission. Inasmuch as the weather maps do not arrive here until the day after the transmission records are made, it is not possible for the observer to be prejudiced. Conclusions as to good or bad transmission were based on observations on Sayville, N. Y., call WSL; Arlington, Va., call NAA; Key West NAR (1,800 m.) Wellfleet, Mass., WCC; San Diego, NPL, and the Lakes stations at Milwaukee, WME; Port Arthur, VBA; Duluth, WDM; Sault Ste. Marie, VBB. For reasons not at once apparent many stations on the Gulf of Mexico or in the Mississippi valley are received here with extraordinary clearness. A good many observations were made on signals from battleships in the Gulf and upon Galveston, WGV; New Orleans, WHK; Ft. Sam Houston, WUJ; Michigan University, 8XA; Ft. Leavenworth, WUV, and others. From the west coast, observations were also made upon Mare Island, NPH; Point Arguello, NPK, and occasionally upon Victoria, VAK. A great many other stations might be mentioned as being heard here when transmission was unusually good. A good many vessels were reported at this station but it was not often possible to locate them very definitely.

Finally, shunted telephone readings have been made on our own signals at Memphis, Tenn., by Br. John Berchmanns, of Christian Brothers College; at St. Louis by Mr. A. S. Blattermann at Washington University; at Boulder Colorado, by Mr. Strock; and by Mr. H. S. Sheppard at Michigan University in connection with certain tests to be reported on jointly in a future paper. Several amateurs at points from 600 to 1,100 miles distant have been kind enough to make written reports on the relative strength of our signals, among these Mr. Stockman at Denver, Colorado, and Mr. Miller, at Bushnell, Ill.

In reference to the influence of barometric pressure, it must be noted that areas of low barometer are always more or less cloudy. In order to settle this point it is necessary to consider the cases where the barometer readings were generally rather high over the areas studied. Of 18 cases which could be put in this class, 11 showed good transmission and 7 poor. But of these 11 cases of good transmission, 4 were reported from the valley of the Mississippi, which the author has reason to believe permits phenomenally good transmission, and 6 were over generally cloudy areas. Of the 7 cases of bad transmission associated with rather high barometer, 5 were over very cloudy areas. The writer does not consider this evidence conclusive, but it might mean that high barometer is unfavorable to transmission. Clear-cut cases for long distances are not easy to find for either the high or the low barometer classes.

On the whole it seems as if the presence of clouds is the controlling factor, modified somewhat perhaps by barometric conditions. Bearing this in mind, it seemed worth while to attempt to find out whether cloudiness would be most beneficial at the sender or at the receiver. Accordingly the evenings of observation were divided as follows:

1. Senders and receiver both in cloudy area.	Good transmission 19; bad 4.
2. Senders and receiver both in clear area.	Good transmission 7; bad 6.
3. Senders, cloudy; receiver, clear.	Good transmission 14; bad 3.
4. Senders, clear; receiver, cloudy.	Good transmission 8; bad 7.

From this analysis it seems that few cases of good transmission are reported when both stations have been in the clear area preceding the night of observation and about the same indifferent result is seen when the sender only has been in the clear. On the other hand, when the sender but not the receiver has been in the cloudy, the ratio of good to bad transmissions is about the same as when the cloudiness has been quite general. This ratio is 5:1 in favor of good transmission. Cloudiness in that portion of the area of transmission near the sender is evidently of the most importance in favoring transmission. This should have an important influence on the formation of any theory which will take account of the variations of nocturnal transmission as a function of the weather of the preceding day.

It seems to the writer that the most serious attempt to correlate fact and theory in long distance transmission problems has been made by Dr. Eccles in the two papers previously mentioned. As he points out, the hypothesis of an upper layer of ionized air was suggested by Heaviside in 1900, and the idea of the production of such ionization by bombardment of cosmic dust has been advanced by Dr. W. J. Humphreys[1] to account for the fact that according to the researches of Newcomb, Yntema, Campbell and Abbott, there is received from the sky a total amount of light which exceeds the total light from the stars. Dr. Eccles seems to prefer however the hypothesis of Professor Schuster,[2] put forward to justify his theory of the diurnal variations of terrestrial magnetism. This would mean a gradual increase in ionization and hence in conductivity with the height, but on the whole a degree of ionization which would create a very great absorption. He points out that a very much smaller degree of ionization would suffice to explain some of the phenomena of long-distance radio transmission.

If the equations of the electromagnetic wave in free space be modified by the addition of a term representing the ionic convection current in the path of the wave, there results an expression for the wave velocity which exceeds that of light in free space. A better way of stating this is perhaps to say that the refractive index of ionized air would be less than unity, just as in the case of thin films of some metals whose refractive indices may be much less than unity for light rays. The effect of a refractive index diminishing with increasing altitude would be to tend to bend the waves back to earth, thus following more or less its curvature.

Dr. Eccles offers the very plausible suggestion in regard to the well-known facts of nocturnal long transmission, that the middle portion of the atmosphere is at night mainly unionized on account of the absence of sunlight, but that partial reflections occur at the very high permanently ionized layer. This reflection would not take place during the day, as there would be no very sharp transition from ionized to unionized atmosphere. His calculations on the amount of bending of long waves during the day time show that a distribution of ionization is possible such that these waves, at certain critical altitudes (ranging from 40 kilometers for a 2,000 m. wave to 100 kilometers for a 200 m. wave) would suffer a refraction so abrupt as to be equivalent to a reflection,

---

[1] W. J. Humphreys, Astrophysical Journal, May, 1912.

[2] Phil. Trans., A, 1907.

thus accounting for the possibility of long distance transmission being better in the daytime with long waves than at night. This has been occasionally reported by Marconi of trans-Atlantic transmission. The writer has taken many observations on the 1,800 m. wave of Key West, on Arlington at 2,500 m. and on Sayville at 2,800 m., but on three occasions only, in the month of December, were any of them heard in the daytime at this station. The exception was Arlington, distant about 1,400 miles. The signals were barely audible, and not to be compared in intensity with the 9:00 P. M. (central time) time signals. The signals of these stations have always been received here stronger as it became later in the evening. The aerial at this station is however not high enough to do long distance receiving in daylight.

The writer does not consider that the evidence which has been presented in this and the preceding paper is in conflict with the theory of Dr. Eccles. On the other hand it is in no wise to be explained by that theory, dealing as it does with refractions and reflections at relatively high altitudes. The author is inclined to accept the idea of a permanently ionized upper layer at great altitude; he is even willing to entertain the notion that the ionized middle region in daylight plays an important rôle in determining the generally large day absorption, but he considers that the evidence here submitted can only be accounted for by assuming a reflection at the cloud level brought about by a more or less abrupt alteration in the velocity of the wave above and below this level. It is not the clouds themselves that reflect, as good transmission between here and the Lake district has often been observed on very clear nights provided that the day has been cloudy. It is rather caused by an electrical discontinuity which persists after the clouds which caused it have perhaps long disappeared. It is difficult to believe that the probable degree of ionization by sunlight at the cloud level could be sufficient to be of influence, but so far no other more plausible suggestion has occurred to the writer. If this ionization is appreciable, then the clouds would in daylight produce a discontinuity layer which might persist for some hours after sunset. By the time this discontinuity fades away the ionization in the whole intermediate region of the atmosphere will be reduced so that waves may reach the permanently ionized upper layer and be reflected by it with little absorption. Thus good transmission will continue until the morning twilight. It naturally follows that general cloudiness would be beneficial in daylight. As far as observations taken at this station go, they fully agree with this. Unfortunately the day range of this station for reception of signals is not sufficiently great to settle this point definitely. The fact that cloudiness at the sender (where the radiant energy would without reflection be highly divergent) is more beneficial that at the receiver, seems to lend support to this theory. The theory leaves us without any adequate explanation of the day absorption which Austin has shown to be very regular in oversea transmission at least. We must therefore either assume that the day time ionization under the cloud level averages much larger than is generally assumed, or that the radiation is divided as follows:

1. A portion reflected from the cloud level, and passing from sender to receiver as between two approximately parallel surfaces, and hence not following the inverse square law of divergence, and not heavily absorbed, since it travels in a feebly ionized medium.

2. A portion entering the middle ionized region and refracted back towards the earth according to the theory of Dr. Eccles. This portion would be absorbed during the day, but very feebly absorbed at night.

3. A portion passing through the middle region and partially reflected at the upper permanently ionized layer. This would be heavily absorbed during the day, and feebly absorbed at night.

4. A portion which passes out into space and is lost.

It is likely that the second portion is of the most importance in the daytime, while the vagaries of long distance nocturnal transmission are due to combinations at the receiver of the first and third portions. Those rapid variations in the strength of signals (swinging), and the slower fluctuations (fading) so familiar to operators in long range work may well be due to interference effects between these two portions.

The rapidity with which these effects often occur strongly suggests the idea of a violent commotion in the lower levels in the wave path.

Accordingly, daylight transmission over a clear area would be carried on mainly by the second portion, the third portion being heavily absorbed. Daylight transmission over a cloudy area (especially where cloudy at sender and its vicinity) would be reinforced by the first portion.

Nocturnal transmission following clear days would be carried on by the second portion reinforced by the third, both portions being feebly absorbed. Nocturnal transmission following cloudiness would in general be carried on by all three portions, but the evidence here presented suggests that the first portion, added to the third, both feebly absorbed, is of great importance.

Since completing this paper the writer has read an interesting account by Nipher, in the Proceedings of the Saint Louis Academy of Sciences, 1913, of local magnetic storms whose origin he believes to have traced to the influence of clouds. He finds also a period of magnetic disturbances coinciding with the well known twilight fluctuations in radiotransmission. Prof. Nipher suggests a variation in the ionization of the *lower* levels caused by variations in the sunlight as the nature of this influence. There seems to be an intimate connection between these phenomena and the variations in radiotransmission.

Radio Station 9*YN*, University, N. D.,
February 21, 1914.

PHASE CHANGE BY REFLECTION—PRIMARILY IN THE ULTRA-VIOLET.

By Oliver H. Gish.

THE first quantitative investigation of absolute phase change was made by Quincke[1] in 1872. This was followed by that of Wernicke,[2] Wiener,[3] Glan,[4] Hennig,[5] Drude,[6] Koenigsberger and Bender.[7] All these investigations were confined to the visible spectrum except that of Koenigsberger and Bender, who, in addition, measured for a few substances the phase change in the infra-red. So far no measurements of this phenomenon have been made in the ultra-violet.

Quincke used a total reflecting prism, a portion of whose reflecting surface was silvered. Light from a *point source, when reflected by this prism* showed interference bands due to the difference in phase of the waves reflected from the silver and those reflected from the glass. He observed variations in these bands with the angle of incidence, and also with the plane of polarization. From measurements of the width of these bands he arrived at values for the phase change from silver relative to that from glass. The complexity of this method made it unsatisfactory.

Wernicke devised a simpler method by which he measured the phase change of silver and several dyes. In this method a thin, plane parallel plate of glass was so mounted that white light reflected from it, entering a spectroscope produced a spectrum that showed vertical light and dark bands. The bands from the silvered portion of the plate showed a shift relative to those from the unsilvered part. From the relative shift the phase change was determined.

Wiener, later, by this method studied silver and obtained results that were in marked disagreement with those of Wernicke.

The work of these men was followed by a more exhaustive study, both theoretical and experimental, by Drude. In his measurements Drude

[1] G. Quincke, Pogg. Ann., 142, p. 192, 1871.

[2] W. Wernicke, Pogg. Ann., 155, p. 87, 1874.

[3] O. Wiener, Wied. Ann., 31, p. 629, 1887.

[4] P. Glan, Wied. Ann., 7, p. 640, 1879; 47, p. 252, 1892.

[5] R. Hennig, Gött. Nachr., 13, p. 365, 1887.

[6] P. Drude, Wied. Ann., 50, p. 595, 1893; 51, p. 77, 1894.

[7] J. Koenigsberger u. R. Bender, Ann. d. Phys., 26, p. 763, 1908.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

---

[1] [illegible]

[2] [illegible]

methods are indirect, yet because of their greater convenience, they have been the more generally used.

The indirect methods: If a sufficiently thin wedge-shaped piece of glass is illuminated with monochromatic light a series of interference bands, due to the interference of waves reflected from its front and back surfaces, may be observed over the plate. If now the back of the plate be coated with some substance, for example, silver, the effect is to shift the interference bands from their original position toward the thinner or thicker portion of the wedge, according to whether the phase change is a retardation or an *acceleration*. By stripping off then, a portion of the coating in a direction at right angles to the bands, two sets of bands are obtained. Their relative displacement serves as a measure of the relative phase change. The phase change by reflection from transparent substances has been thoroughly studied, and theoretically the light (electric vector) suffers no change of phase upon the reflection from air into glass. Accepting this, measurements with the above wedge should give absolute phase change in the transparent region for glass.

A glass plate having parallel faces, should show no interference bands when illuminated with monochromatic light from a broad source; but when white light reflected from it is dispersed by a spectroscope a series of vertical bands extending throughout the spectrum, in ordinary working conditions, may be observed. These bands arise from the fact that waves, of such length that their effective path in the plate is an odd number of half wave-lengths, produce destructive interference in the reflected light. A set of bands from the coated part of the plate and a set from an adjacent uncoated part will be shifted relative to each other. The magnitude of the phase change may be determined from this shift.

The latter method is essentially that of Wernicke; the former that used by Drude, and by Koenigsberger and Bender. Both have been used in the present work.

Because of the convenience of obtaining thin parallel plates mica was used in part of the work, but other advantages led finally to the use of thin wedge-shaped plates of glass. The substances investigated for phase change were silver, fuchsin, doppel-grun, crystal-violet, cyanin, eosin and aniline-orange.

First Method.

In the observations with mica the following plan was followed. A mica plate coated, except for a central strip, with the substance to be tested, was so mounted (Fig. 1), that a source (*s*) was focused by means of a quartz lens (*a*) upon the mica (*p*) at a small angle of incidence (about 2.5 degrees). Then, by means of another quartz lens (*b*) an image of this plate by the reflected light was cast on the slit of a four foot Rowland grating spectroscope. This method requires a source giving a continuous spectrum. Sources fulfilling this requirement and also giving sufficiently intense radiation in the ultra-violet were not available. With a Nernst glower and with exposures eight hours in duration it was found that the limit into the ultra-violet to which observations could be extended was 340 $\mu\mu$.

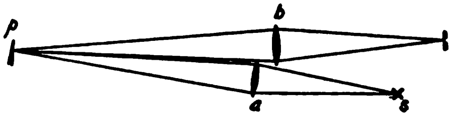


Fig. 1.

Second Method.

For most of the measurements the following method was used, which, since it made possible the application of a discontinuous spectrum, permitted measurements to be extended farther into the ultra-violet region.

Thin glass wedges were selected from several boxes of cover slips and from a small supply of thin glass plates that were at hand. All being discarded that failed to show straight bands of sufficient breadth when illuminated by monochromatic light. The breadth of band which gave the best photograph in the shorter wave-lengths was found from a few trials. These were then coated on the back with the substances whose phase change was to be investigated. Then a strip of the coating was removed in a direction at right angles to that of the bands. At first the glass wedge was simply substituted in place of the mica plate, of the method described above, and the slit of the spectroscope opened to a width of about 4 mm. With the copper arc as a source, images of the slit were distributed throughout the spectrum each showing a set of from three to six bands depending on the wave-length. Due to the achromatism of the quartz lens only a limited portion of the spectrum was in

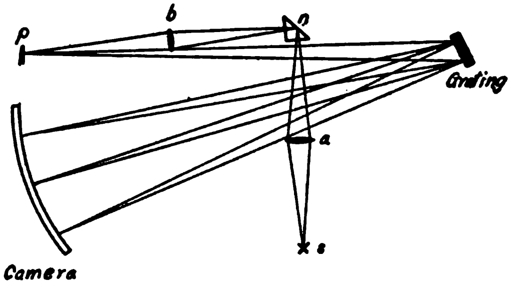


Fig. 2.

focus at a time, so to avoid this, the glass plate itself was diaphragmed down to an aperture of 4 by 10 mm. and mounted in place of the slit of the spectroscope (Fig. 2). By means of two quartz lenses (*a* and *b*) and a total reflecting quartz prism (*n*) an image of the arc was formed on this, the light being incident as before at an angle of about 2.5 degrees. When properly adjusted all the images of the set of bands were found well defined. Photographic records were obtained upon heavy films of such length as to include the first order spectrum and a large portion of the ultra-violet region in the second order. The displacement of the bands was measured with a micrometer microscope.

Method of Measurement.

The difficulty of finding glass plates giving perfect bands was one source of error. To eliminate as much as possible that arising from the curvature of the bands, the cross line of the microscope was first adjusted tangent to some band of one set, and measurements of the shift of all the bands in the set then made. It was then adjusted tangent to a band of the opposite set and the series of readings again taken. Each of these series of readings was repeated, the respective adjustments being on another band of each of the two sets. The mean of these four sets of readings should be practically free from the error arising from curvature, provided that curvature is not abrupt and the points on the bands on which the settings are made are not too far from the line of division of the two sets. The first condition depends on the selection of the glass plates; the second on the care observed in making the settings. A small region between the two sets of bands, owing to the astigmatism of the grating, was not well defined. This necessitated setting on points that were somewhat removed from the real line of division. However this should in no case have caused a greater error than one per cent. The accuracy with which a setting on the center of a band could be repeated depended largely upon the intensity of the photograph.

Method of Depositing Films.

The silver films used were deposited by Brashear's method and were of such density that only a trace of light could be seen on looking through at the bright sky.

In obtaining films of the dyes, these were first dissolved in absolute alcohol and as concentrated a solution was used as could be dried on the plate without the substance crystallizing. The plates were coated by dipping them in the solution and quickly drying over a Bunsen flame. Considerable difficulty was met in obtaining coatings of heavy and uniform thickness. This lack of uniformity in the coatings is the cause of some irregularities observed in the measurements. In the region of the spectrum where the substance is most transparent distortions of the bands probably arising from this cause could usually be observed.

Thickness of Films.

Some measurements of the thickness of the films used were made as follows: Interference bands formed by laying another glass plate on the coated side of the plate holding the film to be measured, in general, showed a shift between the bands over the coated portion and those over the cleared portion of the plate. This shift was measured for two wave-lengths far enough apart so that a measurable difference in path in wave-length could be observed. The shift of the bands due to the thickness of the coating was measured in the direction in which their gain over those from the coating surface took place, as light of shorter wave-length was used. By varying the wave-lengths of the light illuminating the plate it was readily seen that the thickness was, in all measurements, less than a wave-length provided the phase change be neglected. Since fuchsin is very transparent in the red its phase change there should be the same approximately as that of glass, provided its refractive index is greater than one. Under this assumption, that the phase change from glass in air and from fuchsin in air are the same for the red, the relative shift of the bands is a direct measure of the thickness of the film. Values obtained by this method from adjacent parts of one film were 275 and 333 $\mu\mu$. The films of eosin and aniline-orange were so thin as to show Newton's colors.

Observations.

Silver.—The photographs taken for silver on mica showed a relative shift of about three-tenths of a band at 580 $\mu\mu$, decreasing slowly with decreasing wave-length to about 442 $\mu\mu$ where the two sets of bands seem to coincide. The shift with silver on glass was practically the same as for mica except that the position at which the bands coincide seemed to be shifted farther toward the ultra-violet (to about 390 $\mu\mu$). They continued to coincide throughout the transmission region for silver and as far as the photograph showed distinct bands (296 $\mu\mu$). Because of the high reflection coefficient of silver the silvered portion did not give well defined bands in the greater part of the spectrum. The accuracy with which these could be measured did not justify more than qualitative observations.

Drude's formula[1] for the absolute phase change (Δ) at the boundary

---

[1] P. Drude, Wied. Ann., 51, p. 86, 1894.

between a transparent medium of refractive index n_1, and an absorbing medium having an index of absorption k and an index of refraction n is:

$$tg\,\Delta = -\frac{2nn_1k}{n^2 - n^2k^2 - n_1^2}.$$

From this formula, values for the relative phase change were calculated from values for n and k obtained by Minor.[1] These were in close agreement with the observed values for the red, but, being practically constant down to about 320 $\mu\mu$, they are in very poor agreement with the observed values at the shorter wave-lengths. In the region where the bands coincide the calculated values ranged from .38 for 326 $\mu\mu$ to .32 for 275 $\mu\mu$. Minor's observations however were made on massive silver, mine on partially transparent films. The experiments on the variation of phase change with thickness of the film would hence lead one to expect poor agreement in the region of the spectrum where the substance is transparent.

Fuchsin.—The measurements on fuchsin (Table I., Fig. 3) show a decreasing phase change for decreasing wave-length until between 420 and 440 $\mu\mu$ where coincidence, or at least, a minimum phase-change, is observed. Beyond this point the phase change suddenly mounts to its highest value, after which a gradual decrease is observed to 280 $\mu\mu$ where its value is .27 wave-length. The transmission region for this fuchsin film was determined by mounting it before the slit of the spectroscope so that a portion of the light falling on the slit went through the film and

TABLE I.

Fuchsin.

Wave-Length.	Phase Change.	Wave-Length.	Refractive Index of Fuschine.
577.8	0.39	589	2.64 to 2.70
568.5	.38	527	1.85 to 1.91
521.8	.33	486	1.05 to 1.07
510.6	.33	461	0.83
465.1	.26	431	0.95
424.0	.00		
406.3	.60	425	1.00
402.3	.57	413	1.15
382.7	.51	405	1.18
353.0	.39	399	1.24
333.8	.43	397	1.32
296.1	.31	360	1.52
282.3	.27	344	1.60

---

[1] Minor, Ann. d. Phys., 10, p. 617, 1903.

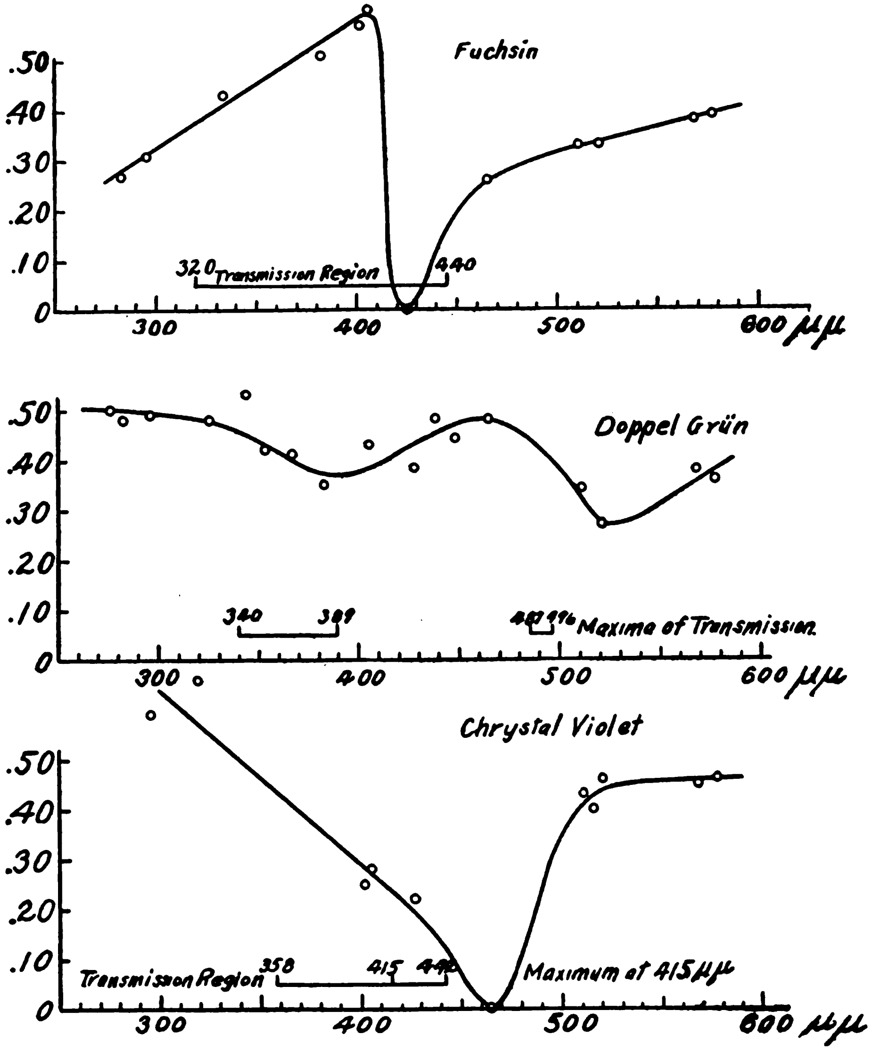


Fig. 3.

the glass plate, while the other passed through the glass plate only. By comparing these two portions in the photograph, it was observed that, between 440 and 320 μμ fuchsin was practically as transparent as glass. The abrupt change in phase difference at 420 μμ from zero to one-half wave-length probably arises from the refractive index of the fuchsin, which is less than glass at 425 μμ, rising above it between 425 and 410 μμ.

Doppel-Grün.—The values for the phase change at the surface of this substance goes through two minima in the portion of the spectrum here

TABLE II.

Doppel-grün.

Copper Arc.		Nernst Glower.	
Wave-Length.	**Phase Change.**	**Wave-Length.**	**Phase Change.**
577.8	.36	580	.34
568.5	.38	570	.25
521.8	.27	560	.25
510.6	.34	550	.28
465.1	.48	540	.23
448.0	.44	530	.21
437.8	.48	520	.21
427.5	.38	510	.20
406.3	.43	500	.18
382.4	.35	490	.18
367.1	.41	480	.30
353.2	.42	470	.39
344.2	.53	460	.45
326.0	.48	450	.47
		440	.41
296.1	.49	430	.35
283.0	.48	420	.35
276.7	.50	410	.39

investigated (Table II., Fig. 3). The transmission of this film was determined in the same way as for fuchsin, and it was found that between 496 and 487 $\mu\mu$, and between 389 and 340 were maxima of transmission. The magnitude of the transmission was considerably less than that for glass.

Crystal-Violet.—For this substance the phase change (Table III., Fig.

TABLE III.

Phase Change.

Wave-Length.	Crystal Violet.	Cyanin.	Eosin.	Aniline Orange.
577.8	0.46	0.23	0.52	0.00
568.2	.45	—	—	—
521.8	.46	.00	—	.33
515.3	.40	—	—	—
510.6	.43	—	.32	—
465.1	.00	.36	.31	.59
456.4	—	.34	—	—
427.5	.22	—	.36	.58
406.2	.28	.48	—	—
402.3	.25	.48	.42	.61
368.7	—	.42	—	—
353.2	—	.48	.32	.61
333.4	—	.46	—	—
330.8	—	.52	—	.60
319.3	.66	.43	.48	—
296.1	.59	.42	.32	.56

A REPLY TO MR. IRVING LANGMUIR'S PAPER "THE EFFECT OF SPACE CHARGE AND RESIDUAL GASES ON THERMIONIC CURRENTS IN HIGH VACUUM."[1]

By J. E. Lilienfeld.

1. Mr. Langmuir does not mention (p. 450), that the author called attention to the experiment of Soddy[2] and first proved[3] that the current from a Wehnelt electrode decreases with the pressure in the tube, not because the decrease of the pressure changes some of the properties of the electrode, but because the electromotive force which is needed to cross the space between the electrodes increases with each improvement of the vacuum owing to the electron density in the space. The author is very glad that Mr. Langmuir has the same opinion on this point.

2. Mr. Langmuir does not mention, that the law

$$i = \text{constant } V^{3/2}$$

has been published[4] by the author as holding accurately for a range of current densities below an upper limiting value of i.

3. For values of i larger than this limiting value of i the author established[5] the law

$$i = \alpha V^2 + \beta.$$

4. If Mr. Langmuir finds in his experiments solely the law $i =$ constant $V^{3/2}$ holding with a rather rough approximation, this is due to the fact that his current densities are below the limiting value mentioned above.

5. Mr. Langmuir claims (p. 483) that he obtained a much higher vacuum than the author. Adopting a criterion suggested by Mr. Langmuir (p. 470) we come rather to the contrary conclusion. Mr. Langmuir's opinion is that the exponent ϵ in the equation $i =$ constant V^{ϵ} has to be $= 3/2$ as far as perfect vacuum is considered. Any increase of pressure increases ϵ. Now the lower part of Curve III., Fig. 5, obtained in Mr. Langmuir's "perfect vacuum" is represented by the equation $i =$ constant $V^{1.71}$. Mr. Langmuir attributes this difference to residual gas. Indeed the author has shown[6] that in the lower part of

---

[1] Phys. Rev., December, 1913, p. 450.

[2] Nature, 77, 54, 1907; also Physik. Ztschr., 9, p. 1 (1), 1908.

[3] Physik. Ztschr., 9 (16), p. 193, 1908; also Ann. d. Phys., 32, p. 674, 1910.

[4] Ann. d. Phys., 32, p. 717–719; also p. 736, 1910.

[5] Ber de Math. Phys. Classe der Kgl. Ges. d. Wiss. zu Leipzig, 9, July 20, 1908; Ann. d. Phys., 32, p. 699.

[6] Ann. d. Phys., 32, p. 717–719; also p. 736, 1910.

his experimental curves the condition $\epsilon = 3/2$ is fulfilled with absolute accuracy. Considering that even in this part of the author's curves the current densities are larger than Mr. Langmuir's, we ought to conclude that the author's vacuum was by no means inferior to the vacuum Mr. Langmuir worked with.

6. Besides, there are other points proving that the author's vacuum was of the very highest degree, for he used liquid and solid hydrogen, with very large and short vacuum connections without changing in any way his results.

As to Mr. Langmuir's conviction that his essential advantage over the author's work consists in his using a pure metallic incandescent electrode instead of Wehnelt cathode, the author refers to the fact that changes of temperature and composition of the Wehnelt electrode do not involve any change in the discharge conditions.[1] Recently[2] the author published the results of his last three years' work, showing also, that not the least difference is caused by using an incandescent pure tantalum cathode instead of the Wehnelt cathode.

As to the anode, the principal thing is that it ought to be freed from gas at a temperature sufficiently higher (500°) than the temperature it assumes when the discharge is passing. The anode has a comparatively large surface, and can be directly cooled by liquid air. And the characteristic of the discharge is not altered by removing the liquid air bath. As the author tried all possible materials for the anodes,[3] obtaining always identical results, there is no possibility that the anodes would be of an essential influence in the experiments.

7. In his papers referred to the author proved by many other experiments that above a lower limit of the current density there is no dependence between the gas density and the discharge characteristic in a high vacuum. Moreover, he stated that above a certain current density there is practically no space charge in the perfect vacuum. He concluded from this as a matter of fact that there is formation of positive charges in the space independently of the gas. He did not call these positive charges ions, as Mr. Langmuir and also Mr. Coolidge[4] suggest in their papers, not having an exact evidence for their *nature*. But there is an absolute mathematical[5] evidence established for their *existence*.

The Physical Institute,
Leipzig University,
February, 1914.

---

[1] Ann. d. Phys., 32, p. 714–715, 1910.

[2] Ann. d. Phys., 43, p. 37–40, 1914.

[3] Ann. d. Phys., 32, p. 706–710. 1910.

[4] Phys. Rev., December, 1913, p. 411.

[5] Ann. d. Phys., 32, p. 725–737 (1910); Ber. d. Math. Phys. Classe der Kgl. Ges. d. Wiss. zu Leipzig 63, 337–339 (1911); Ann. d. Phys. 43, p. 40–44, 1914.

A REPLY TO MR. W. D. COOLIDGE'S PAPER "A POWERFUL RÖNTGEN RAY TUBE WITH A PURE ELECTRON DISCHARGE."[1]

By J. E. Lilienfeld.

Mr. Coolidge objects (p. 412–413) that the author's vacuum "is not high enough to justify the conclusions drawn." In his preceding reply to Mr. Langmuir's objections the author has developed the reasons which make him believe that the vacuum reached in the General Electric Co.'s Laboratory was by no means higher and probably lower than the author's vacuum. As to the freeing the electrodes from gas, the author's opinion is that it is only important to heat the electrodes during the pumping nearly to their melting point and to exhaust as long as gases are developed. If then during the working of the tube the electrode temperature remains sufficiently below the temperature reached during the exhaustion, no more gas can be given out to the vacuum. This is the kind of work the author did, and he obtained nearly perfect results[2] by it. As he does not know which construction of the author's tubes Mr. Coolidge studied, he cannot say why Mr. Coolidge failed in his experiments.

Again, as developed in the preceding reply to Mr. Langmuir, the author never assumed that there is "no such thing as a pure electron discharge." As a matter of fact the author proved that the space charge disappears practically, if the space density of the electrons becomes larger than a certain limiting value. In a space where this limiting value is not reached there may be a perfectly unipolar conductivity. Again, the author did not assume the positive charges to be ions, and even called attention[3] to the fact that owing to the exceedingly small number of ions in his tube there is practically no disintegration of the electrodes. So he cannot agree with Mr. Coolidge's views on any point.

The author intends to publish a paper concerning his own further developed experimental work and limits himself at present to the above reply to Mr. Coolidge's objections.

The Physical Institute,
Leipzig University,
February, 1914.

---

[1] Phys. Rev., December, 1913, p. [illegible].

[2] See the pictures published by Rosenthal, Fortschr. a. d. Gebiete d. Röntgenstrahlen, Vol. XVIII, Tafel XVII (1912), and Vol. XX, Tafel XXII (1913).

[3] Fortschritte, Vol. XVIII, p. [illegible]

THE ENERGY OF PHOTO-ELECTRONS FROM SODIUM AND POTASSIUM AS A FUNCTION OF THE FREQUENCY OF THE INCIDENT LIGHT

By W. H. Kadesch.

THE energy of photo-electrons as a function of the frequency of the incident light has been studied in numerous researches, but with little concordance of results. Ladenburg,[1] who was the first to investigate the subject, concluded that the emission velocity varies directly as the frequency. Joffé[2] showed, however, that Ladenburg's observations were in quite as good agreement with the view that not the velocity of electrons, but their energy, varies as the frequency. Kunz[3] at first found a linear relation between energy and wave length. Later observations led him to develop a theory according to which the velocity varies as the frequency. Wright[4] found a maximum in the energy curve which was taken as a confirmation of the view that the photo-electric effect is a resonance phenomenon. The same conclusion had been reached by Lenard[5] and by Ladenburg and Markau.[6] Hughes[7] found a linear relation between energy and frequency, as did also Richardson and Compton.[8] Cornelius[9] obtained results which were taken to support the theory of Kunz. Compton,[10] however, showed that according to Cornelius's data the energy is more nearly proportional to the cube of the frequency than to the square.

This total lack of agreement in experimental results, and the bearing of photo-electric phenomena on the unitary theories of radiation, render it important that further work be done. It was with the hope of eliminating some of the difficulties and errors that have beset investigators in this field that the present research was undertaken.

[1] E. Ladenburg, Verh. d. D. Phys. Gesell., 9, p. 504, 1907.

[2] A. Joffé, Ann. der Physik, 24, p. 939, 1907.

[3] Jakob Kunz, Phys. Rev., 29, p. 212, 1909, and 33, p. 208, 1911.

[4] J. R. Wright, Phys. Rev., 33, p. 43, 1911.

[5] Lenard, Ann. der Physik, 8, p. 149, 1902.

[6] Ladenburg and Markau, Verh. d. D. Phys. Gesell., 10, p. 562, 1908.

[7] A. L. Hughes, Phil. Trans. (A), 212, p. 205, 1912.

[8] Richardson and Compton, Phil. Mag., 24, p. 575, 1912.

[9] David W. Cornelius, Phys. Rev. (2), 1, p. 16, 1913.

[10] Karl T. Compton, Phys. Rev. (2), 5, p. 382, 1913.

The chief sources of uncertainty in photo-electric work have been the following: (1) The illuminated surfaces have usually been of metals sensitive to only a short range of frequencies. (2) Surface conditions have not been controlled, so that there was no assurance of uniformity throughout a set of observations. (3) There has been in some cases much trouble with reflected light. In order, so far as possible, to obviate these difficulties, the following precautions were taken. (1) Surfaces of the strongly electro-positive metals, sodium and potassium, were illuminated, these being sensitive to long waves as well as short. (2) A device was employed for exposing a fresh surface very readily, and as often as desired.

Apparatus.—The photo-electric cell was of the form shown in Fig. 1.

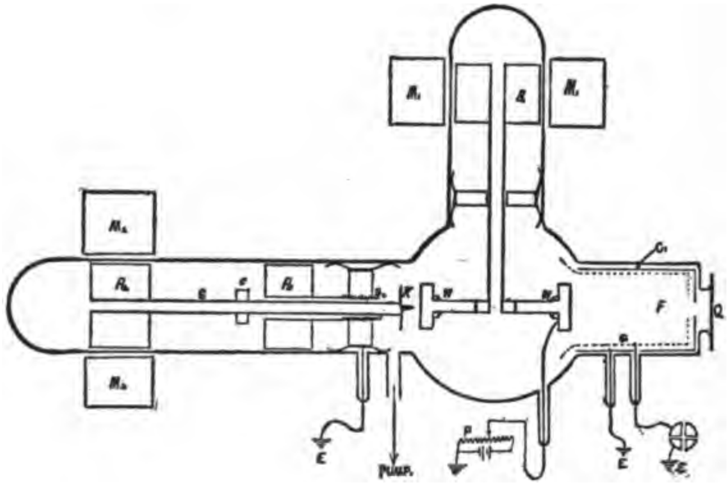


Fig. 1.

W is a brass wheel about 8 cm. in diameter, which could be rotated by means of the electro-magnet M_1, acting on the armature A_1. To the periphery of this wheel, which was insulated from the shaft by means of amber, the electrodes were attached. These were cylindrical in form, 2 cm. in diam. and initially about 8 mm. deep. They were made by pouring the molten metal in an atmosphere of dry CO_2 into a mould whose removable brass bottom was designed to hold the metal firmly, and make metallic contact with it. This base was then screwed into the wheel *W*. *K* is an auger-like knife rotated by means of the electro-magnet M_2 and armature A_2. This knife could also be slid along the tube in the direction of *W*, but the point to which it could be carried was limited by a third armature A_3, and a collar *C*, fixed to the shaft *S*. This armature was connected with the framework by a fine screw S_2, and so, by means of M_2, could itself be advanced or withdrawn. This arrangement made it possible to take off a slice as thin as desired from the electrode, and turn the fresh surface in the direction of F, in position to receive the illumination.

The Faraday cylinder consisted of a fine-meshed copper gauze, blackened by oxidation, and a brass cylinder outside the gauze, concentric with it, and insulated from it by means of ebonite rings. Terminals were led out separately from the brass cylinder, the gauze, the wheel W, and the mechanism of the tube. Those from the mechanism and brass cylinder were put to earth, that from the gauze to an electrometer of sensitiveness about 150 scale divisions per volt, while that from the wheel was connected with a potentiometer arrangement by which any potential desired could be given the electrode.

Extraneous light was excluded by surrounding the tube with a light tight box of sheet iron, painted inside with optical black. This box was also earthed, and helped to eliminate electro-magnetic disturbances, and static effects.

The source of light was a spark between iron terminals. These were joined to the secondary of a large induction coil designed to operate with alternating current. The disturbances attending its use in this way, however,[1] made it necessary to energize the coil with storage cells. Leyden jars were placed in parallel with the spark to increase its instantaneous intensity. The light was passed through a quartz spectrometer, previously calibrated by means of the lines of the mercury arc. During the photo-electric observations the slit width was about 1 mm. for both collimator and telescope. The spark terminals were carried by a clamp fixed to the collimator. In passing from one wave length to another the telescope was allowed to remain in position, only the collimator being moved. The lenses not being achromatic, it was necessary to change the lengths of spectrometer tubes for each new frequency. The lengths required were determined in advance by allowing the light of each mercury line, after traversing the system, to fall upon a screen of uranium sulphate, a satisfactory adjustment being indicated by the sharpness of the focus on the screen. The tube length required at 2,002 A.U. was 22.5 cm., at 3,906 A.U. 28.5 cm. During the process just described the collimator slit was made as narrow as possible while that of the telescope was removed. During the determination of the spectrometer setting corresponding to the various wave-lengths both were in place and narrow.

The whole optical arrangement including induction coil, storage cells,

---

[1] Millikan, Phys. Rev. (2), 1, p. 73, 1913; Pohl and Pringsheim, Ber. d. D. Phys. Gesell., 10, p. 974, 1912.

Leyden jars, and spectrometer, was placed inside a large box, made of sheet iron 2 mm. thick. This was necessary in order to eliminate completely the electro-magnetic disturbances referred to above.

The photo-electric cell was evacuated through a tube about 3 cm. in diameter by means of a Gaede molecular pump. This was kept running throughout every set of observations. A McLeod gauge reading to .000001 mm. of mercury showed no indication. No attempt, however, was made to test for the residual vapors of mercury or of stopcock grease.

Observations.—In determining the energy of the electrons emitted under the influence of any wave-length two methods were employed. In the first, distribution of velocity curves were run in the usual way by plotting as abscissæ the potentials applied to the electrode, and as ordinates the electrometer deflections due to a given period of illumination. The point where this curve met the axis of potentials was taken as a measure of the energy of the swiftest electrons. In the second method a potential was applied to the electrode just sufficient to prevent a deflection of the electrometer. The agreement between the results given by the two methods was very close.

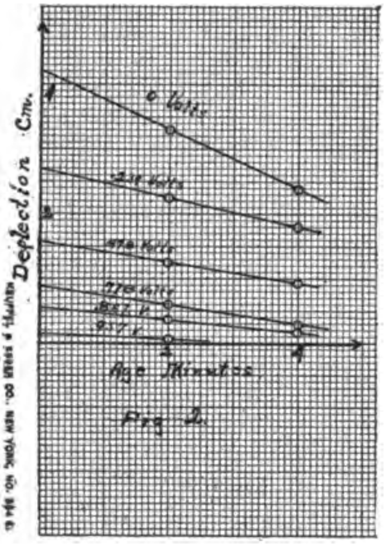


Fig. 2.

It was found that the strength of the photo-electric current fell off very rapidly with increasing age of surface. To determine whether this was due to illumination, or to changes taking place independently of the illumination, observations on the current were made under two conditions. In the one the same surface was illuminated for 30 seconds at intervals of two or three minutes. Curves with ages of surface as abscissæ and the corresponding electrometer deflections as ordinates were then drawn. These were convex toward the axes of coördinates. In the second case a fresh surface was exposed each time, but at different age. The age current curves obtained by this method were straight lines, with negative slope. From this is seen that both age and illumination affect the surface in such a way as to cut down the current. It was thought that an improvement in the method might be made by observing the electrometer deflections as in method two, extending the curve backward to the line of zero age, and taking this point of intersection as the measure of the current from a clean metallic surface. This however was found to be unnecessary, since the slope of these curves became smaller and smaller, approaching zero as the potential applied approached that required to prevent the escape of electrons. This is clearly shown in Fig. 2. In this case only two points on each curve were determined. The method of observation finally adopted was to cut a fresh surface for each potential applied to the electrode, to allow this surface to attain an age of two minutes (about the length of time required to close the box containing the photo-electric cell, and otherwise prepare to make an observation) and then illuminate. The applied potentials were then plotted as abscissæ and the corresponding electrometer deflections as ordinates. Only a small section of the curve was determined in each case, since only the point at which it met the voltage axis was required.

The observations made on sodium by illuminating with four different wave-lengths are graphically shown in Fig. 3. Plotting frequencies as abscissæ, and the corresponding maximum potentials determined as above, as ordinates, the curve in Fig. 4 is obtained. Observations made in the same way on potassium give the points marked by circles in Fig. 5.

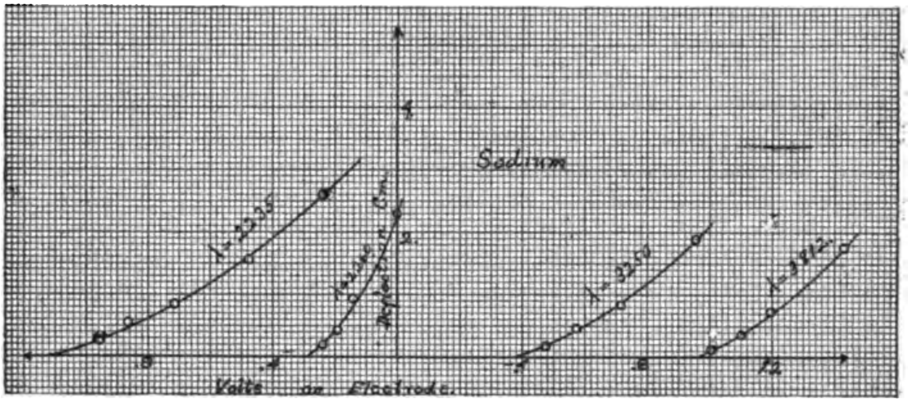


Fig. 3.

In the second method of observation also, namely, that in which a potential was applied to the electrode just sufficient to prevent the escape of electrons, fresh surfaces were frequently cut, especially when the balancing potential was approached. This was done to insure greater accuracy, merely by providing a surface as sensitive as possible to the light. This method was employed only for potassium. The points thus determined are indicated by dots in Fig. 5.

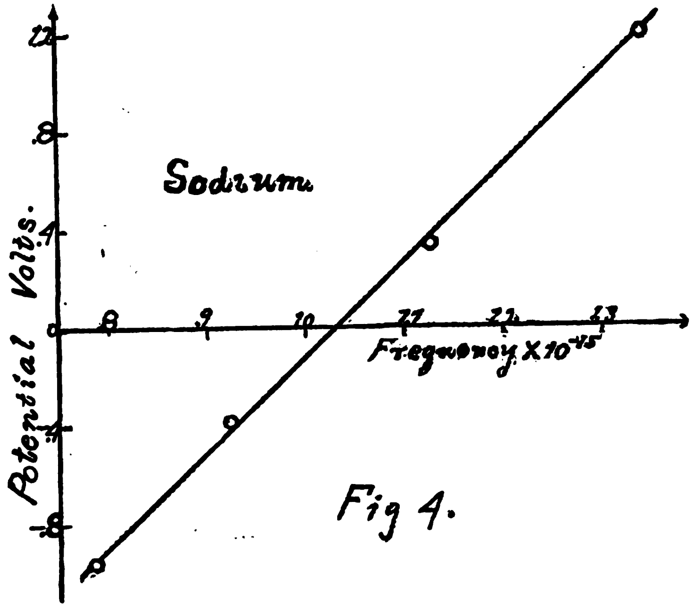


Fig. 4.

Discussion of Results.—The results of the investigation are seen to be in agreement with those of Hughes[1] and of Richardson and Compton.[2] They may be expressed by an equation of the form

$$V = Kn - V_0,$$

in which V is the difference in potential in volts between the electrode and the adjacent parts of the tube, just sufficient to prevent a deflection of the electrometer, n is the frequency of the incident light, and K and V_0 constants.

According to the theory of Einstein[3] the relation between energy and frequency should be represented by the equation

$$Ve = \frac{R}{N}\beta n - P,$$

in which e is the elementary electrical charge, $R\beta/N$ is Planck's constant equal to 6.55×10^{-27}, and P a constant representing the loss of energy suffered by an electron in escaping from the metal.

The observations on sodium gave a value for K equal to 3.87×10^{-15}, those on potassium 3.83×10^{-15}.

Writing the equation in the form given by Einstein, and substituting

---

[1] Loc. cit.

[2] Loc. cit.

[3] Einstein, Ann. der Physik, 20, p. 199, 1905.

for e, 4.772×10^{-10}, the slope for sodium becomes 6.16×10^{-27}, that for potassium 6.09×10^{-27}.

Errors.—In addition to the usual errors due to "personal equation" which in the end would be expected to annul one another, the observations are subject to several others of a systematic sort, depending upon conditions unavoidable in the experiment. First among these may be mentioned electrostatic leaks. In the first method of observation these would have the effect of causing the distribution of velocity curves to approach the axis of potentials at a more acute angle thus rendering the points of contact more uncertain. The tendency would be to assume a positive potential somewhat smaller than the true. This error would be greatest for wave-lengths giving weakest currents. From Fig. 3 these are seen to be the longest and the shortest waves. This would tend to bend the frequency-potential curve in such a way as to make it concave downward. However, since the leak for a deflection of 500 scale divisions never exceed and seldom reached 3 divisions per minute, becoming rapidly smaller with diminishing deflection, the effect on the shape of the curve, as well as on its slope, is negligible.

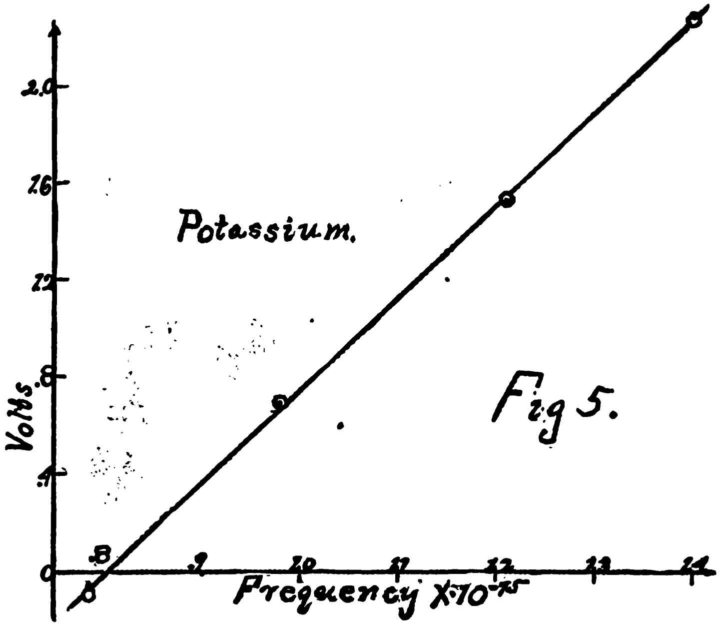


Fig. 5.

The electrostatic capacity of the electrometer and receiving gauze would also introduce an error. This will best be seen by considering the second method of determining electronic energies. Even though the electrical arrangement was fairly sensitive, many electrons would have to pass before an observable deflection would take place. The observed potential, then, is somewhat smaller than the true. Here again the error would be greatest for wave-lengths giving smallest current, and the effect on the frequency potential curve would be the same in character as that due to electrostatic leak, and also very small.

A third error would arise from the effect of reflected light. A ray incident on the receiving gauze would, if of sufficiently high frequency, there release electrons. These would travel to the electrode, and so offset the effect of an equal number passing to the gauze. The observed positive potential would then be smaller than that required to prevent the escape of electrons. Since the surface of the gauze was of copper oxide, not sensitive to long waves, this error would affect only the potentials for the higher frequencies. The curve would therefore have a slope somewhat smaller than the true. Charging the electrode to a high negative potential, however, and illuminating with these waves, gave a negative deflection never exceeding a few hundredths of one per cent. of its positive saturation value. The error due to this cause, then, must also have been small. The total observational error would not account for a difference as large as that between the slopes of the experimental curves and that of Einstein's formula.

In conclusion the writer wishes to acknowledge his obligation to Mr. Fred Pearson and Dr. Harvey B. Lemon for repeated assistance in the course of the investigation, to Mr. Albert E. Hennings, from whom ideas on the mechanism of the tube were freely borrowed, to Mr. Julius Pearson, who constructed the tube and to whose skill and ingenuity its successful operation was largely due, and especially to Professor Millikan, at whose suggestion the research was undertaken, and under whose direction and constant inspiration it was brought to a conclusion.

U. S. NAVAL ACADEMY,
January 12, 1914.

THE HALL EFFECT IN FLAMES.

By Harold A. Wilson.

THE Hall effect in a Bunsen flame was investigated by E. Marx[1] in 1900. A small flat flame between the poles of a large electromagnet was used and a current was passed through this flame in a vertical direction between two horizontal electrodes of platinum wire gauze. The vertical potential gradient was measured by means of two wires one above the other which were connected to a quadrant electrometer. The horizontal potential gradient of the Hall effect was found with a second pair of wires also connected to a quadrant electrometer. If X denotes the horizontal gradient, Y the vertical gradient and H the strength of the magnetic field then Marx found that X/HY had the following values in flames containing the vapors of different alkali metal salts.

Metal.	$-X/HY$.
Cæsium	1.72×10^{-6}
Rubidium	2.70 "
Potassium	3.72 "
Sodium	5.06 "
Lithium	7.86 "
Flame free from salt	10.18 "

The above values of X/HY for salts are those found when strong solutions of the salts were sprayed into the flame. With weaker solutions the values found were more nearly equal to that in the flame free from salt. The conductivity of a flame is increased by the presence in it of an alkali metal salt and the increase is greater the higher the atomic weight of the metal. It appears therefore that in Marx's experiments the Hall effect observed diminished as the conductivity of the flame increased.

If k_1 and k_2 denote the velocities of the positive and negative ions, respectively, due to one volt per cm. then according to the theory of the Hall effect in an ionized gas we have approximately

$$\frac{X}{HY} \times 10^8 = k_1 - k_2,$$

where H is expressed in electromagnetic units. In a Bunsen flame the

---

[1] Ann. der Physik, Band 2, 1900.

velocity of the negative ions is large compared with the velocity of the positive ions so that k_1 can be neglected and we have $k_2 = -X/HY \times 10^8$. Now the negative ions in a Bunsen flame are generally believed to be free electrons so that we should expect k_2 to be independent of the amount and nature of the salt present in the flame.

Marx's results therefore do not agree with the theory that the negative ions are electrons. A possible explanation of this discrepancy was suggested by the writer.[1] In Marx's experiments the horizontal electrodes were about 3 cm. apart and the distance between the two wires used to measure the horizontal gradient X was also about 3 cm. The horizontal electrodes of course are equipotential surfaces so that they must tend to prevent the formation of a horizontal potential gradient in the space between them. This effect we should expect to be greater the greater the conductivity of the flame. It seems possible therefore that the diminution of the Hall effect with increasing conductivity, observed by Marx, may be a spurious effect produced by the nearness of the horizontal electrodes to the place where the Hall effect was measured.

The experiments described below were undertaken with the object of measuring the Hall effect in a Bunsen flame containing different alkali salts under conditions which would permit the full value of the Hall effect gradient to be observed. The results obtained show that the Hall effect is nearly independent of the conductivity of the flame and of the current passing through it in agreement with the theory.

Fig. 1 shows the burner and electrodes used. The burner consisted of a row of seven fused quartz tubes cemented into a brass tube AB. A mixture of gasoline gas, air and spray of a salt solution entered at A and was burnt from the quartz tubes giving a row of seven small Bunsen flames which were in contact as shown. The whole formed a flame about 12 cm. high, 12 cm. wide and 1.5 cm. thick. This flame was placed between the flat poles of a Weiss electromagnet which were 10 cm. in diameter and 3.5 cm. apart. The circle MM' indicates the position of one of the poles. A current could be passed horizontally across the flame between two platinum electrodes E and E' which were kept bright red hot by the flame. These electrodes were about 9 cm. apart and consisted of circular disks 1.5 cm. in diameter supported by stout platinum wires. The Hall effect was measured by means of two platinum wires at H and H' perpendicular to the plane of the paper in Fig. 1. These wires were about 0.2 mm. in diameter and passed right through the flame; they were well insulated and connected to an insulated quadrant

---

[1] Electrical Properties of Flames, page 114.

electrometer. Fig. 2 shows the arrangement used to support the wires *H* and *H′*. *MM′* and *NN′* represent the poles of the magnet and the flame is shown between them. The wires *H* and *H′* were supported by glass tubes *GG* and *G′G′*. These tubes passed through two ebonite plugs

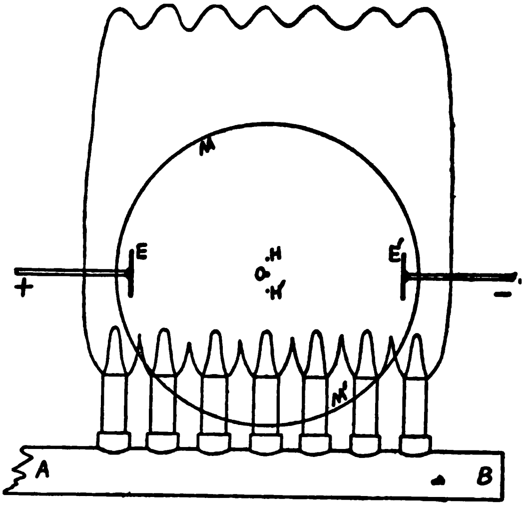


Fig. 1.

P and *P′* fitted tightly into the opposite ends of a brass tube *AB* which could be turned round in the hole bored in the pole *MM′*. *C* is a graduated circle over which a vernier *V* reading to 1/10° turned. This vernier was carried by the tube *AB*. In this way the wires *H* and *H′* could be rotated about an axis at *O* (Fig. 1) and the angle turned through measured.

If a current is passed through the flame between the electrodes *E* and *E′* the equipotential surfaces, near the line *EE′*, in the absence of a magnetic field are approximately vertical planes perpendicular to the faces of the poles of the magnet. If the wires *H* and *H′* are turned round till the electrometer shows that they are at the same potential then they both lie on one of the equipotential surfaces. If now the magnet is

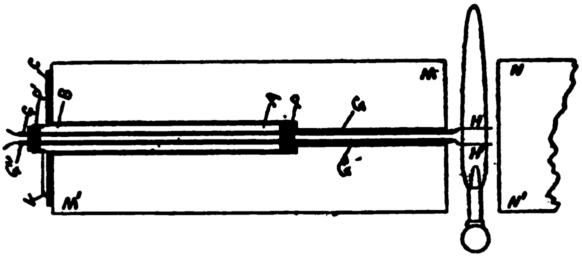


Fig. 2.

excited the equipotential planes are rotated about an axis parallel to the magnetic field and the electrometer is deflected. By turning the wires H and H' round till they are again at the same potential the angle through which the magnetic field rotates the equipotential planes can be determined. If this angle is denoted by θ we have

$$\tan \theta = \frac{X}{Y}.$$

By this method the ratio of the horizontal and vertical potential gradients is obtained from a single observation and it is not necessary to know the sensibility of the electrometer. It was found best to measure the angle of rotation of the equipotential planes first with the magnetic field in one direction and then with it in the opposite direction. The mean of the two angles was taken as a measure of the Hall effect.

Measurements were made with the wires H and H' 3 cm., 1 cm. and 0.5 cm. apart. The angles were nearly the same in each case.

The mixture of gas, air and spray was obtained by means of a Govy sprayer worked by air at a constant pressure of 14.4 cm. of mercury above that of the atmosphere. The gas supply was kept at a constant pressure of 2 cm. of water.

In spite of the careful regulation of the gas and air supplies the flame varied appreciably. This was probably due chiefly to variations in the quality of the gas. In consequence of these variations the results obtained on different days did not agree as well as those obtained nearly at the same time. The variations however were usually less than 5 per cent. The flame used was a well-oxidized flame having sharply defined inner cones on each of the quartz tubes.

When a current is passed horizontally through a Bunsen flame between hot platinum electrodes there is a large drop of potential close to the negative electrode and an uniform potential gradient in the space between the electrodes. This uniform gradient is proportional to the current. If a salt like potassium carbonate is put on the negative electrode the drop of potential there is greatly diminished and the uniform gradient correspondingly increased. The ratio of the uniform gradient to the current remains unchanged provided the potassium carbonate vapor does not get into the flame except near the negative electrode. In making measurements of the Hall effect by the method described above it is difficult to get accurate results unless the potential gradient in the flame is considerable. In all the experiments of which the results are given below potassium carbonate was put on the negative electrode but care was taken that its vapor did not get near to the Hall effect electrodes.

It was found that the potassium carbonate did not change the value of the Hall effect in the flame but it made it much easier to measure.

The sensibility of the quadrant electrometer used was about 500 scale divisions per volt. A rotation of the electrodes H and H' of 1/10 of a degree usually produced an electrometer deflection of several cm. To measure the Hall effect the electrodes H and H' were turned so that the electrometer deflection was zero. A current was then passed through the electromagnet which usually caused the electrometer to be deflected through a large angle of 45° or more. This deflection was reduced to zero by rotating the electrodes. The magnet current was then reversed and the deflection again reduced to zero. The horizontal potential gradient in the flame was varied from about 5 volts per cm. to 30 volts per cm. In most of the experiments it was about 20 volts per cm.

It was found that the Hall effect angle was nearly independent of the current through the flame and therefore of the horizontal potential gradient.

The following results were obtained with the flame containing rubidium chloride and a magnetic field of strength 4,850. The magnetic field was found with a bismuth resistance.

Current in Milliamperes.	Hall Effect Angle.
8	6.6°
12	6.9
16	6.9

The following results were obtained at another time with the flame free from salt and a field 4,850.

Current. $1 = 10^{-4}$ ampere.	Angle.
2.3	6.9°
3.3	6.6
6.0	7.1
6.9	6.9
10.8	6.3

The following table gives the results obtained with different salt solutions and magnetic fields. Each result is the mean of several obtained with different currents passing through the flame. The distance between the Hall effect electrodes was one cm. in most cases.

It will be seen that the Hall effect angle is practically the same for the flame without salt and the flame containing different amounts of rubidium, potassium, sodium or lithium salts. The amounts of the different salts which entered the flame were in all cases sufficient to color it very strongly and to greatly increase its conductivity. When using the 10 per cent. K_2CO_3 solution the quartz tubes became rapidly clogged with solid K_2CO_3.

Solution Sprayed into Flame.	Magnetic Field Strength.	Hall Effect Angle.
Water	7,700	10.2°
Water	4,850	6.3
Water	2,250	3.0
2 per cent. LiCl	7,700	10.9
2 per cent. LiCl	4,850	7.0
2.4 per cent. Na_2CO_3	7,700	10.7
2.4 per cent. Na_2CO_3	4,850	6.9
2.4 per cent. Na_2CO_3	2,250	3.0
10 per cent. K_2CO_3	7,700	11.0
2.6 per cent. K_2CO_3	7,700	10.7
2.6 per cent. K_2CO_3	4,850	7.0
2.6 per cent. K_2CO_3	2,250	3.1
0.26 per cent. K_2CO_3	7,700	10.0
0.26 per cent. K_2CO_3	4,850	6.4
0.26 per cent. K_2CO_3	2,250	3.3
2 per cent. RbCl	7,700	10.8
2 per cent. RbCl	4,850	6.8
2 per cent. RbCl	2,250	3.4

The following are the mean values of the Hall effect angle (θ) found with the three magnetic field strengths (H) used. The values of tan θ and tan θ/H are also given.

Magnetic Field (H).	Hall Effect, Angle (θ).	Tan θ.	$\frac{\tan\theta}{H}$.
7,700	10.6°	0.1871	2.44×10^{-5}
4,850	6.7°	0.1175	2.42×10^{-5}
2,250	3.2°	0.0559	2.48×10^{-5}
Mean			2.45×10^{-5}

It appears that tan θ is nearly proportional to H. According to the theory of the Hall effect in an ionized gas in which the velocity of the negative ions (k_2) is large compared with that of the positive ions we have

$$k_2 = \frac{\tan\theta}{H} \times 10^8.$$

The results obtained therefore give k_2 = 2,450 cm. per sec. for one volt per cm.

A number of attempts[1] to measure the velocity of the negative ions in a Bunsen flame have been made by different physicists and results varying from about 1,000 cm. per sec to 20,000 cm. per sec. obtained. The great variation in the results may be partly due to differences between the flames used but such differences probably cannot account for more

---

[1] See Electrical Properties of Flames.

than a small fraction of the variation. The result just obtained from the Hall effect is probably as likely to be correct as any other but since the theory of the Hall effect is not above suspicion too much reliance ought not to be placed on the absolute value found. There seems no reason to doubt the correctness of the conclusion that the velocity of the negative ions is the same for all alkali metal salts in a particular flame.

Rice Institute,
Houston, Texas,
February 2, 1914.

A SPECTROPHOTOMETRIC STUDY OF THE ABSORPTION, FLUORESCENCE, AND SURFACE COLOR OF MAGNESIUM PLATINUM CYANIDE.

BY FRANCES G. WICK.

THE double cyanides of platinum furnish a group of crystals which possess unusual optical properties. Some of them exhibit two surface colors, dichroic transmission, and dichroic fluorescence, the fluorescent light and that reflected selectively from the surface being polarized. Stokes[1] observed that these salts are fluorescent in the solid condition but not in solution. The dichroic fluorescence of a number of the crystals of this group was discovered by Grailich.[2] An interesting study of magnesium platinum cyanide was made by Lommel[3] who, from the dichroic fluorescence of this crystal, determined the direction of ether vibrations in polarized light.

Magnesium platinum cyanide, $PtMg(CN)_4 7H_2O$, is described by crystallographers[4] as uniaxial, of tetragonal symmetry. It has the form of square-based red prisms and is a positive, doubly refracting crystal, the ordinary ray being purple-red and the extraordinary blood-red.

The sides of the crystal, viewed by reflected light, have a beetle-green surface color which Lommel discovered to be polarized "in a plane perpendicular to the axis of the crystal," *i. e.*, the electric vector is parallel to the axis.

The end faces reflect selectively a blue-violet light which is polarized in such a way that the electric vector is in the plane of incidence.

The sides of the crystal, excited by unpolarized light, emit a fluorescence which, examined through a Nicol prism, shows a difference of color with different positions of the Nicol. If the direction of the electric vector is parallel to the axis of the crystal, the fluorescence appears orange-yellow, if perpendicular to the axis, scarlet-red.

The base of the crystal, excited by unpolarized light, gives unpolarized fluorescence which is scarlet-red.

---

[1] Stokes, Phil. Mag., Vol. 3, p. 385. 1853.

[2] Grailich, Krystallographisch-optische Untersuchungen, 1858.

[3] Lommel, Ann. der Physik, Vol. 8, p. 634, 1879.

[4] Lang, Sitz. Ber. d Akad. d Wiss. Wien, 1902. Horn, N. Jahrbuch f. Min. Uns., 1898, Beil. Band 12, 269.

If polarized exciting light be used, that in which the electric vector is parallel to the principal axis of the crystal always produces the orange-yellow fluorescence; that in which it is perpendicular to the principal axis always produces the scarlet-red. The color of fluorescence depends upon the angle between the axis of the crystal and the direction of the electric vector. A change from yellow to red takes place when the angle which this vector makes with the axis of the crystal changes from 0° to 90°.

In the investigation described in this paper, thin sections of magnesium platinum cyanide were used. These were cut by Steeg and Reuter and mounted between optically tested cover glass free from polarizing influence. It was necessary to have the sections covered since the crystal loses part of its water of crystallization upon exposure to the air, changing to a yellow powder—the pentahydrate. Two sections 8 mm. in diameter were cut parallel to the optic axis, .08 mm. and .15 mm. thick: two sections of corresponding diameter and thickness were cut perpendicular to the axis. The sections parallel to the axis showed the characteristic green surface color of the sides of the crystal: the section perpendicular to the axis showed the violet surface reflection of the base.

TRANSMISSION, FLUORESCENCE AND SURFACE COLOR.

The relation of fluorescence and surface color to transmission is the subject of the first part of this investigation. The existence of both fluorescence and surface color in this crystal gives an unusual opportunity for a comparative study of these phenomena.

The instrument used for the measurements was a Lummer-Brodhun spectrophotometer kindly loaned to the author by Professors Nichols and Merritt, of Cornell University. It was set up in the usual way, the comparison source being an acetylene flame, the light from which was reflected by a mirror through ground glass.

Fig. 1, Curve *T*, gives the per cent. transmission of a section .15 mm. thick cut perpendicular to the axis of the crystal. This shows a region of complete absorption between wave-lengths $.53\mu$ and $.57\mu$, and the edge of another absorption band at about $.45\mu$. By photographic methods, this second absorption band was found to extend as far into the ultra-violet as could be photographed with the glass spectrograph used, the absorption evidently being complete in the region beyond the visible spectrum.

The fluorescence of this same section is shown in Fig. 1, Curve *F*. The section was set up obliquely in front of the slit of the spectrophotometer and the fluorescence excited by light from a Nernst filament which had passed through a deep blue solution of cupric ammonium sulphate. This fluorescence is described by Lommel as "scarlet-red." The band is very narrow and its relation to the absorption band is such as should be expected.

The violet surface reflection of this section is shown in Fig. 1, Curve *S*. To obtain this, the section was placed in front of the slit of the spectrophotometer and rotated about a vertical axis until light from a Nernst filament produced the greatest intensity of violet light as seen through the telescope of the instrument, care being taken to avoid direct reflection from the cover glass. This violet reflected light is polarized, the electric vector being in the plane of incidence. The light from the Nernst filament used to obtain this surface reflection excited a fluorescence which was measurable. This fluorescence, however, was in the red end of the spectrum and did not overlap the violet surface reflection.

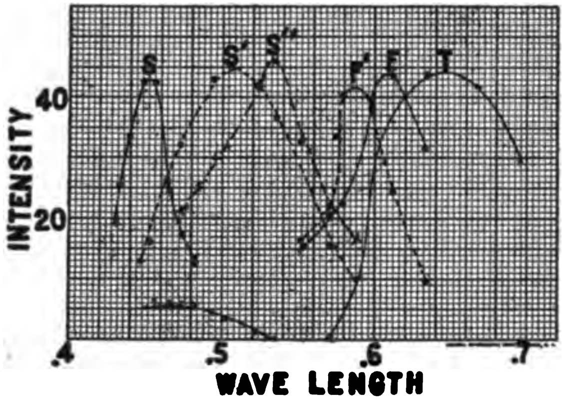


Fig. 1.

Curve *T*. Per cent. transmission of section 15 mm. thick perpendicular to the axis.

Curve *F*. Fluorescence of section 15 mm. thick perpendicular to the axis.

Curve *S*. Violet surface color of section 15 mm. thick perpendicular to the axis.

Curve *F'*. Fluorescence of section parallel to axis excited by polarized light with the electric vector parallel to the axis.

Curve *S'*. Green surface color of section parallel to axis, covered with glass.

Curve *S''*. Green surface color of small crystals without glass cover.

The fluorescence and surface color of a section parallel to the axis were then measured. The fluorescence was less intense than that of a section cut perpendicular to the axis and a carbon arc was used for excitation. Because of the variability of the arc as a source of excitation, these observations were repeated a number of times. The agreement of the results was such as to indicate that, for the length of time required to measure this narrow fluorescence band, the arc was kept in a steady condition.

Light from the arc was passed through a solution of cupric ammonium sulphate and then through a large Nicol prism. This polarized light was used for excitation since the fluorescence of this section is dichroic. The section was placed obliquely in front of the slit of the spectrophotometer with its principal axis vertical. Light polarized so that the electric vector was perpendicular to the axis of the crystal produced the same red fluorescence band as that of the section cut perpendicular to the axis, which is shown in Fig. 1, Curve *F*. Polarized light in which the electric vector was parallel to the axis of the crystal excited the fluorescence shown in Curve *F′* which is polarized in the same sense as the exciting light. Its color is described by Lommel as "orange-yellow."

The green surface color of the section parallel to the axis is shown in Curve *S′*. It was produced by polarized light having the electric vector parallel to the axis of the crystal and was polarized in the same sense as the incident light. The crystal section was placed in front of the slit of the spectrophotometer so that the plane of incidence was parallel to the axis of the crystal. The color, under these conditions, was a vivid green. If the plane of incidence is normal to the axis of the crystal, the reflection from the surface is a blue-green, differing from the vivid green of Curve *S′* in such a way as to indicate that the light strikes the crystal so as to produce both the violet and the green reflections at the same time resulting in a blue-green color.

Since surface color is dependent upon the index of refraction between a substance and the medium with which it is in contact, the presence of the glass cover over the face of the crystal section might be expected to modify the surface color. In order to test this, some of the salt was dissolved in water and re-crystallized on a glass plate. The green surface color of the small crystals which covered the plate was very intense and, with no glass cover, looked a yellower green than the same crystals observed through the glass plate upon which they were deposited. Curve *S″* gives the result of a spectrophotometric measurement of this surface color of the small crystals in contact with air. It will be noticed that the maximum of this band is nearer the region of greatest absorption, shown in Curve *T*, than the maximum of Curve *S′*, the surface color of the section covered with glass. When the plate upon which the small crystals were deposited was covered with a clear, saturated solution of the salt, the color changed to a bluer green, depending for the index of refraction between the crystal and solution. It was impossible to measure the violet surface reflection of the small crystals.

The curves of Fig. 1 are not comparable with respect to absolute value of intensities, the purpose of this figure being to show the relative positions of these bands. For Curve T the ordinate indicates per cent. transmission.

The region of greatest reflection indicated by these curves does not, in any case, correspond to the region of greatest absorption. Haidinger,[1] in a study of surface color, came to the conclusion that surface color is complementary to body color. For many substances this relation does not hold, as later experiments have shown. Absorption has been found to be only one of the factors which determines selective reflection.[2] The reflecting power depends upon the coefficient of absorption and the index of refraction. Other things being equal, an increase in the index of refraction increases the reflecting power. On the red side of an absorption band, the index of refraction is much higher than on the violet side. For this reason the maximum of the reflection band is usually displaced toward the red from the maximum absorption.

The violet surface reflection of magnesium platinum cyanide follows this rule considered in respect to its relation to the ultra-violet absorption band. For the green surface color, however, the region of greatest reflection is toward the violet side of the absorption band with which it seems to be associated. It is evident from Fig. 1, Curve T, which gives the per cent. transmission on the two sides of the absorption band, that the coefficient of absorption for the wave-lengths on the violet side of the absorption band is much greater than that of the wave-lengths on the red side. This may account for the fact that the maximum of the green surface color is displaced toward the violet from the maximum of the absorption band.

The indices of refraction of various wave-lengths for this crystal have been determined by Horn,[3] as follows: $\mu = 1.363$ (C), 1.294 (D), 1.141 (E), 0.974 (F), 0.902 (G). The author hoped to be able to compute the coefficient of absorption for the different wave-lengths but did not feel that the results could be depended upon on account of the surface reflection which was complicated by the presence of the cover glass.

The two fluorescence bands are accounted for by the dichroic transmission. The only relation evident between the surface color and fluorescence is the position of these bands on different sides of the region of greatest absorption. The maximum green surface color is on the side of the absorption band on which the index of refraction is small and the coefficient of absorption great, while the fluorescence is on the side toward the longer wave-lengths where the index of refraction is greatest and the coefficient of absorption least. The plane of the electric vector of this

---

[1] Haidinger, Sitz. Ber. d Akad. d Wiss. Wien, Vol. 8, p. 97, 1852.

[2] Wood, Physical Optics, p. 440.

[3] Horn, N. Jahrbuch f. Min., 1898, Beil. Bd. 12, 269.

green surface reflection is the same as that of the "orange-yellow" fluorescence, *i. e.*, parallel to the axis of the crystal. The violet surface reflection does not seem to be associated with the absorption band which is the source of the fluorescence.

TRANSMISSION OF A SECTION PERPENDICULAR TO THE AXIS IN POLARIZED LIGHT.

In order to investigate further some of the phenomena observed by Lommel,[1] a number of measurements were made of the transmission of the crystal sections in polarized light.

Lommel[1] examined a thin section of a magnesium platinum cyanide crystal cut perpendicular to the optic axis in polarized light. In red light the ordinary system of rings and crosses was observed: in blue light, there were no rings and crosses, the so-called "polarization brushes" appearing instead.

Lommel explained this unusual phenomenon to be a result of the surface reflection which is characteristic of a section of the crystal cut in this direction. When incident light strikes a section cut perpendicular to the axis at an angle of exactly 90°, there is no selective reflection. If the incident light varies so much as 2° from this direction, thus making an angle with the axis of the crystal, that component of the vibration in which the electric vector is in the principal plane, the plane of incidence, is not transmitted but is totally reflected, producing the blue-violet surface reflection which is polarized with the electric vector in the plane of incidence. That component of the incident light in which the electric vector is perpendicular to the plane of incidence and also to a principal section of the crystal, is transmitted. Such a plate acts as a complete polarizer for blue light if the angle of incidence exceeds 2°.

This polarizing effect can, as Lommel suggested, be roughly verified by transmitting light through the crystal section held so that the angle of incidence is very small, then through a Nicol prism and observing it directly with the eye. If red light is used for transmission, no position can be found, upon rotation of the Nicol or the section, in which the light is cut off. When blue light is used, the intensity of the transmitted light varies greatly with a rotation of the Nicol or the section. The positions of maximum and minimum transmission are at right angles to each other.

To test the nature of this transmission, a spectrophotometric study was made of the transmission of a section. 08 mm. thick, cut perpendicular to the axis, for light polarized in different directions. The apparatus was set up as shown in Fig. 2.

---

[1] Lommel, Ann. der Physik., Vol. 9, p. 108, 1880.

The crystal section was placed in a holder *H* designed by Professor Chamberlain and made by Bausch and Lomb. In this holder, the section could be placed directly in front of the slit of the collimator, moved out of the field, and replaced in exactly the same position. The section, which was circular and of larger diameter than the slit, could also be rotated on a horizontal axis in front of the slit, the angle of rotation being measured by the scale attached to the collimator tube. Light from a 100 watt tungsten lamp, *S*, passed through ground glass plates, *P*, was used for transmission, light from the same source diffusely reflected from a block of magnesium carbonate, *M*, being used for comparison. A large Nicol prism, *N*, was placed just in front of the crystal holder. In all these transmission measurements the opening of the collimator slit in front of which the crystal was placed, was small and the peep hole in the focal plane of the telescope was as narrow as the opening in the collimator slit.

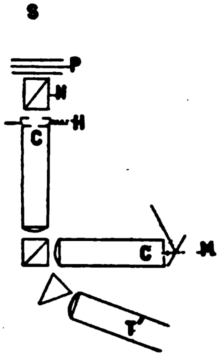


Fig. 2.

Arrangement of Apparatus *S*, **source of light;** *P*, **ground glass plates;** *H*, **crystal holder;** *C*, *C*, **collimator tubes;** *T'*, **telescope.**

To obtain the per cent. transmission for a given wave-length, the crystal section was placed in the holder in front of the slit. The width of the comparison slit was adjusted until a match was obtained and the reading of the micrometer regulating the adjustment of the slit was taken. The crystal was then removed from its position in front of the slit, and another setting was made. To obtain a transmission curve, measurements similar to these were made for wave-lengths at intervals through the visible spectrum, the crystal being replaced in front of the slit in exactly the same position by means of the crystal holder. From the data obtained, the per cent. transmission was computed, no correction being made for surface reflection.

Transmission curves were obtained for a section of the crystal .08 mm. thick cut perpendicular to the axis. The crystal was placed in the holder, its angular position noted, and its transmission measured. A second and third series of measurements were made with the section rotated through angles of 45° and 90°, respectively, from its original position, the Nicol remaining unchanged. No attempt was made to select a special position of the crystal for the first of these measurements since a section of a uniaxial crystal cut perpendicular to the axis should have the same properties regardless of its orientation.

The curves obtained, Fig. 3, show a marked difference in shape. In Curve 2, the per cent. transmission for red light is greater than in Curve

1; that for blue light is less than for Curve 1. This indicates that a rotation of the crystal which increases the transmission for wave-lengths on the red side of the absorption band decreases the transmission for wave-lengths on the blue side of this band.

The appearance of these curves made it seem desirable to investigate the transmission in a different way. Fig. 4 shows a series of curves giving the transmission of this same section for light polarized in a definite direction, the crystal being rotated by 16 steps through 360°.

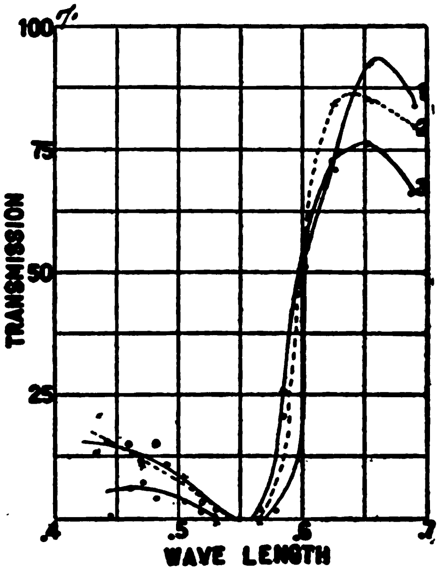


Fig. 3.

Transmission of polarized light at normal incidence through a section perpendicular to the axis .08 mm. thick. The three curves show the transmission with the crystal in three different positions 45° apart. Curve 1, 45° from Curve 2 and 90° from Curve 3.

Wave-length .6015μ which nearly coincides with the position of intersection of Curves 1, 2, and 3 of Fig. 3, shows practically no difference of intensity in different positions. Wave-length .6250μ shows a slight change in intensity upon rotation. Wave-lengths .4808, .4923, and .5050μ, indicate a decided difference in per cent. transmission with different positions of the crystal section.

The appearance of these curves and the phenomena observed when the section was examined in a polariscope with converging polarized light at first suggested that the crystal, instead of being uniaxial, might be orthorhombic, closely approaching tetragonal symmetry. The variation in the maxima of Curves 2, 3, 4 and 5, Fig. 4, seemed to be explained upon the hypothesis that the optical angle was small and the plane of the optical axis changed with wave-length. A section of a uniaxial crystal cut perpendicular to the axis should not show any difference in transmission for a given wave-length upon rotation, the incident light, as in this case being normal to the section.

A more probable explanation of the curves in Figs. 3 and 4 is based upon the supposition that the sections were not, as was supposed, exactly perpendicular to the axis of the crystal but varied so much as 2° from this direction. Lommel's[1] explanation of the polarizing effect of such a plate upon blue light when the angle of incidence exceeds this small value would account for the variation in the intensity of the blue light as shown in Fig. 3, and in Curves 3, 4, and 5 of Fig. 4. The variation in intensity of the blue wave-lengths is due to the surface color. This would account for the phenomena observed upon rotation of the section. The wave-lengths of Curves 3, 4, and 5, Fig. 4, show polarization but not complete

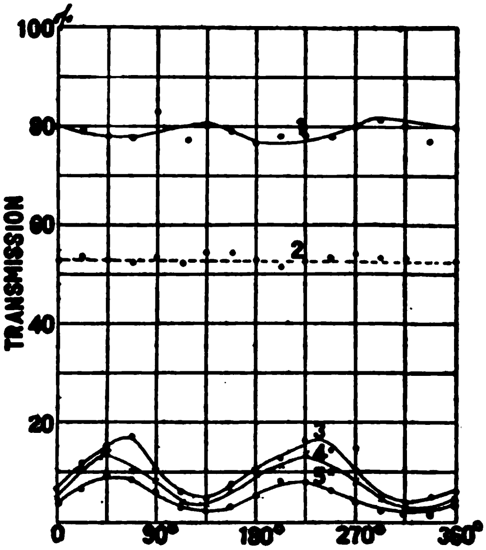


Fig. 4.

Transmission of polarized light through section .08 mm. thick cut perpendicular to the axis for different wave-lengths. The plane of the electric vector of the light used for transmission was kept constant and the section rotated through 365° by 16 steps.

Curve 1, wave-length .6250μ.
Curve 2, wave-length .6015μ.
Curve 3, wave-length .4808μ.
Curve 4, wave-length .4923μ.
Curve 5, wave-length .5050μ.

---

[1] Lommel, Ann. der Physik, Vol. 9, p. 108, 1880.

polarization. The maximum of the blue-violet surface color is shown in Fig. 1, Curve *S*, is toward the shorter wave-lengths from those measured in the curves of Fig. 4.

The variation in transmission of the red end of the curves shown in Fig. 3 and in Curve 1 of Fig. 4 is due to a change in the fluorescence upon rotation of the plate in polarized light. Since the fluorescence changes with a variation in the angle between the axis of the crystal and the direction of the electric vector of the exciting light, the rotation of a plate which was not cut exactly perpendicular to the axis might be expected to produce a change in the fluorescence.

In order to prove that the fluorescence was a decided factor in the transmitted light, the plate was examined in light which had been passed through a deep blue solution of cupric ammonium sulphate. When this light was normally transmitted through the plate to the eye and the plate was rotated upon an axis perpendicular to its own plane, the red color of the fluorescent light was seen in a position at right angles to that which was most transparent to blue light. The incident light contained no red wave-lengths.

It is evident from the curves of Fig. 3 that the position of the crystal section which gives the lowest per cent. transmission for blue light gives the highest for red. This is verified by the curves in Fig. 4. The slight variation in Curve 1 is due to fluorescence, this fluorescence being small in comparison with the intensity of light transmitted from the source. The wave-length of Curve 2 is a region of greater absorption and fluorescent light of this wave-length is absorbed to a greater extent, the transmission, in this case showing practically no change due to fluorescence.

A section .15 mm. thick cut perpendicular to the axis was examined in the same way and a similar change in intensity of both blue and red wave-lengths was observed upon rotation, the position of maximum for blue corresponding aprpoximately that of minimum for red. If the phenomena observed were really due to the plates not being cut exactly perpendicular to the axis, both of the sections examined were in error.

TRANSMISSION OF A SECTION PARALLEL TO THE AXIS IN POLARIZED LIGHT.

A similar study of the transmission of a section parallel to the axis is of interest since the dichroic transmission is evident to the eye when light from a white cloud is passed through the crystal section, then through the Nicol. When the crystal section or the Nicol is rotated, the transmitted light changes from a purple-red color to blood-red upon a rotation of 90°. The purple-red is observed when the electric vector of the light passed through the Nicol is perpendicular to the axis of the crystal; the blood-red when it is parallel to the axis.

Fig. 5 shows a series of curves obtained from a section .08 mm. thick cut parallel to the axis. The crystal section was placed in the crystal holder and the transmission determined for light polarized in a definite direction, the angular position of the crystal being varied for the different curves. In Curve 1, the plane of the electric vector was perpendicular to the axis of the crystal. With the crystal placed in this position there was no green surface color. Observed directly, the transmitted light looks purple-red. Both the blue and the red ends of the spectrum are transmitted. Curve 5 shows the transmission for polarized light in which the electric vector is parallel to the axis of the crystal. The per cent. of red transmission in this case is much greater than that of blue. Light polarized in this direction brings out the green surface color. Observed directly, the transmission color is a much yellower red in this

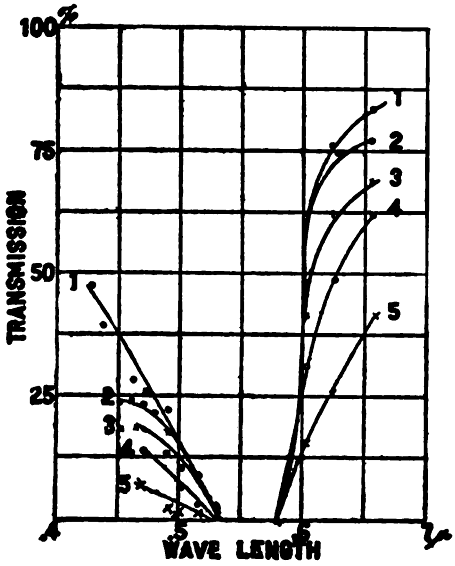


Fig. 5.

Per cent. transmission of section .08 mm. thick cut parallel to the axis for light polarized in different directions.

Curve 1, angle between electric vector and axis of crystal 90°.
Curve 2, angle = 67.5°.
Curve 3, angle = 45°.
Curve 4, angle = 22.5°.
Curve 5, angle = 0°.

position. Transmission for intermediate angles is shown in Curves 2, 3, and 4.

The crystal was then placed in the holder and rotated, keeping the position of the Nicol fixed, in a manner similar to the method used in obtaining the curves of Fig. 4. By this rotation, the angle between the electric vector of the incident light and the axis of the crystal was changed. The change in transmission for definite wave-lengths due to a variation in this angle is shown in the curves of Fig. 6. The form of these curves is such as should be expected.

The apparatus was tested in order to determine whether or not selective transmission of the slit or selective reflection from any of the parts of the spectrophotometer (selective with respect to the plane of vibration) might have a perceptible influence upon results such as these. It was found that errors due to this source might be considered negligible.

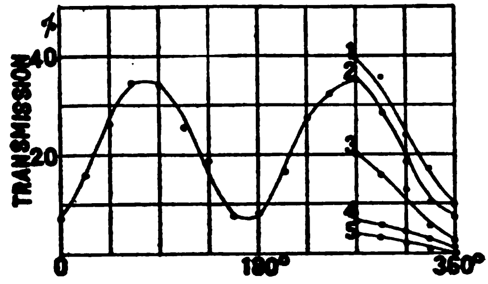


Fig. 6.

Per cent. transmission for polarized light of definite wave-lengths through a section parallel to the axis .08 mm. thick, the angle between the electric vector and the direction of the crystal axis being varied.

Curve 1, wave-length .6543μ.
Curve 2, wave-length .6250μ.
Curve 3, wave-length .6015μ.
Curve 4, wave-length .5050μ.
Curve 5, wave-length .4923μ.

The section used in obtaining the curves of Figs. 5 and 6 was not nearly so transparent as the section cut in the other direction used for the measurements shown in Figs. 3 and 4, although the two sections were of the same thickness. The section parallel to the axis had in it striations, due to the cleavage of the crystal, and the surface, which had a brilliant green surface color, was much less uniform and more highly reflecting than the section cut in the other direction.

In order to determine whether or not a rotation of the crystal plate cut perpendicular to the axis produced a change in surface color as well as in transmission, the apparatus was set up as before. A Nicol prism was placed between the source of light and the crystal section which was supported in front of the slit in a vertical plane in such a way that it could be rotated upon a horizontal axis, everything else being kept fixed.

It was found that, in some positions, the intensity of the surface reflection was greater than in others. Fig. 7 shows this surface reflection in two positions 45° apart, the intensity of the incident light and comparison source being kept constant. There is a difference of intensity and possibly a slight shift in the position of maximum. The polarizer was removed and a difference in intensity was still evident.

This change may be accounted for by the supposition that the section was not exactly perpendicular to the axis. A rotation of the section would change the angle between the axis of the crystal and the incident light, the surface color being more intense at some angles than at others.

Work upon other double cyanides of platinum is now in progress.

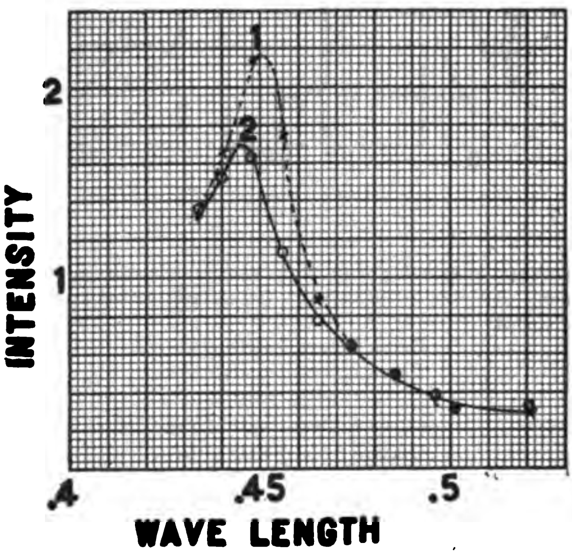


Fig. 7.

Violet surface reflection of a section perpendicular to the axis in polarized light.

The study of these crystals was undertaken at the suggestion of Professors Nichols and Merritt, of Cornell University. To them the author is greatly indebted both for their interest and suggestions during the progress of the work, and for their generosity in providing from their Carnegie grant much of the apparatus and material necessary. A part of the investigation was carried on in their research laboratory.

Grateful acknowledgment is made of the assistance of Professor Gill and Dr. Wilber, of the Cornell Department of Geology, in this study, especially in the interpretation of the transmission curves.

The author wishes to express her appreciation of the interest of Professor Chamberlain, of Vassar College, in this work and of the kindness of Professor Gibbs, of Cornell, in permitting the use of some apparatus he had set up.

Vassar College,
Poughkeepsie, New York.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ADDITIONAL DATA ON THE ILLUMINATION-PHOTO-ELECTRIC CURRENT RELATIONSHIP.[1]

BY HERBERT E. IVES.

IN a previous paper presented before the Society[2] it was shown that the relation between illumination and photo-electric current in potassium cells is not linear, but is different for every cell. It was concluded that the most important influencing factor is the pressure of the gas in the cell. Results were given obtained with a cell which was exhausted to different pressures on the pump and which showed a number of the curves found in individual cells. The new data herewith presented were all obtained from one cell whose construction permitted the passage of a glow discharge between the platinum electrode and the guard ring without affecting the potassium surface. The effect of this discharge was to improve the vacuum, as is well known.

Voltage-current and illumination-current curves were taken at four stages:

1. With the cell in its original condition, gas pressure probably .01 mm. or more.
2. After running the discharge from a small transformer until current no longer passed.
3. After 18 hours running on an induction coil.
4. Upon standing 18 hours thereafter.

RESULTS.

The voltage-current curves show various stages between one extremely convex to the voltage axis, and one extremely concave thereto.

The illumination-current curves correspondingly change from convex to the illumination axis to concave.

Points of interest in the effect of variation of applied voltage will be noted in the complete publication. These results confirm the conclusion from the previous work that the photo-electric current is not as yet proved to be a linear function of illumination.

---

[1] Abstract of a paper presented at New York meeting of Physical Society, February 28, 1914.

[2] Atlanta meeting.

Second Series. *June, 1914* *Vol. III., No. 6.*

THE

PHYSICAL REVIEW.

A STUDY OF THE LONGITUDINAL VIBRATION OF WIRES.

By George A. Lindsay.

I. Introduction.

THE elastic behavior of wires has been very carefully investigated by means of torsional vibrations. This method lends itself most readily, perhaps, to the study of internal friction, for the period may easily be regulated to any desired length, the amplitude may be made large, and, by suitable adjustment of the suspended mass, the free vibration may be continued for a comparatively long time.

Weber[1] was the first to observe that a vibrating body is damped in a vacuum, thus showing with certainty the existence of an internal cause of damping, and O. E. Meyer[2] made the first quantitative study of the phenomenon, by observing the damping of torsional vibrations.

Voight[3] measured the damping of flexural, as well as torsional vibrations, with the view of determining whether, according to Boltzmann's theory, the logarithmic decrement is independent of the period, as the latter shows it should be if damping is caused by the elastic after-effect; or whether there is really internal friction, in which case the logarithmic decrement should depend on the period. The results of his work were not entirely in favor of either theory. For flexular vibrations he found that, for copper and some other metals, the logarithmic decrement varied inversely as the period, thus supporting the internal friction theory, while with aluminum, cast iron, and cadmium the logarithmic decrement was much more nearly constant. In a few cases the decrement actually increased with increasing period, which is at variance with both theories. His conclusion was that in some cases the preponderant factor in damping is internal friction, in other cases it is the after-effect. Voight also found, as Schmidt[4] had done earlier, that the logarithmic decrement varies

---

[1] Pogg. Ann., 34, p. 247, 1835.

[2] Ibid., 113, pp. 77, 193, 1861.

[3] Abh. der Königl. Gesell. der Wiss. zu Göttingen, 38, 1892.

[4] Wied. Ann., 2, p. 48, 1877.

approximately as the square of the amplitude. Streintz,[1] however, found it to be independent of the amplitude in torsional vibrations, and also of the period, if the period were varied by changing the moment of inertia of the suspended mass. Guthe and Sieg[2] found certain platinum-iridium wires, when vibrated torsionally, to give a maximum value of the logarithmic decrement, and the position of the maximum on the decrement-amplitude curve depended on the initial amplitude. This work will be referred to more in detail later in comparing with the damping of longitudinal vibrations. Harris,[3] using bismuth wires, observed a decrease of the logarithmic decrement with decreasing amplitude, but no maximum or minimum values.

Other experiments, notably those of Streintz, Wiechert,[4] and Bouasse[5] and Carriere, have shown that the previous history of the wire very markedly influences the after-effect and the damping. While the after-effect has been carefully observed for longitudinal deformation, as far as the writer has been able to find, little or nothing has been done on the problem of the quantitative measurement of the damping of longitudinal vibrations.

The present investigation is an attempt to measure as accurately as possible the period of longitudinal vibrations of wires, to consider possible causes of difference between this and the theoretical period, and to measure the damping of the vibrations. Both static and dynamic observations will be given which indicate that the modulus of the wires is not exactly a constant with varying extension. An expression for the period involving the amplitude will be derived, which shows that this variation of the modulus cannot account for the observed variation of the period with amplitude. It will also be shown that, with the ordinary assumptions, the variation of the logarithmic decrement with amplitude is not sufficient to explain the variation of the period.

II. ELONGATION OF THE WIRES.

Apparatus.

Four wires were used; one each of copper, steel, phosphor-bronze, and platinum-iridium. The steel wire was new piano-wire; the copper, a piece from a spool of commercial wire. Three of the four wires were about 230 cm. long, while the fourth, the platinum-iridium, was only about

---

[1] Wien. Ber., 69, II. Abt., p. 337, 1874: 80, II. Abt., p. 397, 1879.

[2] PHYS. REV., Vol. 30, No. 4, 1910.

[3] PHYS. REV., Vol. 35, No. 2, 1912.

[4] Wied. Ann., 50, p. 546, 1893.

[5] Ann. de Fac. des Sci. de Toulouse, II., 431; III., 217; IV., 357. Ann. de Chimie et de Physique, 8me Serie, t. 14, p. 190.

140 cm. long. No attempt was made to take account of previous treatment of the wires, since the adjustment for vibration was rather difficult, and it was usually necessary to vibrate the wire for some time before measurements could be made. Excepting the platinum-iridium, which contained 40 per cent. of iridium, and was prepared by Dr. Heraeus, of Hanau, the composition of the wires was not well known, and it is not to be expected that the results are rigidly characteristic of these metals. In fact, it is known that hardness has a great influence on the internal friction of wires. Annealed wires exhibit greater damping than tempered ones of the same material.

A heavy iron bracket was fixed rigidly to the brick wall of the laboratory. A strap of iron was bolted firmly to the front of the bracket; but this was not used as a clamp, for clamping the wire would flatten it, and weaken it at the point where it entered the clamp, besides rendering uncertain the location of the upper end of the vibrating length. Instead, a small slot, only large enough to admit the wire easily, was sawed in the iron strap. This slot was filled with solder, and the upper end of the wire was soldered in, thus attaching the wire very firmly to the support. In order to keep the temperature uniform and fairly constant, the wire was enclosed in a wooden box, the internal cross-section of which was about 16 cm.^{2} The upper end of the box was lightly covered with cotton batting to prevent air currents passing through, yet not so as to interfere with the vibrations. Two thermometers were inserted through the side of the box, one near the top and the other near the bottom.

A fan was installed near the box to keep the air in the room in circulation. Without the fan the temperature of the upper part of the box sometimes became as much as 3 degrees higher than the lower end, especially in colder weather, when the room was heated by pipes near the ceiling. When the fan was working the upper and lower parts of the box differed usually by not more than 0°.1 C. A variation of one or two degrees has very little effect on the period of vibration, since the modulus changes only slightly with the temperature; but in determining statically the elongation due to a certain load, it was very important that the temperature should not change between readings.

The following precautions were taken to straighten the wires before using. The steel and phosphor-bronze wires were suspended and stretched for about one day by ½ the maximum load which they were required to carry. The copper wire was very soft, and was straightened by passing it through a drawplate, using a hole the size of the wire. This straightened the wire without drawing it any smaller. The platinum-iridium wire was moderately loaded and annealed by passing through it an electric current sufficient to raise it to a yellow heat.

Instantaneous Recovery.

In order to make a comparison of static and dynamic moduli, the simple method of measuring the elongation directly was chosen. Consider a wire loaded as in Fig. 1. Let *P* be the position of the lowest point of the wire when at rest. From the elastic forces called out by the distortion, *P* has a tendency to return to some point *O*. This point may not be at all the position of *P* before the load was imposed. It does not even remain constant when *P* moves up and down. The variation of *O* is due to two things: (1) the elastic after-effect; (2) the heating effect of varying the length of the wire. When the wire is at rest, (2) is not to be considered; therefore, disregarding this for the present, let us call $OP = e$ the instantaneous recovery. This is evidently the distance on which the restoring force depends, and this is the distance it is desired to measure.

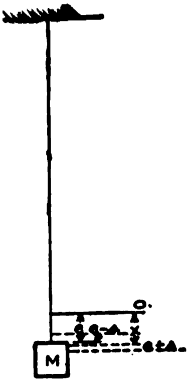


Fig. 1.

Lever Systems for Measuring Recovery.

In order to determine changes occurring very soon after unloading, the device shown in Figs. 2, 3, and 4 was used. Figs. 2 and 3 show two sections at right angles to each other. Fig. 4 shows one of two similar levers, made each of two stips of brass bent and soldered together along one half their length. Small conical hollows were made at *ee*, Fig. 4, to receive the points of *p* in Fig. 3. The arms of the lever were bent just far enough apart so they would hold on the axle *p* without play, and with little friction. The lever was thus free to move about the axis of *p* in a vertical circle. *L*, Fig. 2, is this lever seen from the side. *d* is a small closely fitting pin to one end of which the wire *W* was lightly soldered. *m* is a small mirror with its plane at right angles to the lever, and containing the axis of *p*. One of the levers was used for the wire under test, the other for a comparison wire hung about 2 cm. from the first. The mirrors on the two levers were placed so close together that by means of a single telescope two scales could be viewed at the same time, one reflected from each mirror.

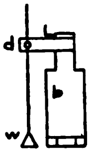


Fig. 2.

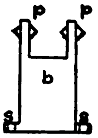


Fig. 3.

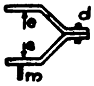


Fig. 4.

Wire No. 2 indicated any sagging of the bracket, and change of temperature. It was found that with the fan running and the box in position the temperature change during the readings necessary for a single determination of the elongation was ordinarily too small to be observed. For measuring the elongation the mass of figure 1 was replaced by a scale pan.

A mass was placed on the pan and after some time a reading was taken on both scales, and the mass was immediately removed. Then readings were taken on the wire under test at the end of 5 sec., 15 sec., 1 min., 2 min., and 3 min. Two or three readings on the comparison wire gave corrections to be applied for sagging of the support, and for temperature changes. The comparative rigidity of the lever system allowed a reliable reading to be taken 5 sec. after removal of the mass. The results are shown for the copper wire in figure 5. The numbers in parentheses refer to different masses removed from the pan as shown in the accompanying table.

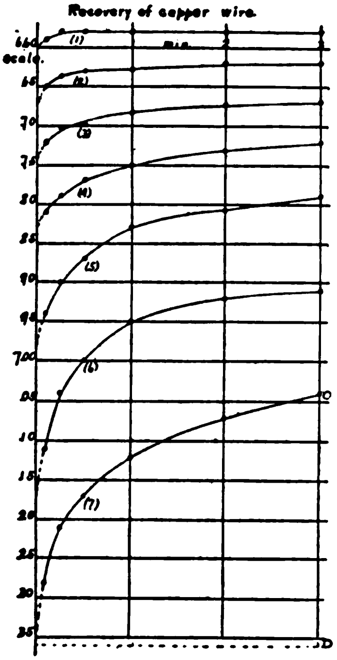


Fig. 5.

Copper.

	Mass, gms.
(1)	461
(2)	930
(3)	1,401
(4)	1,872
(5)	2,343
(6)	2,815
(7)	3,295

Each mass was left on the pan 2 min. The relative positions of the curves in Fig. 5 show how slowly the copper wire recovered from strain. The after-effect and the heating effect are both present in these curves. The curve for a time interval less than 5 sec. is unknown, but producing it as the observed part seems to indicate we would have an intersection on the scale axis as shown by the dotted line.

Owing to the various quantities upon which the computed elongation depends when deduced from the scale readings, and the possibility of error, especially in the motion of the pin *d*, shown in Fig. 2, it was thought best to deter[illegible] apparatus only for the small changes taking place in the [illegible] minute or two, and to measure the entire recovery of the wire sin[illegible] by means of a micrometer microscope focused directly on a point [illegible]. Then the correction shown by Fig. 5, and that [illegible] the sagging [illegible] bracket were applied afterward.

For all experiments it was seen that in one half min. to one min. the wire had nearly recovered from the strain. The microscopic readings for these [illegible] therefore be taken soon after removal of the load. With the copper they were all taken long enough after release so that the change in length had nearly ceased, but the time of each reading was noted, and the proper correction applied from the plots.

Instantaneous Recovery Independent of Period of Deformation.

It was found by means of the lever system that the length of time the load remained on the pan did not influence the instantaneous recovery. The following table shows the instantaneous recovery for various periods of deformation of the copper wire. t is the length of time the weight remained on the pan, e the instantaneous recovery in cm. of the scale. It is the difference between the intersection of the curve with the scale axis (see Fig. 5) and the reading just before release.

TABLE I.

Load = 2 Kg.

t min.	e.
1	11.25
5	11.23
15	11.20
30	11.22
60	11.22
30	11.23
15	11.21
5	11.20
1	11.23

This indicates that although the wire may suffer a gradual change when stressed by a constant force, a given point of the wire has always the same instantaneous recovery.

Since the change observed by aid of the levers and mirrors after the removal of the load is small compared with the total recovery, we may compute the change s in the length of the wire, corresponding to the distance OD shown on the plot of Fig. 5, by the equation

$$s = \frac{1}{2}\frac{r}{a} OD, \qquad (1)$$

where r is the radius of the lever arm and a is the distance from mirror to scale. r was determined by measuring, with a microscope, the diameter of the circle in which the pin d moves when the lever is rotated about the axis. r was thus found to be 2.124 cm.

Temperature Change Due to Loading and Unloading.

The formula for temperature change given by Sir William Thomson[1] is

$$t = \frac{AT\alpha}{\omega c}\Delta p, \qquad (2)$$

where A = the reciprocal of Joule's equivalent.
T = abs. temp.
α = coeff. of linear expansion.
ω = linear density of the wire.
c = specific heat.

Edlund[2] found, experimentally, that this formula gave too high a value for t, and according to his results $A = \frac{1}{68270}$ when Δp is in gm.

When the load is suddenly removed the wire is heated, and as it cools it contracts, which contraction added to the after-effect gives the curves in Fig. 5. To compute the part due to the cooling of the wire we have the change of length due to a change in temperature t,

$$\Delta l = \frac{AT\alpha^2 L}{\omega c}\Delta p. \qquad (3)$$

If we take L = 200 cm.,
and Δp = 3,000 gm., Table II. shows the Δl of equation (3) for each of the four wires. Edlund's value of A is used.

Table II.

Wire	Δl cm.
Steel	0.0010
Copper	0.0004
Phos. br.	0.0020
Pt.-ir.	0.0008

The instantaneous recovery of the wires is given by

$$e = e' - s + \Delta l, \qquad (4)$$

where e' is the elongation as measured by the microscope directly. Δl must be determined for the particular length used in obtaining s; then if this is not the same as the length used in measuring e', $s - \Delta l$ must be reduced to that length before subtracting from e'. For the phosphor-bronze and platinum-iridium $s = \Delta l$ as nearly as the plots will show. For steel, s was a little more than twice Δl, and for copper, nearly ten

---

[1] Math. and Phys. Papers, Vol. 3, p. 66.

[2] Pogg. Ann., 126, p. 539. 1865.

times Δl. This indicates that phosphor-bronze and platinum-iridium have no after-effect, yet this supposition does not agree with the results of timing. Reasons will be given later for supposing that all the wires have an elastic after-effect.

Variation of Instantaneous Recovery with Temperature

To find how the instantaneous recovery varies with the temperature, which is equivalent to finding the variation of the modulus with temperature, the room was kept successively at ten different temperatures ranging from 15°.7 to 26°.4 C., and the instantaneous recovery was determined for each temperature for all the masses concerned in Fig. 5. This test was made for copper only, for the variation of the modulus with temperature is much smaller for the others. According to Pisati it is only one part in 10,000 per degree for steel at temperatures from 0° to 50°. With copper, however, it is large enough to be detected over the range of only 10° employed here, and by plotting instantaneous recoveries and temperatures the equation

$$e_t = e_{23}[1 + 0.0009\,(t - 23)] \qquad (5)$$

was found for the relation between the recovery and the temperature.

Since the word elongation is not to be used in any other sense in this paper, "elongation" will henceforth be used to denote the instantaneous recovery.

Rapidity with Which the Wire Regains Normal Temperature.

The heat evolved by the removal of the load is soon dissipated. A test was made on the copper wire, which, with a diameter of 0.5 mm., was much the largest wire of the four, to see how much time was required for the wire to regain its original temperature. An iron-constantan thermocouple was connected to the wire by separating one of the junctions, passing the separated elements through small holes in the side of the box, and soldering them as lightly as possible to the copper wire, a few cm. apart. The junctions were covered with a little cotton batting so they might cool at most no faster than the remainder of the wire. The other junction of the thermocouple was kept at a constant temperature outside the box. The cross-section of the thermocouple wire was about 1/30 that of the copper wire to which it was attached.

When a mass of 2 kg. was removed from the pan, the deflection of a galvanometer in the thermocouple circuit had practically all disappeared in one minute, showing that in that time the wire had regained its normal temperature. Since the other wires were of less than one half the diameter of the copper wire, the rise in temperature would no doubt disappear in a much shorter time for them.

Results for Elongation.

In Table III. are given the elongations for the various wires. The values of e for copper were all reduced to 23° by formula (5). While the entire set of elongations for copper was taken at 21°, the wires were vibrated at higher temperatures, and it was for comparison with the vibration results that the reduction was made. For all the other wires the variation of modulus with temperature was neglected.

M and e are corresponding masses and elongations, the zero for each being taken with the pan alone suspended.

M includes one half the mass of the wire.

Mass of the pan = 223 gm.

L' = length for which the elongation was measured.

L = vibration length.

e = elongation for the length L.

D = diameter of the wire.

TABLE III.

Copper.
L' = 209.7 cm.
L = 232.1 cm.
D = 0.586 mm.
Temp. 21°.0

Steel.
L' = 154.1 cm.
L = 231.1 cm.
D = 0.217 mm.
Temp. 24°.2

M Gm.	e Cm.	e_{23} Cm.	M/e.	M Gm.	e Cm.	M/e.
957	0.0821	0.0822	11,640	1,000	0.2874	3,478
1,387	0.1182	0.1184	11,710	1,500	0.4309	3,480
1,818	0.1560	0.1563	11,630	2,000	0.5766	3,467
2,248	0.1941	0.1945	11,560	2,500	0.7213	3,465
2,679	0.2315	0.2320	11,550	3,000	0.8675	3,457
3,101	0.2690	0.2695	11,510			

Phosphor-bronze.
L' = 187.6 cm. D = 0.239 mm.
L = 231.5 cm. Temp. = 22°.5.

Platinum-iridium.
L' = 140.5 cm. D = 0.206 mm.
L = 144.6 cm. Temp. = 22°.5.

M Gm.	e Cm.	M/e.	M Gm.	e Cm.	M/e.
953	0.4138	2,303	953	0.1461	6,523
1,383	0.6023	2,296	1,383	0.2119	6,527
1,814	0.7912	2,293	1,814	0.2780	6,525
2,244	0.9816	2,286	2,244	0.3448	6,508
2,675	1.1742	2,278	2,675	0.4137	6,466
			3,097	0.4812	6,436

M/e has no significance for the material of the wire, since it contains the length and diameter, but as long as these are constant it serves to indicate whether Young's modulus is constant or not. Owing to the shortness of the wires used, no great degree of absolute accuracy is claimed for the above elongations, and also, since the computation of the period of vibration does not demand it Young's modulus has not been computed. Its absolute value is of little importance here, but its variation is of great importance.

III. Determination of Frequency of the Vibrations.

Apparatus.

The pan was removed from the wire, and in its place was soldered a brass disk 6½ cm. in diameter, provided with threads on the circumference, so that over it might be screwed a hollow cylindrical shell about 14 cm. long. Inside this shell could be attached five other solid disks, making six different masses which could be used in vibrations. The shell was closed at the bottom, so that for all masses used, the same surface was exposed to the air and the damping due to the air friction was, therefore, constant.

From the lower end of the cylinder a brass rod 8 mm. in diameter projected vertically downward an additional 10 cm., and carried on its lower end a small soft iron armature. The sections of the mass separated from the cylinder are shown in Fig. 6. The electric circuit was arranged, as in Fig. 7, so that the wire was self-driven after the manner of the electrically driven tuning fork. The switch *L* closed both circuits at once. The vibration could be started by raising or lowering the adjustable cup *g* until, when the proper height was reached, the vibration would start and the amplitude could be controlled by the rheostat.

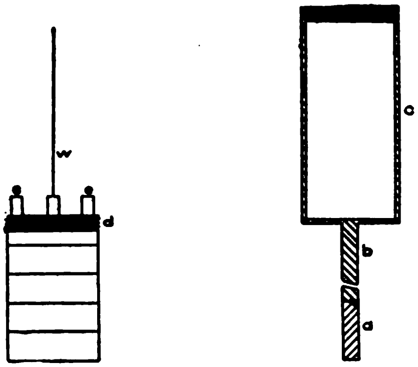


Fig. 6.

a, soft iron armature; *c*, cylindrical shell; *d*, upper disk which screws into the shell.

A tuning fork supplied with adjustable masses for regulating the period, and carrying a lens on one prong, was arranged to vibrate horizontally in front of the wire, so that when a drop of mercury was placed on the wire a Lissajous' figure could be viewed through the vibrating lens by means of a microscope. A phonic wheel was included in the circuit with the tuning fork, so that the fork could be accurately rated while the wire was vibrating. The vibration was so slow that the time required for an elastic pulse to travel the length of the wire was very short compared with the period of the wire, therefore we may consider the wire to be uniformly strained throughout its entire length at all times.

Measuring the Free Period.

This, of course, was a forced vibration of the wire, and the period was therefore slightly less than that of the free vibration. It was found, however, that by adjusting so that the fork was slightly too slow, then shutting off the current driving the wire, the free period could be obtained with considerable accuracy.

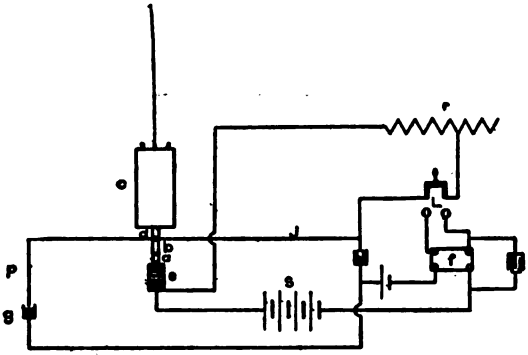


Fig. 7.

e, electromagnet actuated by battery *s*; *f*, relay; *g*, mercury cup; *j*, fine wire soldered to moving system at *d*; *p*, stiff platinum-tipped wire for contact with mercury at *g*.

The free vibration could be observed easily for ¾ min. with the copper wire, about 4 min. with the platinum-iridium wire, and 5 min. with the steel and phosphor-bronze. In case the period varied with the amplitude, as it did with the copper and platinum-iridium, and also to a slight extent with the phosphor-bronze, the fork was set too slow for small amplitudes, and too fast for large ones. By means of the micrometer microscope the amplitude for which the Lissajous' figure was at rest could be satisfactorily determined. This, however, necessitated changing the rate of the fork, and so rating again by the phonic wheel for every amplitude measured, an expenditure of time which was partly avoided by counting the number of seconds elapsing during one cycle of the Lissajous' figure and taking for the mean amplitude, the average of the amplitudes at the beginning and the end of the count.

Relation of Frequency to Amplitude.

For the steel wire no variation of the frequency with amplitude could be detected. The phosphor-bronze showed a very slight increase in frequency with decreasing amplitude, the variation for platinum-iridium was more marked, and the copper wire showed the greatest variation of all. In all cases the plot of frequency and amplitude was practically a straight line, which, produced to the frequency axis, gave the frequency

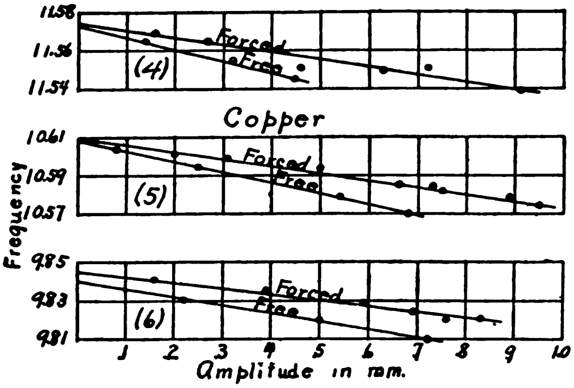


Fig. 8.

for infinitely small vibrations. The equation connecting frequency and amplitude is $n = n_0 - bA$, where b is a positive number. The relation is shown graphically for part of the observations in Figs. 8 and 9. The numbers (4), (5), (6), in parentheses, refer respectively to the largest

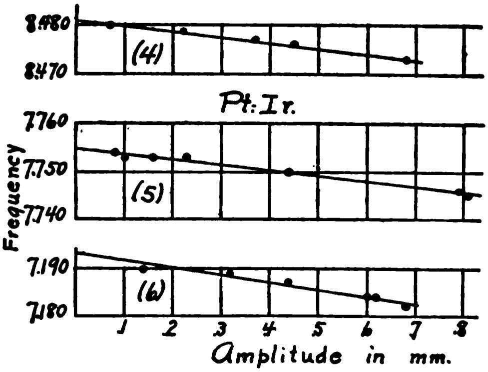


Fig. 9.

three masses given in Tables V. and VI., in order of increasing magnitude. The cause of this variation of period with amplitude will be discussed later.

Free and Forced Vibrations.

In Fig. 8 for copper are included the plots of the forced frequency. It is seen that this also gives a straight line of nearly the same slope as that of the free vibrations, and the forced period differs very little from the free. That there is not a greater difference is due to the fact that the relay included in the circuit aided the induction in delaying the pulse given by the electromagnet. If the pulse were given just at the instant when the armature reached the middle of its downward motion, there would be no difference of the free and forced periods.

Although the force acting on the armature is not simply harmonic with respect to the time yet it may be represented by a Fourier's series, and it may be shown from the difference between the forced and the free periods that for small amplitudes the fundamental of the Fourier's series is in the neighborhood of 65° behind the motion of the armature.

Table IV. is given as an illustration of the manner of timing.

Table IV.

Copper.

$M = 2{,}678$ gm. $\rho = 5/1$. Temp. = 21°.9 C.

N = frequency of fork.
n = frequency of wire.
$\rho = N/n$.

N	Forced.		Free.		Sec. per Cycle.	Wire Slow or Fast.
	Amp. (Mm.)	n	Amp. (Mm.)	n		
			0.08	10.604		
53.020	0.20	10.602			102	slow
	0.31	10.598			34	slow
			0.25	10.593		
	0.50	10.593			∞	——
52.964	0.66	10.586			31	slow
	0.73	10.583			21	slow
			0.54	10.578		
	0.75	10.582			44	fast
52.888	0.89	10.578			∞	——
	0.95	10.574			50	slow
52.860			0.68	10.572		

The 6th column shows the number of seconds required for the Lissajous' figure to pass through one cycle, while the last indicates whether the wire was faster or slower than 1/5 the rate of the fork.

Tables V. and VI. show in condensed form the free amplitudes and frequencies for the various masses.

Such tables are not given for phosphor-bronze and steel for reasons already stated.

TABLE V.

Copper.

Mass, Gm.	Amp., Mm.	n	p	Temp., C.
956	0.10	17.700	5/2	23°.7
	.15	17.693		
	.33	17.676		
1,386	.17	14.715	3/1	23°.8
	.32	14.696		
	.59	14.672		
1,817	.19	12.853	7/2	24°.0
	.24	12.848		
	.40	12.839		
2,247	.14	11.565	4/1	24°.0
	.32	11.555		
	.45	11.545		
2,678	.08	10.604	5/1	21°.7
	.25	10.593		
	.54	10.578		
	.68	10.572		
3,100	.22	9.831	5/1	23°.8
	.50	9.818		
	.72	9.810		

Variation of Frequency with Mass.

Since, if Hooke's Law holds the period is proportional to the square root of the mass, we should have the product of mass and the square of the frequency equal to a constant. From Table III., the ratio M/e is not a constant. It decreases with increasing mass, except for the first two masses of the three wires, copper, steel and platinum-iridium. It would not be concluded from this alone that the elongation is not proportional to the weight removed, for there is considerable uncertainty about the point to which the curves of Fig. 5 should be produced before they reach the axis of ordinates. However the results of timing also show that M/e is not a constant, for Mn^2 is not constant, except for the case of copper. Table VII. shows the masses, frequencies, and Mn^2, for each of the four wires.

The n for the copper and the platinum-iridium is obtained from Figs. 8 and 9. It is the n indicated by the straight line, for the amplitude zero. For copper a small correction to n was made to reduce it to 23° temperature, the same temperature as that for the elongations of Table

Table VI.

Platinum-iridium.

Mass, Gm.	Amp., Mm.	n	p	Temp., C.
953	0.08 .20 .44 .58 .80	13.056 13.053 13.046 13.044 13.037	3/1	23°.0
1,383	0.09 .47 .75	10.836 10.828 10.824	4/1	23°.2
1,814	0.05 .12 .21 .66 .98	9.450 9.449 9.447 9.442 9.439	5/1	24°.4
2,244	0.07 .22 .37 .45 .68	8.480 8.479 8.477 8.476 8.473	5/1	24°.5
2,675	0.08 .10 .16 .23 .44 .79 .81	7.754 7.753 7.753 7.753 7.750 7.746 7.745	5/1	24°.6
3,097	0.14 .32 .44 .60 .62 .68 .78	7.190 7.189 7.187 7.184 7.183 7.182 7.181	6/1	24°.6

III. Since $1/n \propto \sqrt{e}$, one half the correction in per cent. which was made for e, was made here for n: or we might use a formula similar to equation (5)

$$n_t = n_{23}[1 - 0.00045(t - 23)]. \tag{6}$$

For the other three wires the correction was neglected for reasons already stated.

TABLE VII.

Copper.						Steel.			
M[1] Gm.	n	Temp.	Corr.	n_0.	Mn^2.	M Gm.	n	Temp.	Mn^2.
956	17.710	23°.7	+0.006	17.716	3.001×10^5	954	9.525	21°.5	8.655×10^4
1,386	14.732	23°.8	+0.006	14.738	3.011	1,384	7.908	21°.6	8.655
1,817	12.865	24°.0	+0.006	12.871	3.010	1,815	5.903	21°.7	8.649
2,247	11.573	24°.0	+0.005	11.578	3.012	2,245	6.199	23°.1	8.627
2,678	10.607	21°.7	−0.005	10.602	3.010	2,676	5.675	23°.0	8.618
3,100	9.841	23°.8	+0.004	9.845	3.005×10^5	3,098	5.268	22°.7	8.598×10^4

Phosphor-bronze.				Platinum-iridium.			
M Gm.	n	Temp.	Mn^2.	M Gm.	n	Temp.	Mn^2.
953	7.767	21.3	5.749×10^4	953	13.058	23.0	1.625×10^5
1,383	6.437	21.8	5.731	1,383	10.837	23.2	1.624
1,814	5.611	21.9	5.711	1,814	9.450	24.4	1.620
2,244	5.038	22.0	5.696	2,244	8.481	24.5	1.614
2,675	4.594	21.3	5.646×10^4	2,675	7.755	24.6	1.609
				3,097	7.193	24.6	1.602×10^5

In Table VII. all the wires but the copper show a steady decrease in Mn^2 with increase of M. The decrease is very small, or zero, between the first two masses, and it has been noted that there was, in general, no decrease of M/e in Table III., until the second mass was reached.

Relation between M and e.

For all except the small masses the results of both the direct measurement of elongation and of the timing, indicate for steel, phosphor-bronze, and platinum-iridium a greater elongation than that demanded by Hooke's Law. We will therefore assume the relation

$$M = \alpha e + \beta e^2, \tag{7}$$

and deduce the period which would result from oscillations along the curve represented by this equation. Since M/e decreases with increasing M, β will evidently be negative. It is more logical, perhaps, to write

$$e = aM + bM^2,\text{[2]} \tag{8}$$

but for solution of the differential equation given later it is simpler to have M expressed in terms of e, as in (7).

---

[1] M includes one third the mass of the wire, which addition was negligible for all except copper.

[2] J. O. Thompson found the formula $e = aM + bM^2 + cM^3$ to satisfy his observations in static experiments with wires. See Amer. Jour. Science, Vol. 43, p. 32, 1892.

IV. Derivation of the Period.

If we assume small vibrations of the wire, the period, neglecting the damping term, is known to be

$$T = 2\pi \sqrt{\frac{M}{\frac{dM}{de} g}}. \tag{9}$$

From (7) $dM/de = \alpha + 2e\beta$, whence

$$n = \frac{1}{2\pi} \sqrt{\frac{g(\alpha + 2\beta e)}{M}}. \tag{10}$$

Since the period has been shown by Figs. 8 and 9 to depend on the amplitude, the following derivation is given to show whether vibration along the curve represented by equation (7) causes the period to vary appreciably with the amplitude or not.

Returning to Fig. 1, let x be the distance from O to P at the time t. Let M' be the mass which by equation (7) corresponds to the elongation x. Let F' represent the force of restitution at the time t. M' will be less than M when x is less than e, and greater than M if x is greater than e. Then from equation (7)

$$F' = M'g = Mg\frac{M'}{M} = Mg\frac{\alpha x + \beta x^2}{\alpha e + \beta e^2}. \tag{11}$$

In equation (3) let $h = \dfrac{\Delta l}{\Delta p} = \dfrac{AT\alpha^2 L}{\omega c}$

$$\Delta l = \Delta x$$

$$\Delta p = M' - M = \alpha(x - e) + \beta(x^2 - e^2).$$

Δx is the increase in length due to the shifting of the position of O by temperature changes in the wire, the temperature changes being caused by the vibration. Then

$$\Delta x = h\,\Delta p = h[\alpha(x - e) + \beta(x^2 - e^2)]. \tag{12}$$

Since equation (7) does not contain this temperature effect, we must add Δx to the x of that equation, and, instead of x, write $x + h[\alpha(x - e) + \beta(x^2 - e^2)]$, Δx is negative when $x < e$. $\Delta x = 0$ when $x = e$. Thus we take the temperature of the wire to be that of the room when $x = e$. We will also suppose the vibrations to be so rapid that there is no time for the wire to receive or to give out heat, but the vibrations take place under adiabatic conditions. Then we have, for the elastic force acting on the mass M, when the distance OP is x

$$F' = Mg\frac{\alpha\{x + h[\alpha(x-e) + \beta(x^2 - e^2)]\} + \beta\{x + h[\alpha(x-e) + \beta(x^2 - e^2)]\}^2}{\alpha e + \beta e^2}. \tag{13}$$

Since the effect of the weight of the wire itself on the vibrations is equivalent to the effect of one third such weight suspended from the lower end, in what follows, M will denote the suspended mass plus one third the mass of the wire. Except for the copper wire, however, this addition was less than ½ gram, and was neglected.

Let

$$F = F' - Mg. \tag{14}$$

Then if we neglect terms of the order of $h\alpha\beta(x^2 - e^2)$ and $h\alpha\beta x(x - e)$, which are small compared with αx and $\alpha^2 h(x - e)$ we shall have from (13) and (14)

$$F = Mg\frac{\alpha(1 + h\alpha)(x - e) + \beta(x^2 - e^2)}{\alpha e + \beta e^2} = g[\alpha(1 + h\alpha)(x - e) + \beta(x^2 - e^2)]. \tag{15}$$

The external and the internal friction are each assumed proportional to the velocity, and the two terms representing them may be combined thus,

$$\mu\frac{dx}{dt} + \eta\frac{dx}{dt} = \sigma\frac{dx}{dt}, \tag{16}$$

where μ is the external damping coefficient, and η the internal.

As the mass M moves up and down, O (Fig. 1), the point to which the lower end of the wire tends to return, will also oscillate, because of the after-effect. This motion of O will doubtless be somewhat behind the motion of P in phase. The complete vibration requiring only about 1/5 sec. for the lowest frequency observed, there would be only a short time for the wire to recover between vibrations, but immediately after release the motion of O due to the after-effect is comparatively rapid, so it is not at all certain that this motion may be disregarded; in fact, a later discussion will indicate that this is perhaps an important factor in determining the period.

Kohlrausch proposed the formula $-dy/dt = \alpha(y/t)$, or $y = c/t^{\alpha}$, where y is the deformation due to the after-effect at the time t after the distorting force has ceased to act, and α is a constant. If this were approximately true for small t, we should have a very large dy/dt, but all his observations were taken after 10 sec. and as far as the writer has observed, practically nothing is known of the behavior of the after-effect during the first second after removal of the distorting force. Since an assumption would be worth little without the support of observational data and also since it would doubtless greatly complicate the equation, this effect will for the present be neglected.

The differential equation of motion may then be written

$$\frac{d^2x}{dt^2} + \sigma\frac{dx}{dt} + g\frac{\beta x^2}{M} + \frac{g\alpha(1 + h\alpha)}{M}x - \frac{g\alpha^2he + gM}{M} = 0. \tag{17}$$

If we neglect h and β, then $M = \alpha e$, and (17) becomes

$$\frac{d^2x}{dt^2} + \sigma\frac{dx}{dt} + \frac{g}{e}(x - e) = 0, \tag{18}$$

which is the well-known equation representing damped vibrations, the solution being

$$x = e + Ae^{-\sigma t \div 2}\cos\sqrt{\frac{g}{e} - \frac{\sigma^2}{4}} \cdot t, \tag{19}$$

where the time is counted from the lowest point of the vibration, at which point $x = e + A$, A being the amplitude. The period of this motion is

$$T = \frac{2\pi}{\sqrt{\frac{g}{e} - \frac{\sigma^2}{4}}}. \tag{20}$$

If β is neglected, but h is not, we have

$$T = \frac{2\pi}{\sqrt{\frac{g(1 + h\alpha)}{e} - \frac{\sigma^2}{4}}}. \tag{21}$$

From measurements of σ discussed later it will appear that for the largest value of σ found, $\sigma^2/4$ compares with g/e about as 1 with 10^6, showing that under the assumption that the frictional resistance varies as the velocity, the damping has no appreciable effect on the period. Hence, if in (17) we neglect $\sigma(dx/dt)$, we have left

$$\frac{d^2x}{dt^2} + \frac{g}{M}[\beta x^2 + \alpha(1 + h\alpha)x - (\alpha^2he + M)] = 0. \tag{22}$$

This equation represents undamped vibrations, but since we desire only the period that fact is of little importance.

Solution of the Equation.

Let

$$\frac{\beta}{3} = \gamma$$

$$\frac{\alpha(1 + h\alpha)}{2} = \delta$$

$$M + \alpha^2he = \zeta$$

and (22) becomes

$$\frac{d^2x}{dt^2} + \frac{g}{M}(3\gamma x^2 + 2\delta x - \zeta) = 0. \tag{23}$$

By a first integration we obtain

$$\frac{p^2}{2} = -\frac{g}{M}\gamma\left(x^3 + \frac{\delta}{\gamma}x^2 - \frac{\zeta}{\gamma}x + D\right), \tag{24}$$

where $p = dx/dt$, and D is the constant of integration.

$$p = \frac{dx}{dt} = \sqrt{\frac{-2g\beta}{3M}}\sqrt{x^3 + \frac{\delta}{\gamma}x^2 - \frac{\zeta}{\gamma}x + D}. \tag{25}$$

D may be determined from the condition, that when $x = e - A$, $p = 0$.

If we let $f(x) = x^3 + (\delta/\gamma)x^2 - (\zeta/\gamma)x + D$ then $f(x) = 0$ when $p = 0$,

$$D = -(e - A)^3 - \frac{\delta}{\gamma}(e - A)^2 + \frac{\zeta}{\gamma}(e - A), \tag{26}$$

and is thus a function of the amplitude.

If $A = e$, which is the greatest amplitude possible, $D = 0$.

This amplitude is always impracticable on account of the tendency of the wire to vibrate transversely when this point is nearly reached.

Equation (25), solved for t, is

$$t = \sqrt{\frac{3M}{-2g\beta}}\int_{x_0}^{x}\frac{dx}{\sqrt{x^3 + \frac{\delta}{\gamma}x^2 - \frac{\zeta}{\gamma}x + D}}. \tag{27}$$

Equation (27) gives the time for any part of the vibration, according to the limits assigned to x. If the extreme positions of P are taken as limits the value of t will be ½T.

To reduce the elliptic integral to the standard form of the first class,

$$F(k, \varphi) = \int_0^{\phi}\frac{d\varphi}{\sqrt{1 - k^2\sin^2\varphi}} = \int_0^{x}\frac{dx}{\sqrt{(1 - x^2)(1 - k^2x^2)}},$$

we must find the roots of $f(x) = 0$.

Since the 4th power of x is lacking, we have at once that one root is ∞, and D has been chosen so that another root is $e - A$. If we substitute the value of D from equation (26) in $f(x) = 0$, and divide by $x - (e - A)$, we obtain

$$x^2 + x\left(e - A + \frac{\delta}{\gamma}\right) + (e - A)^2 + \frac{\delta}{\gamma}(e - A) - \frac{\zeta}{\gamma} = 0, \tag{28}$$

whence

$$x = -\frac{e - A + \frac{\delta}{\gamma}}{2} \pm \frac{1}{2}\sqrt{(e - A)^2 + 2\frac{\delta}{\gamma}(e - A) + \frac{\delta^2}{\gamma^2} - 4(e - A)^2 - 4\frac{\delta}{\gamma}(e - A) + 4\frac{\zeta}{\gamma}}. \tag{29}$$

ζ may be expressed in terms of δ and γ.

$$\begin{aligned}\zeta = M + \alpha^2 he &= \alpha e + \beta e^2 + \alpha^2 he \\ &= \alpha e(1 + h\alpha) + \beta e^2 \\ &= 2\delta e + 3\gamma e^2\end{aligned}$$

$$4\frac{\zeta}{\gamma} = 8\frac{\delta e}{\gamma} + 12e^2. \tag{30}$$

Substitute this value of $4\frac{\zeta}{\gamma}$ in (29) and the equation becomes

$$x = \frac{1}{2}\left(-e + A - \frac{\delta}{\gamma} \pm \sqrt{9e^2 + A^2 + \frac{\delta^2}{\gamma^2} + 6eA + 6\frac{\delta}{\gamma}e + 2\frac{\delta}{\gamma}A - 4A^2}\right). \tag{31}$$

The expression under the radical differs from the square of $3e + A + \delta/\gamma$ only by $4A^2$. For the largest value of A observed

$$\frac{4A^2}{\frac{(\delta)^2}{(\gamma)^2}} = \frac{1}{90000} \text{ for platinum-iridium,}$$

$$= \frac{1}{250{,}000} \text{ for phosphor-bronze,}$$

$$= \frac{1}{640{,}000} \text{ for steel.}$$

For very small amplitudes the ratio is much smaller. Hence $4A^2$ may be neglected and we may write

$$x = \tfrac{1}{2}\left[-e + A - \frac{\delta}{\gamma} \pm \left(3e + A + \frac{\delta}{\gamma}\right)\right]. \tag{32}$$

$$\therefore \left\{\begin{aligned} x_3 &= e + A \\ x_4 &= -2e - \frac{\delta}{\gamma}\end{aligned}\right\} \tag{33}$$

are the remaining two roots of $f(x) = 0$.

It was to be expected that if $e - A$ is one root, $e + A$ is very nearly another, which simply means that in the vibration P moves very nearly as far below the point $x = e$ as it does above that point.

If we assume $e - A$ and $e + A$ to be two of the roots, the third root comes easily from the relation between the roots and the coefficients, for if ω_1, ω_2 and ω_3 are the roots, and

$$\omega_1 = e - A,$$

$$\omega_2 = e + A,$$

then

$$\Sigma\omega = -\frac{\delta}{\gamma}, \tag{34}$$

and

$$\omega_3 = -2e - \frac{\delta}{\gamma}.$$

To obtain the integral in (27) in the standard form we have to transform the roots

$$\infty,\ e - A,\ e + A,\ -\frac{\delta}{\gamma} - 2e$$

respectively into

$$-\frac{1}{k},\ -1,\ 1,\ \frac{1}{k}.$$

The bilinear transformation is

$$x = \frac{py + r}{qy + s}.$$

Determining the constants, we find

$$\begin{aligned} q &= 1, \\ s &= \frac{1}{k}, \\ p &= e + \frac{A}{k}, \\ r &= \frac{e}{k} + A. \end{aligned} \tag{35}$$

If $A = e$, $p = r$.

If $A = 0$, $k = 0$, and $s = r = \infty$.

$$\int_{x_0}^{x_1} \frac{dx}{\sqrt{f(x)}} = \frac{ps - qr}{\sqrt{M'}} \int_{y_0}^{y_1} \frac{dy}{\sqrt{(1 - y^2)(1 - k^2y^2)}}.$$

$$M' = \frac{\sqrt{b_0}}{k},\ b_0 = q^4 f\left(\frac{p}{q}\right),\ = f(p),\ \text{for } q = 1;$$

$$\therefore\ \frac{ps - qr}{\sqrt{M'}} = \frac{e + \frac{A}{k} - kA - e}{\sqrt{f(p)}} = \frac{\frac{A}{k} - kA}{\sqrt{f(p)}}, \tag{36}$$

$$k = \frac{1 - \sqrt{a}}{1 + \sqrt{a}},\ \text{where } a = \frac{\omega_4 - \omega_3}{\omega_4 - \omega_2} \cdot \frac{\omega_1 - \omega_2}{\omega_1 - \omega_3}. \tag{37}$$

The three finite roots are all positive, and the graph of the function appears somewhat as in Fig. 10. The integration takes place from $\omega_2 = e - A$ to $\omega_3 = e + A$, and is therefore real.

D is negative except when $A = e$ in which case it is zero.

$$a = \frac{\frac{\delta}{\gamma} + 3e + A}{\frac{\delta}{\gamma} + 3e - A}. \tag{38}$$

Let $c = -(\delta/\gamma) - 3e$, a positive quantity. Then

$$k = \frac{1 - \sqrt{\dfrac{c - A}{c + A}}}{1 + \sqrt{\dfrac{c - A}{c + A}}} = \frac{c - \sqrt{c^2 - A^2}}{A}. \tag{39}$$

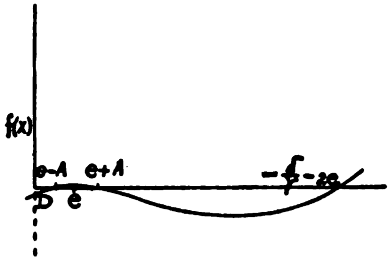


Fig. 10.

When $A = 0$, $k = 0$, and the last member of equations (36) becomes indeterminate. To evaluate it, from (39)

$$\frac{A}{k} = \frac{A}{\dfrac{c - \sqrt{c^2 - A^2}}{A}} = c + \sqrt{c^2 - A^2}, \tag{40}$$

hence,

$$\lim_{A=0} \frac{A}{k} = 2c, \tag{41}$$

also from (39),

$$Ak = c - \sqrt{c^2 - A^2}; \tag{42}$$

$$\therefore \frac{A}{k} - kA = 2\sqrt{c^2 - A^2} \tag{43}$$

and

$$\frac{ps - qr}{\sqrt{M'}} = \frac{2\sqrt{c^2 - A^2}}{\sqrt{f(p)}}; \tag{44}$$

$$\begin{aligned} \therefore t = \sqrt{\frac{3M}{-2g\beta}} \int_{x_0}^{x_1} \frac{dx}{\sqrt{f(x)}} &= \frac{2\sqrt{c^2 - A^2}}{\sqrt{f(p)}} \\ &\times \sqrt{\frac{3M}{-2g\beta}} \int_{y_0}^{y_1} \frac{dy}{\sqrt{(1 - y^2)(1 - k^2y^2)}}. \end{aligned} \tag{45}$$

When $x_0 = e - A$, $y_0 = -1$; when $x_1 = e + A$, $y_1 = 1$. Integrating between these limits we have $\frac{1}{2}T$. Hence the period is given by

$$T = \frac{8\sqrt{c^2 - A^2}}{\sqrt{f(p)}} \sqrt{\frac{3M}{-2g\beta}} K, \tag{46}$$

Copper	1.0021
Steel	1.0013
Phosphor-bronze	1.0015
Platinum-iridium	1.0011

The heating effect has therefore little influence on the frequency.

It will be noticed on the steel and platinum-iridium plots that when M is small Mn^2 is less than it should be. This may be explained by supposing that the wire obeys Hooke's Law for small elongations. Also, as will appear later in comparing the results for direct elongation, the wires seem not to be entirely straightened out until the second mass is reached, in spite of the precautions, already noted, which were taken to straighten them. The phosphor-bronze wire does not exhibit this deficiency in Mn^2 because the elongation of that wire was relatively greater, and the first weight took the wire beyond the region where the elongation is proportional to the load. The largest weight used was too great for the phosphor-bronze wire, and although no permanent elongation could be observed when this mass was removed, yet it is plainly evident from the

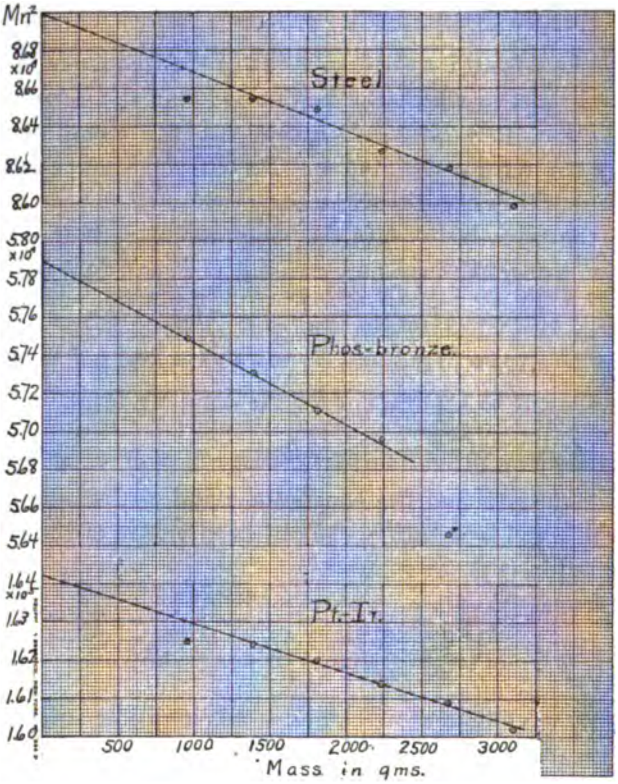


Fig. 11.

small value of Mn^2 for this mass that the rate of elongation of the wire at this point was greater than that which is given by $M = \alpha e + \beta e^2$.

For the copper wire, Mn^2 is a constant within the range of error, but it is to be noted that the greatest elongation is only about the same as the range for which Hooke's Law holds in the case of the steel and platinum-iridium wires. If there is any range for which equation (7) represents the behavior of the copper wire, that range is very limited, for the product of Mn^2 is a constant as far as observed, and the wire could sustain only a little more than the heaviest weight without passing the elastic limit.

From Fig. 11 the following equations were obtained.

$$\text{Steel: } M = 3{,}498\, e - 22.0\, e^2. \tag{56}$$

$$\text{Phosphor-bronze: } M = 2{,}327\, e - 19.6\, e^2. \tag{57}$$

$$\text{Platinum-iridium: } M = 6{,}602\, e - 166\, e^2. \tag{58}$$

To show with what degree of accuracy these represent the observed frequencies, we write eq. (53) in the form

$$n = \frac{1}{2\pi}\sqrt{\frac{g\alpha(1 + h\alpha)}{M} + 2\frac{\beta}{\alpha}g}, \tag{59}$$

and compute n for each mass, comparing the observed with the computed values.

TABLE VIII.

Steel.				Phosphor-bronze.				Platinum-iridium.			
M Gm.	n_0.	n_c.	n_0-n_c.	M Gm.	n_0.	n_c.	n_0-n_c.	M Gm.	n_0.	n_c.	n_0-n_c.
954	9.525	9.531	−0.006	953	7.767	7.766	+0.001	953	13.058	13.076	−0.018
1,384	7.908	7.908	.000	1,383	6.437	6.436	+0.001	1,383	10.837	10.836	+0.001
1,815	6.903	6.900	+ .003	1,814	5.611	5.611	.000	1,814	9.450	9.449	+0.001
2,245	6.199	6.199	.000	2,244	5.038	5.037	+ .001	2,244	8.481	8.479	+0.002
2,676	5.675	5.673	+ .002	2,675	4.594	4.606	− .012	2,675	7.755	7.753	+0.002
3,098	5.268	5.269	−0.001					3,097	7.193	7.193	0.000

n_0 = observed value of the frequency for infinitely small vibrations, taken from Fig. 9 for platinum-iridium.

n_c = frequency computed from equation (59).

The above residuals show that the frequency is very well represented by equation (59) except for the first masses of steel and platinum-iridium and the last of phosphor-bronze. For the smallest masses it is not certain that the wires were fully straightened, but on examining the results for all the wires including the copper we must conclude that for small distortions, the elongation is proportional to the distorting force, beyond that there is a region where the wire very closely obeys the law expressed by equation (7), then the elongation increases more rapidly

TABLE IX.

Copper.					Phosphor-bronze.					Platinum-iridium.				
M[1] Gm.	e_0 Cm.	n_0.	n_c.	n_0-n_c.	M gm.	e_0 Cm.	n_0.	n_c.	n_0-n_c.	M Gm.	e_0 Cm.	n_0.	n_c.	n_0-n_c.
956	0.0822	17.716	17.397	+0.319	953	0.4138	7.767	7.752	+0.015	953	0.1461	13.058	13.044	+0.014
1,386	0.1184	14.738	14.496	.242	1,383	.6023	6.437	6.426	+0.011	1,383	.2119	10.837	10.831	+0.006
1,817	0.1563	12.871	12.617	.254	1,814	.7912	5.611	5.606	+0.005	1,814	.2780	9.450	9.456	−0.006
2,247	0.1945	11.578	11.310	.268	2,244	.9816	5.038	5.033	+0.005	2,244	.3448	8.481	8.491	−0.010
2,678	0.2320	10.602	10.356	.246	2,675	1.1742	4.594	4.602	−0.008	2,675	.4137	7.755	7.752	+0.003
3,100	0.2695	9.845	9.609	+0.236						3,097	.4812	7.193	7.187	+0.006

[1] M does not include the mass of the scale-pan, which was 223 gm. e_0 is the change in elongation due to M. For the vibrations, M is the tota mass suspended.

even than this formula demands, and finally the strain becomes so great that the wire gives way. The weaker parts of the wire pass through these stages in advance of the stronger parts, and their cross-section being lessened, they elongate more and more rapidly, until rupture takes place at one of these points.

Computation of Frequency for Wires Obeying Hooke's Law.

Formula (21) gives the period if the wire obeys Hooke's Law and if we measure the elongation directly. For small elongations we might expect this formula to give a period agreeing well with the observed, but it does not. In all cases the e observed directly and substituted in (21) gives too small values for n, indicating that the observed e is too large.

Table IX gives the values of n_e computed from formula (21), using the values of e observed directly. The masses are the same as those used in the vibrations, except for steel. For this reason steel is given separately in Table X.

At first sight it might be supposed that these results for phosphor, bronze and platinum-iridium are satisfactory, with the exception-perhaps, of the smallest mass; and that formula (21) gives the period more closely than (59): but it must be remembered that formula (21) assumes that $e \propto M$. Therefore we have no right to substitute in it the values of e_0 in Table IX, because the ratio e_0/M is not constant, and we need to use a different ratio of e_0/M for each one, which is contrary to the hypothesis on which (21) is derived.

TABLE X.

Steel.

M Gm.	$\frac{e}{M}$.	M Gm.	e Cm.	n_0.	n_e.	$n_0 - n_e$.
1,000	2.874×10^{-4}	954	0.2754	9.525	9.501	+0.024
1,500	2.873	1,384	.3996	7.908	7.888	+0.020
2,000	2.883	1,815	.5240	6.903	6.888	+ .015
2,500	2.885	2,245	.6481	6.199	6.193	+ .006
3,000	2.892	2,676	.7726	5.675	5.673	+ .002
Mean...	2.887×10^{-4}	3,098	.8944	5.268	5.272	− .004

Columns 3 and 4, Table X, give the vibrating masses and the corresponding elongations, which were computed from the mean e/M by multiplying by the mass used in vibration. n_e is the frequency from

$$n = \frac{1}{2\pi}\sqrt{\frac{g(1 + h\alpha)}{e}},$$

using the e of column 4. Table X. shows, as the values of Mn^2 of Table VII. also do, that no constant value of M/e will satisfy the observed frequencies.

Comparison of e from Static and Dynamic Observations.

Finally the elongations corresponding to the observed frequencies were computed for all the wires. For the copper wire the formula, $e = g(1 + h\alpha)/4\pi^2n^2$ was used. For the others formulæ (56), (57), and (58) were inverted, giving e in the form of equation (8).

$$\text{Steel: } e = 2.859 \times 10^{-4}M + 5.1 \times 10^{-10}M^2. \quad (60)$$

$$\text{Phosphor-bronze: } e = 4.297 \times 10^{-4}M + 1.6 \times 10^{-9}M^2. \quad (61)$$

$$\text{Platinum-iridium: } e = 1.515 \times 10^{-4}M + 5.9 \times 10^{-10}M^2. \quad (62)$$

For these three wires e_c was computed for the given load plus the pan, then for the pan alone, and the difference compared with the elongation, e_0, observed directly. In the case of copper since the product of Mn^2 was a constant no computation was made for the initial load.

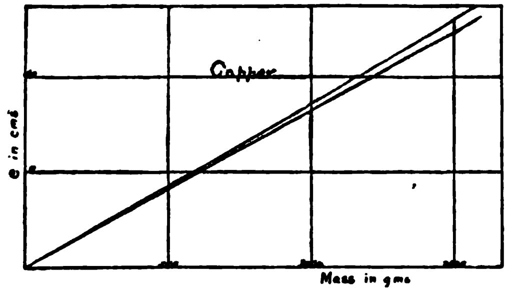


Fig. 12.

Fig. 12 shows e_0 and e_c for copper as ordinates with M on the axis of abscissas. e_c and M give a straight line, while e_0 and M do not. For the other wires neither curve is a straight line, and they lie so near together that they have not been plotted. $e_0 - e_c$ is always positive, however, for all the wires, and increases with M.

V. Discussion of Results.

The dynamic modulus of metals has been found by other methods to be greater than the static modulus. The same is true for these longitudinal vibrations, as shown in the last paragraph. No attempt has been made to determine the absolute value of either modulus, it being outside the purpose of this investigation.

If we consider the modulus to be proportional to dM/de, we have from equation (7) $dM/de = \alpha + 2e\beta$, which may easily be computed by equations (56), (57) and (58). For copper, since $\beta = 0$, we have $M/e = 4\pi^2Mn^2/g(1 + h\alpha)$.

Possible After-effect in All the Wires.

A large after-effect is shown in Fig. 5 for copper, and some is also exhibited by similar curves for steel. Since the recovery is rapid at first, it seems quite possible that the point of instantaneous recovery may be far beyond that indicated by the dotted continuation of the curves. The greater part of the recovery may be during the first second or two following release, or even while the load is being removed. The curves for copper unquestionably show that it is rapid at first, for very little of the effect there indicated comes from the heating of the wire. For phosphor-bronze and platinum-iridium there is *apparently* no after-effect, but the recovery may be so rapid that it is complete before an observation can be taken. This theory would explain the discrepancy between the observed elongation and that computed from the results of vibrations, which is equivalent to saying it would account for the difference between the static and dynamic moduli.

We may suppose, then, that the observed values of the elongation are all too large. The deformation due to the after-effect is much larger than would be supposed from usual observation, for it decreases very rapidly when the load is first removed, and by the time an observation can be made a great part of it has disappeared. Thus there may be considerable after-effect in wires which apparently show none; the wire may have entirely recovered by the time the first observation can be made.

Influence of the After-effect on the Period.

Considering again Fig. 1, as the point P oscillates, O will also oscillate with a certain amplitude depending on the period, the distance OP, and the material of the wire, as well as its condition as to hardness, temperature, etc. The phase difference between the motions of O and P will depend on the period and the manner in which the wire recovers after removal of the load. This last is an important element, and also an uncertain one. If the phase difference were zero, then P and O would both move downward through their mean positions at the same instant. In the half of the period when P is below its mean position, O would also be below its mean position. As a result the force of restitution would be less than if O remained at rest, and the period would be increased. When P and O were above the mean positions there would be a greater elastic tension on account of the displacement of O, and this would also increase the period, so that we have a decrease in frequency due to the motion of O. It may be noted that this is just opposite to the effect of the motion of O due to the heating and cooling of the wire. (Comp. the term $h\alpha$ in equation (53).)

But we must suppose that *O* is somewhat behind *P* in phase. Then when the two points are on opposite sides of their respective positions of rest the frequency would tend to increase, when they are on the same side it would tend to decrease. Unless the motion of *O* became 90° or more behind that of *P*, the frequency would probably be decreased by this motion of *O*.

That this does not account for the variation in Mn^2 for steel, phosphor-bronze, and platinum-iridium, appears from the fact that Mn^2 did not vary appreciably in the case of copper, which is just the one in which the after-effect was greatest. It is true that the recovery of copper is not so rapid as that of the other three metals, and hence the amplitude of *O* may not be as great, but we should expect at least a noticeable variation in Mn^2.

VI. The Damping of Longitudinal Vibrations.

Apparatus.

The amplitude of the vibrations when the wire is only about two meters long cannot be very great; consequently the accurate measurement of the damping becomes a matter of some difficulty. The following method has yielded fairly satisfactory results.

A fiber of glass was attached to the wire, and allowed to project about 1 cm. at right angles to it. The fiber pointed towards a specially constructed camera. The lens, which was one used in an ordinary galvanometer telescope, and had a focal length of about 15 cm., was stopped down until the aperture was only about 5 mm. At the back of the camera was fixed a drum, 40 cm. in circumference, rotating about a vertical axis. The axis was a screw, so that as the drum revolved, it moved parallel to the axis. A small drop of mercury was placed on the end of the glass strip next to the camera, the drop was brightly illuminated by the light from an electric arc, and the camera was so placed that the image of the drop fell on the drum. Owing to the great curvature of the small mercury drop, a sharp spot of light was obtained. A rapid photographic film was attached to the drum, and rotated as the wire vibrated, thus obtaining a record of the vibration. The mercury drop could not be placed directly on the wire, because of the fogging of the film by light reflected from the wire. The glass fiber was colored red, so that any light reflected therefrom would not affect the record. Fig. 13 shows a section of a record for steel.

Since the purpose was only to measure the amplitude, uniformity of motion of the drum was unnecessary. It was therefore turned by hand, a handle outside the camera box serving that purpose. The mass was set vibrating and the drum started. Then the current driving the wire

PHYSICAL REVIEW, VOL. III., SECOND SERIES
June, 1914.

PLATE I.
To face page 428.

Fig. 13. Steel.

GEORGE A. LINDSAY.

was shut off and at the same time the drum was stopped for an instant. The several vibrations thus heaped up together indicated where the damping began.

The measurements of the amplitude were made on a measuring engine of the Detroit Observatory, the plate-holder of the engine being mounted to revolve about an axis parallel to the axis of the microscope. This permitted an easy adjustment of the cross hair tangent to two adjacent waves. For all the wires except copper, 1,000 vibrations could easily be measured. Beyond that number they were so small that a relatively large error in the logarithm of the amplitude was introduced. The lens was so placed that the amplitude on the film was about equal to the actual amplitude of the point on the wire. The motion might easily have been magnified, but what was gained in this way was lost in definition of the trace. The largest double amplitude measured was about 4 mm. on the film, the smallest about 0.3 mm. Ordinarily the measurements ran from 3 mm. to 0.5 mm. The measuring engine read directly to 0.005 mm.

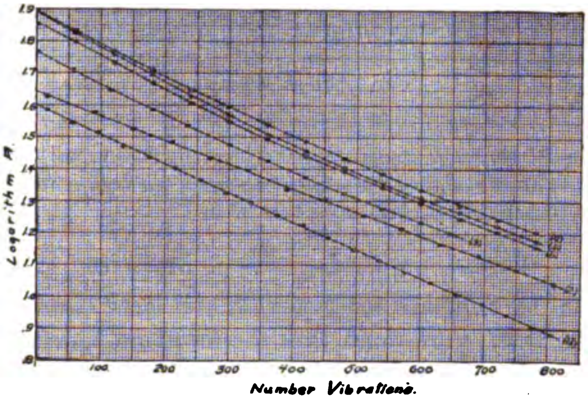


Fig. 14.

Decrement curves for steel.

Two records were made for each mass suspended from the copper wire, because the rapid damping allowed room for two on the film. For the other metals the damping was so small that only one record was made on each film. Every 30th vibration was measured and the logarithms of these were averaged by pairs, so that the plots show only the logarithms for every 60th vibration. Figs. 14 and 15 represent graphically the decrements for the masses given in Table XI. in order of increasing magnitude. Similar curves were drawn for copper, and the logarithmic decrements of Table XI. were obtained from these curves.

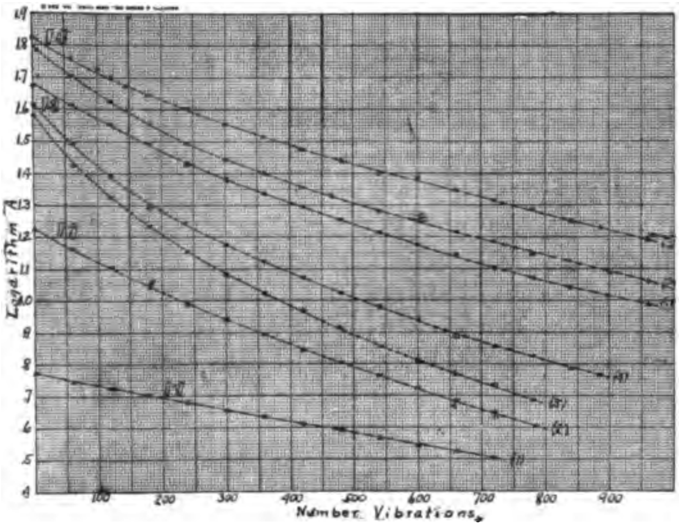


Fig. 15.

Decrement curves, ⊙, for platinum-iridium; △, for phosphor bronze. The scale is the same for all; but to avoid confusion the origin of ordinates has been shifted up or down for certain curves, as indicated by the logarithms in brackets.

Variation of the Logarithmic Decrement.

It was found by Schmidt[1] for torsional, and later also by Voight[2] for flexural and torsional vibrations, that the logarithmic decrement varied with the amplitude. They expressed the relation in the form

$$\lambda = \lambda_0 + bA^2,$$

where λ_0 is the logarithmic decrement for very small vibrations.

The values of Table XI. for copper are plotted in Fig. 16. Although the rate of increase is different for different masses, the increase is nearly proportional to the increase in amplitude[3] in all cases, and

$$\lambda = \lambda_0 + bA$$

represents the relation. The second mass gave an abnormally large decrement for the larger amplitudes, as seen from Table XI. There is no apparent reason for this. Both records taken of this mass show the same peculiarity.

While with the other wires, the logarithmic decrement for a rough approximation, increased in proportion to the increase of amplitude, the increase was much less than with copper, and less regular. The logarith-

---

[1] Loc. cit.

[2] Loc. cit.

[3] Bouasse and Carriere found $\lambda = bA$ for torsional vibrations of copper. (See Ann. de Chim. et de Physique, 8me Serie, t. 14, p. 208.)

TABLE XI.

Log. Decr.—Amplitude. Copper.

λ in common logarithms.

Mass. Gm.	Log. A.		1.8	1.7	1.6	1.5	1.4	1.3°	1.2	1.1	1.0	.9	.8	Temp. C.	n_0
	A_0	A	6.31	5.01	3.98	3.16	2.51	1.99	1.58	1.26	1.00	.79	.63		
956	2.30	λ						.00274	247	224	206	179		21°.9	17.716
	1.55									.00222	198	181	169		
1,386	2.75							.00475	384	305	259	226		24 .2	14.738
	2.85						.00571	494	377	274	232				
1,817	5.95			.00559	470	394	362	308	277	256	226	219		24 .3	12.871
	6.30			.00546	475	410	367	309	277	240	225				
2,247	3.80					.00354	320	292	252	228	208	203		22 .9	11.578
	3.95					.00342	329	283	254	219	205	198			
2,678	5.20				.00453	404	386	348	323	293	263	250		24 .2	10.602
	5.20				.00454	420	374	339	294	280	264	251			
3,100	4.05					.00408	364	320	296	270	239	221		24 .2	9.845
	6.55			.00562	490	436	370	325	292	259	242	230			

Steel.

M Gm.	A_0	A	6.31	5.01	3.98	3.16	2.51	1.99	1.58	1.26	1.00	Temp. C.	n_0
954	4.00	λ				.00091	90	90	90	88	85	23°.6	9.525
1,384	4.35				.00079	77	74	74	72	70		23 .6	7.908
1,815	6.15			.00103	99	91	84	79				23 .8	6.903
2,246	8.15		.00102	99	92	89	84	80				22 .7	6.199
2,676	8.25		.00114	107	100	92	85	78				22 .5	5.675
3,098	7.70			.00110	107	98	91	85	80	76		22 .3	5.268

TABLE XI.—*Continued.*

Phosphor-bronze.

M Gm.	A_0	A	6.31	5.01	3.98	3.16	2.51	1.99	1.58	1.26	1.00	Temp. C.	n_0
1,383	6.05			.00040	37							21 .7	6.437
2,244	5.60				.00100	87	78	69	64			21 .8	5.038

Platinum-iridium.

M Gm.	A_0	A	6.31	5.01	3.98	3.16	2.51	1.99	1.58	1.26	1.00	Temp. C.	n_0
953	4.95				.00107	101	82	71	63	58	45	23 .7	13.058
1,383	6.50			.00153	115	93	72	61	57	49		23 .9	10.837
1,814	4.35				.00108	92	77	65	54	52	50	24 .3	9.450
2,240	7.15			.00188	156	126	102	85	76	70	57	24 .2	8.481
2,675	6.70			.00245	190	157	139	115	96	89	75	24 .2	7.755

The column A_0 contains the largest amplitude measured on each film. The last two columns give the temperatures inside the box when the photographs were taken, and the frequencies for small amplitudes.

mic decrement for steel, especially for the smaller masses, is very nearly constant.

For phosphor-bronze only two masses were used and there is a remarkable difference in the decrement in these two cases. The decrement for the small mass, 1,383 gm., is only about one third that for the larger mass, 2,244 gm., and that for the smaller mass is very nearly constant. In 700 vibrations this amplitude decreased from 6.04 to 3.27, while for the larger mass in the same number of vibrations it decreased from 5.56 to 1.48. For the other metals there is no apparent dependence of λ on the period. If we produce the straight lines of Fig. 16, backward to the axis we get for λ_0, omitting No. 2

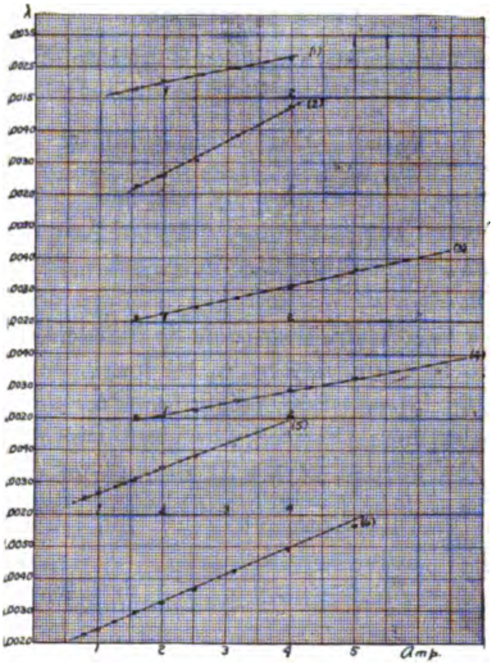


Fig. 16. Copper.

Mass.	λ_0.
(1)	.00121
(2)	———
(3)	.00136
(4)	.00130
(5)	.00186
(6)	.00160

With the largest mass suspended from the copper wire a single test was made of the effect of starting with a larger amplitude. In the case of the greater initial amplitude the decrement is slightly higher for large amplitudes, but as the amplitudes decrease the decrements in the two cases approach equality.

The temperatures were nearly the same in all cases, so little variation can be expected from this source.

It would be very desirable to test more fully a single wire, carrying a constant load, to determine the effect of change of temperature, and previous treatment of the wire, as well as the variations of other conditions for which there was not opportunity in this limited investigation.

Cause of Damping.

If the damping were caused by internal friction of the particles, and the friction were assumed proportional to the velocity, then we should have $\lambda \propto \frac{T}{M} \propto n$, or $\lambda/n =$ a const. That this is not fulfilled at all by any of the wires is plainly seen by reference to Table XI., and by comparing λ for equal amplitudes and different frequencies. The phosphor-bronze shows a marked variation in the other direction; λ decreases with increase of frequency.

In Boltzmann's theory the decrement is independent of the period, and this seems to be nearer the truth, for longitudinal vibrations. As already stated in the introduction, Voight found for torsional and flexural vibrations that some metals showed, as phosphor-bronze has done in the present instance, an increase of λ with decrease of n. A definite conclusion can not be reached for phosphor-bronze, however, since but two frequencies were used.

Correction for Air Damping.

A correction for the damping due to the friction of the air was made as follows. The cylindrical shell shown in Fig. 6 with the rod attached as when used for vibrations, was suspended in a horizontal position by a bifilar thread, so as to swing in a direction parallel to the axis, thus exposing the same surface and giving it the same motion through the air. The wire in longitudinal vibration presented only a small surface compared with the shell, and its effect would be nearly compensated by the friction of the bifilar threads mentioned above. The logarithmic decrement of this pendulum system was then determined for the different masses.

From equation (16) $\mu = 2\lambda_0/T_0$, where λ_0 and T_0 are respectively the logarithmic decrement, and period of the pendulum vibrations.

$\eta = 2(\lambda/T - \lambda_0/T_0) = 2\lambda_m/T_m$, where λ_m is the logarithmic decrement due to the internal damping alone. T_m is the period as it would be if there were no air damping, and is practically identical with T.

$$\therefore \lambda_m = \lambda - \lambda_0 \frac{T}{T_0}.$$

Thus $\lambda_0(T/T_0)$ is the correction to be subtracted from the measured value of λ to obtain the decrement due to the metal alone.

For small amplitudes the following were observed.

Mass.	λ_0.	T sec.
2,244	0.00027	3.44
3,097	0.00027	3.44

The greatest correction to be applied is for the smallest value of n. The smallest value of n was for phosphor-bronze, where for $M = 2{,}244$ gm., $n = 5.04 \dfrac{\text{vibs.}}{\text{sec.}}$

There was no mass of 3,097 gm. used with phosphor-bronze, but for steel

$$M = 3{,}097 \text{ gm.},\quad n = 5.27$$
$$M = 2{,}244 \text{ gm.},\quad n = 6.20$$

Thus we have for phosphor-bronze,

M gm.	$\frac{\lambda_0 T}{T_0}$.
2,244	0.000019

for steel,

M gm.	$\frac{\lambda_0 T}{T_0}$.
2,244	0.000015
3,097	0.000016

Therefore the maximum correction to be applied to λ given in Table XI. is 0.00002. For the copper it would be about half this value, and hence, when compared with the decrement for internal damping, is small enough to be neglected.

The Platinum-Iridium Wire.

The platinum-iridium wire was chosen because of the peculiar behavior of such wires noticed by Guthe,[1] and later investigated further by the same author and Sieg.[2] They found an excessive damping of torsional vibrations for platinum-iridium wires containing 40 per cent. of iridium, which is the same composition as that of the wire used in the present instance. It was accordingly expected that the damping of the longitudinal vibrations would also be large. The result was a decrement comparable to that of steel and phosphor-bronze, and far below that of the copper. When the wire was later suspended and vibrated torsionally, it was found that neither did this wire exhibit unusually large damping of

---

[1] Proc. Iowa Ac. Sci., 15, p. 147, 1908.

[2] Phys. Rev., Vol. XXX., No. 4, 1910.

torsional vibrations. The highest decrement observed for the torsional vibrations was 0.00270, when the initial amplitude was 825°. The decrement decreased considerably with the amplitude. Since the length of the wire under discussion was 145 cm. and the one used by Guthe and Sieg was 40 cm., an angle of 825° is about double the twist per unit length for which they observed a logarithmic decrement some 2½ times as large. The diameter of the wire used here was 0.206 mm., as compared with 0.194 mm. for theirs. Their wire showed a difference in period of 2 per cent. between large and small amplitudes. The period of this wire was found to be 18.069 sec. for 11° amp., 18.133 sec. for 550° amp., a difference of only ⅓ per cent. There is, therefore, evidently a difference in the composition of the two wires, or else previous treatment is very influential in determining their behavior.

Variation of Period with Amplitude.

The effect of damping on the period is given by

$$T = \frac{2\pi}{\sqrt{\frac{g}{e} - \frac{\sigma^2}{4}}},$$

where $\sigma = 2\lambda/T$.

For copper, which exhibited the greatest damping, let us take $\lambda = 0.010$ in natural logarithms, which corresponds to the highest λ computed in common logarithms. Also take $T = 0.07$ sec., which is approximately the period for $M = 1{,}386$ gm. Then

$$\sigma = \frac{.02}{.07} = 0.29, \quad \frac{\sigma^2}{4} = 0.020,$$

$$\frac{g}{e} = \frac{980}{.12} = 8170.$$

Hence $\sigma^2/4$ compares with g/e about as 1 with 400,000. The observed variation of T was ⅓ per cent., hence the variation was not caused by the change in λ, provided σ enters into the equation for the period as shown above. The fact that λ varies so greatly with the amplitude shows however, that the internal friction, whatever may be its nature, is *not* proportional to the velocity.

The equation (46) is an expression for the period which involves the amplitude. The largest value of A observed in timing was 0.1 cm. Substituting this in equation (46) we find that for platinum-iridium, $\sqrt{c^2 - A^2}$ differs from c by 1 part in 700,000, and in the denominator, $\sqrt{f(p)}$ differs, when $A = 0$, and when $A = 0.1$ cm. by only 1 part in 3,000,000. It has already been stated that $K[= F(k, \pi/2)]$ is not perceptibly affected by changing A within the limits of the experiment; hence the vibration along the curve represented by (60), (61), or (62) will not account for the variation of T. This also appears by considering that for copper the dynamic modulus was a constant, yet the greatest variation of period with amplitude was observed here.

By comparing elongations from static and dynamic observations as in Fig. 12 it is found that the differences $e_0 - e_c$ per unit length, in the order of magnitude beginning with the largest, place the metals in the following order: Copper, platinum-iridium, phosphor-bronze, steel.

This is the order of variation of period with amplitude; the copper showed the greatest variation, the platinum-iridium considerable, the phosphor-bronze very little and none was detected for steel.

The position of the wires with regard to the magnitude of λ is uncertain for all except copper, which again undoubtedly stands at the head.

The indication is that the wires having the largest after-effect, have also the greatest variation of period with amplitude, and the largest decrement, although it is to be noted that *rapidity of recovery* from after-effect is of as much importance in affecting the period as the total magnitude of the after-effect.

VII. Summary.

1. As a result of the measurement of the frequency of longitudinal vibrations of wires, carrying various loads, it appears in Section IV. that for small loads, the modulus is a constant; for greater loads the modulus decreases with increasing load, although the wire is still far within the elastic limit.

2. These two regions are of different relative extent in different wires. A soft copper wire showed a constant modulus until the elastic limit was very nearly reached (see Table VII.). Steel, phosphor-bronze and platinum-iridium, showed a relatively large range of elongation where the frequencies for small amplitudes are satisfied by an equation of the form

$$n = \frac{1}{2\pi}\sqrt{\frac{g[\alpha(1 + h\alpha) + 2\beta e]}{M}} \text{ (see Table VIII.),}$$

where, for a given wire α and β are constants, e is the elongation for the mass M, and e and M are connected by the relation $M = \alpha e + \beta e^2$. h is a small constant depending on temperature changes in the wire as the wire vibrates.

3. The modulus determined dynamically is, as usual, larger than that measured under static conditions (see Fig. 12).

4. This difference in moduli may be explained as the result of a large after-effect, the greater part of which disappears very rapidly after the removal of load (see Sec. V.).

5. The frequency decreases with increase of amplitude, in the case of copper and platinum-iridium. The relation may be represented by $n = n_0 - bA$ where b is a positive quantity. b is greater for large frequencies than for small (Tables V. and VI.). The variation for phosphor-bronze was exceedingly small, and for steel piano-wire n was evidently independent of the amplitude.

6. The wire which showed the greatest variation of period with amplitude also showed the greatest damping and the greatest after-effect.

7. The logarithmic decrement was measured and found to vary with the amplitude (Sec. VI.). For copper, at least, the increase of λ was very nearly proportional to increase of amplitude (Fig. 16). The logarithmic decrement does not vary with different frequencies in such a manner as to indicate that the damping is due to internal friction.

The writer is under obligation to Professor Guthe for proposing the investigation, and for making valuable suggestions during the progress of the work, to Professor Randall for advice in regard to some of the experimental part, and to Professor Curtiss for the use of a measuring engine of the Detroit Observatory.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
March, 1914.

A COMPARISON OF ACTUAL AND BLACK-BODY TEMPERATURES

By Charles C. Bidwell.

THE use of an optical pyrometer to determine the temperature of a metal gives an approximation to the true temperature only when the metal is enclosed, as in a furnace, the walls of which are practically all at the same temperature. The more completely the enclosed region above the metal surface approximates a uniform temperature, the more accurate will be the temperature given by the pryometer. If the metal is in an open crucible with its surface radiating freely into open space and receiving no light from the surroundings there is then a complete departure from black-body conditions. The radiation is selective in such a case and is characteristic of the particular surface. An optical pyrometer sighted upon such a surface will always give temperatures too low. The corrections which must be made to such optical readings have been determined in only a few cases. And the comparisons which have been made by various observers are in rather poor agreement. Recent observations by Stubbs and Prideaux[1] on the emissivity of gold near its melting point and by Stubbs[2] on silver and copper show great changes in emissivity with wave-length. This may account in large measure for the lack of agreement of different observers. The absorbing glasses used in the various pyrometers are never strictly monochromatic. One red glass, admitting a wider range of light than another, may give quite a different value for the black-body temperature. In order to extend our knowledge concerning the laws of selective radiation from metallic and other surfaces there is need of more observations made with monochromatic light. The data submitted in this paper are not intended to meet that requirement fully but they may be of some practical value.

The author has made comparisons of actual and black-body temperatures for several metals through a wide temperature range. A Morse pyrometer, which is of the disappearing filament type, was used with a red absorbing glass. The glass used is one of the best obtainable as regards mono-chromatism. The per cents. of light of the various

---

[1] Proc. Roy. Soc., Ser. A, Vol. 87, Oct. 1912, p. 451.

[2] Proc. Roy. Soc., Ser. A, Vol. 88, Mar., 1913, p. 195.

wave-lengths transmitted through this glass are given in Fig. 1. The corrections to optical readings which the author has determined for various metals are approximate for any pyrometer in which an absorbing glass transmitting between 0.60μ and 0.70μ is used. They are probably exact only when the absorbing glass is exactly like the one here used. The comparisons are shown for silver, gold, copper, nickel and iron in Fig. 2. Using data from the curves in Fig. 2 the author has computed relative emissivities for these metals through a temperature range of more than 1000 degrees. The relation between relative emissivity and temperature is shown in Fig. 3.

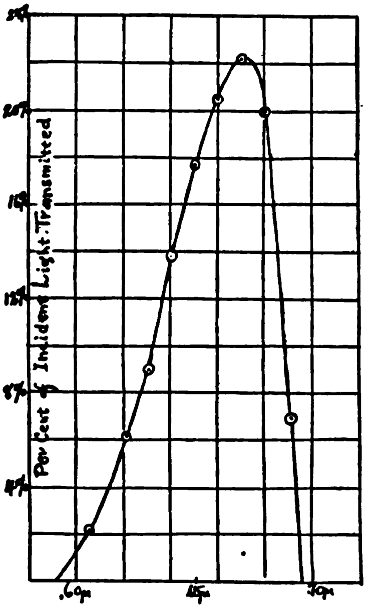


Fig. 1.

Transmission through the absorbing glass used in the Morse pyrometer.

The methods by which actual temperatures were obtained for the various metals in the solid and liquid states, the precautions required in individual cases and the method of computing emissivities are discussed in the following pages.

The pyrometer was calibrated to read "black-body" temperatures first, by sighting into a Reichsanstalt "black-body," the temperature of which was determined by means of a platinum, platinum-rhodium thermo-junction which had been calibrated by the Bureau of Standards. Calibration points as high as 1600° C. were obtained in this way. Beyond this a calibration point was obtained at the melting point of platinum which was taken as 1775° C. A piece of pure platinum was placed in a carbon cavity with a small opening at the top. A small platinum wire projected through this opening from the top of the specimen within. Melting of the specimen was shown by movement of the wire. The cavity was heated electrically and the pyrometer sighted into the opening from above. Additional points between 1600° C. and 1800° were obtained by use of a Wanner pyrometer, for the calibration of which only two points are necessary, the extrapolation being based on Wien's law. The Wanner and the Morse were sighted simultaneously into the black-body cavity in the carbon rod. Calibration points for the Morse were thus obtained at 1625° C., 1725° C. and 1810° C. The point obtained on the melting-point of platinum was in very good agreement with these points. The author's calibration was found to agree exactly with that furnished by the manufacturer.

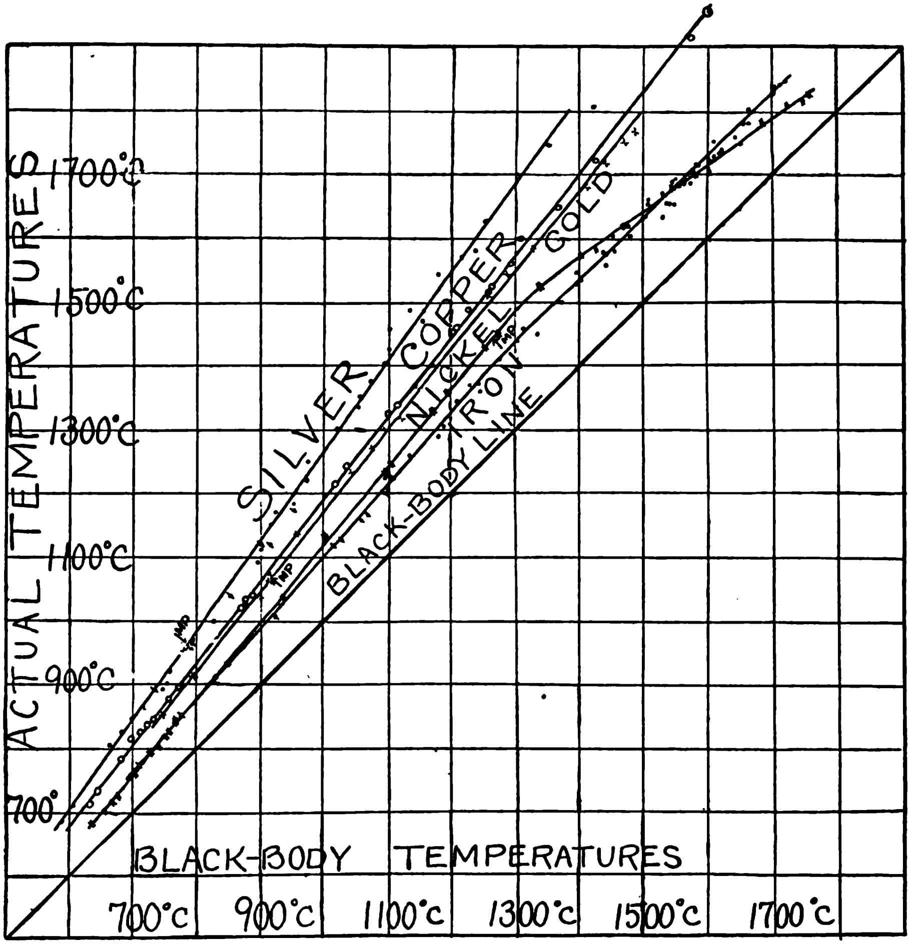


Fig. 2.

Black-body temperatures as compared with actual temperatures for various metals. The deviations of optical readings from actual temperatures are indicated by the vertical heights above the 45 degree, or "black-body" line.

Silver.—Points indicated by small circles with lines were taken with a platinum, platinum rhodium junction encased in quartz. The other points indicated by small circles were taken as described in the text.

Copper.—Points indicated by large circles.

Gold.—Points indicated by crosses.

Nickel.—Points indicated by double circles with crosses were taken by means of a carbon-graphite thermo-junction, the tips of which were frozen into the metal as it solidified from the molten state. The other points for nickel are indicated by small circles with crosses. These were taken as described in the text.

Iron.—Points indicated by small circles were taken on molten iron, those indicated by small circles with lines were taken on solid iron.

The real problem involved in the work was the determination of actual temperatures. The material to be studied was placed in a small cavity in a carbon rod which was heated electrically by a current from a low tension transformer. Observations were made on the free surface of the heated substance and actual temperatures taken simultaneously by means of thermo-junctions or otherwise as described later. Care was taken that the material not only filled the cavity but projected above the upper surface of the carbon rod, thus avoiding any chance of light reaching the surface from the surroundings. There were no surrounding walls, the carbon being heated in the open air. Thus the radiation from the surface was that of a body radiating freely into open space and receiving and reflecting no light from its surroundings. The transformer was of 40 kilowatt capacity and used on a 2200-volt circuit. It was capable of stepping the voltage down to 30 in the secondary when the latter was on open circuit. With the secondary short-circuited through the carbon heating rods probably several hundred amperes were ordinarily required. By using carbons of different sizes any desired temperature between 600° C. and 2200° C. could be obtained.

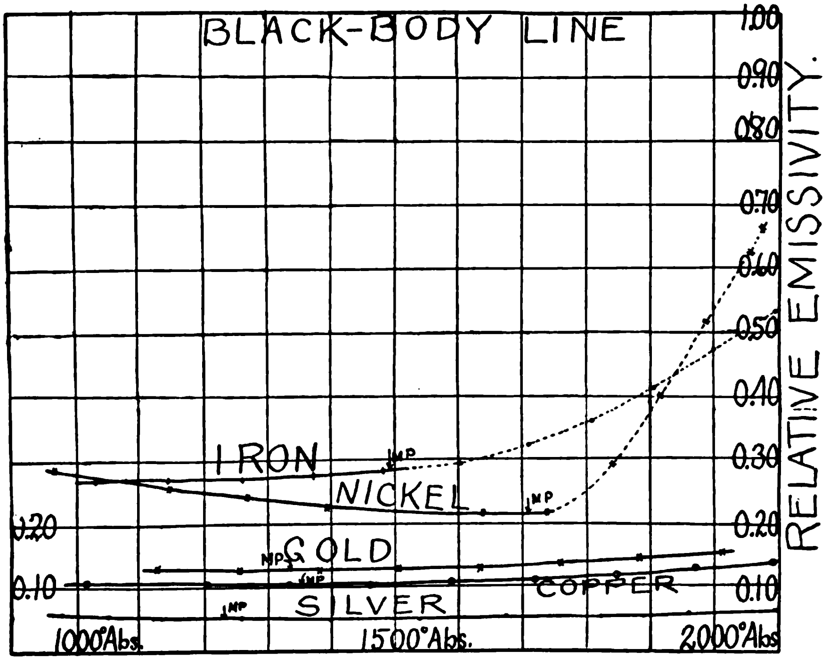


Fig. 3.

Relative emissivity and absolute temperature. (Light of wave-length approximately 0.66μ.)

For the determination of actual temperatures a thermo-junction of platinum and platinum with 10 per cent. rhodium, fused into the surface, offered a satisfactory method for solids, but, for convenience and rapidity, optical readings in a hole about 2 mm. deep by 1 mm. wide were taken as giving true temperatures for the surface. The hole was bored with a drill which made the bottom conical. A test of these readings was made by fusing a thermo-junction into the edge of the cavity about flush with the surface. The observations taken in this test are as follows:

Optical Readings in Cavity.	Thermojunction Readings.
1003° C.	990° C.
1005	1000
1015	1010
1050	1045
1075	1060
1130	1125

These readings are seen to agree within the range of accuracy possible with an optical pyrometer. The advantage of the optical method lay in the fact that the pyrometer could be sighted, first on the cavity, then on the surface, then back on the cavity, all within a few seconds and with the one instrument, while thermo-junction measurements involved balancing a potentiometer, which required considerably longer time. And absolutely steady conditions for any length of time were quite out of the question.

In the observations both on solid and molten metals extreme precautions were taken to obtain clear uncontaminated metallic surfaces. In the case of molten metals little trouble was experienced since slag and oxide always float to the edges of the crucible leaving a clear brilliant surface in the middle of the globule. A study of the surface of solid metals brought out the fact that the radiation was altered very greatly by slight changes in the surface. The brilliancy of the polish, the presence of very slight amounts of the polishing materials (rouge, etc.), or an imperceptible film of oxide changed the radiation decidedly. Consistent, reproducible results were only obtained on surfaces procured by solidification from the molten state, the freezing taking place in an atmosphere of hydrogen or nitrogen and the metal kept in such an atmosphere throughout the observations.

With such surfaces no abrupt change in the character of the radiation on passing from solid to liquid or vice versa was observed. A molten metal on freezing will ordinarily be observed to flash up brightly. This does not occur in a reducing atmosphere unless undercooling has taken place.

MOLTEN IRON.

In the case of molten iron a small carbon cavity was immersed in the metal with the opening in the cavity flush with the surface of the iron. Thermo-junction tests showed that cavity readings taken with the pyrometer indicated true temperatures at the surface very accurately. For these observations a large graphite crucible (about 5 cm. deep and 5 cm. inside diameter) was placed in a trough between fire-clay bricks and the trough filled with granular carbon packed tightly around the crucible. Current from the low tension transformer passed through this tightly packed carbon would quickly bring it to any desired temperature. A small carbon rod was fitted into a hole in the bottom of the crucible in such a way as to project vertically up through the middle of the crucible until flush with the top. A small cavity 5 mm. deep by 2 mm. wide drilled into the top of this rod constituted the black-body. The crucible surrounding the rod contained the molten iron. Simultaneous readings were taken at various temperatures in cavity and on iron surface.

As a check on the true temperature, a platinum, platinum-rhodium junction encased in a quartz capillary was pressed into the surface and the temperature readings thus taken compared with the optical readings on the free surface. Extended observations were not possible owing to the softening of the quartz and consequent destruction of the junctions. Two readings which were taken under steady temperature conditions are as follows:

Surface reading....1250° C.	Thermojunction reading....1360° C.
Surface reading....1275° C.	Thermojunction reading....1385° C.

This shows surface readings to be about 110° low. The cavity indicates surface readings to be about 130° low in this temperature region. It is to be expected that the junction readings would not be high enough. The junction was simply laid on the surface and pressed down but not immersed and there must be a temperature gradient from the iron surface through the quartz to the junction. If the junction is pressed beneath the surface, readings depend entirely on the depth of immersion and are no indication of the surface temperature. Hence the cavity readings being slightly higher than the junction readings, as taken above, are to be regarded as probably the truest indication obtainable of the surface temperature. Considerable difficulty was experienced in keeping conditions steady long enough to get satisfactory readings. The best results were obtained while the temperature was slowly rising or slowly falling. The cavity reading was first taken then the surface, and finally the cavity again. The mean of the cavity readings was taken as giving the actual temperature of the surface. The following set of data is a sample of many runs taken on molten iron. The curve for iron (Fig. 2) records the data of six such runs covering the temperature range from 1200° C. to 1850° C.

Sample Set of Readings on Molten Iron.

Actual Temperatures.		Black Body Temperatures of Surface.
Cavity Readings.	**Mean.**	
Temp. rising:		
1550°–1580° C.	1565° C.	1440° C.
1580 –1625	1603	1480
1625 –1645	1635	1500
1645 –1665	1655	1505
1665 –1655	1660	1505
1655 –1655	1655	1535
1655 –1685	1670	1530
1685 –1705	1695	1552
Temp. falling:		
1425 –1395	1410	1272
1395 –1320	1357	1240
1320 –1255	1287	1175
1225 –1185	1205	1095

SOLID IRON AND OTHER METALS.

For solid iron the surface studied was obtained by solidification from the molten metal. A small carbon rod was punched into the metal as it was solidifying and in the pasty condition. The frozen surface layer was thus pressed down and the still liquid mass below caused to flow up over it from around the edges and while so doing to solidify. All was carried on beneath burning hydrogen. A brilliant reflecting surface was thus obtained. Readings on such a surface give a curve continuous with the curve for the liquid surface (see Fig. 2). A surface obtained by simply high burnishing does not retain its luster and does not give a curve continuous with that for the molten metal. The cavity used for the "black body" was the hole left by the carbon rod mentioned above. The same method was used for all the metals studied. Only thus could a clear uncontaminated metallic surface be obtained. In some cases the metal was cooled through change of state and down to room temperature in a hydrogen or nitrogen atmosphere and a small hole then drilled into it to serve as a black-body. Only surfaces carefully protected from oxidation give consistent reproducible results.

MOLTEN METALS—GOLD, SILVER, COPPER AND NICKEL.

For gold, silver, nickel and copper in the molten state actual temperatures were determined by means of a thermo-junction of carbon and graphite.

A suitable junction of these materials as finally developed in the course of this work was composed of rods of carbon and graphite about 30 cm. long by 2 mm. diameter clamped side by side but insulated from each other by an air space. The junction was closed across the surface of the metal into which the rods were plunged. The cold ends of the rods were fitted into heavier pieces of carbon and graphite at the farther ends of which were fastened the copper wires which completed the circuit through the galvanometer or potentiometer. For a further description of these junctions with methods of calibration and precautions to be taken in their preparation and use, see following article on "Note on Carbon-Graphite Thermo-junction."

A small globule of the silver or other metal was placed in a cavity bored in the side of a carbon rod, the carbon rod being fitted horizontally into graphite electrodes and heated electrically. The cavity was usually about 10 mm. wide by 6 mm. deep. Enough metal was used to fill the cavity completely with the rounded surface protruding well above the surface of the rod. The thermo-junction points were adjusted to just penetrate the surface. Optical readings were made on the surface as close as possible to the junction. The thermo-electric circuit was completed through a resistance of 10,000 ohms with a high resistance galvanometer shunted around 1000 of these. The galvanometer deflections were calibrated to read temperatures direct. Several runs were made in this way on each metal from temperatures ranging from the melting point to 1900° C. As the junction rods oxidized rapidly in the air above the metal new junctions were required for each run. Hence the data is not dependent upon a single run and a single calibration but in each case on several different junctions each independently calibrated.

On molten silver a set of observations was taken in which actual temperatures were measured with a platinum, platinum-rhodium thermo-junction encased in a very fine quartz tube, the junction being pressed upon the surface of the metal. These readings are, as was expected, slightly lower than the carbon junction measurements (see Fig. 2). On solid nickel a set of observations were taken, in which actual temperatures were measured by means of a carbon-graphite junction which was "frozen" into the metal as it solidified from the molten state. These readings (see Fig. 2) agree well with the observations taken by the "black-body" cavity method.

RELATIVE EMISSIVITY.

The relative emissivities for the different metallic surfaces for the whole temperature range from 600° C. to 1850° C. were computed in the following way. If I_a is the intensity of light emitted by any hot body and T_a the corresponding "black-body" temperature, by Wien's law the relation between the two is

$$I_a = c_1\lambda^{-5}e^{-\frac{C_2}{\lambda T_a}} \tag{1}$$

For a full radiator at the same actual temperature we have

$$I = c_1\lambda^{-5}e^{-\frac{C_2}{\lambda T}} \tag{2}$$

Dividing (1) by (2) we get

$$\frac{I_a}{I} = \frac{e^{\frac{C_2}{\lambda T}}}{e^{\frac{C_2}{\lambda T_a}}}. \tag{3}$$

Now $I_a/I = E$ (relative emissivity). We may then write (3) as

$$\log_{10} E = \frac{C_2 \times .434}{\lambda}\left(\frac{T_a - T}{TT_a}\right). \tag{4}$$

If C_2 is taken as 14,500 and λ as 0.66μ then (4) becomes

$$\log_{10} E = 9{,}535\left(\frac{T_a - T}{TT_a}\right).$$

Thus (E) may be determined.

This expression requires the light to be monochromatic and the question now arises whether the light admitted to the pyrometer field is sufficiently monochromatic to justify its use. Fig. 1 shows that about 80 per cent. of the light is between wave-lengths 0.635μ and 0.685μ, with the average at 0.660μ. Computations of the emissivity of nickel at 2078° absolute (using data from the curve, Fig. 2) on the basis that the light is all of wave-length 0.635μ give 0.653 for E. On the basis that the light is all of wave-length 0.685μ we get for E the value 0.673. As the light is fairly evenly distributed between these limits the value of E for the whole band cannot be far from the mean of these values, which is obtained if the light is taken as of wave-length 0.66μ.

A more extreme case is that of silver at 1823° absolute. If all light were of wave-length 0.635μ (E) would be 0.051; if it were all of wave-length 0.685μ, (E) would be 0.063. The value of (E) must lie between these limits and the mean is obtained if we assume the light to be all of wave-length 0.66μ. The error introduced by regarding the light as monochromatic and of wave-length 0.66μ is therefore small and the use of Wien's equation is justified.

Fig. 3 shows the relation between relative emissivities and absolute temperatures. The low emissivity of silver is remarkable. At 1800° C. it radiates like a "black-body" at 1400°. Its emissivity is only about

5 per cent. that of a full radiator. Through the red glass the molten silver appears as a dark spot surrounded by the white hot carbon, yet carbon and silver are at approximately the same temperature.

Molten nickel takes up carbon from the crucible rapidly and beyond 1800° C. becomes a semi-solid pasty mass. On cooling the carbon which was either in solution or combined as carbide crystallizes out as graphite the mass becoming fluid again. The freezing point appears not to be affected by this absorption and expulsion of carbon. It is probable that the emissivity of molten nickel is modified by this absorbed carbon, the sharp rise shown on the curve being due to an actual change in composition which might not occur if the nickel were melted in some other sort of container. The effect was observed with iron also but not at all with gold, silver or copper. On account of this effect the emissivity curves for molten iron and nickel are given as dotted lines since they probably represent changes due to change in composition of the metal.

The relative emissivity which by Kirchhoff's law is the same as the absorptivity is shown to be practically constant for silver, copper and gold through the whole temperature range from 600° C to 1800° C. The values agree also with absorptivities at room temperatures as determined by Hagen and Rubens.[1] The table shows a comparison of Hagen and Rubens' values at 25° C. and the author's values at high temperatures. For silver, copper and gold a knowledge of the reflecting power at ordinary temperature is all that is required for a determination of optical pyrometer corrections at any temperature. The author believes that this has never been verified through a wide temperature range before. Unfortunately for the generality of the above relation, nickel seems to have a temperature coefficient of relative emissivity. Taking the value of this coefficient from the curve as − .000125, the value of the relative emissivity for 25° C. is found by computation to be .355 per cent. The fact that Hagen and Rubens have found practically that value is rather interesting.

	Hagen and Rubens—Absorptivity.			**The Author.**
	0.60 μ.	**0.65 μ.**	**0.70 μ.**	**0.66 μ (Approx.)**
Silver	.074	.065	.054	.055
Gold	.156	.111	.077	.125
Copper	.165	.110	.093	.105
Nickel	.35	.34	.31	[.355–(?)]
Steel	.45	.44	.42	.27–.29 (Iron)

---

[1] Annalen der Physik, 8, 912, p. 1.

All the curves show some evidence of an increase in emissivity at extreme high temperatures.

With regard to emissivity and change of state there is no evidence here of a sudden change occurring, as has been reported by some observers. Attention is called to the data taken on both the molten and solid metals near the melting points, especially for silver, gold and nickel. Except for the movement of slag at the edges of the liquid globule it is impossible to tell optically whether the metal is liquid or solid when near the melting-point. Surfaces artificially prepared, on the other hand, no matter how brilliantly polished always show a sudden drop in emissivity on melting. When a molten metal solidifies *in air* a rise in emissivity occurs as shown by a sudden brightening or flashing up. Evidently these changes are due to the formation of an oxide film or, in the case of the prepared surfaces to the presence of foreign material in the "pores" of the metal.

Cornell University,
February, 1914.

NOTE ON A THERMO-JUNCTION OF CARBON AND GRAPHITE.

By Charles C. Bidwell.

IN the course of certain studies on the radiation from molten metals[1] the need of some means of measuring temperature where optical methods were not applicable led to the utilization of the thermal E.M.F. between carbon and graphite and the construction of thermo-junctions, by means of which temperatures as high as 2200° C. were read. Although there is no mention in the scientific literature of the use of such a junction, it has been learned since the above mentioned work was performed that the Bristol Mfg. Co., of Waterbury, Conn., holds a patent granted in 1905 on a thermo-junction of carbon and graphite with adjustable tips. They have never developed the junction into a commercial instrument, probably on account of the variation in E.M.F. which necessitates constant re-calibration and is sufficiently serious to preclude its use in industrial processes. The junction however offers certain possibilities in the region beyond the reach of the platinum, platinum-rhodium couple in cases where radiation methods cannot be used. For scientific purposes therefore it may be valuable and worth a description.

The junction, as finally constructed, was designed to measure the temperature of molten metals. It was composed of rods of carbon and graphite about 30 cm. long by 2 mm. diameter clamped side by side but insulated from each other by an air space. The ends that dipped into the metal were narrowed to points and nearly met where they penetrated the surface of the metal. The thermo-electric circuit was thus closed through the metal. The cold ends of the rods were fitted into heavier pieces of carbon and graphite, thus giving each an additional length of 50 cm. At the farther ends of these heavier rods, were fastened the copper wires which completed the circuit through the galvanometer or potentiometer. The copper-carbon and copper-graphite contacts which constituted the cold junctions were wrapped in asbestos and maintained at room temperature.

Certain precautions were required in the preparation and use of these junctions. The E.M.F. is large, approximately 0.02 microvolts per

---

[1] See preceding article on A Comparison of Actual and Black-Body Temperatures.

degree and very nearly linear up to 2000° C., but rather erratic and untrustworthy if the carbons and graphites are used without special previous heat treatment. Electrically heating to about 2000° C. for several minutes seems to drive off impurities. At least the E.M.F. thereafter is fairly steady. If such a junction is now calibrated it will be found that the calibration will hold as long as the tips last. The rods oxidize in the air just above the crucible, the tips beneath the metal undergoing little change. If the tips are broken off and the junction rods pushed down into the metal again the original calibration may or may not be correct; usually a new calibration must be made. As long as the tips last the calibration is good.

The variation of the thermal E.M.F. with different rods and for different regions along the same rod may be due to partial graphitization

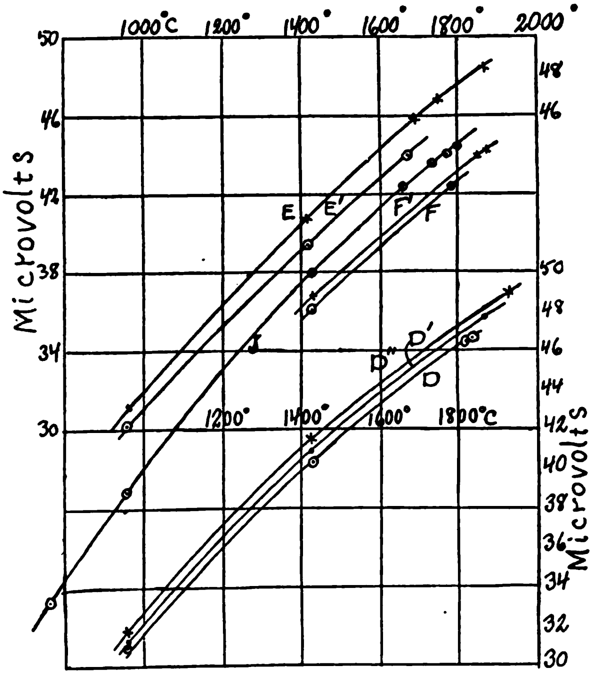


Fig. 1.
Calibration curves for carbon-graphite thermojunctions.

of the carbon or to incomplete graphitization of the graphite. Both the carbon and graphite seem to be at fault. The carbon rods were ground down from National Carbon Co. electric light carbons, the graphite was the artificial product made by the Acheson Graphite Co. The extent of the variation may be seen by consulting the calibration curves for the rods actually used in the author's work on optical and black-body temperatures of metals. These are shown in the figure.

The curves marked D, D', D'' are calibrations for the same pieces of graphite and carbon. D was for the original pieces; D', the calibration after the original tips were oxidized away and the rods again ground down to points; D'' after regrinding a second time. Likewise E and E' are calibrations for another junction, E' after grinding down new tips. Similarly, F and F'. It is evident that the variation in E.M.F. even for a few millimeters along the same piece of carbon or graphite is large enough to invalidate temperature readings unless the calibration is constantly checked.

For calibration the junction was immersed in molten silver which was allowed to cool through its freezing point. A high resistance galvanometer in series with the junction was observed during the cooling. At the freezing point the motion was arrested, the reading remaining stationary for several seconds. The point for 960° C. was thus obtained. The process was repeated with nickel. Undercooling occurred usually with nickel and was so considerable that the galvanometer could not keep pace with the quick rise in temperature which occurred when the solidification did take place, and the cooling would begin again before the galvanometer had swung back to the melting-point. Cooling curves were taken to determine the seriousness of this lag. It was found that the galvanometer would usually get back to within 10 degrees of the melting-point when cooling began again. 1430° C. was taken as the melting point of nickel and allowance made for the lag when undercooling occurred. For higher temperature points the junction tips were immersed in a globule of molten iron, optical readings taken on the surface, and the correction as already determined for iron applied. Calibration points in iron as high as 1900° C. were thus obtained.

If samples of carbon and graphite of greater purity than was available for this work could be obtained and the filaments protected where exposed to oxidation a serviceable instrument might be made of this junction.

CORNELL UNIVERSITY,
February, 1914.

DISCHARGE POTENTIALS ACROSS VERY SHORT DISTANCES.

By Edna Carter.

PASCHEN'S law states that the potential required to produce a discharge through a gas is a function of the product (*p.d*) of the pressure and the distance between the electrodes. Paschen[1] worked with pressures above the critical pressure and found the potential very nearly proportional to *p.d.* Carr[2] extended the measurements to lower pressures and smaller distances and found that the potential reached a minimum value and then increased with a further decrease in *p.d* and finally it was very nearly inversely proportional to this product. The work of Almy[3] and Williams[4] indicates that this would also be true even at atmospheric pressure, if the distances were made sufficiently small and the discharge could be forced to go across the shortest distance.

By means of a Chamberlain[5] compound interferometer with its massive carriage and accurate ways, it was quite easy to test these results and show that down to a distance of 0.5 wave-length of Na light the minimum spark potential of about 270 volts is still required to produce a discharge in dry air. Williams has proved that in this case the spark does not pass across the shortest distance. It was hoped that measurements could be made inside of 0.5 wave-length with this interferometer which can be made to measure distances to 1/40 of a wave-length, but it was impossible to say that the sparks which were obtained over shorter distances at lower potentials were not due to the yielding of the material under the electrostatic force so that the electrodes were first brought into contact.

Meurer[6] was unable to detect any effect of a magnetic field, transverse or longitudinal, on the potential required to start a spark discharge in air at atmospheric pressure, although such effects are obtainable at reduced pressures. It was thought that at the knee of the curve an effect might be found upon the minimum spark potential. To investigate

---

[1] Wied. Ann., 37, p. 79, 1889.

[2] Phil. Trans., *A*, Vol. 201, 1903.

[3] Phil. Mag. (6), Vol. 16, 1908.

[4] Phys. Rev., 31, p. 216, 1911.

[5] Phys. Rev., 23, p. 187, 1906.

[6] Ann. der Physik, 28, p. 199, 1909.

this point an electromagnet was made out of a rod of iron 1.5 cm. in diameter cast into the form of a ring about 15 cm. in diameter and wound with two layers of heavy copper wire. A gap 1.5 mm. wide was left in the ring and the iron at the gap was tapered to half its diameter. The spark gap between the iridium electrodes was introduced into this space so the magnetic field was transverse. No attempt was made to measure the strength of the magnetic field, but a current of 30 amperes through the electromagnet produced no measurable effect upon the discharge potential.

J. J. Thomson in his "Conduction of Electricity through Gases" has shown how on theoretical grounds one might expect the curve showing the relation between potential and $p.d$ to have two branches. Assuming that the curve obtained in Carr's experiments has become the hyperbola demanded by the Thomson theory for small values of $p.d$ and extrapolating for still smaller values, Madelung[7] found that the potentials obtained by experiment were very much lower than those demanded by the theory. When the pressure was reduced to about 0.07 mm. with a distance between the electrodes of 0.05 mm., the discharge took the form of a spark across the shortest distance. For this value of $p.d$ the theory requires a potential difference of about 60,000 volts. In reality it was only 9,000 volts. As the pressure was reduced in Madelung's experiments, the potential did not increase proportionally but seemed to reach a limiting value which was very nearly proportional to the spark length. This limiting value of the potential gradient he sets at 400,000 volts pro cm. He extends his curves showing the relation between potential and spark length to the origin.

Perhaps we ought not to expect Paschen's law to hold for these low pressures on account of the probable lack of uniformity in the distribution of the gas. It seemed of interest however to know what happens at distances equal to a few wave-lengths of Na light and also to find out if there is a limiting value of the potential gradient when every effort is made to rid the electrodes of gas. It was also hoped that some light would be thrown on the questions concerning electrical contact and the expulsion of electrons by metals.

An arrangement was attached to a Chamberlain interferometer in such a way that by means of a separate screw and a flexible copper disk two iridium electrodes, about 1 mm. in diameter, the one pointed and the other flat, could be brought together and separated inside the vacuum. With the aid of an additional iridium contact outside the tube, the distance apart of the electrodes could be measured in wave-lengths with as much

---

[7] Phys. Zeits., Feb., 1907.

accuracy as has been warranted so far by the results. The electrodes were contained in a glass tube about 2 cm. long and 2 cm. in diameter. The discharge could be observed in a low power microscope. The necessary voltages were obtained from a 1,600-volt battery of small accumulators and a high potential machine capable of furnishing any voltage up to 4,000. A Braun electrometer was used to measure the potential difference. A graphite resistance of 10^7 ohms was contained in the circuit and there was a cadmium iodide resistance permanently connected to the machine. The vacuum was secured by means of a Gaede mercury pump and cocoanut charcoal cooled in liquid air. One cannot claim for this anything higher than 0.0001 mm. The state of the vacuum was judged by the discharge through an attached Pflücker tube with large capillary. With the best vacuum conditions no visible discharge was produced in this tube by an induction coil capable of furnishing 60,000 volts.

When the tube was first evacuated, bluish white sparks passed rather easily and very irregularly. They resembled the explosions of occluded gases which one sees on the electrodes in any discharge tube. As the vacuum was maintained a longer time and the discharge passed through at intervals, these irregular sparks became less frequent. The discharge almost invariably began with a faint glow on one or both electrodes, which grew brighter as the electrodes were made to approach each other; and often after long continued maintenance of the vacuum the two glows simply melted together without any sudden intense lighting up of the field and disappeared at contact. When the graphite resistance was removed, the glow appeared as usual and just before contact very brilliant sparks of the same color were seen. These were surely due to the metal vapor. On one or two occasions yellowish sparks distinctly different from the white ones were observed. These may have been due to impurities in the metal or to the presence of some other gas. The phenomena were very irregular, but the distance at which the glow first appeared and a galvanometer gave the first indication of a current was fairly well defined and was approximately proportional to the voltage used.

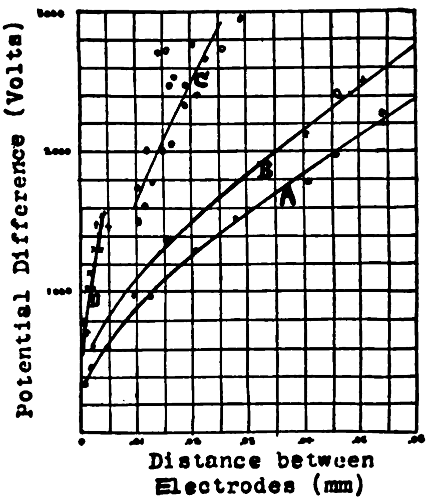


Fig. 1.

The curves represent the relation of the voltage to the distance between the electrodes when the glow first appeared. Curve *A* was obtained soon after the tube was evacuated and curve *B* a day later. The values in the neighborhood of *C* were obtained with the high potential machine after various means had been used to remove the gas from the electrodes. The values about the curve *D* were obtained with the battery after using what seemed to be the most effective method of removing the gas. Enough air was introduced so that a glow discharge was produced across the gap by an induction coil. After allowing this discharge to pass for several minutes the tube was quickly evacuated again. Taking out the graphite resistance and allowing a series of brilliant sparks to pass across, while the high vacuum was maintained, seemed to increase also for a time the potential gradient necessary to start the discharge. Later the electrodes were inserted in a quartz tube about 20 cm. long and 0.5 cm. in diameter where by means of an electric furnace they could be heated for hours to a bright red heat with the evacuation going on at the same time. The heating did not seem to have so much effect as the earlier methods and the phenomena in this smaller tube were more irregular, the discharge having a tendency to start at points back on the copper wires to which the iridium electrodes were soldered. Keeping away the mercury vapor by inserting a tube constantly surrounded by liquid CO_2 in acetone produced no noticeable effect.

The results show a minimum discharge potential in the neighborhood of 300 volts. Curve *A* corresponds rather closely to the potential gradient set by Madelung as the limiting value. Curve *C* gives a potential of 10^6 volts pro cm. and curve *D* 3.10^6 volts pro cm. Since the results are so irregular and seem to depend upon the condition of the electrodes rather than the exact state of the surrounding vacuum and since the value of the potential gradient seems to be increased by any means which would drive gas out of the electrodes, it is very probable that the discharge takes place in a gas of considerably greater density than is indicated by the state of the vacuum. This gas may permeate the electrodes but it also seems to cling fast to their surfaces. The presence of this gas may make impossible a complete confirmation of the Thomson interpretation of Paschen's law for small values of $p.d$, but another approximation may be made by using tungsten electrodes which can be more readily and more nearly completely freed from gas.

These investigations were carried out in the physical laboratory of the University at Wurzburg. My sincerest thanks are due Professor Wien and the other members of the department for their stimulating interest and helpful advice.

VASSAR COLLEGE.

NOTE ON THE FLUORESCENCE OF FROZEN SOLUTIONS OF THE URANYL SALTS.

By Edward L. Nichols and Ernest Merritt.

THAT aqueous solutions of the uranyl salts exhibit fluorescence similar to that of the salts themselves but of a feebler intensity has long been known. To determine whether the nearly equidistant bands, of which in general the fluorescence spectra of these solutions consist, retain their character when the solutions are frozen and reduced to the temperature of liquid air or whether resolution into groups of narrower bands occurs, was the purpose of the experiments to be described in this preliminary note.

To this end solutions of uranyl sulphate, uranyl potassium sulphate, uranyl nitrate and uranyl acetate of widely varying concentrations were used.

The solutions were placed in a test-tube *F* (Fig. 1) within a cylindrical Dewar flask *M* with unsilvered walls. Fluorescence was excited by a conical beam from a right-angled carbon arc *L* and the spectrum was observed with a Hilger spectroscope, the collimator of which is shown at *N*. For this spectroscope a suitable spectrograph could be substituted when photographs were desired.

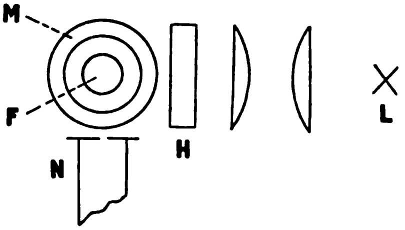


Fig. 1.

A ray filter *H* absorbed all light from about wave-length .47 μ to the extreme red so that the fluorescence bands appeared upon a dark background.

In no case, with the exception of uranyl acetate in alcohol, was a resolution of the fluorescence of aqueous solutions into narrow line-like bands observable; but there were certain striking changes in the character of the spectra when temperature and concentration were varied. These are noted briefly in the following paragraphs:

A. AQUEOUS SOLUTIONS.

1. *Uranyl Sulphate.*—The solutions of this salt present the simplest case; that of a single set of rather broad bands essentially unmodified either by temperature or dilution excepting as to breadth and intensity. In this preliminary survey a set of solutions were made by diluting the concentrated solution successively with ten parts of water. Measurements were made of the stronger bands at the temperature of liquid air to determine approximately the location of the crests.

The results are given in Table I. In this table the bands measured are designated arbitrarily by letters *c*, *d*, *e*, *f*, and *g;* there being two bands, *a* and *b*, of longer wave-length discernible in the spectroscope which do not appear in the photographs.

TABLE I.

Uranyl Sulphate in Water —185° *C.*

Concentration.	Band *c*.	Band *d*.	Band *e*.	Band *f*.	Band *g*.
1.00	.5631μ	.5380μ	.5131μ	.4915μ	.4807μ
0.10	.5625	.5377	.5130	.4915	.4797
0.01	.5626	.5380	.5131	.4916	.4796
0.001	.5626	.5376	.5129	.4915	.4804
0.0001	.5632	.5388	.5138	.4929	?

Estimations of width were also made but these are not included in the table because in a photograph the apparent width of a band depends on the intensity of the exciting light, the time of exposure and the development of the negative. As development progresses the crests appear first and darkening extends laterally outwards in both directions.

The widths as they appear in the photographs were roughly about 60 Ångström units for band *c*, 80 units for bands *d*, *e* and *f* and 50 units for band *g*.

Within the errors of observation, which would appear to be one or two Ångström units in the case of the more intense bands *e* and *f*, two or three units for band *d*, three or four units for band *c* and perhaps ten units for band *g* which was very vague, broad and weak, there is no shift with the concentration, ascertainable by this method, until a dilution to .001 is passed. In the weakest solution (.0001) however the bands are shifted to the red. The movement is about fourteen units for band *f*, eight or ten units for bands *d* and *e* and not more than five units for band *c*. The location of band *g* for this solution was not possible on account of weakness of the spectrum and the disturbance due to the presence of the neighboring absorption band of liquid air.

No attempt was made to secure photographs of the spectra of still weaker solutions, but a series of visual observations made by freezing and exciting aqueous solutions each of which contained twice the proportion of water of the preceding one showed that the two brightest bands (*e* and *f*) were still dimly visible when a solution containing *one part of the concentrated solution to 500,000 of water* was excited at the temperature of liquid air.

2. *Uranyl Nitrate.*—The concentrated aqueous solution of this salt when frozen and excited to fluorescence showed a double series of bright bands alternately narrow and broad. The narrower bands were on the side towards the violet, perhaps a third as wide as the accompanying broad band and less intense. The spectrum increased rapidly in brightness as cooling proceeded.

When the solution was diluted to 1/10, the fluorescence on cooling first appeared as a single very broad continuous band from red to blue but was rapidly resolved into a double series as in the spectrum of the concentrated solution.

With further diminution of concentration the double banded spectrum is observed although not so bright; at least until 1/1000 is reached. In solution with 10,000 parts of water however the narrower bands could no longer be distinguished.

The location of the bands, in the case of the nitrate, as shown in Table II. is somewhat less satisfactory than with the sulphate. The drift towards longer wave-lengths as the dilution increases is however not less marked. Band *g*, as in Table I., is encroached upon by the absorption band of liquid air to such an extent that the location of the crest is open to a considerable correction and the apparent absence of drift is probably not significant.

TABLE II.

Uranyl Nitrate in Water at —185° C.

Conc.	Band.		Band.		Band.		Band.		Band.	
	c.	*c'.*	*d.*	*d'.*	*e.*	*e'.*	*f.*	*f'.*	.	*g'.*
1.00	.5681μ	.5596μ	.5430μ	.5334μ	.5185μ	.5092μ	.4964μ	.4873μ	.4802μ	.4724μ
0.10	.5682	.5595	.5435	.5338	.5190	.5091	.4970	.4870	.4799	
0.01			.5432	.5330	.5196	.5089	.4970	.4875	.4804	
0.002					.5207	.5103	.4977	.4882	.4803	
0.001					.5211	.5100	.4985		.4805	

3. *Uranyl Acetate.*—The behavior of frozen solutions of uranyl acetate is much more interesting and remarkable than that of the sulphate or nitrate. In concentrated solution this salt has a fluorescence spectrum which to the eye appears to consist of a single very broad and faint band. At the temperature of liquid air this is resolved into a group of brilliant bands nearly equally spaced and in their general appearance similar to those of the sulphate but differently located (see Table III.). Upon dilution to 1/160 the resolved spectrum consists of broad very strong bands between which, at very low temperatures, much narrower and very much fainter bands appear.

Further dilution to 1/1600 produces another marked change. The broad and narrow bands are now supplanted, as if by partial fusion, by very broad and rather feeble bands having an intermediate position. Of the two which it is possible to locate with certainty in the photograph taken of the spectrum of this solution the one of shorter wave-length is clearly double although overlapping, having broad crests at approximately .5086 μ and .5215 μ. The other broad band having its middle about .5491 μ cannot be even partially resolved. The weakest solution upon which observations were made had a concentration of 1/16000. Its spectrum consisted of broad dim unresolved bands, the two strongest of which had their crests at about .5024 μ and .5239 μ. The outlying bands in the neighborhood of .48 μ and .54 μ were too vague to be located in the photograph.

The bands upon which measurements were attempted are given in the following table. Whether the changes in position should be ascribed, as in the case of the other salts, to a shift with concentration can be determined only by further observations.

TABLE III.

Uranyl Acetate in Water —185° C.

Concentration.	Character of Bands.							
	Broad.	Narrow.	Broad.	Narrow.	Broad.	Narrow.	Broad.	Narrow.
1 : 000	.5641μ		.5398μ		.5145μ		.4936μ	
1 : 160	.5640	.5533μ	.5398	.5284μ	.5152	.5048μ	.4931	.4837μ

	Very Broad.	Very Broad.	Very Broad.
1 : 1600	.5419μ	.5213μ	.5086μ
1 : 16000		.5239	.5024

4. *Uranyl Potassium Sulphate.*—Only a cursory examination of this substance was made. The concentrated aqueous solution when frozen

and excited showed broad bright bands without any trace of resolution at the temperature of liquid air. Diluted successively to 1/10, 1/100, 1/1000, and 1/10000 the spectrum retained the same appearance but the bands became broader as the concentration diminished and with the higher dilutions much dimmer.

B. Alcoholic Solutions.

Some of the uranyl salts, notably the acetate and nitrate, are soluble in ethyl alcohol. The concentrated alcoholic solution of the nitrate when reduced to the temperature of liquid air has a fluorescence spectrum consisting of alternately broad and narrow bands located as shown in Table IV.

The wave-lengths of the narrow bands is approximately the same as in the case of the aqueous solution of the nitrate but the broad bands are greatly shifted towards the red. In dilute solutions the pairs of bands are replaced by single broad bands having intermediate positions.

Table IV.

Uranyl Nitrate in Alcohol at —185° C.

Conc.	Broad.	Narrow.	Broad.	Narrow.	Broad.	Narrow.	Broad.	Narrow.
1/1	.5480	.5337	.5214	.5096	.5011	——	.4875	.4819
1/50	.5520	——	.5270	——	.5034	——	.4886	.4815?
1/500	.5522	——	.5271	——	.5040	——	.4882	.4821?
1/5000	.5521	——	.5273	——	.5041	——	——	.4806?

The narrow band at .4819 was vaguely discernible at higher dilutions but the position as indicated in the table was in question. The location of the bands of the dilute solutions does not seem to be very simply related to that of the bands of the concentrated solution although it remains nearly or quite unchanged for dilutions between 1/50 and 1/5000. This is easily explained if we consider these bands as resulting from the merging of neighboring bands of the concentrated solution and that the relative brightness of neighboring bands in the spectrum of the concentrated solution differs as we pass from red to violet.

The spectrum of the frozen alcoholic solution of uranyl acetate was altogether different from the various spectra already considered. It consisted, both for concentrated and dilute solutions, of numerous very narrow line-like bands superimposed upon an unresolved back ground; as though in this case a portion of the dissolved acetate had been thrown out on freezing.

The sharply resolved bands of this spectrum however, although they fall into equally spaced series, as is the case with the spectra of the solid uranyl salts at low temperatures, do not correspond in position, nor as to interval, with the bands of the solid acetate.

In Fig. 2 the arrangement and approximate width of the various

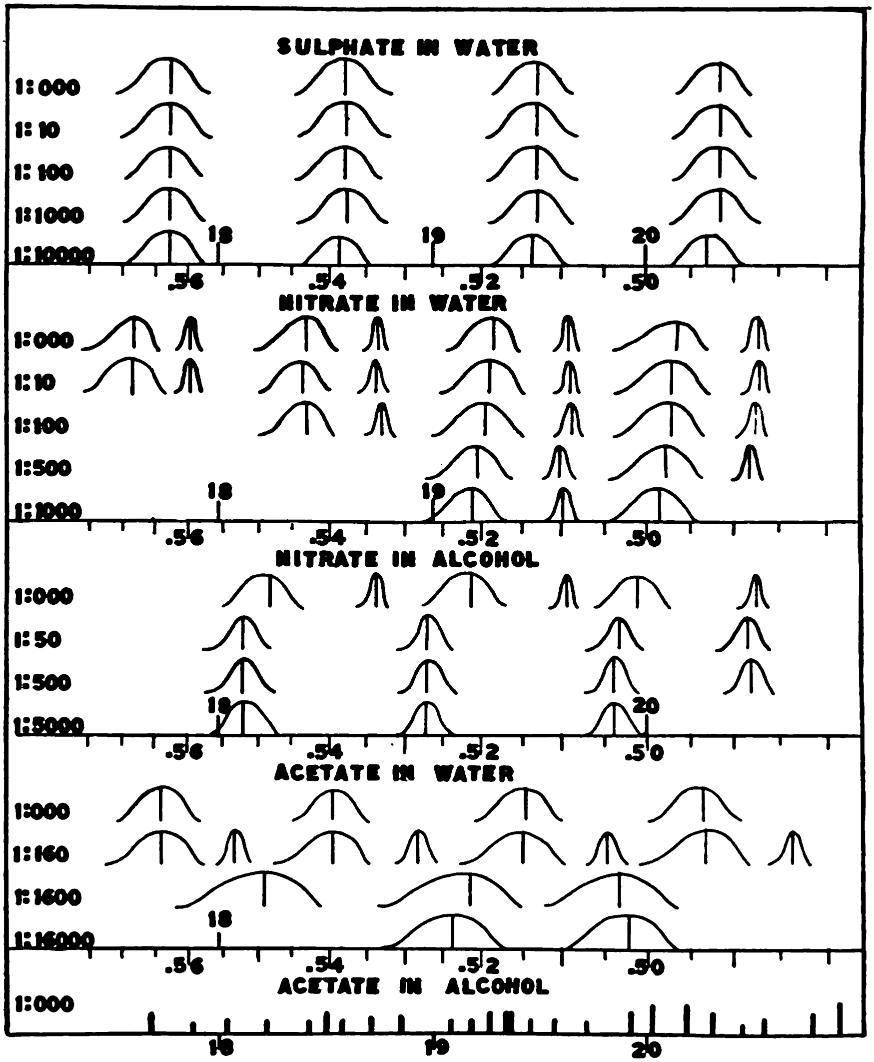


Fig. 2.

fluorescence bands already described are shown graphically in a diagram in which the abscissæ are frequencies. A scale of wave-lengths is also given for each spectrum. The positions of the narrow line-like bands in the spectrum of the acetate in alcohol are indicated at the bottom of the figure.

It will be seen that the frequency-interval between neighboring broad bands and also between narrow bands is approximately the same in all of these spectra; the average interval being about 86×10^{-4} where the wave-length is expressed in Ångström units. The only serious exception is in the case of the dilute solution of uranyl acetate in water (1 : 1600) where very broad bands have replaced the doublets of the more concentrated solution (1 : 160).

In the course of the observations recorded in this note, equally striking changes and shifts were found to occur when the temperature of a given solution was varied. A description of these phenomena may be expected as the result of a systematic study now being made by Mr. H. L. Howes, who has assisted the authors throughout this preliminary survey of the subject.

Physical Laboratory,
Cornell University,
March 30, 1914.

AN ATTEMPT AT AN ELECTROMAGNETIC EMISSION THEORY OF LIGHT.

By Jakob Kunz.

THE principle of relativity gives a consistent explanation of the phenomena of aberration of light, of the experiments of Fizeau and Michelson-Morley, and of the increasing mass of the electron as function of the velocity. The new principle rejects the ether, in which according to the older theory light waves are propagated and in which the electric and the magnetic energies have their seat. We are concerned again with actions at a distance, without a medium, but with actions proceeding with the velocity of light.

The mathematical simplicity of the original principle of relativity was mainly due to the fact that it used a fundamental constant, the velocity of light c as an absolute constant, so that the Lorentz transformation can be applied to Maxwell's equations, which remain unchanged.

Recently A. Einstein[1] generalized the original principle and applying it to the field of gravity came to the conclusion that c must not be considered as a constant but as a function of the coördinates. If the conclusion of this investigation is confirmed by the experiment, then the original theory of relativity fails and if it is not confirmed, the theory of relativity will be beset with great difficulties. In either case it will only be an approximation to the physical reality.

If we consider the material bodies as completely separated but exerting forces on each other, then the action at a distance remains incomprehensible at all events; but if there is no medium, we should expect in accordance with the Newtonian theory of gravity an action at a distance with infinite velocity, and as a matter of fact we do not know whether gravity proceeds with finite or infinite velocity. If however in the theories of relativity it is assumed that the action proceeds with constant or variable finite velocity, then the phenomena become even more mysterious.

The principle of relativity, even in its simple original form, affects our

---

[1] A. Einstein, "Entwurf einer verallgemeinerten Relativitätstheorie," Zeitschrift für Mathematik und Physik, Band 62, p. 225, 1914.

notions of space and time. Time, once absolute, dwindles to a mere shadow. The simultaneity of two events and the equality of two time intervals become relative, the parallelogram of velocities appears only as an approximation, an absolutely solid body is impossible and the mass of a body depends on its velocity.

When a physical theory which is mathematically complicated and is only an approximation cuts so deeply in our fundamental notions, and renders the phenomena so incomprehensible, the freedom of advancing other theories, which, though more conservative, attempt to coördinate the various phenomena in question should be granted. In the following a theory will be developed which agrees with that of relativity in many features, but gives an entirely different aspect of the world.

§ 1. Fundamental Assumptions.

1. One of the theories other than that of relativity is the electromagnetic emission theory of light. It is a compromise between the emission theory and the wave theory. Each electric charge is supposed to be surrounded by an electromagnetic field residing in the medium, which field itself forms the mass of the charge. Thus instead of having a continuous medium, ether, we have as many media as there are electric charges. Each individual electromagnetic field extends throughout the universe, but is essentially concentrated in the immediate neighborhood of the electron. No assumption is made as to the structure of the elementary medium.

2. Maxwell's equations will be applied to the molecular fields. The expressions for the masses of fields at rest will be extended to fields in motion.

3. The velocity of light is always equal to c for a vacuum. While in a mechanical emission theory the velocity v of the source is added geometrically to the velocity c, we have in the present theory, through a process of compensation, the velocity of light always equal to c, and independent of the velocity of the source. The difference between a mechanical emission theory, the undulatory theory and the electromagnetic emission theory of light can be illustrated by the following figures.

The source of light moves with the velocity v per second from A to B towards the observer. In the mechanical emission theory the light particles emitted in the point A with the velocity c would lie after a second on the sphere with radius c and with the center B. Thus the center of the wave front would always coincide with the source itself. In the undulatory theory, where the light is carried through the continuous independent medium, the center of the disturbance would always coincide with the point A in which it has been emitted. In the electromagnetic emission theory the center of the disturbance would coincide with the moving source but the wave surface would be an ellipsoid of revolution whose equatorial plane is perpendicular to the direction of motion. In the second and third cases the velocity of light is always equal to c. In the second case the motion of the material luminous source has an influence on the optical phenomena, so we could hope to discover the motion of the source with respect to the ether and if the ether were at rest we could hope to discover the absolute motion of the source. This is impossible by mechanical methods according to Newton's principle of relativity. In the first and third theory we could not discover the absolute motion of the source. The critical velocity c of light in the vacuum is in Maxwell's theory equal to the ratio of the electrostatic to the electromagnetic unit of electric charge. If we consider c as constant and maintain Maxwell's equations unchanged for an electromagnetic field in motion, we consider that ratio of the two units also as independent of the motion. This means that the ratio of the force which on the one hand unit charge exerts upon another charge in a given distance to the force which on the other hand the same unit charge, when in motion exerts upon a magnet is independent of a uniform motion of the whole system. It is sufficient, but not necessary, for this purpose to assume that an electric charge

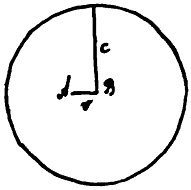


Fig. 1.

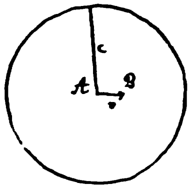


Fig. 2.

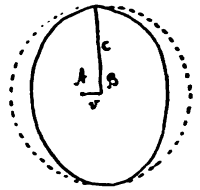


Fig. 3.

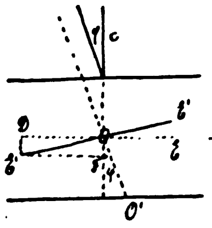


Fig. 4.

k μ v

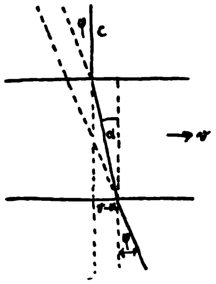


Fig. 5.

exerts upon another charge the same force, no matter whether both are at rest or in uniform motion; further, that an electric current exerts the same influence upon a magnet independent of the state of rest or of uniform motion of the whole system. In this way may be explained the facts that the electrostatic field of the earth, revolving round the sun, produces no magnetic effects, and the magnetic field of the earth no electric effects by electromagnetic induction upon bodies which are rigidly connected with the earth.

4. As there is no independent medium like ether, we are only concerned with relative motions between charges, magnets, sources of light and observers. An absolute motion of an electromagnetic system with constant velocity in a straight line can not be defined nor measured with optical and electrical methods.

The third and fourth assumptions lead to the Lorentz transformation of Maxwell's equations. There is however another transformation carried out by Maxwell and Hertz who found that the essential form of the equations remains unchanged if they are related to a system of axes at rest with respect to the ether or in motion similar to that of a rigid body; in other words, the absolute translation or rotation of a rigid system of bodies has no influence upon its internal electromagnetic phenomena, provided that all bodies of the system, the atomic fields included, take part in the motion. The electric and magnetic fields seem to be rigidly connected with the material bodies. The laws of geometrical optics are therefore independent of the motion of the earth.

The question still arises why according to this theory we can only discover relative motions between charges or magnets and between light sources and observers. In the first examples of course the reason lies in the interaction of the fields, but why should the field around a source of light contract in the equatorial plane if it approaches an observer? The reason may lie in the pressure which the light exerts upon the observer and which the observer exerts on the source. It might finally be possible that all the fields with which we can carry our experiments are imbedded as it were in a universal field of force.

§ 2. The Mass of the Electron.

An electron moves slowly in a medium whose permeability and dielectric constant are equal to unity. It is accompanied by a material electric field which, for small velocities, is symmetrical round about the spherical electron so that in a distance v from the center the electric force E is equal to $E = e/r^2$ and the magnetic force is equal to $H = ev \sin \vartheta / r^2 = Ev \sin \vartheta$; the magnetic energy per unit volume is equal to

$$E_1 = \frac{\mu H^2}{8\pi} = \frac{\mu E^2 v^2 \sin^2 \vartheta}{8\pi} = \frac{1}{2} m_1 v^2.$$

m_1 is the mass per unit volume.

$$m_1 = E^2 n' n^2/4\pi = \frac{\mu E^2 \sin^2 \vartheta}{4\pi}$$

or for $\mu = 1$

$$m_1 = \frac{E^2 \sin^2 \vartheta}{4\pi}$$

in general

$$m_1 = \frac{\mu k^2 E^2 \sin^2 \vartheta}{4\pi}.$$

μ is the permeability and k the dielectric constant. For the following considerations it will be sufficient to put μ and k equal to 1. The mass dm of an infinitesimal ring will be equal to:

$$dm = \frac{e^2}{4\pi r^4} \sin^2 \vartheta \; 2\pi r^2 dr \sin \vartheta \, d\vartheta$$

and the whole mass will be equal to:

$$m = \frac{2}{3} \frac{e2}{a} = m_0,$$

where a is the radius, e the charge of the electron. This mass extends for an isolated electron throughout the whole space, but half of the mass is concentrated in the immediate neighborhood of the electron, that is in a sphere whose radius $a_1 = 2a$.

If the electron moves with finite velocity, then the electric field changes in such a way that the lines of electric force rotate towards the equatorial plane, which is perpendicular to the direction of motion v. At the same time the lines of magnetic force accumulate more and more in that plane as the velocity v increases. If finally the critical velocity c is reached, the whole electromagnetic field will be concentrated in that plane and the mass of the electron will increase indefinitely, so that an electric charge can not move with a velocity greater than that of light. We see also that in this limiting case the electron must cease to emit light in the direction of motion.

For a velocity v smaller than c we have:

$$E = \frac{e\left(1 - \frac{v^2}{c^2}\right)}{r^2\left(1 - \frac{v^2}{c^2}\sin^2 \vartheta\right)^{\frac{3}{2}}},$$

$$dm = \frac{e^2\left(1 - \frac{v^2}{c^2}\right)^2 \sin^2 \vartheta}{4\pi r^4\left(1 - \frac{v^2}{c^2}\sin^2 \vartheta\right)^3} 2\pi r^2 dr \sin \vartheta \, d\vartheta,$$

whence

$$m = \frac{1}{2}e^2\left(1 - \frac{v^2}{c^2}\right)^2 \int\int \frac{dr}{r^2} \frac{\sin^3 \vartheta \, d\vartheta}{\left(1 - \frac{v^2}{c^2}\sin^2 \vartheta\right)^3}.$$

The integrations are to be extended over the whole field outside the electron. We do not know the shape of the electron, be it at rest or in motion. But there is a tension in the direction of electrical lines of force, and hence a resultant tension acting on the electron, especially round about the equator and the electron will assume the shape of an ellipsoid of revolution. According to the law which governs the equilibrium between internal and external forces, the mass as function of the velocity will be different. The integration will be carried out for three different conditions as follows:

1. The electron preserves the shape of a sphere during the motion.[1] The result of the integration is this:

$$\frac{m}{m_0} = \frac{3}{16}\left\{\frac{c^2 - v^2}{v^2} + 3 + \frac{c^2}{v^2}\left[\frac{3v}{(c^2 - v^2)^{\frac{1}{2}}} - \frac{(c^2 - v^2)^{\frac{1}{2}}}{v}\right] \operatorname{arctg} \frac{v}{\sqrt{c^2 - v^2}}\right\}.$$

2. The form of the electron changes according to the law

$$\frac{a}{b} = \sqrt{1 - \frac{v^2}{c^2}},$$

the integration yields the result

$$\frac{m}{m_0} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

the expression which relativity gives for the transversal mass of the electron.

3. The electron changes according to:

$$\frac{b}{a} = 1 - \frac{v^2}{c^2};$$

the integration gives

$$\frac{m}{m_0} = \frac{3}{8}\frac{c}{v}\frac{c^2 - v^2}{v^2}\left(\frac{c^2}{c^2 - v^2} - \frac{3}{4}\right)\log\frac{1 + \frac{v}{c}}{1 - \frac{v}{c}} + \frac{3c^4\left[2 - 3\left(1 - \frac{v^2}{c^2}\right)\right]}{16(c^2 - v^2)v^2}.$$

The first formula gives results which are smaller by 1 . . . 3 per cent. than the experimental values of C. E. Guye and S. Ratnowsky, which are however a little larger than those calculated by means of Abraham's

---

[1] J. Kunz, "Détermination théorique de la variation de la masse de l'électron en fonction de la vitesse," Archives des sciences physiques et naturelles de Genève, 1913.

formula. The third formula gives values too large and increasing too rapidly, while the second formula corresponding to relativity is in best agreement with the facts observed.

§ 3. THE ELECTROMAGNETIC MOMENTUM AND THE PRESSURE OF A BEAM OF LIGHT.

It follows from Maxwell's equations that there is a tension in the direction of the lines of force, which per unit area perpendicular to the line is equal to the density of the energy. The pressure perpendicular to the lines of force is just as large. It follows that the pressure of a beam of light per unit area is equal to the electromagnetic energy per unit volume. We can now determine this pressure by means of the electromagnetic mass and momentum. A beam of light consists in the present theory of oscillating and advancing electromagnetic mass. The electric force is perpendicular to the direction of propagation, $\sin \vartheta = 1$ and if $\mu = k = 1$, then

$$m_1 = \frac{E^2}{4\pi}.$$

The momentum per unit volume is equal to

$$M = m_1 c,$$

the energy per unit volume will be

$$\frac{1}{2} m_1 c^2 = \frac{E^2 c^2}{8\pi} = \frac{H^2}{8\pi}$$

and the pressure per unit area is equal to

$$p = Mc = \frac{H^2}{4\pi}.$$

If

$$H = H_a \cos \frac{2\pi}{T}\left(t - \frac{x}{c}\right)$$

then

$$\overline{H^2} = \frac{1}{2} H_a^2$$

and

$$p = Mc = \frac{1}{8\pi} H_a^2;$$

this is the energy of the beam per unit volume.

If k and μ are both equal to 1, then

$$p = m_1 c^2 = E, \quad m = m_1 = \frac{E}{c^2},$$

or by differentiation

$$dm = \frac{dE}{c^2}.$$

Hence it follows that a source of radiation, which emits energy, loses a part of its electromagnetic mass. The sun loses yearly about 10^{14} tons of electromagnetic inertia. On the other hand if a body absorbs energy, its mass must increase proportionally to the energy absorbed, and if an electric charge is set in motion, it will have more magnetic energy than at rest. If this electromagnetic mass were granular and could be broken up into smaller units, such as $E = hn$, then such a unit would have the mass for yellow light $m_1 = 3_1 F.10^{-33}$, about 100,000 times smaller than the mass of the electron at rest.

§ 4. On Newton's Dynamical Equations.

Every atom possesses at least one electron. If the velocity of an atom changes, the inertia will change also. Newton's dynamical equations require therefore a correction which for all ordinary velocities of material ponderable bodies is insignificant, but which becomes very large, if the velocity v approaches that of light. The law of conservation of mass does not hold rigorously, but the law of conservation of momentum remains exact.

The total momentum remains constant in an enclosed system of heavy bodies, electrical charges, magnets, currents and sources of light. If a source emits a beam in a definite direction, it will lose momentum and be driven in the opposite direction. If on the other hand an electric wave strikes a charge, or if a beam is absorbed by a surface, then the material bodies gain as much momentum as disappears from the space. A force is defined in Newton's dynamics by the following equation:

$$F = \frac{dM}{dt},$$

but since

$$\frac{dM}{dt} = \frac{d(mv)}{dt},$$

$$F = \frac{mdv}{dt} + \frac{vdm}{dt}$$

and

$$Fdt = m\,dv + v\,dm.$$

If the mass moves through space dl during time dt, then the increase of energy is equal to:

$$dE = F\,dl = F\frac{dl}{dt}dt = Fvdt = dmv^2 + mvdv = c^2dm,$$

$$dm(c^2 - v^2) = mv\,dv,$$

$$dm\left(1 - \frac{v^2}{c^2}\right) = \frac{m}{c^2}v\,dv.$$

This equation has been integrated by Lewis and Tolman. Putting $v/c = x$, we get:

$$\frac{dm}{m} = -\frac{1}{2}\frac{d(1 - x^2)}{1 - x^2},$$

$$\log m = \log (1 - x^2)^{-\frac{1}{2}} + \log m_0,$$

$$\frac{m}{m_0} = \frac{1}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}};$$

hence we find again for the increase of the mass the expression given by relativity.

The corrected equation of Newton holds not only for the ordinary inert bodies, but also for the radiations in a cavity. In a cavity bounded by perfect mirrors, we may find for the radiant energy E, the expression

$$E = mc^2,$$

or the energy of radiation possesses inertia. If moreover this electromagnetic inertia is subject to gravity, then the weight of such a cavity will be equal to:

$$mg = \frac{Eg}{c^2}.$$

If further the electromagnetic mass is at the same time heavy, then the gravity of the earth will exert on a certain body a force in a given point, which depends on the state of motion or rest of the body. An ordinary potential of gravity, as a function of the coördinates, only exists no more, for it now depends on the velocity of the falling body as well.

If the electromagnetic mass is subject to gravity, then a beam of light from a fixed star, passing through the field of attraction of the sun, will be attracted and therefore the position of the star will appear displaced. This very important problem may be solved by this phenomenon or also by observations made with pendulums of radioactive substances which are very rich in electrons. Let us consider two geometrically similar pendulums, the first consisting of a radioactive substance, such as radium, the second of non-radioactive substance. We shall assume the weight Mg of the two pendulums to be the same, but the mass M of the radioactive substance to be $m_1 + m$, where m_1 shall be subject to gravity, the electromagnetic mass m independent of gravity. The periods of the two pendulums will be

$$T_1 = 2\pi\frac{\sqrt{(m_1 + m)r^2}}{Mgs},$$

$$T_2 = 2\pi\frac{\sqrt{m_1 r^2}}{Mgs}.$$

The radioactive pendulum would have a longer period than the ordinary one. 1 gr. radium contains about 1/13 mgr. more mass in the active state than after the transformations. In recent years it has been shown by Eötvös that for ordinary bodies the inertia is exactly proportional to the weight up to 10^{-7}. But nevertheless we have not yet a direct experimental proof that the electromagnetic mass is subject to gravity.

§ 5. THE EXPERIMENT OF MICHELSON-MORLEY.

As there is no independent medium, the motion of the earth has no influence upon geometrical optics and the result will remain the same whether we place the interference apparatus of Michelson-Morley in the direction of the motion of the earth or perpendicular to it. Even if the source of light were not connected with the apparatus, but were in motion, as for instance if the light of canal rays were made use of or the light of a star, in no case would we observe a displacement of the interference fringes through a rotation of the apparatus. Here appears a distinct difference between the electromagnetic and the mechanical emission theories. According to the latter theory we should expect an effect in the experiment of Michelson-Morley, if the light were incident from a star.

§ 6. THE EXPERIMENT OF TRONTON AND NOBLE.

The energy of an electric condenser of two plane parallel plates is independent of the direction of the motion of the earth; this experimental fact follows immediately from our assumptions. In the theory of an independent ether however the condenser would possess more energy if the plates were parallel to the velocity v of the earth, than if they were perpendicular to it. A charged and suspended condenser would produce a couple in the first position tending to bring it into the second position.

§ 7. ABERRATION OF THE LIGHT FROM FIXED STARS.

While the light of a fixed star travels from the objective A of the telescope to O', the earth moves with the velocity v from O to O'. The phenomenon of aberration was always evidence in favor of an emission theory or led to the assumption of a stationary ether, through which the earth moves.

$$\frac{OO'}{O'A} = \frac{v}{c} = \frac{\sin \Phi}{\sin \vartheta} = 20''49.$$

Φ is the angle of aberration, v/c the constant of aberration of the light from fixed stars.

§ 8. The Experiments of Airy and Fizeau.

As the constant of aberration v/c depends only on v and c, Airy thought that it must change, if c changes. He filled therefore the telescope with water and expected a different angle of aberration, as the velocity of light in water is equal to c/r, if r is the index of refraction of water. Airy found however no change of the constant of aberration and he concluded that the water carries the ether with it, so that the velocity v is diminished by the same measure as c. If the water were carrying the ether with it with its own velocity, then no aberration would be possible, it must therefore communicate to the ether only a fraction of its own velocity. If the oscillating and advancing mass of a beam of light falls upon a transparent substance containing bound electrons, these charges will be set in motion and emit electromagnetic mass themselves. If moreover the substance struck by light is in motion, the electrons will be deviated from their original direction and oscillate in a new path. The light emitted will be perpendicular to this new direction and the original beam of light appears to be deflected from the original direction.

A beam of light strikes a column of water with plane surfaces, which move with constant velocity v perpendicular to the beam of light. Let us consider in a given point O of Fig. 4 an electron, which, if the water is at rest, under the action of the electric force OE, is deflected in the direction OD. The magnetic force would have no influence. If however the electron together with the water is set in motion with the velocity v, then the magnetic field of the light will act upon the charge in motion tending to deflect it in the direction OF. The resulting deflection and oscillation will be along OE'; the new beam will travel in a path perpendicular to this direction, that is from O to O'.

$$OD = eE,$$

$$OF = \frac{evH}{c^2} \quad H = cE,$$

$$OF = \frac{evE}{c},$$

$$\sin \Phi = \frac{OF}{OD} = \frac{v}{c};$$

this means that the angle of aberration Φ is independent of the specific properties k and r of the medium. Hence Fizeau's experiment follows immediately.

The water communicates to the beam a part of its own velocity v, so that the beam travels in the direction of v with a velocity u. It will strike a point A on the lower side of the layer of water, and be deflected, so that Φ represents again the angle of deviation between the real and the observed beam. Now we have

$$\sin \alpha = \frac{v - u}{V},$$

$$\frac{\sin \Phi}{\sin \alpha} = r, \quad c = Vr,$$

$$\sin \Phi = r \sin \alpha = \frac{r(v - u)}{V} = \frac{r^2(v - u)}{c}.$$

This angle however is independent of the specific properties of the flowing substance; hence for the vacuum:

$$r = 1, \quad u = 0,$$

$$\sin \Phi = \frac{v}{c},$$

$$\frac{v}{c} = \frac{r^2}{c}(v - u), \quad (v - u)r^2 = v,$$

$$u = v\left(1 - \frac{1}{r^2}\right).$$

This is according to Fresnel and Fizeau the fraction of the motion, which the flowing water communicates to the beam of light.

If we observe a point at rest through a rotating disc of glass, it will appear to be deflected from its natural position. If we use a Roentgen ray instead of a beam of light then r the index of refraction is equal to 1 and therefore $u = 0$, that is, we would expect that Fizeau's experiment gives a negative result with Roentgen rays.

RECENT LITERATURE.

The present attempt at an electromagnetic emission theory is based upon the works of Faraday, Maxwell, H. A. Lorentz and other investigators. J. J. Thomson especially has in various investigations treated the electromagnetic field of an elementary charge as something individual, endowed with mass, momentum and energy. He has however, so far as I know, not extended the theory to the critical phenomena here treated. Contributions to the present theory have been made by N. R. Campbell in his book on modern electrical theory, by D. Comstock, PHYSICAL REVIEW, 30, p. 267, 1910; R. C. Tolman, PHYSICAL REVIEW, 31, p. 26, 1910; 35, p. 136, 1912; O. M. Stewart, PHYSICAL REVIEW, 32, p. 418, 1911, and J. Kunz, American Journal of Science, 30, p. 313, 1910.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
March 12, 1914.

NOTE ON THE EVALUATION OF THE CONSTANT C_2 IN PLANCK'S RADIATION EQUATION.

By Charles N. Haskins.

THE methods hitherto used[1] for the evaluation of C_2 in Planck's equation

$$J = \frac{C_1}{\lambda^5}\frac{1}{e^{C_2/\lambda\theta} - 1} \qquad (1)$$

depend essentially upon graphical processes, *i. e.*, upon processes whose precision is limited by conditions entirely independent of those which control the accuracy of the experimental data. It seems therefore worth while to point out a purely numerical method by means of which C_2 may be found from the experimental results without the necessity of recourse to such graphical methods.

In the present note such a method is developed. The problem is reduced to the solution of an equation of the form

$$u^n - u + A = 0,$$

where n is a positive quantity greater than unity but not necessarily an integer. This equation may be solved by any one of several well-known methods. The details of one of these methods are, for completeness, indicated, and the applicability of the process tested by applying it to data computed by means of equation (1). It is found that the assumed value of C_2 is reproduced with all the precision of which the logarithmic tables used are capable.

Reduction of the Equation.—Let J_1, λ_1, θ_1; J_2, λ_2, θ_2 be two sets of observed corresponding values of J, λ and θ. Let $\lambda_2\theta_2 > \lambda_1\theta_1$. Then

$$J_1 = \frac{C_1}{\lambda_1{}^5}\frac{1}{e^{C_2/\lambda_1\theta_1} - 1}, \quad J_2 = \frac{C_1}{\lambda_1{}^5}\frac{1}{e^{C_2/\lambda_2\theta_2} - 1}. \qquad (2)$$

Hence

$$\frac{e^{C_2/\lambda_1\theta_1} - 1}{e^{C_2/\lambda_2\theta_2} - 1} = \frac{J_2\lambda_2{}^5}{J_1\lambda_1{}^5}. \qquad (3)$$

Put now

$$n = \frac{\lambda_2\theta_2}{\lambda_1\theta_1},$$

---

[1] Cf. Buckingham and Dellinger, Bulletin, Bureau of Standards, 7, 393–406, 1911.

$$x = e^{C_2/\lambda_2\theta_2},$$

$$C = \frac{J_2\lambda_2^5}{J_1\lambda_1^5}.$$

Then since $\lambda_2\theta_2 > \lambda_1\theta_1 > 0$, and $C_2 > 0$; $n > 1$, $x > 1$, $C > 1$. Equation (3) now becomes

$$\frac{x^n - 1}{x - 1} = C,$$

or

$$x^n - Cx + C - 1 = 0. \tag{4}$$

This is an equation of the well-known "trinomial form" and may be solved, for example, by Newton's Method, by the method of Gaussian logarithms, or by iteration.[1]

If we put further

$$u = \frac{x}{C^{1/n-1}} = \frac{e^{C_2/\lambda_2\theta_2}}{C^{1/n-1}},$$

whence

$$C_2 = \frac{\lambda_2\theta_2}{\log_{10} e}\left(\frac{1}{n-1}\log_{10} C + \log_{10} u\right), \tag{5}$$

and

$$A = \frac{C-1}{C^{n/n-1}}, \quad 0 < A < 1,$$

equation (4) becomes

$$u^n - u + A = 0. \tag{6}$$

Equation (4) has two and only two positive roots. One is the trivial value $x = 1$ corresponding to $C_2 = 0$, the other is greater than unity and corresponds to the value of C_2 sought. Hence equation (6) has two positive roots of which the greater gives the desired value of C_2. It is easily seen that both roots of (6) lie between zero and unity. Write now equation (6) in the form

$$u = (u - A)^{1/n}. \tag{7}$$

If we consider the curves

$$y = u, \quad z = (u - A)^{1/n}$$

and note that $y(A) = A > z(A) = 0$, while $y(1) = 1 > z(1) = (1 - A)^{1/n}$ we see that in the neighborhood of the greater root of (6)

$$1 = \frac{dy}{du} > \frac{dz}{du} > 0.$$

Hence[2] if by substitution in (6) we find a rough approximation u_0

---

[1] Cf. Runge, Praxis der Gleichungen, pp. 52, 141, 81; and especially p. 147, where an equation of form (4) arising from a financial problem is solved by the method of Gaussian logarithms.

[2] Cf. Osgood, Calculus, p. 403.

to the greater root the successive approximations given by

$$\begin{aligned} u_1 &= (u_0 - A)^{1/n}, \\ u_2 &= (u_1 - A)^{1/n}, \\ &\cdots\cdots\cdots \\ u_{m+1} &= (u_m - A)^{1/n}, \end{aligned}$$

will converge to the desired root u. When this value has been found C_2 is given by

$$C_2 = \frac{\lambda_2 \theta_2}{\log_{10} e}\left(\frac{1}{n-1}\log_{10} C + \log_{10} u\right).$$

Numerical Example of the Method.—A test of the above process *as a method of computation* is best obtained by applying it to values of J computed from (1) with assumed values of C_1 and C_2 and noting the precision and rapidity with which the assumed value of C_2 is reproduced.

The following data were assumed:

$$C_1 = 5.29 \times 10^5,\ C_2 = 1.46 \times 10^4,\ \lambda_1 = 2,\ \theta_1 = 800,$$

$\lambda_2 = 5$, $\theta_2 = 1{,}600$ and it was found that

$$J_1 = 1.801,\ J_2 = 32.54,\ u = 5,\ C = 1764,\ A = 0.1542$$

The equation to be solved is therefore

$$f(u) = u^5 - u - 0.1542 \quad 0.$$

Substitution gives $f(0.9) = -0.155$, $f(1) = A = 0.154$. Hence the root sought is approximately $u_0 = 0.95$.

The following table gives the result of the successive approximations.

m	u_m	C
0	0.95	1.454×10^4
1	0.9554	1.459×10^4
2	0.9565	1.460×10^4
3	0.9570	1.460×10^4
4	0.9570	

The computations were made with four place logarithmic tables. It is seen that the convergence of the process is completed with $u_4 = u_3$ but that u_1 approximately and u_2 exactly reproduces the assumed value of C_2.

Though the precision of experimental data would not justify the use of seven place tables, it was deemed desirable to test the *method* by a computation with such tables. The convergence of the u's (to seven places) was complete at $u_9 = u_8$, but u_6 gave $C_2 = 1.459999 \times 10^4$, and u_7, u_8, u_9, gave $C_2 = 1.460000 \times 10^4$.

DARTMOUTH COLLEGE,
HANOVER, NEW HAMPSHIRE,
March 29, 1914.

PROPOSED INVESTIGATION OF THE EFFECT ON THE PROPAGATION OF ELECTRIC WAVES OF THE TOTAL ECLIPSE OF THE SUN, 21st AUGUST, 1914.[1]

THE forthcoming total eclipse of the sun affords an exceptional and important opportunity of adding to existing knowledge of the propagation of electric waves through air in sunlight and in darkness, and across the boundaries of illuminated and unilluminated regions. The eclipse will be total along a strip extending from Greenland across Norway, Sweden, Russia and Persia to the mouths of the Indus. In Russia the duration of totality will be a little more than two minutes.

There are two main points calling for investigation during the eclipse. In the first place, the propagation of signal-bearing waves through air in the umbra and penumbra will probably obey laws different as regards absorption and refraction from those obeyed in illuminated air. In the second place, the strength, frequency and character of natural electric waves, and of atmospheric discharges, may vary. The variations may occur either because the propagation of natural waves from distant sources is facilitated or impeded by the eclipse, or, possibly, because the production of natural electric waves or atmospheric discharges is for some unknown reason affected by the eclipse.

These points have previously been investigated to only a slight extent. The observers of signals during the solar eclipse of 17th April, 1912, nearly all agreed that the strength of the signals was greater during the eclipse than an hour before or after. There was only one special observation of strays during the same eclipse, when very pronounced and remarkable variations were recorded during the passage of the shadow-cone across Europe.

To investigate the propagation of signals across the umbra it will be necessary to arrange for wireless telegraph stations on either side of the central line of the eclipse to transmit signals at intervals while the umbra passes between them. This transit of the umbra occupies about two minutes. It is thus very desirable that the Scandinavian and Russian stations should transmit frequently throughout several minutes before, during, and after totality. But stations other than those favored by their proximity to the central line should endeavor to keep a complete record of the variations of signals during the eclipse. Stations in Europe west of the central line and stations in the Mediterranean and in Asia Minor may find noticeable changes in the strength of signals, particularly long distance signals, between the hours of 10 a.m. and

---

[1] Received from the Committee for Radiotelegraphic Investigation of the British Association for the Advancement of Science.

3 p.m., Greenwich time; and it is probable that the stations of India and East Africa, and ships in the Indian Ocean, may feel the effect of the penumbra in the afternoon. On the other hand, ships in the Atlantic, and fixed stations in eastern Canada and the United States, will probably be affected by the penumbra in the early morning. At Montreal the eclipse (partial) is at its greatest phase at 5.52 a.m. Standard time. It is possible that the eclipse may have some influence even when it is invisible.

The investigation of strays is of as great interest as that of signals. So far as is yet known, the natural electric waves reaching wireless telegraph stations in latitudes higher than 50° appear to travel mostly from the south. Thus the greatest changes produced in strays by the eclipse will probably be experienced at stations in Scandinavia and Russia, to reach which the waves must cross the path of the umbra. At the same time changes of some kind are to be expected in other districts than these, and it is therefore desirable that statistical observations of natural electric waves be made all over the world, and especially at places within an earth quadrant of southern Russia. It is also desirable that meteorological observations, including those of atmospheric ionization and potential gradient, should be at the disposal of the Committee when considering the records of strays and signals.

The Committee propose to prepare and circulate special forms for the collection of statistics of signals and strays, especially within the hemisphere likely to be affected by the eclipse; they will endeavor to make provision for the transmission of special signals at times to be indicated on the forms; and they will offer for the consideration of the authorities controlling stations near the central line a simple programme of work. The discussion of the observations, and the comparison with meteorological data, will be carried out by the Committee; and digests of the statistics, together with the conclusions drawn from the analysis, will be published in due course.

The Committee would be greatly aided in the organization of this investigation if those possessing the necessary facilities and willing to make observations during the eclipse would communicate with the Hon. Secretary, Dr. W. Eccles, University College, London, W.C., at the earliest possible date.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

WASHINGTON MEETING, APRIL 24 AND 25, 1914.

MINUTES OF THE SEVENTY-SECOND MEETING.

A REGULAR meeting of the Physical Society was held at the Bureau of Standards, Washington, April 24 and 25, 1914. This was a joint meeting with the Electrophysics Committee of the American Institution of Electrical Engineers. The programs of the two morning and of the Saturday afternoon sessions were in charge of the Physical Society with President Merritt in the chair. The Friday evening session was in charge of the A. I. E. E. with Chairman J. B. Whitehead in the chair. The Friday afternoon session was given to a lecture by Sir Ernest Rutherford, F.R.S., of the University of Manchester, Eng., "On X-ray and Gamma-ray Spectra," complimentary to the American Physical Society.

Special features of the meeting were the opening of the new electrical building of the Bureau of Standards, and an exhibit of physical apparatus. This exhibit was arranged under the direction of a committee of the American Physical Society with Dr. F. A. Wolff as chairman. It was a large and representative exhibit, participated in by thirty-two manufacturers, importers and industrial research laboratores, ten universities and educational institutions, and eight federal scientific bureaus.

Members of the Physical Society were especially invited by the National Academy of Sciences to attend the William Ellery Hale lectures by Sir Ernest Rutherford upon "The Constitution of Matter and the Evolution of the Elements." These were given in the auditorium of the National Museum on April 21 and 23, and were attended by a large number of the Physical Society members.

All in attendance at the meetings were the guests of the scientific staff of the Bureau of Standards at luncheon on both days of the meeting. After the Friday evening session the local branch of the A. I. E. E. gave a smoker which was largely attended.

At a short business session of the Physical Society the following items of business were transacted:

On recommendation of the council, it was voted to establish a new grade of foreign members, to be defined as non-residents of North America, to pay dues of $4 with no initiation fee and to receive the PHYSICAL REVIEW (with *Science Abstracts* on additional payment of $2) and having all rights of regular members in the Society. Also to make such changes in the by-laws as the establishment of this new grade of membership would necessitate.

On motion it was voted to approve and authorize an International Congress of Physics to be held in Washington in October, 1915, in case it should appear that it can be properly financed. (A committee of nine was appointed by the council to determine this question.)

It was voted that the president appoint a committee of three to express the deep sense of loss felt by the members of this Society in the death of their former president, Professor B. O. Peirce.

The Society voted to express to the director and members of the National Bureau of Standards its high appreciation of the generous hospitality extended to the Society throughout the meeting, also to the Washington Section of the American Association of Electrical Engineers for arranging trips and providing guides to various places of scientific interest in the city and its neighborhood.

The attendance at all sessions was exceptionally large—at none less than one hundred and fifty. The Friday afternoon lecture was heard by about three hundred. One hundred and fifty-seven members registered.

At the Friday evening session (in charge of the A. I. E. E.) the following papers were presented:

Solenoids. C. R. UNDERHILL.

Some Investigations of Lighting Protection for Buildings. DEBLOIS.

Some Simple Examples of Transmission Line Surges. (By title.) W. S. FRANKLIN.

At the three sessions in charge of the American Physical Society the following papers were presented:

High Temperature Measurements with the Stefan-Boltzmann Law. C. E. MENDENHALL and W. E. FORSYTHE.

Cold-end Compensator for Thermocouples. (Apparatus shown.) CHARLES B. THWING.

The Emissivity of Metals and Oxides. I; Nickel Oxide (NiO) in the Range 600° to 1,300° C. G. K. BURGESS and P. D. FOOTE.

Formulæ for the Ordinary Mercury Contact Thermostat, and Some Practical Conclusions Deduced from Them. (By title.) W. P. WHITE.

The Specific Heats of Mixtures of Water and Alcohol, and of Solutions of Non-Electrolytes in these Mixtures. W. F. MAGIE.

The Extension of the Spectrum in the Extreme Ultra-Violet. (By title.) THEODORE LYMAN.

The Infra-red Arc Spectrum of Barium. H. M. RANDALL.

On the Growth and Decay of Color Sensation. M. LUCKIESH. (Read by A. G. Worthing.)

Some Effects of Diffraction on Brightness Measurements Made with the

Holborn-Kurlbaum Optical Pyrometer. A. G. Worthing and W. E. Forsythe.

Displacement of Arc Lines not Due to Pressure. Chas. E. St. John and H. D. Babcock. (Read by C. G. Abbott.)

On the Accuracy of Terrestrial-Magnetic Measurements. L. A. Bauer.

The Gamma-Ray Comparison of Specimens of Radium Salts. N. Ernest Dorsey.

The Results of the Atmospheric Electric Observations on the Second Cruise of the 'Carnegie,' June 1910 to December, 1913. C. W. Hewlett.

Apparatus for the Spectroscopic Synthesis of Color. H. E. Ives and E. J. Brady.

New Methods for Measuring Time Constants of Low Resistances. Frank Wenner, Ernest Weibel and F. B. Silsbee.

A Sensitive Moving Coil Galvanometer. F. Wenner, E. Weibel and F. C. Weaver.

Some Peculiarities in the Thermal Expansion of Invar. Arthur W. Gray.

A New Turbidimeter. P. V. Wells.

The Diurnal System of Convection. Wm. H. Blair.

The Control of the Wave-length-Sensibility Curves for Selenium. E. O. Dieterich.

Some Records of the Wireless Time Signals Made with a Physiological Recorder. C. W. Waggoner.

Electric Conduction and Thermo-electric Action in Metals. E. H. Hall.

Electrochemical Indicators and Recorders. Instruments for Showing Continuously the Chemical Content of Solutions. F. A. Harvey.

Characteristic Curves of Tungsten Filament Incandescent Lamps and their Application in Heterochromatic Precision Photometry. G. W. Middlekauff and J. F. Skogland.

The Thomson E.M.F. in and the Thermal Conductivity of Tungsten at Incandescent Temperatures. A. G. Worthing.

A Direct Determination of "h." R. A. Millikan.

Reversible Transitions Between Solids at High Pressures. P. W. Bridgman.

Surface Leakage over Insulators. H. L. Curtis.

Spark Potentials in a Magnetic Field. (By title.) R. F. Earhart.

Further Experiments on the Use of the Photo-Electric Cell in Stellar Photometry. Jakob Kunz, J. Stebbins and W. F. Schulz.

Note on the Photo-Electric Effect with Potassium Surfaces in Very High Vacuum. Saul Dushman.

On the Relation Between the Photo-electric Potential and the Frequency of Light for Potassium. S. Karrer.

Reflection and Scattering of Slow-moving Electrons. Albert W. Hull.

Wave-Length Sensibility Curves of Potassium Photo-Electric Cells. H. E. Ives.

The Photo-Electric Effect of Carbon as Influenced by its Absorbed Gases. Otto Stuhlmann, Jr. and R. J. Piersol.

The Relation of Residual Gases to the Photo-Electric Sensitiveness and the Contact E.M.F. of Sodium. R. A. MILLIKAN and W. H. SOUDER.

Effect of Glass Walls on Thermionic Currents. SAUL DUSHMAN.

Corona Produced by Continuous Potentials. S. P. FARWELL.

Theory of the Corona. BERGEN DAVIS.

A Milli-Ampere Current Transformer. EDWARD BENNETT.

Some Points with Regard to the Variation of the Specific Magnetization of a Substance with Temperature. W. F. G. SWANN.

High Frequency Verification of Kirchoff's Capacity Formulæ. (By title.) F. C. BLAKE and CHAS. SHEARD.

An Electromagnetic Puzzle. F. J. ROGERS.

A Significant Instance of Galvanometer Instability. W. P. WHITE.

A New Design of Flicker Photometer for Laboratory Colored-Light Photometry. H. E. IVES and E. J. BRADY.

Note on the Physiological Effect of the Current. F. J. ROGERS.

Examples of the Precision Attainable in Determinations of Thermal Expansivity. ARTHUR W. GRAY.

Dioptric Formulæ for Combined Cylindrical Lenses at Oblique Axes. (By title.) CHARLES SHEARD.

The Testing of Potentiometers. FRANK WENNER and ERNEST WEIBEL.

An Absorbing Solution for Eliminating Color Differences in Photometry. H. E. IVES and E. F. KINGSBURY.

Photographs of Retrograde Rays, (*a*) from the Cold Cathode, (*b*) from the Hot Lime Cathode. O. H. SMITH.

A. D. COLE,
Secretary.

ON METALLIC CONDUCTION AND THERMOELECTRIC ACTION IN METALS.[1]

BY EDWIN H. HALL.

IN this paper[2] an attempt is made to consider and compare the functions of (A) electrons transferred from atom to atom during collisions or contacts and of (B) electrons relatively free between the atoms.

The proposition is advanced that thermoelectric action cannot be accounted for without assigning thermal capacity to the electrons, and the idea that such thermal capacity is a function of the temperature is introduced by treating R, of the equation $pv = RT$, as a variable for electrons, $= k_rT^p$, where k_r and p are constants.

The main conclusions are that the free electrons (B) are essential for the

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

[2] Acting upon information which I had not examined with sufficient care, I stated at Washington that pure metals, when heated under such pressure conditions as not to suffer change of volume, show a decrease of resistance. This statement is true regarding liquid mercury, as Barus found long ago, but it is not true of metals in the solid state. After going carefully over the ground of my investigation once more I find that the mistake which I had made in this particular did not affect my general conclusions, which remain unchanged.

phenomena of thermoelectricity, but play an unimportant part in electric conduction.

The relation between the Peltier effect and the Volta effect is discussed.

A table of data concerning change of volume and change of resistance in the fusion of metals is given in an Appendix.

Cambridge, Mass.,
May 26, 1914.

Some Points with Regard to the Variation of the Specific Magnetization of a Substance with Temperature.[1]

By W. F. G. Swann.

According to the theory of Weiss the molecular magnetic theory of a solid may be treated on the lines of that for a gas provided that the applied field H is replaced by $H + H_m$, where H_m is a field which represents the effects of the molecular actions. H_m is assumed to be of the form NI where I is the intensity of magnetization and N is a constant for the substance.

Weiss has shown that in order to account for the variations of the specific magnetization with temperature above the Curie point, it is necessary to assume that the number of magnetons in a molecule changes abruptly at certain temperatures. In the present communication it is shown that this is not all that is necessary to account for the facts, but that the constant N must also vary abruptly with the temperature and in some cases must even acquire a negative value.

A change in the number of magnetons is usually not accompanied by an abrupt change in the coefficient of magnetization, which fact seems to indicate a tendency on the part of the substance to make a change in the number of magnetons, only when the temperature conditions are such that it can do so without altering that part of the energy which is purely magnetic.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington.

Characteristic Curves of Tungsten Filament Incandescent Lamps and Their Application in Heterochromatic Precision Photometry.[1]

By G. W. Middlekauff and J. F. Skogland.

As the international candle is maintained by means of carbon filament incandescent lamps operated at four watts per candle, the standardization of lamps of higher efficiency involves photometric difficulties due to color difference. Although differences in color may be reduced or eliminated in the direct comparison of the lamps either by the use of blue glass screens placed in the path of the light from the carbon standards, or by the substitution of secondary standards of the same color as the lamps to be measured, nevertheless the difficulties mentioned must be encountered in calibrating the screens and the secondary standards.

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

On the assumption that the radiating properties of pure tungsten wire in the form of a filament in vacuo are constant, the authors concluded that if the candle-power-voltage relation could be accurately expressed by means of an equation, candle-power values of tungsten standards at the higher efficiencies could be determined from single values at color match with carbon standards with greater precision by computation than by actual measurement with color difference. It would then be possible, in the calibration of glass screens and incandescent lamps at high efficiencies, to avoid all measurements with color differences except those necessary in the determination of the equation which would be carefully and accurately made once for all.

To investigate this subject, a group of 60-watt, 110-volt, drawn wire tungsten lamps were standardized through the range of color met with in the standardizing work of the Bureau of Standards, and it was found, as expected, that not only the candle-power-voltage relation but every other characteristic relation for each and every lamp of the group could be accurately expressed by a simple equation of the form

$$y = Ax^2 + Bx + C,$$

in which x = log voltage; y = log candlepower, log watts, log current, or log watts per candle; and A, B and C are constants whose numerical values depend upon the significance of y. C depends also upon the candle-power value of the lamp considered while the values of A and B are invariable for the same relation when applied to any lamp of the group investigated.

It was found that the equations generally employed to express characteristic relations could not be used except through a limited range and that the adjustment is in no case as precise as that obtained by means of the above equation.

As watts per candle is the only independent variable, it must be known before computing characteristic values. Therefore the general equations for the group of lamps had, necessarily, to be arranged for the substitution of percentage values with unity taken at some chosen efficiency. In this case 1.20 w.p.c. was found to be most practical. Volt ratios thus have their base at this point, and in the general equations which are also of the form given above, x = log per voltage and y = log per candlepower, log per watts, log per current, or log actual watts per candle. C is equal to zero except in the equation for watts per candle evaluation where it has the value log 1.20. To the constants A and B, values are assigned which give practically perfect adjustment of candle-power and watts of these lamps and also permit extrapolation to 0.7 w.p.c. and all intermediate points as has been verified by a check with independent groups of lamps. The range from 0.7 to 0.5 w.p.c. has not yet been investigated, but it seems probable that this further extension is possible. The equations have been found to apply to tungsten lamps of sizes from 20 to 100 watts, including those of most recent manufacture.

Derived equations permit the reduction of candle-power and voltage values at any efficiency to those at 1.20 watts per candle. This reduction is the first essential in computing characteristic values.

Tables will be published[1] showing, (*a*) values of per cent. candle-power and per cent. voltage at 1.20 watts per candle from any given efficiency within the range from 2.0 to 0.7 and probably to 0.5 in steps of 0.02 watts per candle, and (*b*) percentage values of watts and candle-power and actual watts per andle for every volt ratio from 0.6 to 1.3 and probably to 1.6. Tabular differences will be given and their use explained. From these tables others based on any efficiency included can be easily calculated.

Bureau of Standards,
Washington, D. C.,
April 1, 1914.

A Displacement of Arc Lines Not Due to Pressure.[2]

By Charles E. St. John and Harold D. Babcock.

When the light from the different parts of the iron arc is examined by a powerful spectrograph, it is found that there are variations in the wave-lengths of the lines depending upon the portion of the arc used. A direct comparison has been made by us between the center of the iron arc and the region very near the negative pole. It has been extremely difficult and in fact practically impossible to obtain with certainty non-simultaneous photographs of spectra and comparisons that do not show minute relative displacements which must be referred to the instrumental conditions, even though the apparatus is very stable and the optical parts are in a constant temperature underground compartment.

By an arrangement of prisms over the slit of the plane grating spectrograph of 30-foot focus we now obtain *simultaneous* exposures, and are able to determine the absolute shifts between the pole and the center of the arc. There are some groups of lines—groups *a*, *b*, and *c* 4 of the Mount Wilson classification —that show no determinable displacements between the center and the negative pole, there are other groups, such as *c* 5, *d*, and *e*, the wave-lengths of which vary with the portion of the arc used, by such increments that, if pressure were the cause, a pressure difference of more than an atmosphere would be indicated between pole and center. The pressure shift for lines of group *b* in the red is 0.009 Å per atmosphere, as found by Gale and Adams. These lines are among the best lines in the iron spectrum, and they do not show displacements greater than the accidental errors of measurement which in the case of these lines do not amount to 0.001 Å.

It appears then that the displacements shown by the groups *c* 5, *d* and *e* between pole and center are not due to pressure. In general these lines are widened unsymmetrically at the negative pole, and the displacement was at first ascribed to the unsymmetrical broadening as the negative pole was approached, but the intensity curves obtained by Koch's *microphotometer* show that the maxima are displaced in the direction and by the amount

---

[1] Bulletin of the Bureau of Standards.

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

indicated by the measured shift. Provisionally we are inclined to ascribe these displacements to increase of density, but the effects of other conditions are still under investigation.

The following table shows the results in the case of a few typical lines:

Negative Pole minus Center of the Arc.

Group *a*.		Group *b*.		Group *d*.		Group *e*.	
λ	*P−C*	λ	*P−C*	λ	*P−C*	λ	*P−C*
5,323	−0.0000Å.	6,136	+0.0007Å.	5,281	+0.018Å.	5,364	−0.022Å.
5,332	−0.0002	6,137	−0.0004	5,283	+0.019	5,367	−0.026
5,341	−0.0006	6,213	+0.0003	5,324	+0.022	5,369	−0.020
5,497	−0.0003	6,219	+0.0010	5,339	+0.016	5,383	−0.024
5,501	−0.0004	6,230	+0.0004	5,393	+0.017	5,400	−0.024
5,506	+0.0004	6,252	+0.0000	5,653	+0.014	5,410	−0.024
Mean............	+0.0002Å.		+0.0003Å.		+0.018Å.		−0.023Å.
Displ. per atm....	+0.0036		+0.0094		+0.015		−0.018

MT. WILSON OBSERVATORY,
CALIFORNIA.

ON THE GROWTH AND DECAY OF COLOR SENSATIONS IN FLICKER PHOTOMETRY.[1]

BY M. LUCKIESH.

IT has been well established that photometric measurements obtained by the direct comparison and flicker methods do not agree in most cases. Under favorable conditions this disagreement is only a few per cent., but where there is a large color difference such as obtains when red or green lights are compared with "white" light or with each other the results by the two methods often differ by many per cent. A comparative study has been made of the two methods and a further study has been made of the phenomena involved in the flicker method in order to account for the difference between the results by the two methods. The results by both methods are of course primarily effected by the variations in the color vision of various observers. For instance observers having so-called normal color vision on comparing red or blue with "white" light obtain results differing by as much as 100 per cent. But the fact that the two methods give different results indicates that the different phenomena underlying these two methods are of importance.

When flickering lights are observed it is at once obvious that the rates of growth and decay of the color sensations are liable to be involved. Broca and Sulzer have shown that there is an overshooting of luminous sensation varying with the intensity and color of the light. The writer has used complementary colors, red and blue-green, in studying the phenomena involved in flicker photometry. These have been intercompared in various ways and also com-

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

pared with "white" light. It has been verified that the ratios of the intensities of these two lights differ by many per cent. by the direct comparison and flicker methods.

The maximum values of sensation produced by these colored lights differ considerably at all frequencies of flicker up to vanishing-flicker frequencies. The speed at which flicker disappears is always lower for the blue-green light for equal intensities as measured by the direct comparison method. When blue-green light is flickered upon a steady red field the speed at which flicker disappears is much lower than for the case of red light flickering upon a steady green field. In these cases the illuminations on the photometer screen are balanced for equality by the direct comparison method. The speed or frequency at which a balance is made with the flicker photometer is found to be lower than the speeds of vanishing flicker for the two lights. There is a considerably greater overshooting of luminous sensation in the case of the red light flickering upon a steady blue-green field than in the case of blue-green light flickering upon a steady red field.

It is also found that the vanishing flicker frequency depends upon the shape of the "illumination wave," that is upon the contour of flicker. This suggests a possibility that flicker photometers differing in principle may give different results. The results indicate that the importance of the different rates of growth and decay of color sensations have not been considered seriously enough in connection with flicker photometry. It seems that the differences between the results by the direct comparison and flicker methods can be largely accounted for in the above phenomena.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Cleveland, Ohio.

Reversible Transitions between Solids at High Pressures.[1]

By P. W. Bridgman.

A large number of substances have been examined over the range from 0° to 200° and from atmospheric pressure to 12,000 kgm. per sq. cm. The reversible transitions from one solid to another which occur within this range have been studied, and the relation between pressure and temperature along the transition lines, the difference of volume between the different forms, and the latent heat of transition have been determined. Data have been obtained for the following substances: AgI, NH_4NO_3, HgI_2, C_2Cl_6, KNO_3, $KClO_3$, $AgNO_3$, KSCN, NH_4SCN, KNO_2, and $CsNO_3$. Of these NH_4NO_3, $KClO_3$ and KNO_2 have each one new form not known before, and KNO_3 has two new forms. Particularly striking are the very rapid curvature of the $AgNO_3$ line, and the fact that there is a maximum temperature of transition between the red and the yellow modifications of HgI_2. The results for these various substances show nearly all possible kinds of behavior. This is different

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

from the behavior on the transition curve from liquid to solid, where all substances give results of only one type.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

SURFACE LEAKAGE OVER INSULATORS.[1]

BY HARVEY L. CURTIS.

THE resistance between two conductors insulated by a solid dielectric usually depends very largely on the surface condition of the dielectric. If the insulator is in a humid atmosphere, condensation of moisture is known to take place on the surface and this increases the surface leakage. This paper will attempt to find a connection between the moisture condensed and the surface leakage.

The surface resistivity is defined as the resistance between two opposite edges of a surface film which is one centimeter square. The surface conductivity is the reciprocal of this. The surface resistance of most insulators varies greatly with the humidity of the surrounding air. In one case (hard rubber which had been exposed to the sunlight) the surface resistivity in very dry air was nearly one trillion (10^{12}) times as large as in very humid air. With waxy materials such as paraffin, ozokerite and beeswax, there is very little change with the humidity but all other insulators show marked changes. A factor of 10^5 or 10^6 between high and low humidities is not uncommon. It is to be expected that this change in surface resistivity is due to condensed moisture.

The thickness of the surface film of water upon quartz and glass has been determined by weighing. Knowing this thickness and the surface resistivity, the conductivity of the surface film is readily computed.

Ihmori[2] found the thickness of the water film on quartz by weighing. With cleaned specimens at about 90 per cent. humidity the thickness was about 0.5×10^{-6} centimeters. With uncleaned specimens the thickness was found to vary from 1.4×10^{-6} to 6.2×10^{-6}. The surface resistivity of quartz at 90 per cent. humidity which had been carefully cleaned was found to be about 10^{12} ohms per centimeter square. This gives the conductivity of the water of the film as 2×10^{-6} reciprocal ohms per centimeter cube, which corresponds to a high grade of distilled water. With the uncleaned specimens the surface resistivity was as low as 10^8 ohms per cm. square. Assuming that this corresponds to the thickest film found by Ihmori, the conductivity of the water is 0.0017 reciprocal ohms per centimeter cube. Since the quartz is insoluble, the increased conductivity is due to soluble salts which were present on the surface. If it were entirely due to sodium-chloride, there must have been 6×10^{-9} gram of the salt on each square centimeter.

In the case of glass, it was found that careful cleaning produced much less change in the surface resistivity than in the case of quartz. In fact with soft

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

[2] Wied Ann., 31, p. 1006; 1887.

German glass there was very little if any change. A number of samples were measured, the lowest value of 2×10^7 ohms being for a soft glass. Parks[1] has found the thickness of the water film on glass to be about 10^{-6} cm. Hence for soft glass, the conductivity of the water in the surface film is 5×10^{-8} reciprocal ohms per centimeter cube. This can be accounted for by the solubility of glass in water.

In the case of the waxy materials, water does not spread over the surface, but collects in drops. Hence we would not expect any change of surface resistivity with humidity. That such is the case has already been noted.

The presence of inorganic salts on the surface of insulators may not only lower the conductivity of the film, but it may also increase its thickness. This was shown by the measurements of Ihmori already quoted. Hence in the case of rubber which has deteriorated by exposure to the light, thereby forming considerable quantities of deliquescent salts on the surface, the resistivity changes through a very wide range due to changes of humidity.

An oil film has a much higher resistance than a water film, but in the case of the very best insulators such a film may lower the surface resistivity at low humidities. With moderate insulators, however, it may have a beneficial effect.

Bureau of Standards,
Washington, D. C.

A Significant Instance of Galvanometer Instability.[2]

By W. P. White.

A CERTAIN moving coil galvanometer, whose coil was very well balanced, showed for some time great steadiness while standing on a stone shelf. Subsequently, it showed in the same situation great sensitiveness to certain tremors of the building. There was no visible jiggling of the coil, but the slamming of doors, moving of heavy boxes, or pounding, in certain locations, caused a deflection often exceeding a millimeter at a meter's distance. The deflection was such as might have been produced by slight tipping of the galvanometer. It was a radial field instrument and, like most of its kind, very sensitive to changes of level. An investigation seemed to indicate that the shelf was too flexible, and the galvanometer was fastened to a stout iron bracket which was secured to two boards which had been built into the wall for such purposes. The trouble entirely disappeared, and for some time the galvanometer was almost perfectly steady again. Subsequently, the trouble reappeared as badly as before. An examination indicated that the wooden boards were not quite firmly fastened to the wall. The iron shelf was then fastened directly and firmly to the brickwork of the wall itself, and the trouble again disappeared. Conclusions: (1) It is clear that if the stone shelf had not been steady at first, or if the wooden boards had been loose from the wall at the

---

[1] Phil. Mag. (6), *5*, p. 517; 1903.

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

outset, the real nature of the trouble would probably never have been discovered. The reasonable inference would have been drawn that the tremors of the building as such were too much for the galvanometer, and some unnecessarily elaborate protection would have been installed. (2) It is clear that moving coil galvanometers, at any rate those with a radial field, may suffer serious perturbations which are not the direct result of oscillations or jiggling of the coil. If in this case the perturbations had been accompanied by a small amount of jiggling, the latter would of course have been blamed. It is quite possible, therefore, that changes of level, weak fastening of shelves, and other similar preventable causes may now be responsible for much galvanometer disturbance, but are not recognized and remedied because some jiggling is also present and gets credit for the whole trouble. (3) This seems very likely to be the case where a Julius suspension of the old type, with three wires, is used, since the ordinary breezes of the room, acting on these fine wires, may produce slight irregular expansions and contractions, which cause changes of level, and therefore deflections. In such a case, the conclusion might easily be drawn that the deflections are due to the vibrations of the building, that they therefore show that the suspension is inadequate, and that no further help is possible, whereas the case may be quite otherwise. Of course, if any effect of this sort is suspected with a Julius suspension, a test can easily be made which will show whether it is present or not.

Geophysical Laboratory,
Washington, D. C.

High Temperature Measurements with the Stefan-Boltzmann Law.[1]

By C. E. Mendenhall and W. E. Forsythe.

In view of the increasing use of extremely high temperatures (2000–3000° C.) the establishment of a reliable scale for this reason becomes increasingly important. Above 1550° C., the limit this far attained with the gas thermometer, the only method available is some form of radiation pyrometer. Of these we may use for a perfect radiator, either the one based on a measurement of the total radiation or one depending upon the spectral distribution. While in many cases the latter is more convenient to use, the former is the more sound from a theoretical standpoint, for the reason the Stefan-Boltzmann law has been chosen as defining the temperature scale.

This work may be considered in three parts: (1) A comparison of the Stefan-Boltzmann scale of temperature with the Day and Sosman scale between 1063° C. and 1549° C. (the melting points of gold and palladium). (2) A determination of the melting point of platinum in terms of the Stefan-Boltzmann scale. (3) A comparison of the optical temperature scale based on the application of Wien's Law to a pyrometer of the Holborn-Kurlbaum type with the Stefan-Boltzmann scale up to 2820° C.

Apparatus.—The optical pyrometers were calibrated by observations on a

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

black body furnace held at the melting points of palladium and gold respectively. For the intermediate points and for extending the scale rotating sectors of known aperture were used, combined with Wien's distribution law in which C_2 was taken as 14,500 and the wave-length used was 0.658 μ. To obtain the high temperature the carbon tube furnace described in the Astrophysical Journal, December, 1911, page 353, was used. The arrangement of this furnace was altered somewhat to allow for a series of water-cooled diaphragms that served both to protect the receiving thermocouple and also to limit the beam of radiation. The inside of the furnace was carefully washed out with nitrogen before any attempt was made to make any determination of temperature, by measuring the total radiation. The receiving thermocouple consisted of a single junction of Bi-Sb and Sb-Cd alloys, the hot junction being soldered to a light receiving disc of silver foil 3 mm. in diameter. This receiving disc was blackened with acetelyne smoke and mounted at the center of a hemispherical concave mirror. Under these circumstances the receiver has been assumed to be a perfect absorber, since only differential errors would be introduced if this assumption were not quite correct.

If a certain deflection D of the galvanometer connected to the thermopile, is obtained at a temperature T_1 (always the gold or palladium melting point) with clear aperture, and the same deflection is obtained through a rotating sector whose transmission is S (< 1) at a temperature T_2 then $T_2 = T_1 / \sqrt[4]{S}$ which determines the temperature on the Stefan-Boltzmann scale.

Twelve comparisons were made of the Stefan-Boltzmann scale and the gas scale between 1063° C. and 1549° C. The total radiation sector having been cut in the ratio $(1{,}063 + 273/1{,}549 + 273)^4$ the ratio of the corresponding deflections should have been unity, the observed mean ratio was 1.001, the maximum ratio being 1.007, the minimum 0.998. Our value for the melting point of platinum depends upon three very concordant direct determinations of the melting point in a graphite tube black body furnace carried out by Mr. C. G. Peters. The platinum was enclosed in porcelain and protected from the action of the reducing gases by a flow of nitrogen. The average value was 1753° C. The temperature scale based on the Stefan-Boltzmann law and that based on the Wien Distribution law, were compared at the following points with the results indicated:

Number of Comparisons.	Temperature ° C.	$T_W - T_{S-R}$	Range of Observations.
9	1750	Less than ± 0.5° C.	
7	2200	Less than + 2.	2° C
3	2500	About + 2.	4
4	2820	About + 4.	7

Department of Physics,
University of Wisconsin.

COLD-END COMPENSATOR FOR THERMOCOUPLES.[1]

BY CHARLES B. THWING.

THE method of compensating for variations in the temperature of the cold ends of a thermocouple used in connection with a direct reading indicator or recorder consists in placing in series with the couple at the cold end a Wheatstone bridge of low resistance. Three arms of the bridge are of manganin, the fourth of nickel. The current through the bridge is so adjusted by resistance in the battery circuit as to give direct readings of temperature at the bridge when the thermocouple is not in circuit. When couple and bridge are connected in series the readings of bridge and thermocouple are combined to give true temperature readings. Otherwise expressed, the bridge automatically sets the zero of the indicator to cold end temperature. (The apparatus was exhibited, attached to a recording pyrometer.)

PHILADELPHIA, PA.,
March 24, 1914.

THE EMISSIVITY OF METALS AND OXIDES. I: NICKEL OXIDE (NiO) IN THE RANGE 600 TO 1300° C.[1]

BY G. K. BURGESS AND P. D. FOOTE.

THE monochromatic emissivity, E_λ, throughout the visible spectrum and the total emissivity, E, of nickel oxide (NiO) have been measured for the temperature interval 600 to 1300° C. The monochromatic emissivity increases linearly with increasing wave-length and decreases linearly with increasing temperature over the region investigated. For example, at 1160° C., E_λ increases from 0.865 at $0.5\,\mu$ to 0.882 at $0.7\,\mu$, and for $\lambda = 0.65\,\mu$, E_λ decreases from 0.958 at 800° C. to 0.845 at 1300° C. The total emissivity increases with increasing temperature, but the relation is not linear. Temperatures and E have respectively values as follows: 600°, 0.54; 800°, 0.68; 1000°, 0.76; 1200°, 0.85; 1300°, 0.87.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

SOME EFFECTS OF DIFFRACTION ON BRIGHTNESS MEASUREMENTS MADE WITH THE HOLBORN-KURLBAUM OPTICAL PYROMETER.[1]

BY A. G. WORTHING AND W. E. FORSYTHE.

IT has generally been assumed that, when the pyrometer filament in a Holborn-Kurlbaum optical pyrometer apparently matched the background image in brightness, the filament and the image were at the same brightness. However, in attempting to compare temperature measurements on a tungsten filament made with an ordinary Holborn-Kurlbaum optical pyrometer with those made with a modified one as described below, such was found not to be the case.

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

The apparatus was arranged as indicated in Fig. 1 where we have shown also the dimensions. It was found that varying the size of the opening at C, that is varying the angle α, keeping, however, the angle α greater than the angle β, necessitated a change in the brightness of the pyrometer filament in order to maintain the apparent match in brightness with the background image. In a special case, keeping all other parts of the apparatus constant, and varying only the angle α, an apparent change in the brightness of the background image of 60 per cent. was caused. Other conditions being the same, the smaller the angle and the larger the pyrometer filament, the brighter the background image appeared as compared with the brightness of the pyrometer filament. When the angle α was changed by varying the opening in C only in a direction perpendicular to the axis of the pyrometer filament, the apparent change in brightness was the same as when the aperture in C was increased in all directions.

On blocking out the central portion of the objective lens so that, from geometrical considerations only, no light from the background in the immediate neighborhood of the point where the pyrometer filament is seen projected, can enter the eyepiece opening, the filament is still seen apparently illuminated, even though no current is passing through it. When an eye piece of high enough resolving power was used, this brightness of the pyrometer filament was seen to consist of bright streaks along its edge. Because of these and other effects it was decided that the apparent change in brightness of the pyrometer filament was due to diffraction of the light from the background at the pyrometer filament.

Some necessary working conditions for avoiding difficulties arising from diffraction and other causes in optical pyrometry are added:

1. The sources to be studied should be used as backgrounds and not as pyrometer filaments.
2. A single pyrometer filament should be used throughout an intercomparison.
3. The angles α and β should be definitely fixed. This can be best done by having limiting diaphragms at C and E which are at fixed distances from the pyrometer filament, preferably as far away as possible.
4. The apparatus should be so adjusted that there is approximate axial symmetry.
5. The resolving power of the eyepiece should not be so great as to prevent the practical disappearance of the pyrometer filament against the background image.
6. The image of the background should be large in comparison with the pyrometer filament.
7. The magnifying power of the eyepiece should be sufficiently large so that no difficulty is experienced by the observer in fixing on the intersection and so that the effects due to the eye's imperfections are largely eliminated.

If in addition, the following desirable conditions are fulfilled, it will be found that brightness matches can be more easily obtained.

1. The eyepiece should have as high a resolving power as possible, but still with the condition that when the pyrometer lamp filament is balanced in brightness against the background, there will be disappearance.

2. An eyepiece and eyepiece diaphragm combination which gives comparatively large clear images is of course desirable.

3. Considerable depends upon the pyrometer lamp. In general the writers have found filaments in either hairpin loops or single straight filaments mounted in spherical bulbs to be the most satisfactory. In general the larger bulbs have been found more free from imperfections than the smaller bulbs.

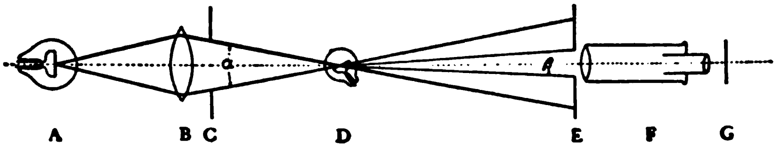


Diagram showing arrangement of apparatus. *A*, background; *B*, objective lens; *C*, entrance cone diaphragm; *D*, pyrometer filament; *E*, eyepiece diaphragm; *F*, eyepiece; *G*, monochromatic glass filler. *AB* = 25 cm., *BD* = 128 cm., *DE* = 185 cm. Diameter of aperture at *E*, 9 mm.

4. For the sake of ease of adjustments, particularly in obtaining axial symmetry, it is very desirable to have the diaphragm *C* one with a variable aperture.

5. In cases where high accuracy is demanded a gain may sometimes be made by using light of the shorter wave-lengths.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Cleveland, Ohio.

THE RESULTS OF THE ATMOSPHERIC ELECTRIC OBSERVATIONS ON THE SECOND CRUISE OF THE "CARNEGIE", JUNE, 1910, TO DECEMBER, 1913.[1]

By C. W. Hewlett.

A SYSTEMATIC series of observations extending over three years has been made on the potential gradient, conductivity, and the radioactivity of the atmosphere during fifteen passages in the Atlantic, Indian, and Pacific Oceans. The results will be elsewhere analyzed and treated in detail. The mean values for the conductivity vary considerably in the different Oceans, but in all cases were high in comparison with the results previously found on land and on sea. The values were of the order of from 50 to 100 per cent. greater than those usually found for land and seemed to show very little connection with the radioactivity of the atmosphere. Only in the Atlantic Ocean was an appreciable amount of radioactivity observed. The average activity here being 8 (in Elster and Geitel units).

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

The average value for the potential gradient in the Atlantic Ocean was about equal to that in the Pacific and about 60 per cent. greater than the value in the Indian Ocean. With the exception of one observation the potential gradient was always positive when even the observations were made during rain. The relations of the elements among themselves and with the various meteorological factors is in accordance with what would be expected from theoretical considerations.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington.

A Sensitive Moving-Coil Galvanometer.[1]

By F. Wenner, E. Weibel and F. C. Weaver.

THE galvanometer is designed for use in bridge, potentiometer, and similar work where the resistance of the apparatus is fairly low and a high sensitivity is required. To distinguish the design described here from others we shall refer to it as type *m*.

The coil is 8 × 12 mm. in mean area and has $27\frac{1}{2}$ turns of .080 mm. (No. 40 American wire gauge) single silk-covered copper wire. It is wound in such a way that there is a loop at both the top and bottom to which the suspensions and mirror are attached. A second loop is brought out both at the top and the bottom and extends to the front. These with a wire added later form a truss to stiffen the coil. Before the coil is removed from the form on which is is wound it is treated chemically to remove all traces of iron in the insulation and on the surface of the wire. After thorough washing and drying the coil, still on the form, is dipped in a thin solution of collodion which when dry binds the winding firmly together.

The mirror is 1 cm. in diameter and .6 mm. in thickness.

The suspensions are made from .015 mm. copper wire rolled flat. They are each about 4 cm. long and by means of a spring are held taut, the tension being of the order of 1,000 dynes.

The point to which the lower end of the lower suspension is attached is not directly under the point to which the upper end of the upper suspension is attached, but is from 1 to 3 mm. to the front. Thus the coil rotates about an axis making a small angle with the vertical. In balancing the coil the adjustment is made so that the center of mass is a fraction of a mm. to the front of the axis of rotation. This gives the moving system a small gravity control opposing the control of the suspensions. By changing the level of the instrument the gravity control may be changed and consequently the period of the moving system changed as desired.

The iron core is 6 mm. in diameter and 1 cm. long. The pole pieces are of the same length as the core and have a radius of 4 mm. In assembling the spacing is such that the air gaps are 2 mm. at the center and slightly less under the pole tips, making the field very nearly radial.

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

A strong magnet is used and it is provided with an adjustable shunt so that the intensity of the field in the air gap can easily be varied over a considerable range.

With the period adjusted to 10 seconds and the field strength adjusted so as to make the external critical resistance 20 ohms the sensitivity is approximately 20 mm. per micro-volt, with the scale at a distance of 1 meter.

As compared with the most sensitive "low resistance" galvanometers on the market, taking the mean of the operating constants of three instruments of different designs, we have, approximately—external critical resistance 65 ohms —period 6 seconds—and sensitivity 2 mm. per micro-volt.

It is probable that further experience with this design will suggest minor changes in the construction.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

THE CONTROL OF THE WAVE-LENGTH-SENSIBILITY CURVES FOR SELENIUM.[1]

BY E. O. DIETERICH.

AN investigation of the conditions governing the shape of the sensibility curves for selenium led to the production of several new types of cells, which may be classified into two general groups; those that have a maximum sensibility for wave-lengths longer than 640 $\mu\mu$, and those that show very little sensitiveness in this region, but have a maximum for wave-lengths shorter than 640 $\mu\mu$. The location of the maximum for the different types produced thus far is as follows: 440 $\mu\mu$, 500 $\mu\mu$, 550 $\mu\mu$, 700 $\mu\mu$, 720 $\mu\mu$, and 800 $\mu\mu$. Those that show a maximum in the red also have a pronounced minimum at 640 $\mu\mu$, and a broad maximum at the shorter wave-lengths. Some, however, have two well-defined maxima; those that have a maximum at 440 $\mu\mu$ also show one at 700 $\mu\mu$ or 720 $\mu\mu$, and a minimum at 640 $\mu\mu$.

The location of the maximum seems to be determined entirely by the method of "annealing" the cells. The samples annealed at 210° C., or higher, all show a maximum below 640 $\mu\mu$, and no maximum at all in the longer wave-lengths. Those annealed at lower temperatures, 180° C., all show a maximum at wave-lengths greater than 640 $\mu\mu$, which is higher than the broad, undefined maximum in the shorter wave-lengths. When the samples are annealed at temperatures between 180° C. and 210° C., the height of the maximum in the red, relative to that in the blue, becomes less and less, until at about 210° C. it disappears. Further work, to determine more accurately the governing conditions, is in progress.

THE PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.

THE TESTING OF POTENTIOMETERS.[1]

BY FRANK WENNER AND ERNEST WEIBEL.

FOR precise measurements with a potentiometer the errors in the adjustment of the resistance sections or coils in the apparatus must be known.

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914. To be published in the Bulletin of the Bureau of Standards and reprinted as Scientific Paper No. 223.

These errors can be determined by measurements of the resistances of the various sections but, without some systematic method of applying corrections, are not easily allowed for, in the use of the potentiometer.

We have found that it is convenient to express the relation between the known electromotive force, the unknown electromotive force, the readings and the corrections by the formula

$$E = f[(e_1 + a_1) + (e_2 + a_2) + \text{etc.}]\,(1 + b + c + d) \qquad (1)$$

where E is the value of the unknown electromotive force
f is the range reading,
e_1 is the reading of the highest dial,
e_2 is the reading of the next highest dial, etc.,

$$c = \frac{S - s}{s},$$

where S is the value of the known electromotive force and s is the reading of the known electromotive force dial or dials, and b, d, a_1 and a_2, etc., are small corrections due to errors in the adjustment of the various resistance sections. The correction a_1 depends only on the reading e_1, a_2 depends only on e_2, etc., b depends only upon the reading s and d depends only upon f. A table can therefore be constructed for each dial giving the corrections corresponding to its various readings.

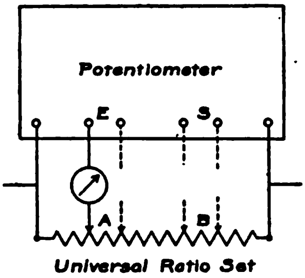


Fig. 1.

Let R_e be the resistance in the potentiometer between the E terminals and R_s that between the S terminals. Then if the total current is independent of the settings of the various switches, plugs, etc.,

$$E = SR_e/R_s = f[(e_1 + a_1) + (e_2 + a_2) + \text{etc.}]\,(1 + b + c + d). \qquad (2)$$

Thus if R_e/R_s is determined for the various readings of f, of e, and of s the corrections b, d, a_1, a_2, etc., can be determined.

In order to measure R_e/R_s readily to a reasonably high accuracy, a special piece of apparatus was designed and has been in use during the past two years. This apparatus, which we have designated a "Universal Ratio Set," is equivalent to 211110 resistance coils, of .01 ohm each, connected in series (connection to the terminals of any coil being possible). This is accomplished with 100 coils and 5 dial switches of the usual construction. If this apparatus be connected in parallel with the potentiometer to be tested a Matthiessen Hockin bridge is formed.

Now if for any setting of the potentiometer four balances are made as indicated in the figure we have

$$Re/R_s = A/B \qquad (3)$$

The value of A/B is readily determined from the readings and known corrections to the ratio set. If such measurements are made for all settings of each of the dial switches, range switches or plugs, etc., we have data from which all the corrections of equation (1) can be calculated. In use certain adjustments are made (which cannot be explained in a short abstract) such that the calculations are very simple. The apparatus has been found to furnish a rapid and direct means for calibrating any type of potentiometer.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

SOME RECORDS OF THE WIRELESS TIME SIGNALS MADE WITH A PHYSIOLOGICAL RECORDER.[1]

BY C. W. WAGGONER.

THE intensity of the wireless time signals from Arlington, Va., which are received on a small aerial at W. Va. University, led the writer to try a muscle-nerve preparation of a frog and it was found that this preparation responds very well to the stimulus sent from the navy station.

The sciatic nerve was connected to the receiving circuit in place of the high resistance telephones, the gastrocnemius muscle having been attached to a long lever operating over a smoked-drum kymograph. A number of complete five-minute records showing the fatigue of the muscle. Records of the weather reports were made, but the speed was too high to make it possible to follow with this type of recorder.

MORGANTOWN, W. VA.,
March 23, 1914.

AN ELECTROMAGNETIC PUZZLE.[1]

BY F. J. ROGERS.

IF an electric current flows through a long straight tube the return part of the circuit being at a great distance, or still better, symmetrically distributed on opposite sides of the tube, there will be *no magnetic field* inside of the tube at any time whether the current is constant or varying at any rate.

If a wire threads through the tube there will be an induced current in it when the current in the tube varies. This induced E.M.F. is proportional to the length of the tube and is equal (though slightly greater) to the induced E.M.F. in a wire just outside of the tube and very close to it.

This is a case of induction which is evidently not the same as is in mind when a conductor sweeps across lines of magnetic flux or when lines of magnetic flux are thought of as sweeping across a fixed conductor.

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1914.

In our case there is no magnetic field at any time inside the tube where the induced E.M.F. exists.

How are we to look upon this case of induction? To those who are completely satisfied with the statement that the induced E.M.F. in a circuit is equal to the rate of variation of the flux through the surface of which this circuit is the contour nothing more need be said. For this case of induction is perfectly in accord with that statement. To those who admit that the above statement is only short-hand mathematics and not physics it may be worth while to say that this statement ascribes an effect (the induced E.M.F. in a wire inside a tube) to a cause (a variation in magnetic flux outside of the tube) which does not exist where the effect is produced.

Can we save our face in this matter and still preserve the imagery of an induced E.M.F. being produced by lines of magnetic flux sweeping across the fixed conductor? I think we may do so in the following manner: Suppose when the current in the tube is being built up from a zero value that closed lines of flux of molecular dimensions originate in the *substance* of the tube and expand with rising current until they surround the tube. In expanding each line must cut across the tubular space and in doing so contribute its part to the induced E.M.F. in the interior of the tube. This method of imagining the process of induction will probably appear satisfactory to many but still the difficulty remains that induction takes place inside the tube while the resultant field is zero everywhere and at all times. The flux lines which we have imagined to be snapping across the tube come symmetrically from all sides in such a way that they mutually cancel each other with regard to the production of a magnetic field. Here enters an idea which seems to me worth consideration. Inside the tube we have a vector field which may be looked upon as the sum of two equal and opposite vectors and therefore a field of zero intensity. However, if these two equal and opposite components are varying, their inductive effects are arithmetically additive and a zero magnetic field is not a field of nothingness but still possesses electromagnetic properties.

I am perfectly aware of the fact that the induction in the case of a transformer in which the primary is uniformly wound on a ring and is overwound uniformly by the secondary is of exactly the same character as the case of induction I have been discussing. The case of the tube was the form in which this "puzzle" first appealed to me, but the fact that this condition occurs in such a familiar case does not make it any the less a puzzle.

Princeton University.

Note on the Physiological Effect of the Current.[1]

By F. J. Rogers.

For some years I have regularly required students to measure the resistance of their own bodies when current flows from one hand to the other, and to observe the maximum current, from a direct current source, that they were

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

willing to endure. Of course the resistance depends greatly on the character and area of contact. The maximum current which the average person is willing to endure proves to be not greatly different in different individuals. If the whole hand is immersed in water or if the electrodes are large, metal handles or plates grasped firmly, then practically every one is willing to endure 20 milliamperes of direct current, on the other hand I have seen not more than one or two who would not say enough before the current reached 40 milliamperes.

Even this difference is principally due, on the one hand to those who are disinclined to endure a little physical pain and on the other to those, who through emulation or otherwise, will not cry enough until their pain has become rather intense.

I have had this experiment performed on scores of students before paying heed to the very occasional remark that the pain was more intense in one arm than in the other. Finally with fewer students to pass through the ordeal and coming across one who was more insistent on the difference in sensation in the two arms or wrists, I reversed the current, when he declared the pain was now greater in the other wrist. With this beginning I proceeded to extend operations upon every one I could drag up to be tested, with uniformly the same result for all persons, male and female, old and young. This difference is not an absolute one. When the sensation is mild there is practically no difference in sensation according to the direction of the current, but just as soon as the painful sensation becomes rather intense the victim uniformly says that the pain is decidedly greater in one wrist or arm than in the other and this always proves to be the cathode arm, the one out of which the current is flowing.

The same condition prevails when the current flows from one finger to the corresponding finger of the other hand. In this case the pain is most intense in the cathode finger although still more or less distant from the electrode. If, however, the electrodes are in contact with the little finger of one hand and the thumb of the other hand, the pain is more intense in the little finger, no matter in which direction the current flows.

Without having attempted experimentation on others in this regard I at least know in my own case that when the current flows from one foot to the other the pain is more intense in the cathode ankle than in the other one.

When current flows through a moderately small electrode in contact with a sensitive portion of the skin, as for example the arm, the pain, in this case a sort of burning sensation, is always more intense at the surface immediately in contact with the electrode; this is well known but is not the fact which I have been trying to describe. It is not however well known to physiologists that when current flows through electrodes in contact with the outside of the face that a decided taste sensation is caused in the proper place for such sensations. I tried the same experiment with sugar and salt in my mouth (on separate occasions) to see whether epicures might possibly derive greater pleasure from such stimuli, however with negative results.

It is well known among physiologists that when a nerve is stimulated by an electric current, the sensation is more intense at the cathode than at the anode. However in my experiments with a large electrode in contact with the palms of the hands practically no sensation was produced at either electrode while at a distance from the electrode, namely in the wrist and forearm the sensation, when it become intense, depended upon the direction of the current, being more painful in the cathode wrist.

This fact which the physiologists seem not to know about may be harmonized with the greater sensitiveness at the cathode by making use in our explanation of what are called physiological cathodes. Wherever current flows from nerve tissue across a surface of separation into another kind of tissue such as muscle or tendon we have a change of material in the path of the current and physiologists call this a physiological cathode. Now I am told that in the wrist there are a great many sensory nerve endings which terminate in tendons. If these are called physiological cathodes when the corresponding hand is the cathode, the greater pain in the cathode wrist is brought into line with the greater sensitiveness of the cathode in nerve stimulation.

PRINCETON UNIVERSITY.

PHOTOGRAPHS OF RETROGRADE RAYS, (*a*) FROM THE COLD CATHODE, (*b*) FROM THE HOT LIME CATHODE.[1]

BY O. H. SMITH.

AT the Thanksgiving, 1912, meeting of the American Physical Society several photographs were exhibited by Knipp showing retrograde rays. Thomson had photographed them, however with limited detail, a few months before. The present paper deals with a more extended photographic study of these rays using both the cold and the hot lime cathodes. The apparatus employed is essentially that described by Knipp.[2]

(*a*) The photographs, in the case of the cold cathode, with very weak deflecting fields, show in a very striking manner the three kinds of carriers—the electron, the carriers atomic in size with a negative charge, and carriers atomic in size with a positive charge. For a given magnetic field these heavy ions show a deflection that is 2 or 3 per cent. of that of the electron. For strong deflecting fields the electrons are blown off the plate and in place of the single line representing each the heavy positively and negatively charged ions there appear a number of parabolic lines characteristic of the gas in the discharge vessel. Under favorable conditions some of the negative lines are duplicated on the positive side, *i. e.*, a negative line having a corresponding positive component.

(*b*) For the case of the hot lime the problem presents additional difficulty. First, in lining up the cathode, and second, apparently the heavy carriers do not possess sufficient energy to affect the photographic plate upon which they

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

[2] Phil. Mag., December, 1911; PHYS. REV., XXXIV., March, 1912.

fall. The lining up of the cathode is accomplished by mounting it upon a sort of universal joint which is actuated from without by means of taps. Even then the direction of the cathodic beam changes with the heating current and destroys the alignment necessitating continual adjustment. The energy of the ions is increased by passing them through an accelerating field. With very weak deflecting fields and with an accelerating gradient of about 2,500 volts per centimeter the photographic plates show both the electrons and the negative ions. When the accelerating field is reversed the positive ions are revealed and, of course, the electrons and negative ions in turn are suppressed. The retrograde rays show but very indistinctly even for the largest accelerating fields employed which was about 3,000 volts per centimeter. Their distinctness on the photographic plate depends in a marked way upon the electrical conditions within the discharge vessel, for instance the positive ions show best on the plate when the metallic parts within are grounded while the negative ions are more distinct when the connection within is to the anode. The photographs indicate that the positive rays are more intense than the negative ones.

A number of photographs showing the deflections under the above named conditions accompany the paper.

PHYSICAL LABORATORY, UNIVERSITY OF ILLINOIS.

AN EXTENSION OF THE SPECTRUM IN THE EXTREME-VIOLET.[1]

BY THEODORE LYMAN.

THE researches of Schumann led him to extend the spectrum to the neighborhood of wave-length 1,250. His limiting wave-length was determined by the absorption of the fluorite which formed a necessary part of his apparatus. In 1904, I succeeded in pushing the limit to wave-length 1,030 by the use of a concave diffraction grating.

Recently I have renewed the attack on the problem with the result that I have succeeded in photographing the spectrum of hydrogen to wave-length 905. The extension is due not so much to any fundamental change in the nature of the apparatus as to an improvement in technique consequent on an experience of ten years.

It is a characteristic of the region investigated by Schumann between wave-lengths 1,850 and 1,250, that while hydrogen yields a rich secondary spectrum, with the possible exception of one line, no radiation has been discovered belonging to the primary spectrum. On the other hand, in the new region between the limit set by fluorite and wave-length 905, a disruptive discharge in hydrogen produces a primary spectrum of great interest made up of perhaps a dozen lines. These lines are always accompanied in pure hydrogen by members of the secondary spectrum but they may be obtained alone if helium containing a trace of hydrogen is employed.

Results obtained from vacuum tubes when a strong disruptive discharge is used, must always be interpreted with caution since the material torn from the

---

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1914.

tube itself sometimes furnishes impurities. In the present case, it will be some time before the effect of such impurities can be estimated. However, it may be stated with some degree of certainty that the diffuse series predicted in this region by Ritz has been discovered. The first member at 1,216 is found to be greatly intensified by the disruptive discharge and the next line at 1,026 appears also, though very faintly. This diffuse series bears a simple relation to Balmer's formula. Following the same kind of argument, a sharp series corresponding to the Pickering series might be expected. The new region appears to yield two lines belonging to such a relation at positions demanded by calculation.

Jefferson Physical Laboratory, Harvard University,
April 20, 1914.

ERRATUM.

Pages 50 and 52. In the paper by A. K. Ångström entitled "Some Observations on Selective Reflection from Solutions in the Infra-red," cuts 1 and 3 should be interchanged; as printed these cuts and the descriptive captions underneath do not corrrespond.

Index to Volume III., Series II.

I

Jra

Vibr

Wag

Wate

Weat

Weav

Weibe

Weibe

Wenn

Wenn