PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XLVII.

FROM MAY 1911, TO MAY 1912.

MDCCLXXX

BOSTON:
PUBLISHED BY THE ACADEMY
1912

University Press:
John Wilson and Son, Cambridge, U.S.A.

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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 1. — May, 1911.

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By Harvey C. Hayes.

With Six Plates.

Investigations on Light and Heat published with Aid from the Rumford Fund.

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AN INVESTIGATION OF THE ERRORS IN COOLING CURVES AND METHODS FOR AVOIDING THESE ERRORS; ALSO A NEW FORM OF CRUCIBLE.

By Harvey C. Hayes.

Presented by John Trowbridge, February 8, 1911. Received December 29, 1910.

Two main difficulties are encountered by one who attempts to make an accurate study of the physical properties of alloys. The first difficulty is the preparation of an alloy which shall contain only the desired elements in its make-up. Foreign elements may enter the alloy through lack of purity in the component metals (and the difficulty of getting chemically pure metals is never appreciated until one has attempted it), also impurities are almost sure to get into the alloy from the crucible. The chemist can, with sufficient pains, prepare pure samples of nearly all the metals; but thus far science has not produced a crucible that will keep them pure while melting them into an alloy. Impurities from this source have been a hindrance to the study of alloys, especially a study of their magnetic properties, and have been a cause for more or less error in the work that has thus far been done.

Roberts-Austen, in his classic experiment, showed that solids diffuse, even at comparatively low temperatures. This makes doubtful the possibility of finding a crucible that will not diffuse somewhat into the alloy at such a temperature as the melting point of most metals. One solid that does not seem to diffuse into metals, and apparently the only one that does not, is quicklime. A block of lime with a hollow scooped out ofttimes serves the chemist for a crucible, for all that he requires of a crucible is that it shall hold together long enough to melt a small portion of metal and then slowly cool. But for the study of alloys such a crucible will not suffice, as it is often necessary to chill the melt. A block of lime will not stand such treatment; and even if it would, the lime is so poor a conductor of heat that it would be impossible to chill an alloy through the comparatively thick walls of such a crucible.

The crucible. — The ideal crucible for work on alloys would be one made from thin metal, if we could find some metal that would not diffuse, for we could then readily study the effects of chilling, as the crucible would be a good heat conductor. But since all metals diffuse, even in the solid state, we cannot hope for such a crucible. The best substitute would be one made from thin metal and lined with a thin coating of lime.

The need for such a crucible has been felt by all who have attempted to make anything like an accurate study of alloys, and attempts have been made to perfect one, but until now without success. The author has finally succeeded in lining a steel crucible with a thin coating of lime. These linings are fairly durable so long as they are kept free from moisture, but if left in a damp place the lime slacks and cracks off. With a lining two tenths of a millimeter in thickness I have made seventeen melts, each time chilling in an ice-bath, and at the end of this time the lining was almost intact.

These linings are made from a mixture of finely powdered quicklime and calcium nitrate, about four parts by weight of the lime to one by weight of the nitrate. Care must be taken that the powders are thoroughly mixed. Such a mixture fuses to solid lime when sufficient heat is applied to drive off all the nitric acid.

This last fact is not new. It is often made use of in the chemical department of Harvard University for preparing small boat-shaped crucibles suitable for melting small portions of metal. But one meets with considerable difficulty in keeping the powder in place on the steep sides of the crucible while it is being fused.

The method finally employed is to use a cylindrical-shaped crucible. This is clamped, open end outward, in the chuck of a high-speed lathe and then set spinning. The mixed powder is then carefully blown inside the crucible where the centrifugal force holds it firmly on the sides in the form of an even coating. The spinning crucible is then heated with a blast lamp until all the acid is driven off. It is then removed from the lathe, set in an upright position, and the bottom sprinkled with a coating of the powder. This is finally fused on, the force of gravity keeping the powder in place.

By this method it is possible to give the crucible a very even coating of almost any desired thickness, though the first attempts are usually discouraging. I have found it possible to chill an alloy very satisfactorily through these thin linings.

For work on weakly magnetic alloys, especially for such as fuse above eight hundred degrees centigrade, a factor of safety is added by using for the crucible some weakly magnetic metal such as platinum, as traces of the crucible might diffuse through the thin porous linings: but with linings two millimeters or more in thickness there can be little or no danger from this source.

The perfection of this crucible now makes it possible to prepare an alloy of definite constitution, and this removes one of the main difficulties in the study of alloys.

INVESTIGATION OF THE ERRORS IN COOLING CURVES.

More information concerning an alloy can be had from its cooling curve than from any other one source, providing the cooling curve is accurate; and more information can be had from the temperature-time curve than from any other of the various forms. The difficulty of getting such curves is not great providing the cooling is slow; but when one attempts to take a curve for rapid cooling or chilling numerous difficulties arise. The remainder of this paper is devoted to a consideration of these difficulties, the errors that as a result have crept into some of the work on metals, and methods for overcoming these difficulties.

The errors. — The difficulties that arise when one attempts to take a cooling curve where the cooling is rapid, and the errors that arise therefrom, are due to temperature lag and lag in the galvanometer. Temperature lag takes place through the protection tube, through imperfect contact between the tube and the enclosed thermo-couple, and finally through the couple itself. Lag in the galvanometer is a function of the period of this instrument, probably nearly proportional to the period. This lag, which for simplicity will be called the electrical lag, can be almost entirely eliminated by using an Einthoven form of galvanometer (a fine conducting filament suspended in a strong magnetic field), for here the inertia of the moving parts is reduced to a minimum, and the period can be made very short without great loss of sensitiveness. By thus eliminating the electrical lag, I have been able to study the temperature lag in its various phases. The work has been carried out in much the following order:

a. Lag due to all three causes, — tube lag, contact lag, and lag in the junction.

b. Contact lag and lag in the junction.

c. Lag in the junction itself.

Method. — The apparatus used in this work, which is described in detail farther on, consisted essentially of an Einthoven galvanometer with a commutator arrangement, such that this instrument could be thrown in series with either of two thermo-couples. These couples were made of copper against constantan, and were so arranged that one gave the temperature just outside the protection tube, while the other gave the temperature from the inside after the usual manner.

Arrangement of thermo-couples. — The arrangement of these junctions was as follows: A cylindrical copper block five inches long and three inches in diameter had two holes, each three inches deep, drilled symmetrically in one end. A constantan wire was fused to the bottom of one hole, thus forming a junction with the copper block as one element. This couple gave at all times the temperature of that portion of the block which formed the bottom of the hole. Moreover, since the two holes were symmetrically placed and the cooling was made symmetrical, this junction gave the temperature at the bottom of the other hole.

In this second hole an ordinary protection tube was placed with a copper-constantan junction inside. The protection tube was surrounded with a thin film of lead, so that the tube experienced the same external conditions that are met with in taking the cooling curve of a molten metal or alloy. A protection tube open at the end was placed in the hole first mentioned, so that the heat capacity of the two holes should be the same.

Because of its short period — less than one fiftieth of a second — it was possible to alternate the galvanometer rapidly between the two thermo-couples. For most work, however, an alternation of about once a second was found satisfactory.

The cold junction of each couple was kept at the temperature of melting ice, so the deflection of the fiber in the galvanometer was always proportional to the temperature of the hot junction of the couple with which it was in series. This deflection was photographed on a sensitive film which was rotated on the drum of a chronograph. In this way it was possible to photograph on the same film the two curves, one giving the temperature just outside the protection tube, and the other giving the temperature inside the tube, according to the usual manner. These curves were traced by a succession of fine dots, but the alternations were so rapid that in the case of slow cooling the curves appear as an unbroken line. These curves had millivolts for ordinates and time for abscissae, and the apparatus was so arranged that these coördinates were photographed on the film. The difference in height between the two curves at any instant was evidently a measure of the temperature lag due to all three causes, — tube lag, contact lag, and lag in the junction; but thus far there was nothing to indicate what part of this lag was due to each of the three causes.

The curves of the annexed plates, reproduced from the actual photographs, show this lag for both quartz and porcelain protection tubes for different rates of cooling. These curves are reduced to one fifth the original size. The highest temperature in each case was about 550 degrees centigrade.

Similarity of the thermo-couples and calibration. — Curve 1, Plate **1**, which traverses the sheet four times, due to four revolutions of the drum, was taken at a very slow rate of cooling, the time of exposure being about four hours. In place of the ordinary protection tube closed at the end, the tube used in this case was open at the lower end except for a thin film of mica. Here the temperature lag between the two junctions must have been practically zero, because of the slow rate of cooling and because of the thinness of the film separating them. The curve, which is in reality double, shows that the two couples were practically identical throughout the temperature range covered.

A calibration curve for one of these couples was obtained by taking the melting points of pure tin, lead, zinc, and aluminum, also the boiling point of water. These results are given in Table I.

TABLE I.

	Temperature. Deg. Centigrade.	Millivolts (obs.).	Millivolts (calc.).
Boiling water	100	3.85	3.85
Melting tin	232	9.70	9.65
Melting lead	327	14.15	14.19
Melting zinc	419	19.40	19.34
Melting aluminum	657	33.70	33.70

The third column, marked Millivolts (calc.), was obtained by applying the well-known formula connecting temperature and electromotive force,

$$E = a\theta + b\theta^2.$$

Here E is the e. m. f. in millivolts and θ is in degrees centigrade. Substituting in this equation the values of E and θ, as found for boiling water and melting Al, the values of a and b were found to be 0.0362 and 0.0000229 respectively; and since the variation between the observed and calculated results lies within the limit of error, the curve

$$E = 0.0362\,\theta + 0.0000229\,\theta^2$$

has been taken as the calibration curve for the two junctions.

Referring to this formula, it is comparatively easy to find the difference in temperature between the two junctions at any instant during the cooling. Let E_1 be the e. m. f. of the junction within the protection tube, and Θ_1 be the temperature of that junction. Let E_2 and Θ_2 be the e. m. f. and temperature respectively of the other junction at the same instant. Then

$$(\Theta_1 - \Theta_2) = (\sqrt{4\,bE_1 + a^2} - \sqrt{4\,bE_2 + a^2})/2\,b,$$

the maximum temperature lag through quartz and porcelain protection tubes for different rates of cooling, is given in Table II. This is computed from the curves of the accompanying plate (Plates **1** to **6**).

TABLE II.

Quartz.		Porcelain.		
Data of Curve No.	Lag.	Data of Curve No.	Lag.	Time Coördinates. One Division equals
2 Plate **1**	13 deg.	2a Plate **2**	49 deg.	30 sec.
3 Plate **2**	45 "	3a Plate **2**	118 "	15 "
4 Plate **3**	80 "	4a Plate **3**	190 "	10 "
5 Plate **3**	179 "	5a Plate **4**	355 "	5 "
6 Plate **4**	270 "	6a Plate **4**	480 "	3 "

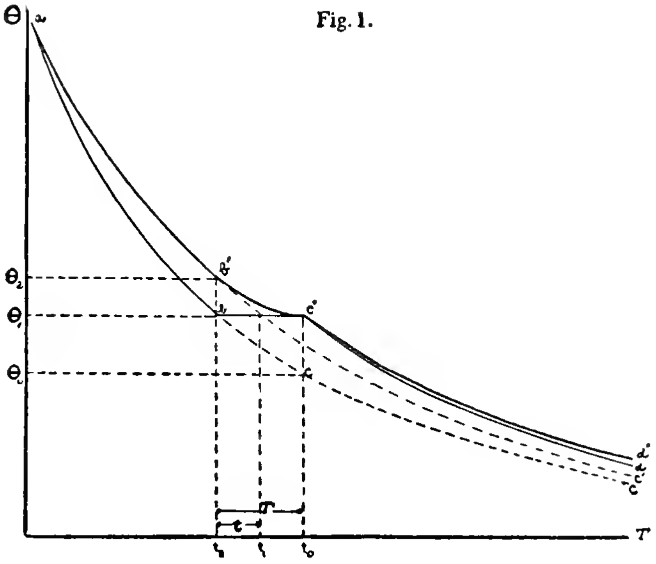
No simple relation between the two curves. — These results show that the error in the cooling curve as usually taken (i. e. by means of a thermo-couple placed inside a protection tube) is large, especially if the rate of cooling is at all large. The question then arises : Is it possible to find a relation between the correct curve and the incorrect curve such that the correct curve can be obtained from the incorrect one, i. e. from the curve taken. Curve 8 (Plate **5**) enables us to answer this question.

In taking this curve, time coördinates of which were three seconds for one space, the copper block was first dipped for an instant to a depth of two inches in ice-water, then removed, then redipped, then removed, etc. The lower line, which is very irregular, as we should expect, is the correct cooling curve. The upper one is the curve obtained by the ordinary method, a junction inside a protection tube. The relation between the two curves is far from simple, and any formula giving this relation must needs be complicated. Thus far no formula has been found.

Incorrect curve may give correct temperature of transformation. — Much of the information, however, that comes from a cooling curve can be had from a curve that is not absolutely correct; for this information comes from the irregularities of the curve, not from the regular parts. In general, any change in the constitution of a metal is accompanied by a liberation or absorption of heat, thereby causing a kink in the cooling curve. How erroneous can the cooling curve be and still give the temperature of transformation with considerable accuracy?

For simplicity, let us take the case of finding the melting point of a pure metal. In this case the cooling curve for that portion of time in which transformation takes place is a straight line parallel to the time axis. In Figure 1 let the line *abc'd* represent the true cooling curve, while line *abc* represents the cooling curve if no transformation takes place. Let the line *ab'c'd'* represent the cooling curve given by the couple inside the protection tube, and the line *ab'e'* the corresponding curve if no transformation takes place. Then the temperature lag at the beginning of transformation is $\theta_2 - \theta_1$, and the corresponding time lag is $t_2 - t_1$. The time through which transformation takes place is $t_0 - t_1$, while $\theta_1 - \theta_0$ is the number of degrees through which the melt would cool if no transformation takes place.

Fig. 1.



It will be seen that

$$\theta_2 - \theta_1 = \frac{d\theta_2}{dT} \cdot \tfrac{1}{2}\,(t_2 - t_1),$$

if we assume that $\frac{1 d\theta_2}{2 dT}$ is the averate rate of cooling during the period required for θ to drop to the temperature of transformation, and that $\frac{d\theta_2}{dT}$ is the rate of cooling at the beginning of transformation. Also,

$$M(\theta_1 - \theta_0) \cdot \bar{S} = ML,$$

where M is the mass in grams of the melt, $\bar{S}$ is the average specific heat, and L is the latent heat of melting. But

$$\Theta_1 - \Theta_0 = \frac{d\Theta_1}{dT} \cdot T$$

approximately, where $\frac{d\Theta_1}{dT}$ is the actual rate of cooling at the beginning of transformation. Therefore

$$\bar{S}\frac{d\Theta_1}{dT} \cdot T = L.$$

For safety,

$$2\,(t_1 - t_2) \leqq T,$$

otherwise the irregularity in Θ_2 will lie wholly above the temperature of transformation.

Therefore, for safety,

$$\bar{S}\frac{d\Theta_1}{dT} \cdot \frac{\Theta_2 - \Theta_1}{\frac{d\Theta_2}{dT}} \leqq L, \qquad \text{or} \qquad \Theta_2 - \Theta_1 \stackrel{=}{<} \frac{L}{\bar{S}} \cdot \frac{\frac{d\Theta_2}{dT}}{\frac{d\Theta_1}{dT}}.$$

For slow cooling $\frac{d\Theta_1}{dT} = \frac{d\Theta_2}{dT}$ approximately. Then

$$\Theta_2 - \Theta_1 \stackrel{=}{<} \frac{L}{\bar{S}}.$$

For rapid cooling $\frac{d\Theta_2}{dT} > \frac{d\Theta_1}{dT}$ throughout most of the temperature range covered, and our formula becomes

$$\Theta_2 - \Theta_1 << \frac{L}{\bar{S}},$$

which is meaningless.

For slow cooling, then, the cooling curve will give us the correct temperature of the melting point, providing the temperature lag is less than the ratio between the latent heat of melting and the average specific heat of the metal during the transformation. This value for the specific heat is about equal to the average between the specific heats corresponding to the liquid and solid states, and therefore in general more than the specific heat of the solid. This ratio always gives a fairly large value for $\Theta_2 - \Theta_1$, so we may be fairly sure of obtaining the correct temperature of melting, even though the temperature lag is considerable.

In general an incorrect curve gives incorrect data. — However, in the case of many transformations, such as a change of allotropy, the latent heat of transformation is small, so the ratio $L/\bar{S}$ is small, and the value of $\theta_2 - \theta_1$ must be small if the transformation temperature is to be given with accuracy. This requires that the cooling curve must be nearly correct. Yet Curve 3 shows that for comparatively slow cooling the temperature lag is 45 degrees for quartz protection tubes, and much more for porcelain tubes. The conclusion follows that the ordinary method for taking cooling curves fails to give with accuracy the temperature of such transformations as involve slight absorption or evolution of heat.

Ordinary method of correcting for temperature lag. — This error due to temperature lag has been long recognized, and the following method employed to correct it. Both a cooling and a heating curve is taken. The cooling curve gives a temperature above, while the heating curve gives a temperature below the temperature of transformation. Assuming that the rate of change of temperature is constant, and that the lag is proportional to the rate of change of temperature, then the correct temperature can be obtained as follows :

Let θ_c be the transformation temperature given by the cooling curve,
" θ_h " " " " " " heating "
" a " rate of cooling, assumed uniform,
" b " " heating, " "
" k " temperature lag for unit rate of cooling,
" θ " correct temperature of transformation.

Then
$$\theta_c = \theta + ka$$
$$\theta_h = \theta - kb$$
$$\frac{\theta - \theta_c}{\theta - \theta_h} = -\frac{a}{b}.$$

Therefore
$$\theta = \frac{b}{a+b}\theta_c + \frac{a}{a+b}\theta_h.$$

This method erroneous. — The value of this formula depends upon the correctness of the two assumptions upon which it is based. The rate of change of temperature can be regarded as fairly constant over a considerable period of time when the cooling is slow. The accuracy of the second assumption — that the temperature lag is proportional to the rate of change of temperature — can be tested by the aid of Curves 1′ and 2 (Plate 1), for we can readily find the temperature lag at any time, and also the rate of cooling, and hence the value for k.

On each of these two curves three points were chosen, and the value of $\Theta_2 - \Theta_1$, $\frac{d\Theta}{dT}$, and k computed with the following results (Table III):

TABLE III.

Curve 1′, *Plate* 1.

Point.	$\Theta_2 - \Theta_1$.	$\frac{d\Theta}{dT}$.	k.	Difference.
1	5.25 degrees	0.373	13.9	1.3
2	3.06 "	0.201	15.2	1.6
3	2.12 "	0.128	16.8	

Curve 2, *Plate* 1.

Point.	$\Theta_2 - \Theta_1$.	$\frac{d\Theta}{dT}$.	k.	Difference.
1	11.2 degrees	0.622	18.0	1.7
2	8.34 "	0.422	19.7	1.9
3	5.88 "	0.268	21.6	

These results show that the lag is not proportional to the rate of cooling, but that the value of k increases as the value of $d\Theta/dT$ decreases, and that this change in k is nearly linear. This increase in the value of k cannot be accounted for by the fact that the rate of cooling to the point at which the value of k was computed had not been constant but had been decreasing, so that in each case the lag was more than it would have been had the rate of cooling been constant and of the value at the point in question. The lag would be greater in proportion for the higher points as the decrease in the rate of cooling is greater for the portion of the curves before those points.

The true cause for this variation in the value for k does not concern us here. The fact is that the second assumption is not correct, and, unless the heating and cooling curves have the same slope, the formula does not give the correct value for Θ. Moreover, a comparison of the results obtained from Curves 1′ and 2 shows that even under these last named conditions the formula is not trustworthy. Curve 1′ gives a lag of 5.25 degrees centigrade for a rate of cooling of 0.373 degrees per second, while Curve 2 gives a lag of 5.88 degrees centigrade for a rate of cooling of only 0.268 degrees per second.

Contact lag is variable. — These curves were taken with the same quartz protection tube and the same thermo-couples, and the discrepancy is not due to variation in the thermo-couples, as they were tested after each curve and found to have remained constant. The variation was apparently due to change in the contact lag, and this variation is liable to occur between any two curves, as, for instance, between the heating and cooling curves used in determining Θ.

If so much variation can be due to change in the contact lag, it would seem that this lag must be great, perhaps furnishing a large part of the entire lag. A consideration of the ordinary form of thermo-junction should lead one to suspect this, even though the results obtained from Curves 1′ and 2 had not disclosed the fact.

The two elements forming the couple are usually fused together in the form of a bead nearly spherical in shape. Under the most favorable conditions this bead rests on the bottom of the protection tube, though ofttimes it takes a position as shown in Figure 2. In either case the contact between the tube and bead is imperfect. In the first case we have a point, or, at most, a very small surface of contact, and in the second case no contact at all. In the first case the junction can lose its heat by conduction and radiation, though mostly by radiation; and in the second case its heat must leave wholly by radiation. In either case it would seem that the contact lag must be large, and that it would vary with the position of the junction in the tube.

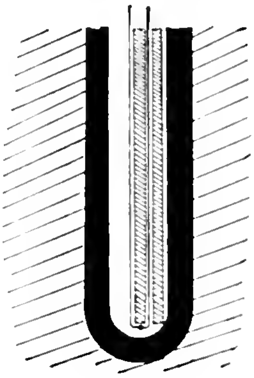


Fig. 2.

Contact lag is great. — To test out the lag due to imperfect contact between tube and junction, a protection tube open at the bottom was used. This allowed the bead of the junction to rest directly on the copper. Here the lag was due to imperfect contact and lag in the couple itself. The lag in the couple was very small, as the material of the couple was a good heat conductor, and because the heat capacity of the couple was small. Several curves were taken with this arrangement of the couples, and in each case the lag was nearly as great as that given by the ordinary arrangement with the same rate of cooling. Curve 10, Plate 5, is a typical example. Here the rate of cooling was the same as that employed in Curves 4 and 4_a.

It is to be noticed that the lag is nearly as great as that registered in Curve 4. This lag is not all due to imperfect contact and lag in the junction, for a thin film of oxide always formed on the surface of the copper, even when the surface was polished before the experiment; and this oxide is a poor heat conductor. However, the experiment gives conclusive proof that the contact lag is great.

Means for reducing this lag. — The only way to reduce this lag is to use a different form of junction. The lag can be materially reduced by pounding the bead down to a thin sheet and fitting it to the bottom of the tube; but even then the contact lag forms a large part of the total lag. A much better form of couple is one in which the tube forms one element, with the other element fused to the inside bottom of this tube.

Such a couple has been patented by C. B. Thwing, and is made by James G. Biddle, Philadelphia. This form of junction, as marketed, has the outer element and tube made thick and heavy, in order to prolong the life of the junction which comes in direct contact with the molten metal. The junction is useless for accurate work on alloys, as it contaminates the melt; but the form of the junction is correct since the tube lag is made small, the tube being a good heat conductor, and the contact lag is entirely eliminated.

Improved form of thermo-couple. — The author makes use of a couple of this form, but places a thin coating of lime on the outside of the tube to avoid contamination. The metal tube which forms one element of the junction is made very thin, thus reducing the lag in the couple itself. The tubes are deposited electrolytically on a wax form; the wire leading from the tube, and the second element leading from the bottom of the tube, having been placed in position on the wax form. These wires are thus sealed to the tube by the process of deposition. In this manner the couples can be made nearly any desired size.

The temperature lag in these junctions is reduced to a minimum. The lime coating can be made very thin, thus causing little lag through the protection tube. The contact lag is small and constant, since the whole surface of the couple is in close contact with the lime coating. Finally the lag in the junction itself is nearly zero, as the heat capacity of the junction is nearly zero.

Comparison of old and improved form. — Curve 11, Plate **5**, really two separate curves on the same sheet, gives a comparison of the lag due to the two junctions. The curve on the left was taken under the most favorable conditions applicable to the ordinary method. The protection tube was made of thin quartz, and the junction rested on the bottom of the tube. The curve on the right shows the corresponding lag when the tube-form of couple is used. Here the apparent lag is more than the actual lag, as the tube couple gave a higher e. m. f. than the couple of which the copper block formed one element. The rate of cooling was the same for both curves, and was obtained by immersing the copper block in oil.

In all the curves taken, the protection tube was surrounded with a thin film of lead; yet the cooling curves, except faintly in Curve 1′, give no indication of the freezing point of the lead. This point, however, is plainly shown in the cooling curve taken with the tube-form of couple, even though the rate of cooling was high.

The fact that the heat liberated by the freezing lead causes no irregularity in the cooling curves taken by the ordinary method, leads one to believe that not only does that method fail to give the temperature of transformation with accuracy, but it may fail to give any indication of the existence of a transformation. On the other hand the possibilities of the tube-form of couple are great. These possibilities are not fully shown by Curve 11, as the junction was fairly heavy and the lime coating much thicker than necessary. With a refined couple this lag can be greatly reduced.

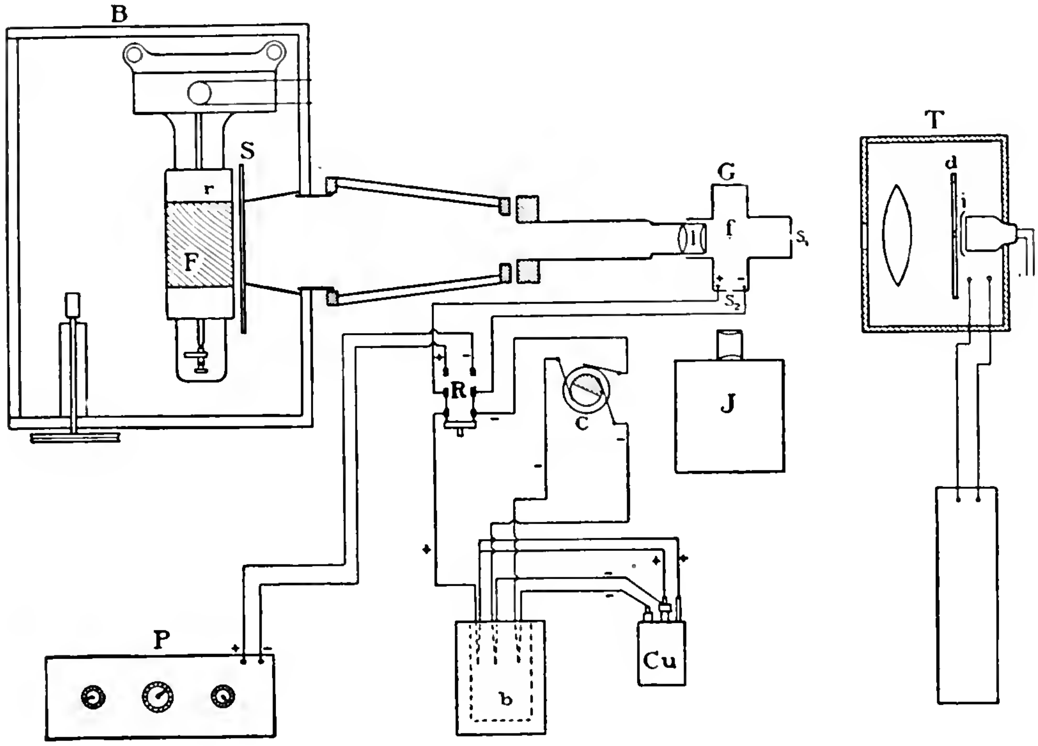


Fig. 3.

The cooling employed in taking Curve 11 was about the same that is employed in the oil-tempering of steel. At this rate of cooling a refined couple would give very little lag, and should give curves sufficiently accurate to throw considerable light on the processes of chilling and tempering.

Against the correcting for temperature lag by means of heating curve. — A study of alloys in the light of Gibb's "Phase Rule" leads one to believe that their characteristics depend greatly on their past history. Having prepared an alloy, it is doubtful if its properties will be the same after it has been remelted. It is then highly desirable that the cooling curve be correct as first taken. The usual method requires the taking of the heating curve, i. e. the remelting of the alloy, in order that we may apply an incorrect formula to give us the temperature of such transformations as are registered on these insensitive curves. This method is cumbersome and, unless the rate of cooling is very slow, is inaccurate. And when we have taken the heating and cooling curves and found the so-called temperature of transformation, it is a question as to what alloy the data belongs.

The tube-form of couple makes it possible to take an accurate cooling curve for slow rates of cooling, and even such rates as are employed in tempering can be taken with a fair degree of accuracy. Thus the second main difficulty in the study of alloys is largely removed.

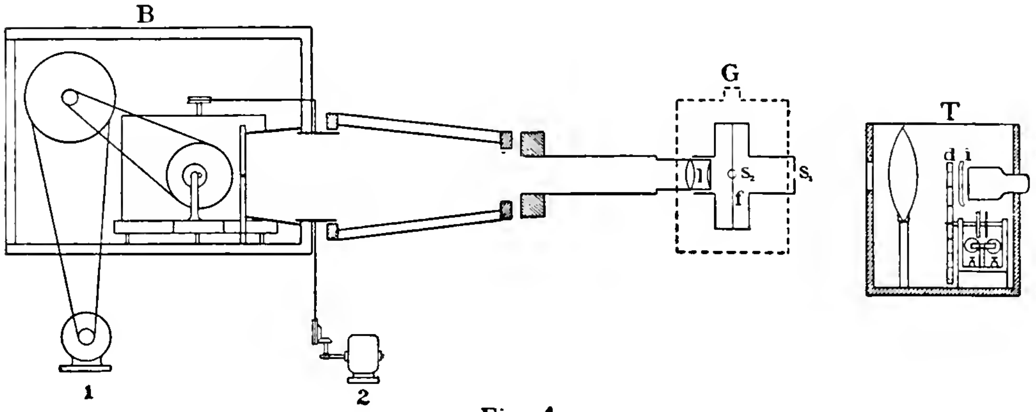


Fig. 4.

Description of the Apparatus.

The recording device. — Figures 3 and 4 represent a top and side view, respectively, of the recording part of the apparatus. A simplified form of Einthoven galvanometer G, in circuit with a thermo-couple, gives the difference in temperature between the hot and cold junction. An ordinary projecting lantern J throws a beam of light through S_2 and illuminates the filament *f* of the galvanometer. By means of the lenses *l*, the light from the filament is focussed on the drum *r* of a chronograph. The screen S carries a narrow slit parallel to the axis of the drum, and thus allows only a spot of light to reach the sensitive film F which is fastened about the drum. A variation in the temperature of the hot junction causes the spot of light to move along the drum in a direction parallel to its axis. If such a movement takes place while the drum rotates, a curve is photographed on the film, the coördinates of which are temperature and time.

Placing the time coördinates. — The chronograph is so arranged that it can be run with either of two motors 1 or 2 (Figure 4). One-tenth horse power A. C. motors are used for this work, as they give to the drum a more uniform rotation than the ordinary clockwork arrangement. Motor 2 is connected to a variable gear, such that the time of rotation for the drum can be varied from forty seconds to two hours. This motor is used to turn the drum whenever a cooling curve is being photographed, the gearing always being so adjusted that the drum rotates about once while the cooling takes place. Box T contains an arrangement for throwing a periodic flash through S_1 of the galvanometer. This light finally passes through the slit in the screen and gives a fine white line on the film. If the drum rotates uniformly and the flashes occur at the end of equal periods of time, and if at the same time a curve is traced by the spot of light coming from the filament, we should have, upon developing the film, a temperature vs. time curve with the time coördinates drawn.

Placing the e. m. f. coördinates. — By means of the double switch R a potentiometer P can be thrown into circuit with the galvanometer, and this instrument can then be made to register millivolts. This arrangement makes it possible to place electromotive force coördinates, on the film. First rotate the drum with no e. m. f. through the galvanometer. The spot of light then traces the zero line on the film. Then repeat this operation for each millivolt, or whatever increment of e. m. f. is desired, until the range of e. m. f. covered by the thermocouple is passed. For this work motor 2 is used, as the gearing here is such that the drum rotates about once in ten seconds.

In order that these coördinates should have the same intensity as the curve, the time of exposure should be the same. This causes a great loss of time, as the period of rotation for the drum is more than one hour when the cooling is slow. This waste of time is avoided by widening the slit S while these coördinates are being made. By making the slit one millimeter wide, the time required for recording one coördinate line is about ten seconds. Thus the total time required for adding the e. m. f. coördinates to one of the curves of this paper is about ten minutes. This method for adding the e. m. f. coördinates amounts to calibrating the galvanometer for each curve, so that the results are largely insured against variation in the galvanometer.

This recording apparatus is essentially the same as that devised by Einthoven and described at length in Annalen der Physik, 1903, Vierte Folge, Band 12. It is without doubt the best form thus far devised for recording rapid cooling, but the expense of the apparatus has tended to prohibit its general use. It therefore seems desirable to describe briefly the simplified form used in this work. Only ordinary ingenuity is required for its construction, and the cost is comparatively small.

The galvanometer. — Figure 5 shows the construction of the galvanometer. The magnetic field is furnished by eight cast-iron ring magnets, arranged in two sections of four. One section is placed above the focussing lenses l, and the other section directly beneath this. A thin brass chamber fitted between the jaws of the compound magnet carries the filament, a platinum fiber about one ten-thousandths of an inch in diameter. These three pieces, with some simple device for varying the tension on the fiber, completes the galvanometer.

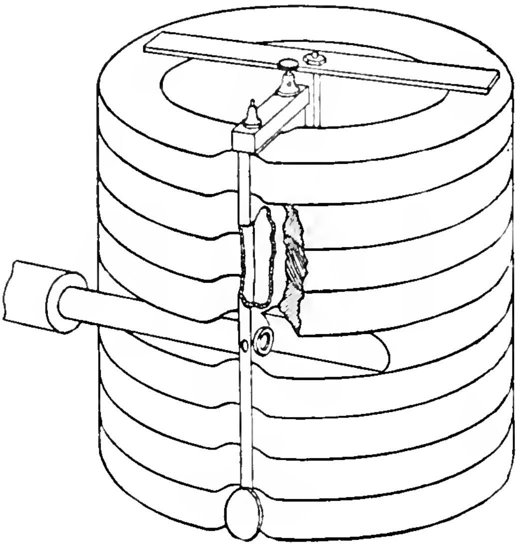


Fig. 5.

Periodic flashes for giving time coördinates. — Figures 6 and 7 show in some detail the mechanism employed for giving periodic flashes. Two rachet wheels, each carrying sixty teeth, are fastened rigidly to an axle (Figure 7). A double electromagnet *m* attracts the armature *a* and causes the clutch *x* to turn the axle. Clutch *y* is so adjusted that the rotation is allowed to proceed only a distance of one tooth. So long as the current continues through *m* the axle is held firmly in position; but whenever this current is broken the armature is pulled back by spring *s* so that clutch *x* falls behind another tooth. Upon making the circuit again, the axle is again rotated a distance of one tooth. A relay operated by a separate circuit is so connected into the circuit which traverses the magnet *m*, that when its armature is back the circuit is made through *m*. The relay is operated by a circuit that is made for an instant once a second, a seconds pendulum being used for accomplishing this. Thus the circuit *m* is broken for an instant once a second, and the axle, therefore, is rotated one division every second.

A thin aluminium disk twenty centimeters in diameter is clamped to the end of the axle by means of a thum-screw. Narrow slits are cut radially into the edge of the disc as shown in Figure 7. This disc is interposed between a Nernst glower and slit S_1 of the galvanometer. Figure 4. An iron screen *i* before the glower allows only a narrow beam of light to fall upon the disc; and whenever a slit in the disc moves across this beam of light a momentary flash passes into S_1. By varying the number of slits in the disc, the period between flashes can be made nearly any length between one second and one minute.

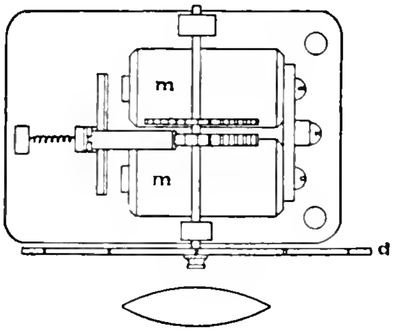


Fig. 6.

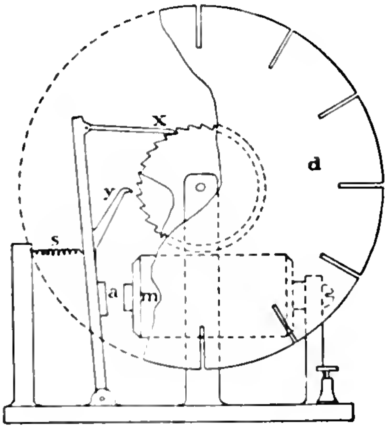


Fig. 7.

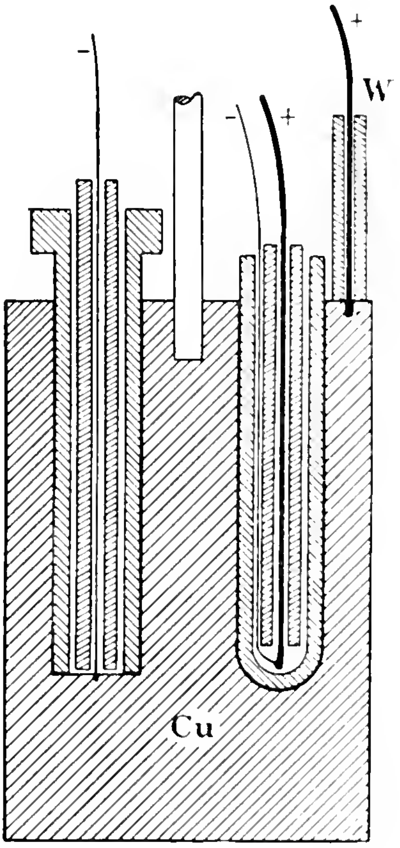


Fig. 8.

The Heating Part of the Apparatus.

The copper block and thermo-couples. — The heating part of the apparatus may be briefly described with the aid of Figures 8 and 9. Figure 8 represents the cross-section of a copper cylinder five inches long and three inches in diameter. Two holes, each three inches deep, are symmetrically drilled in the top of the cylinder. These holes have a diameter nearly one millimeter greater than the diameter of the protection tube to be experimented upon. A protection tube is placed in each of the holes in order that the heat capacity may be the same for each. One of these tubes is closed at the lower end and the other one left open. Within the closed tube an ordinary copper-constantan junction is placed, and a constantan wire is passed through the open tube and fused to the copper block. A copper wire *w* is fused to the top of the copper block, and protected from the hot gases of the furnace by means of a short porcelain tube. The space between the closed tube and the copper block is filled with lead. Thus the closed tube experiences the same conditions that are met with in taking an ordinary cooling curve for a molten metal or alloy.

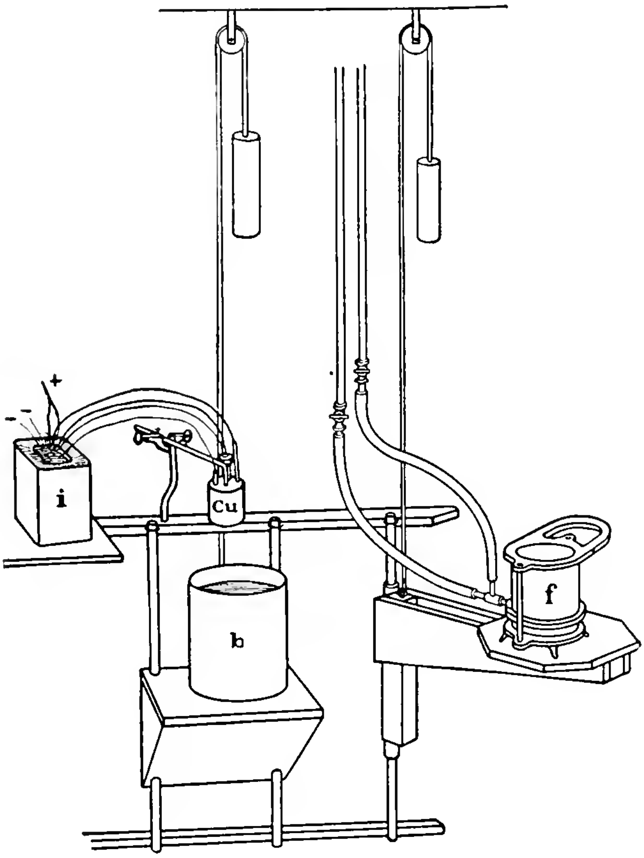


Fig. 9.

The commutator. — The commutator arrangement, by means of which the two thermo-junctions are alternately thrown in series with the galvanometer, is shown in *c*, Figure 3. It might be added that several curves could be photographed on the film by simply changing the form of the commutator. The alternations were about once a second throughout this work, but the period of the galvanometer was only one fiftieth of a second, and the damping very rapid, so that as many as five alternations per second could be made. This means that at least ten such curves could be placed on the same film, and even a greater number when the rate of cooling is slow.

Copper-constantan couples were used throughout this work, principally for the reason that it made possible the use of a copper block. Several reasons made it desirable to use copper. The copper has no transition points in the temperature range covered, so the cooling curves would have no irregularities due to such transitions. Copper being an excellent heat conductor, the temperature at the bottom of the two holes will be nearly the same, even if there are some slight irregularities in the cooling at the surface. Copper and lead is one of the few combinations of metals that do not alloy more or less readily. Lastly, copper against constantan makes a thermo-couple that gives a high thermo-electromotive force.

Validity of the method employed for determining the lag through the protection tube, etc. — Since the validity of this whole paper depends on the condition that the temperature at the bottom of the two holes shall be the same at all times, numerous tests were made to see if this condition were fulfilled. To test this condition, a constantan wire was fused to the bottom of each hole in the block, and the two curves giving the temperature at the bottom of each of the two holes were taken for various rates of cooling. These curves overlapped in nearly all cases, the variation scarcely ever being more than the width of the line. Curve 14, Plate 6, gives such a set of curves for rapid cooling. The curves show the temperature variation between the two junctions at its greatest. On this curve, one space on the time axis represents three seconds.

It might be urged that a large portion of the lag recorded in all cases was due to lag through the lead film which surrounded the tube. Curve 13 (Plate 6), a curve resulting from an accident, offsets this argument. Just after the cooling had started, the tube broke and allowed the lead to come in contact with the junction. This break occurred when the temperature of the block was only a little above the melting-point of the lead. After the experiment was over, the bead of the junction was found about half imbedded in the lead. The cooling here was rapid, having been caused by dipping the copper block in ice-water. The irregularities in the curve, and probably the breaking of the tube, were caused by the water boiling over on the top of the block. Despite this, however, the curves coincide throughout most of their length. This proves conclusively that there was little lag through the lead film.

Furnace and cooling bath arrangement. — Figure 9 shows the arrangement for heating and cooling the copper block. Because of the presence of the thermo-couples it was difficult to move the block from the furnace to the cooling bath. This difficulty was avoided by counterpoising the furnace and bath so that either could be brought to the block. The cooling bath was arranged to slide up and down, being guided in this movement by two vertical rods. The depth to which the block was submerged was regulated by fastening a clamp on one of the guiding rods. The furnace was counterpoised on an arm which could turn about a single guiding rod and thus be brought beneath the block. With this arrangement, the block could be transferred from the furnace to the bath as quickly as it could if the block were movable. The cold junction of both couples were kept at the temperature of melting ice by means of an ice-bath *i*, Figure 9.

Variation in the rate of cooling. — Variation in the rate of cooling was provided as follows: For rapid cooling, the block of copper was surrounded by ice-water to within one centimeter of the top. For the next slower rate the block was dipped in warm water to a depth of one centimeter. The next slower rate was obtained by surrounding the block with oil. A still slower rate was given by setting the copper block on a block of iron that was surrounded by water. The next slower rate was given by allowing the block to cool in air. Finally, the slowest rate was obtained by allowing the block to cool in the furnace. The rate of cooling was thus varied from about half a minute to over two hours.

Need for the research recorded in this paper became apparent to the author upon attempting to study the magnetic properties of some weakly magnetic alloys. The two difficulties which the paper discusses were at once encountered, and had to be overcome before the work could proceed. These difficulties have been largely overcome, and the road now seems to be fairly clear to a large and much neglected field of research.

JEFFERSON PHYSICAL LABORATORY
CAMBRIDGE, MASS.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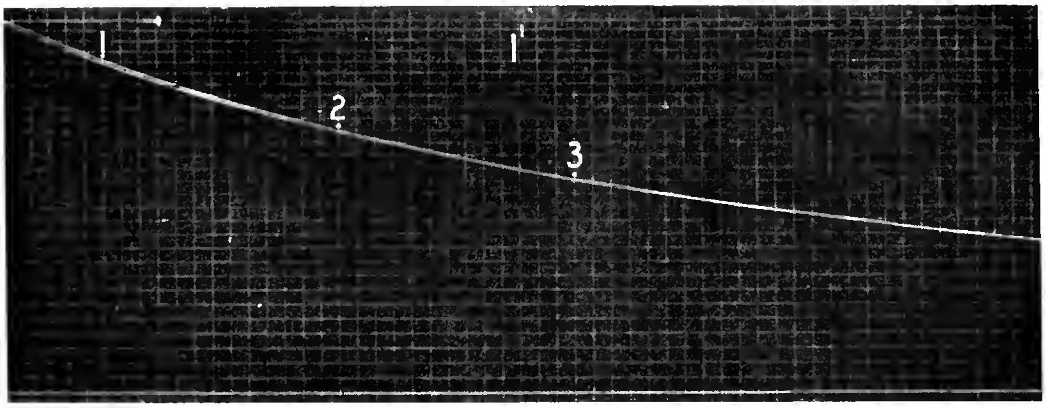
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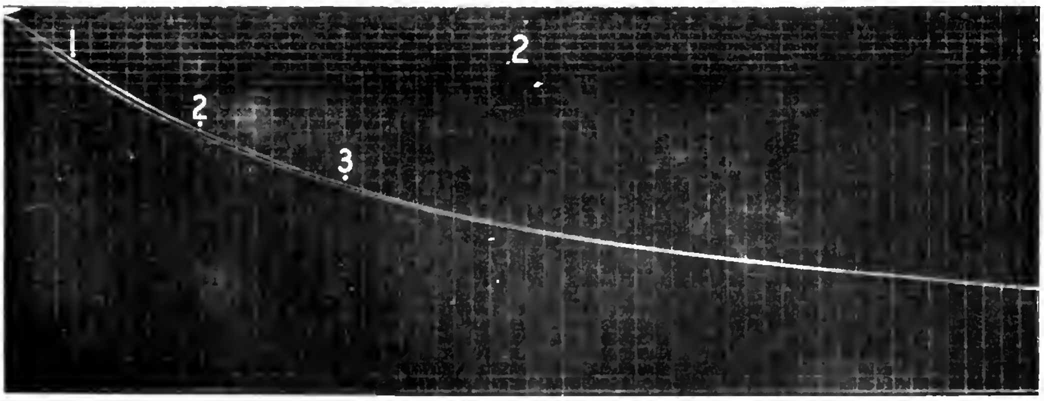
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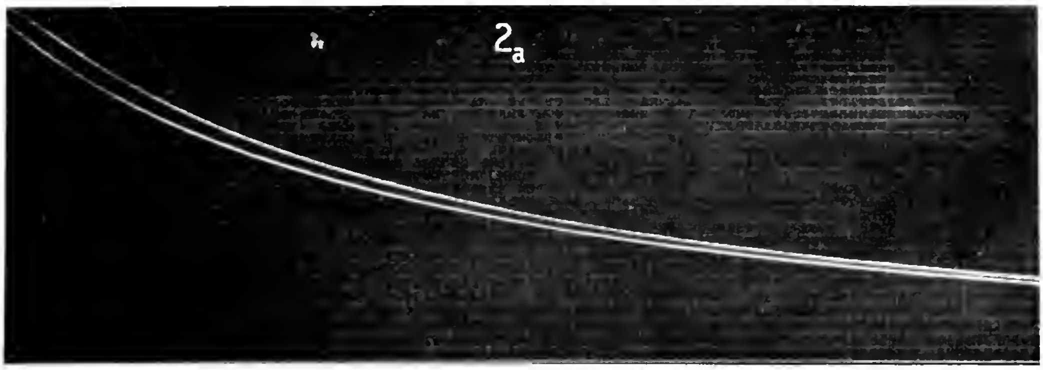
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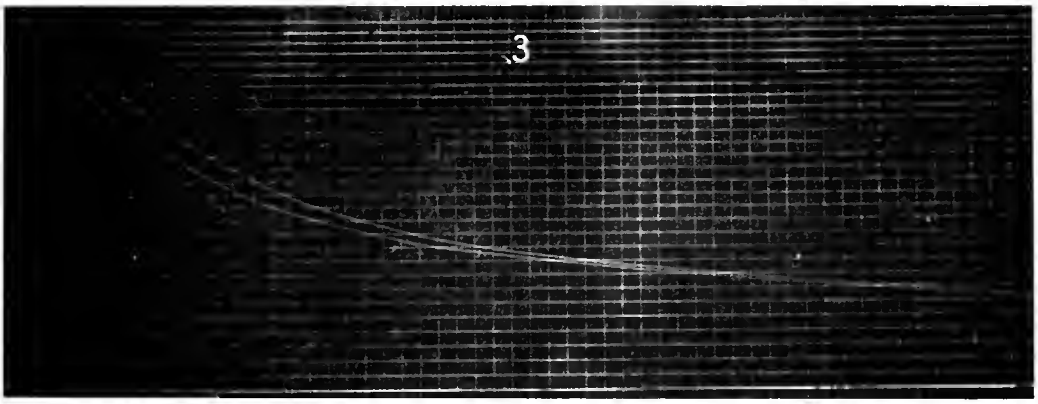
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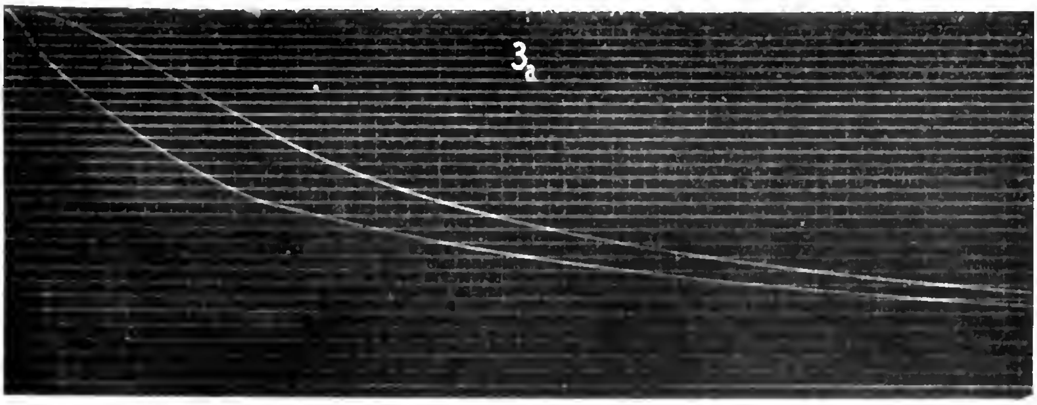
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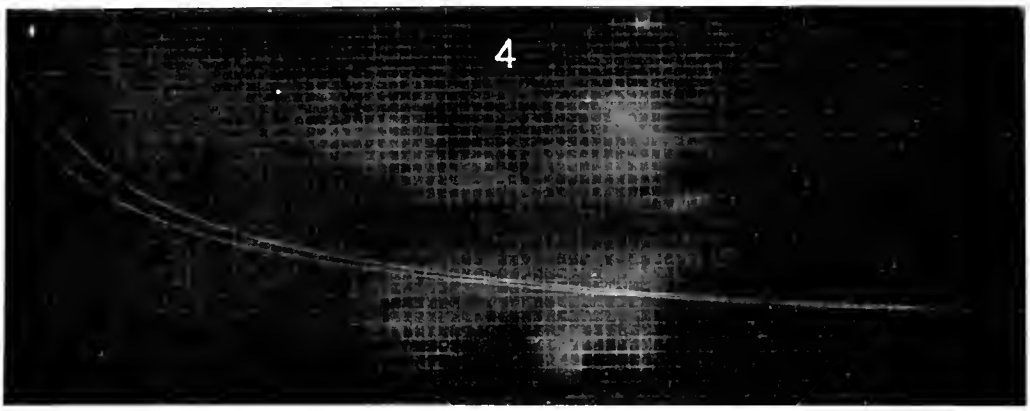

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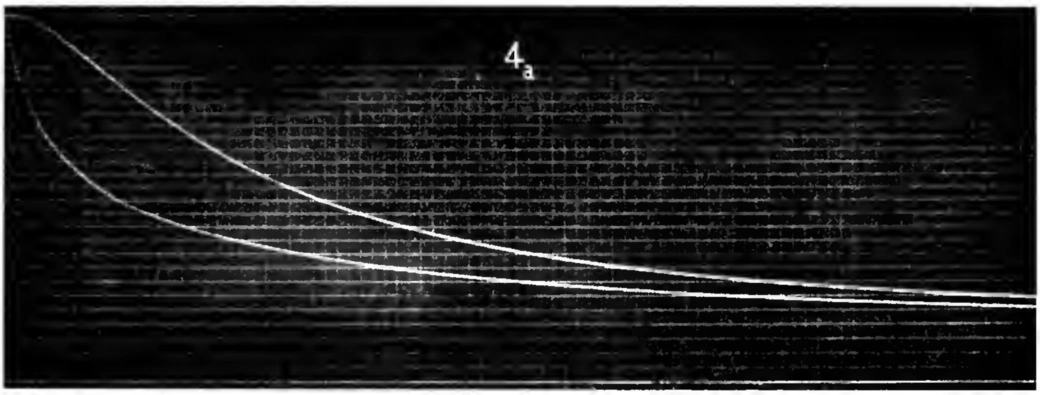

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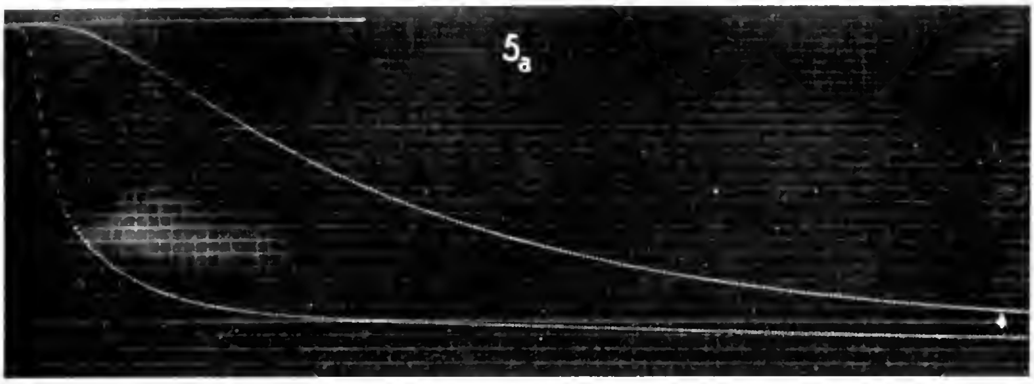

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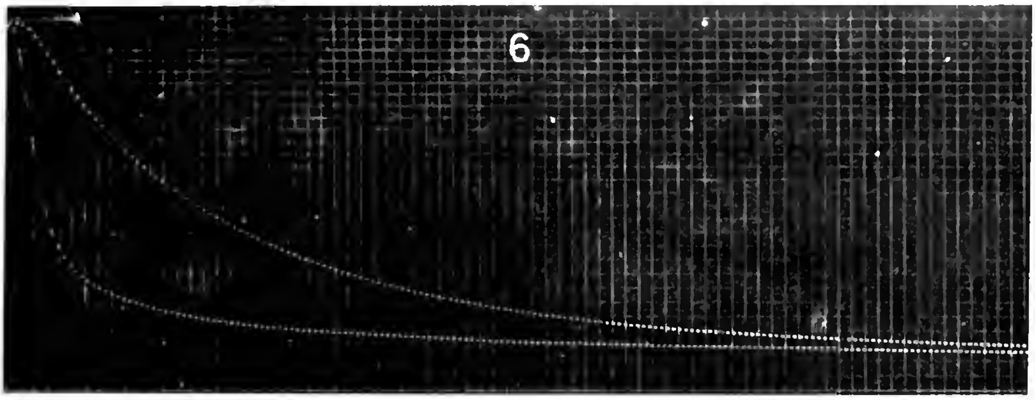

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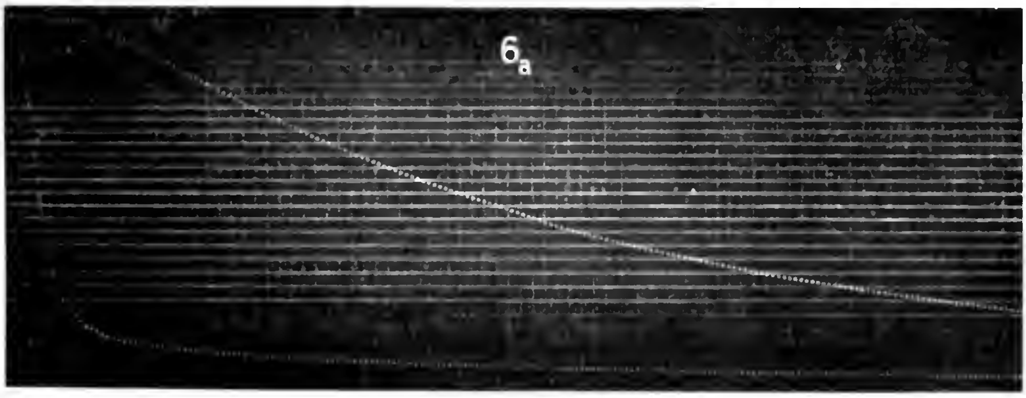

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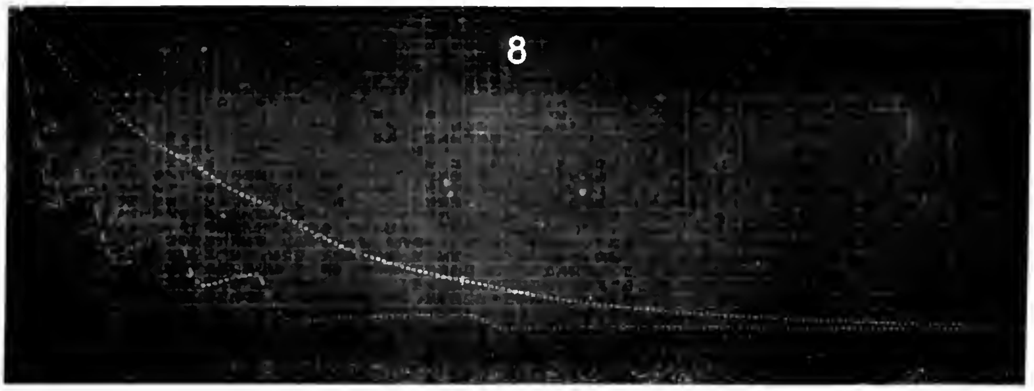
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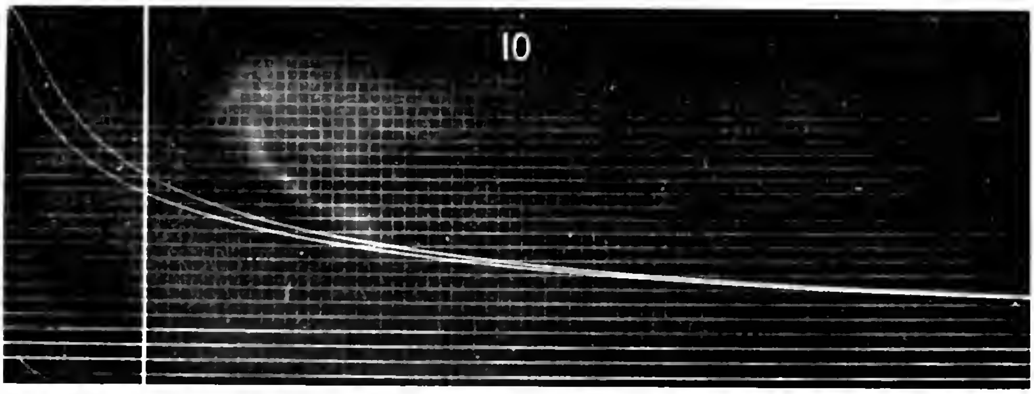
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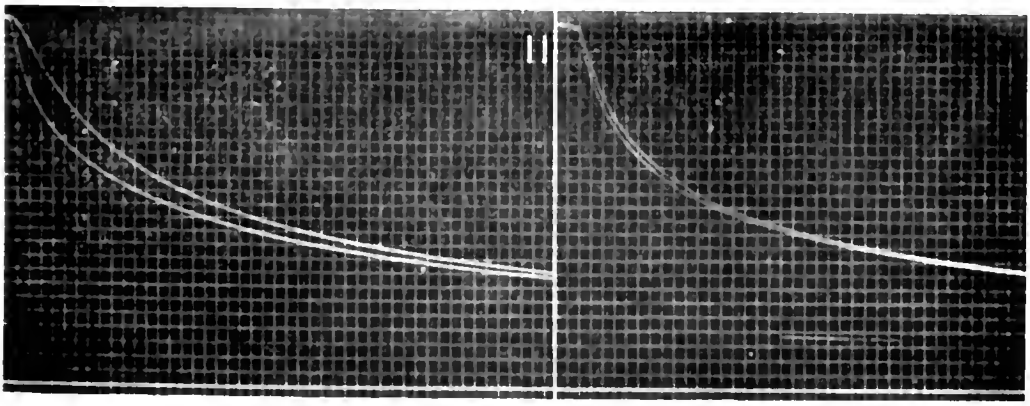
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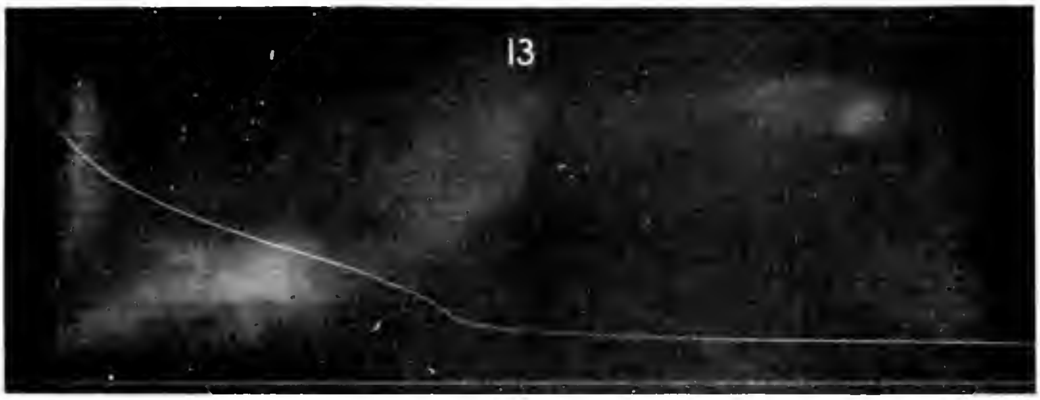
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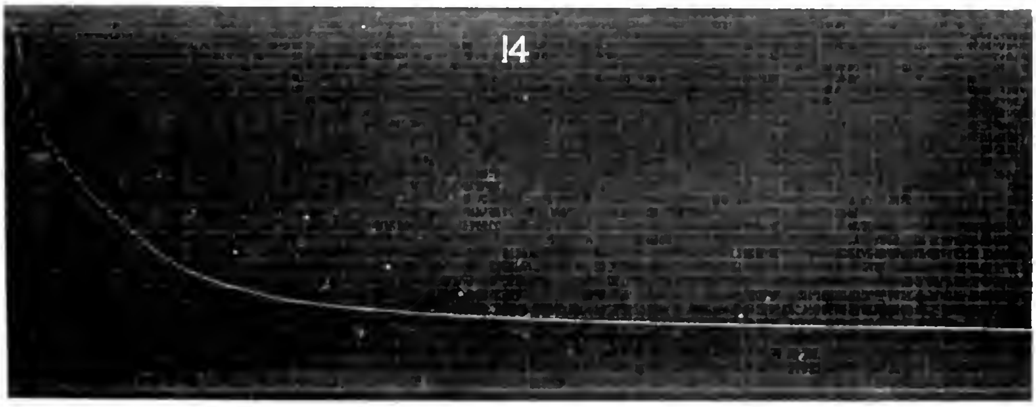
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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 2. — May, 1911.

DETERMINATION OF THE ALTITUDE OF AEROPLANES.

By Robert W. Willson.

With Two Plates.

DETERMINATION OF THE ALTITUDE OF AEROPLANES.

By Robert W. Willson.

Presented February 8, 1911. Received December 31, 1910.

The object of this paper is to add something to the discussion of a somewhat novel problem which has arisen as a result of certain developments in the art of aviation during the past year.

Up to the time of the aviation meet at Los Angeles in February, 1910, no greater height had been recorded in the flight of a "heavier than air" machine than about fifteen hundred feet. At that meet Paulhan, in a Blériot machine, reached a height of 4165 feet, the height being determined by triangulation. The reading of his aneroid was 4600 feet.

At the Montreal meeting, in June, Walter E. Brookins attained an altitude of 3523 feet, determined by triangulation, his baroscope reading 200 or 300 feet higher; and at Atlantic City, in July, the same aviator raised the record to 6175 feet, as determined by a triangulation similar to that of the first method described in the following pages. The height by barograph was 6200 feet.

When the project of an aviation meeting at Cambridge was being discussed, the writer agreed to be responsible for the accurate measure of altitudes; and the results obtained and the methods used form the subject of this paper. At that time no official accounts of the experience at other places in making such measurements had been published, but it was agreed that it would be acceptable to the aviators that they should attempt to reach their greatest altitudes when in a vertical plane passing through the starting line of the course, and as nearly as possible at a point over the grandstand. It was also agreed that only one machine should be under observation at any time. Under these conditions the arrangements now to be described were planned. The accompanying map (Plate 1) of the Squantum peninsula and the surrounding country will serve to make the situation clear. The map shows the positions of the two base lines, and gives the ground plan of the flight of Brookins on September 8.

First Method, — The Field Base.

A measured base of 5000 feet was established on the line NS reaching from the extreme northern limit of the course, across the field, passing above the center of the grandstand, and terminating at a point just beyond the boulevard recently built by the Metropolitan Park Commission. The north and south direction was chosen in order that the observations might not be interfered with by the sun at the times of day most favorable for flight. It was expected that the aviators would cross this line near its center on each coil of the ascending spiral, and that the greatest height attained at such a crossing would be taken as the height of record.

At each end of the field base was placed a sextant mounted on a stand (Plate **2**), with its plane in the vertical plane of the base line, and the line of sight pointed toward the grandstand, which was nearly midway between the stations. A target placed in the line of sight at a sufficient distance from each sextant served as a substitute for the horizon line, and when the image of the aeroplane was brought to coincide with the target, as it crossed the plane of reference, the altitude was read directly from the vernier of the sextant. The height of the northern station was eighteen feet and of the southern station twenty-six feet above mean low water; it is sufficiently accurate to assume that the sextants were in the same horizontal plane twenty-two feet above mean low water and nine feet above the center of the field.

After some experiments the target was given the form shown in Plate **2**. The central lozenge was one foot square and the extreme horizontal length four feet. The wings served to make an approximate setting as the aeroplane approached the plane from either side. The horizon mirror of the sextant was replaced by a larger mirror extending about three inches from the sextant plane, the silvering being removed from a strip one eighth of an inch wide perpendicular to the plane of the sextant. Through this opening the target could be seen by the naked eye placed somewhat to the left of the telescope, and the aeroplane could thus be picked up and followed and an approximate setting made some time before coming to the reference plane. At the critical moment the eye was placed at the telescope and the image of the aeroplane made to cross the center of the lozenge of the target. The use of a light blue shade between the index and horizon glass greatly facilitated the observation by cutting off the glare of the sky. The clamp of the index was replaced by a roller turned by a good-sized milled head, and forming a very convenient "quick slow motion." A "finding plane" of a size corresponding to the new horizon glass was attached to the index glass and carried a level perpendicular to the plane of the sextant, by means of which that plane might be made vertical. These three modifications are all plainly shown in Plate **2**.

The observers were connected with each other and with the committee room at the grandstand by a telephone line devoted to this use alone. A chart, shown about one eighth size (Figure 1), was at hand from which the height corresponding to simultaneous observations of the altitude at either end of the base could be read off.

The abscissas and ordinates represent the angles N and S respectively, and the curves give the values of h for each 100 feet, computed from the above formula. The scale was one quarter of an inch for each degree of N° or S°, and on this scale it was not difficult to read with an error of less than ten feet up to altitudes of 15,000 feet.

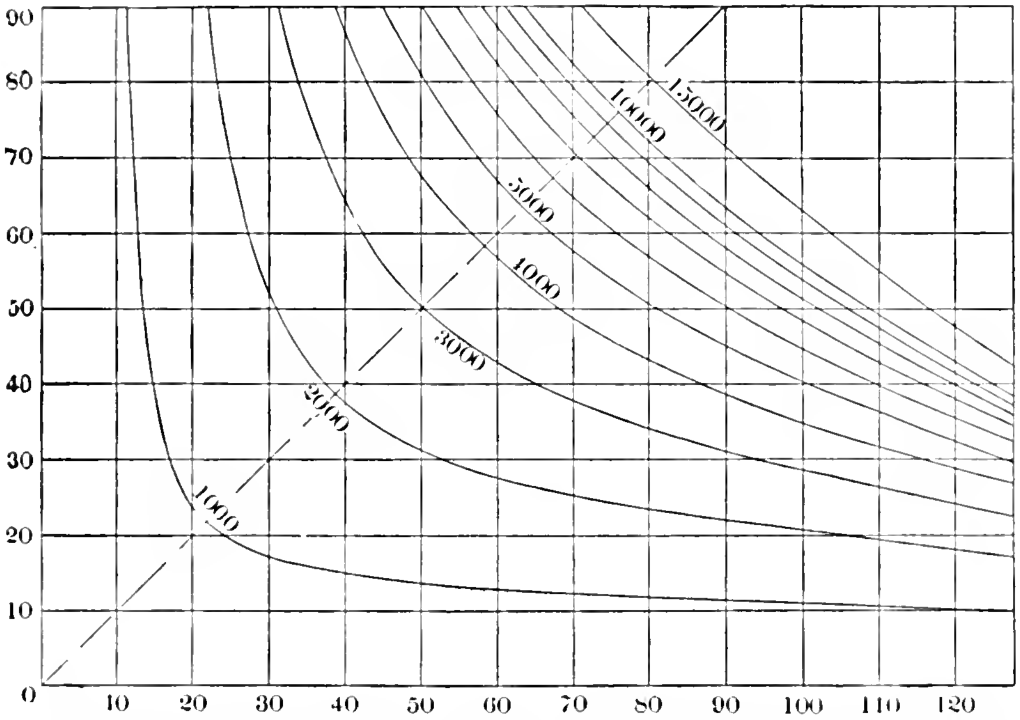

Figure 1. Chart for determining approximate altitude from sextant observations.

This chart was not used, as was expected, to give out the altitude a few seconds after each crossing, since the committee deemed it wiser not to make any announcements of altitudes till the end of the day.

The Distant Base.

As a check on the observation at the field, and in order to give data for a closer investigation of all the circumstances of the flight, a second base was occupied lying nearly east and west, about two and a half miles south of the aviation field. Satisfactory stations were found, one on Forbes Hill in Quincy, at a height of 128 feet above the aviation field (141 feet above mean low water), and the other on the estate of Mrs. E. M. Carey, in Milton, at a height of 71 feet. The length of the base line (QM upon the map, Plate 1) was 6236 feet. The stations were visible to each other, and, although the grandstand was visible from neither, aeroplanes could be observed as soon as they had risen to the height of 50 or 75 feet.

The position of the base was selected so that observations could not at any time be interfered with by the sun, and that the angle of elevation could be measured without an eye prism up to an altitude of more than 15,000 feet above the center of the field.

The distance from the field was not so great that it was necessary to read the angles with great accuracy, while it was sufficiently great to reduce materially the difficulty in following the rapidly moving aeroplanes, so that it was possible to observe quickly and accurately both horizontal and vertical angles without a finding device.

The instruments used were a special theodolite by C. L. Berger reading horizontal angles to 10″ and vertical angles to 20″, and a Buff mining transit reading both horizontal and vertical angles to 20″. Both instruments had full vertical circles, and inverting eyepieces magnifying about thirty diameters.

Through the kindness of Mr. Carl Keller, the New England Telephone Company connected the two end stations and the central station at the field during the entire period of the meet.

It was thus possible to insure simultaneous observations at the two stations in both coördinates. That they were practically simultaneous is clearly shown by the tables which follow, in which the approximate times are given as noted at each station. Where the times differ it is almost always possible to make an exact agreement by altering one or both by a single second, so that the mean of the times would rarely be in error by that amount.

The error of the observers' watches was found by a telephone comparison with the official chronometer on the field immediately before each flight.

By combination of the observations we were able not only to compute the altitudes of the aeroplanes at intervals of forty seconds or less, but also to locate their corresponding positions as projected vertically on the ground plane, and thus to plot so many points of the spiral both in ascent and descent as to form an interesting and useful record of all the details of the flight.

It may here be remarked that the use of this method seems preferable to any that requires the aviator to attain his maximum height at a given point or line. If thus restricted, the Blériot monoplane especially is at a disadvantage, as its construction renders it extremely difficult for the operator to see the ground at points anywhere near directly beneath him. The discussion of his ascending spiral, checked by observations of his descent, fixes his highest point quite accurately without placing any burden upon the aviator himself. (In reference to this point, see the flight of Grahame-White discussed on p. 42.)

The character of the results obtained may best be shown by the records of some of the flights and the methods of discussing them which follow.

To illustrate the whole process, we may take the observations of the flight of Brookins, September 12, the last day when any considerable flight was made, and at a time when the observers had had several days of practice. No great altitude was reached, but the flight was in many respects typical, and exemplifies some of the advantages of the two methods used, as controlling and checking each other.

TABLE I.

Flight of Brookins, Sept. 12, 1910, as Measured by Sextants. Base Line, Distance between Stations, 5000 feet. Sextants 9 feet above Course.

North Station.				South Station.			
No.	Direction.	Time.	Vert. Angle.	Time.	Vert. Angle.	Computed.	Chart.
1	1st, E	$5^h\ 58^m\ 30^s$	17° 7′	$5^h\ 58^m\ 35^s$	13° 57′	697 ft.	694 ft.
2	2nd, W		obtuse[1]	6 0 49	8 56		
3	2nd, E	6 6 55	39 28	7 4	25 50	1533	1529
4	3rd, W	10 45	24 4	10 53	60 26	1791	1799
5	3rd, E	12 35	47 50	39	31 15	1967	1964
6	4th, W	13 10	71 8	17	20 34	1672	1664
7	4th, E	13 35	42 24	45	20 12	1338	1314

[1] Too large to be measured by the sextant.

If the angular altitudes at the two stations are N° and S° respectively, and the length of the field base 5000 feet, the altitude in feet, h, given in column 7, is computed by the expression

$$h = \frac{5000}{\cot N + \cot S}.$$

The values given in column 8 were read directly from the chart referred to above on page 27. A correction of 9 feet has been added to each value, as the sextant base was higher than the middle of the field by that amount.

Only four crossings were well observed in the ascent and two in the descending spiral. The second observation, however, though incomplete, served a purpose, as will appear later. Not only the altitudes, but the projections of the crossing points on the ground line are given by the observations, since the distances of the projection from the north and south stations are $h \cot N$ and $h \cot S$ respectively, and six points in the spiral are thus fixed, making, with the start and finish, eight points in all thus completely determined.

Observations at the Distant Base.

As compared with the eight determinations made by the sextants, twenty-one simultaneous observations were made at the Quincy-Milton base. These are shown in detail in Table II. For purposes of comparison the results of the sextant observations are inserted, unnumbered but in chronological order.

The values of the altitudes in columns 5 and 9 are computed as follows:

Let h be the height of the aeroplane above the center of the field,
C, the length of the base line, 6236 feet,
$q = 128$, and $m = 71$ feet, the heights of Q and M above the center of the field,
α and β, the horizontal angles between the aeroplane and base line at Q and M respectively,
A and B, the angular altitude of the aeroplane at Q and M respectively.

Then
$$\begin{aligned} h &= C \tan A \sin \beta \operatorname{cosec} (\alpha + \beta) + q, \\ &= C \tan B \sin \alpha \operatorname{cosec} (\alpha + \beta) + m. \end{aligned}$$

All effects due to the curvature of the earth and refraction are neglected as being less than the errors of measurement which were expected to occur. The accuracy actually attained would seem, however, to justify the application of such corrections.

TABLE II.

FLIGHT OF BROOKINS, SEPT. 12, 1910, AS MEASURED BY TRANSITS. BASE LINE, DISTANCE BETWEEN STATIONS, 6236 FEET. COURSE 13 FEET ABOVE MEAN LOW WATER.

	QUINCY STATION Height above Course 128 ft.				MILTON STATION Height above Course 71 ft.			
No.	Time.	Vert. Angle.	Hor. Angle.	Alt.	Time.	Vert. Angle.	Hor. Angle.	Alt.
1	$5^h\ 57^m\ 31^s$	1° 54′	70° 35′	576 ft.	$5^h\ 57^m\ 30^s$	2° 17′	82° 10′	583ft.
2	58 12	2 18	74 30	649	58 13	2 36	77 31	653
	58 32	by sextants		687				
3	58 43	2° 33′	77° 50′	700	58 40	2 47	74 19	705
4	59 24	2 45	83 3	769	59 22	2 51	70 47	770
5	6 0 20	2 39	77 59	861	6 0 20	[2 53]	79 15	865 [1]
	0 49	by sextants		940				
6	2 2	3° 24′	67° 53′	1052	2 00	[3 54]	88 29	1054
7	3 8	4 4	65 6	1169	3 10	4 49	89 42	1190
8	3 53	4 44	67 13	1274	3 51	5 23	86 4	1276
9	4 42	5 22	65 31	1358	4 42	6 10	86 7	1362
10	5 13	5 42	63 12	1402	5 13	6 40	87 35	1404
11	5 55	6 13	62 58	1431	5 53	7 16	85 43	1434
12	6 32	6 17	70 48	1482	6 32	6 50	79 19	1488
	7 0	by sextants		1524				
13	7 3	6° 1′	76° 40′	1518	7 2	6 17	76 1	1527
14	7 42	5 45	83 45	1565	7 41	5 44	71 44	1571
15	8 15	5 57	87 53	1597	8 15	5 45	67 55	1602
16	9 16	6 38	86 56	1633	9 15	6 21	66 47	1636
17	10 2	7 24	83 14	1693	10 0	7 10	68 4	1693
18	10 40	8 10	79 59	1759	10 38	8 1	69 10	1758
	10 49	by sextants		1782				
19	11 41	9° 14′	72° 12′	1889	11 40	9 37	74 10	1887
20	12 25	8 7	73 25	1949	12 23	8 34	78 2	1955
	12 37	by sextants		1958				
21	13 11	6° 4′	75° 58′	1674	13 10	6 22	79 8	1674
	13 14	by sextants		1663				
	13 40	by sextants		1311				
	14 40	alighted						

[1] In the case of observations 5 and 6 the vertical angles as read off at Milton have each been decreased by 1°. This correction is justified not only by the agreement thus brought about between the two stations, but by the sextant observation at $6^h\ 0^m\ 49^s$ which, as is shown on page 34, indicates an altitude of 940 feet.

To find the horizontal distances D_q and D_m from Q and M, we have, with little extra work and from the same data of computation,

$$D_q = C \sin\beta \operatorname{cosec}(\alpha + \beta) \quad \text{and} \quad D_m = C \sin\alpha \operatorname{cosec}(\alpha + \beta),$$

and by use of these two distances the points are easily plotted with reference to the base line. It is sufficiently accurate, however, and more convenient, to determine the points graphically by drawing lines at the proper angles with the base by means of a protractor and straight edge, and marking their intersection as the position of the aeroplane.

The computations were quickly made on mimeographed forms following the scheme shown on page 33, which gives the original computations for observations 5 and 6 of Table II, using, of course, the uncorrected data. The discrepancy of these results pointed out at once the faulty observations.

The general agreement of the values at the two stations seems to show that the height is fixed by each observation with an error of less than five feet; but observations 5 and 6 at Quincy and Milton, as computed from the recorded data, show differences too large to be ascribed to error of observation. The sextant observation at $6^h\ 0^m\ 49^s$, although the angle was too great to be measured at the north sextant station (the spiral being far out beyond the course), still shows that the observations at the Quincy station give the correct value, and there seems to be good reason for assuming that the vertical angles were read 1° too large in each case at the Milton station. It appears in the discussion of all the flights that the error most frequently made was in reading the vertical angles. In the whole series of observations but two errors are indicated in the reading of the horizontal angles, one of which will be referred to later.

Time-Altitude Curves.

By plotting the successive values of h, given in Table II as abscissas, with the corresponding times as ordinates, we have the curve given below, Figure 2 (right), the slope of which gives the rate of ascent in feet per minute. The points corresponding to transit observations are indicated by circles, the sextant observations by crosses. The rate of ascent is about 100 feet per minute, and the descent nearly ten times as rapid.

Computation of Altitude from the Fifth, and Sixth Observations of Table II.

Date 1910, Sept. 12
Aviator, Brookins
A, a, q = alt., az. and elevation at Quincy Station.
B, β, m = alt., az. and elevation at Milton Station.

C = base line
h = height

Time	$6^h\ 0^m\ 20^s$	Time	$6^h\ 0^m\ 20^s$	Time	$6^h\ 2^m\ 2^s$	Time	$6^h\ 2^m\ 0^s$
A	2° 39′	B	3° 53′	A	3° 21′	A	4° 54′
β	79 15	a	77 59	β	88 29	a	67 53
$a + \beta$	157 14	$a + \beta$		$a + \beta$	156 22	$a + \beta$	
log C	3.79493	log C	3.79493	log C	3.79493	log C	3.79493
tan A	8.66543	tan B	8.83175	tan A	8.77387	tan B	8.93313
sin β	9.99231	sin a	9.99038	sin β	9.99985	sin a	9.96681
csc $(a + \beta)$	0.41231	csc $(a + \beta)$	0.41231	csc $(a + \beta)$	0.39698	csc $(a + \beta)$	0.39698
log $(h - q)$	2.86498	log $(h - m)$	3.02937	log $(h - q)$	2.96563	log $(h - m)$	3.09185
$h - q$	733	$h - m$	1070	$h - q$	924	$h - m$	1236
q	128	m	71	q	128	m	71
h	861	h	1111	h	1052	h	1307

Representation of the Spiral.

From the observations of Table II we may plot the ground plan of the spiral described in the ascent, and, with somewhat less certainty, that of the much more rapid descent. Each of the sextant observations, too, fixes a point on the spiral, although taken alone they would give little information as to the actual path of the aviator.

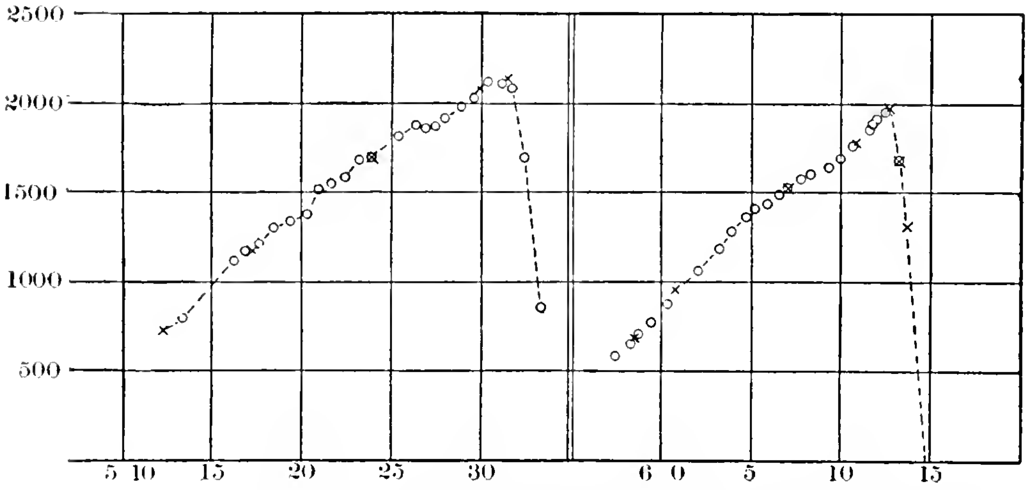

Figure 2. Time-altitude curves of Grahame-White (left) and of Brookins (right), September 12.

In Figure 3 are plotted the points as thus determined, each being numbered to correspond with the observation of Table II on which it depends. The points of crossing the base line are determined by the sextant observations of Table I.

The elevation of the path, as shown in the lower half of the figure, is determined by combining the altitudes from Table I and II with the projections of the observed points of the spiral above.

It is noteworthy that the spiral serves to give with some accuracy the height at the point of the crossing at $6^h\ 0^m\ 49^s$, where the angle was too great to be measured at the north end of the base. The figure shows that the projection of that point, which is marked by the dot between points 5 and 6 of the spiral, is about 900 feet north of that station, or 5900 feet from the south station, at which the vertical angle was measured as 8° 56′. This gives a height of 940 feet (assuming the elevation of the station as 13 feet), and a little further investigation shows that the angle at the north station was about 134°, and confirms the record of the observer that it was not measurable, as the sextant reads only to 128°. The error in position of the projected point is probably less than 150 feet, corresponding to an uncertainty of about 24 feet in the deduced height and 3° in the angular altitude at the north station.

In order that an intelligent judgment may be formed of the general accuracy attained, of the nature and frequency of erroneous observations, which must always occur in such a series, of the possibility of

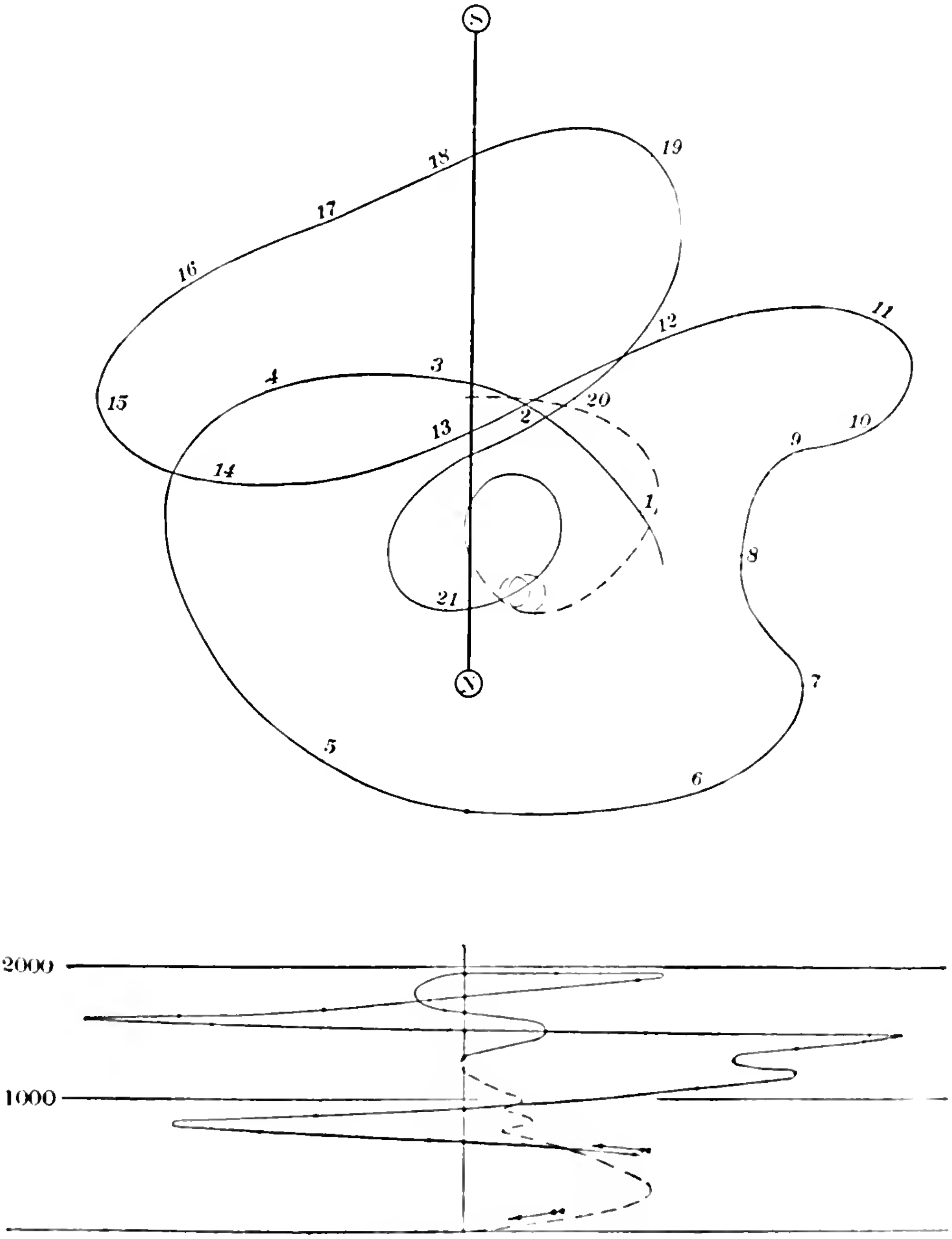

Figure 3. Spiral of Brookins, September 12, plotted from observations of Tables I and II.

correcting such observations, and the effect of rejecting them, three additional sets are given in Tables III, IV, and V. The first is that of Brookins on September 10, in which he reached the greatest altitude of the meet, with three discordant observations, one of which has been corrected, apparently with reason, by altering the vertical angle at the Quincy station by 1°. The others would be brought into line by changes of 10′ and 30′ in the vertical angles at Milton station, but no outside evidence is furnished by the sextants or spiral to justify such a change. In both cases the spiral, Figure 5, indicates that the horizontal angles were probably correctly recorded.

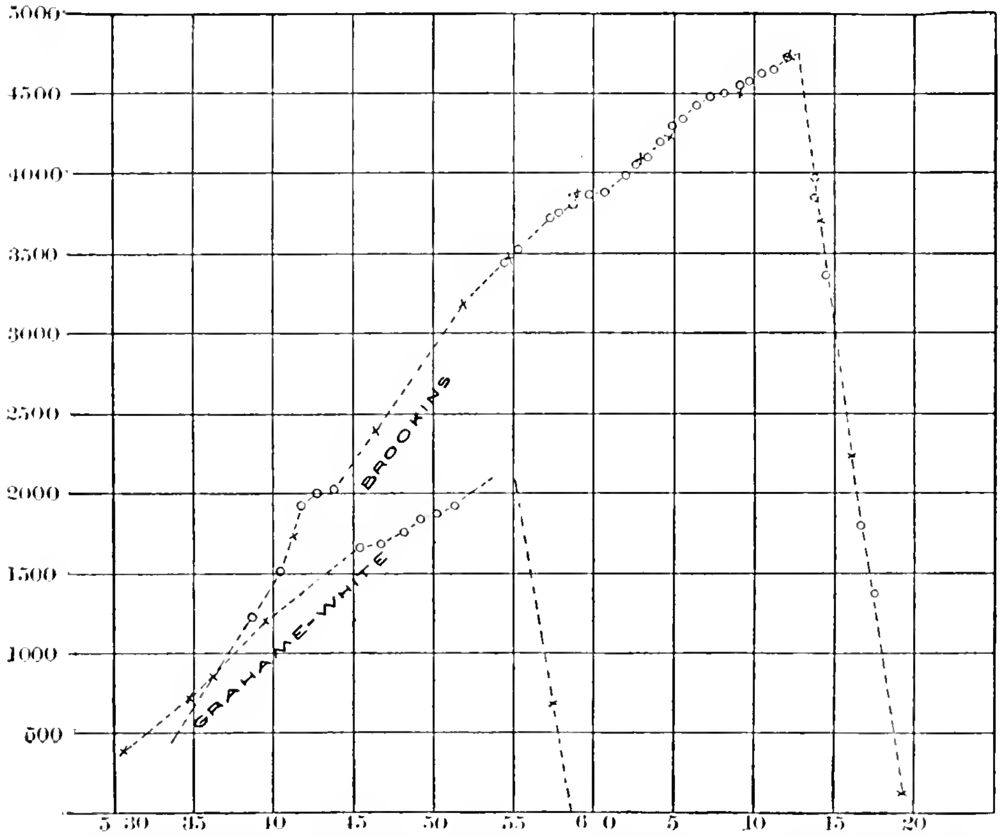

Figure 4. Flights of September 10: Brookins (Wright biplane), Grahame-White (Farman biplane).

The second flight, that of Brookins on September 8, shows two corrections of vertical angle and one change of the time of observation at Quincy, three vertical angles unrecorded at Milton, and one observation marked worthless, the result from which differs 17 feet from that at Quincy. This was on the second occasion of making observations, and naturally contains more errors and uncertainties, but in no case is the height uncertain by so much as five feet.

TABLE III.

FLIGHT OF BROOKINS, SEPT. 10, 1910. WRIGHT BIPLANE. BASE LINE 6236 FEET, COURSE 13 FEET ABOVE MEAN LOW WATER.

	Quincy Station. Height above Course 128 ft.				Milton Station. Height above Course 71 ft.			
No.	Time.	Vert. Angle.	Hor. Angle.	Altitude.	Time.	Vert. Angle.	Hor. Angle.	Altitude.
1	5^{h} 38^{m} 37^{s}	3° 54′	68° 59′	1220 ft.	5^{h} 38^{m} 40^{s}	4° 24′	88° 7′	1222 ft.
2	40 22	5 47	68 28	1511	40 30	6 28	84 30	1518
3	41 40	[7] 56	80 41	1910[1]	41 44	7 55	71 44	1919
4	42 41	7 44	90 59	2005	42 45	7 8	64 54	1981
5	43 42	7 12	90 20	2019	43 46	6 51	67 6	2023
6	54 13	11 12	69 49	3432	54 19	12 10	88 15	3450
7	55 11	11 53	82 51	3514	55 15	11 49	75 9	3527
8	57 10	15 3	85 36	3713	57 15	14 19	68 35	3715
9	57 52	15 43	82 34	3753	57 55	15 11	70 19	3753
10	58 35	16 16	79 5	3803	58 40	16 16	72 42	3849
11	59 41	16 50	73 42	3858	59 45	17 20	76 48	3865
12	6 0 35	16 36	69 31	3874	0 40	17 43	81 7	3877
13	1 55	15 13	66 1	3986	2 0	10 48	87 55	3986
14	2 37	14 21	71 21	4039	2 36	15 18	84 41	4050
15	3 15	14 29	80 20	4092	3 20	14 29	76 24	4091
16	4 5	16 52	81 48	4201	4 10	16 27	72 0	4199
17	4 50	17 52	74 43	4295	4 55	18 17	77 13	4295
18	5 30	17 58	68 8	4338	5 34	19 23	83 22	4339
19	6 22	17 23	60 27	4419	6 26	20 3	92 31	4427
20	7 14	15 36	58 32	4472	7 19	18 12	98 5	4478
21	8 2	14 33	63 25	4496	8 6	16 21	94 55	4503
22	9 2	14 24	73 2	4530	9 7	15 14	85 42	4549
23	9 39	14 48	78 48	4569	9 42	15 3	79 47	4576
24	10 20	15 29	85 33	4616	10 25	15 5	72 52	4626
25	11 9	17 41	87 2	4646	11 14	16 46	68 45	4645
26	12 2	18 59	76 43	4719	12 6	19 13	76 17	4731
27	13 39	13 45	68 5	3974	13 42	14 30	88 33	3844
28	14 24	11 21	81 10	3356	14 28	11 24	76 40	3364
29	16 34	7 18	67 52	1789	16 38	8 8	83 35	1799
30	17 24	4 41	65 55	1375	17 28	5 23	89 54	1381

[1] Vert. angle at Q has been changed from the recorded value of 6° 56′.

The third flight, Figure 2 (left), is that of Grahame-White on September 12, immediately preceding that of Brookins. The seventh observation shows a corrected vertical angle at Milton, and the twelfth a correction of the horizontal angle at the same station, — one of two instances de-

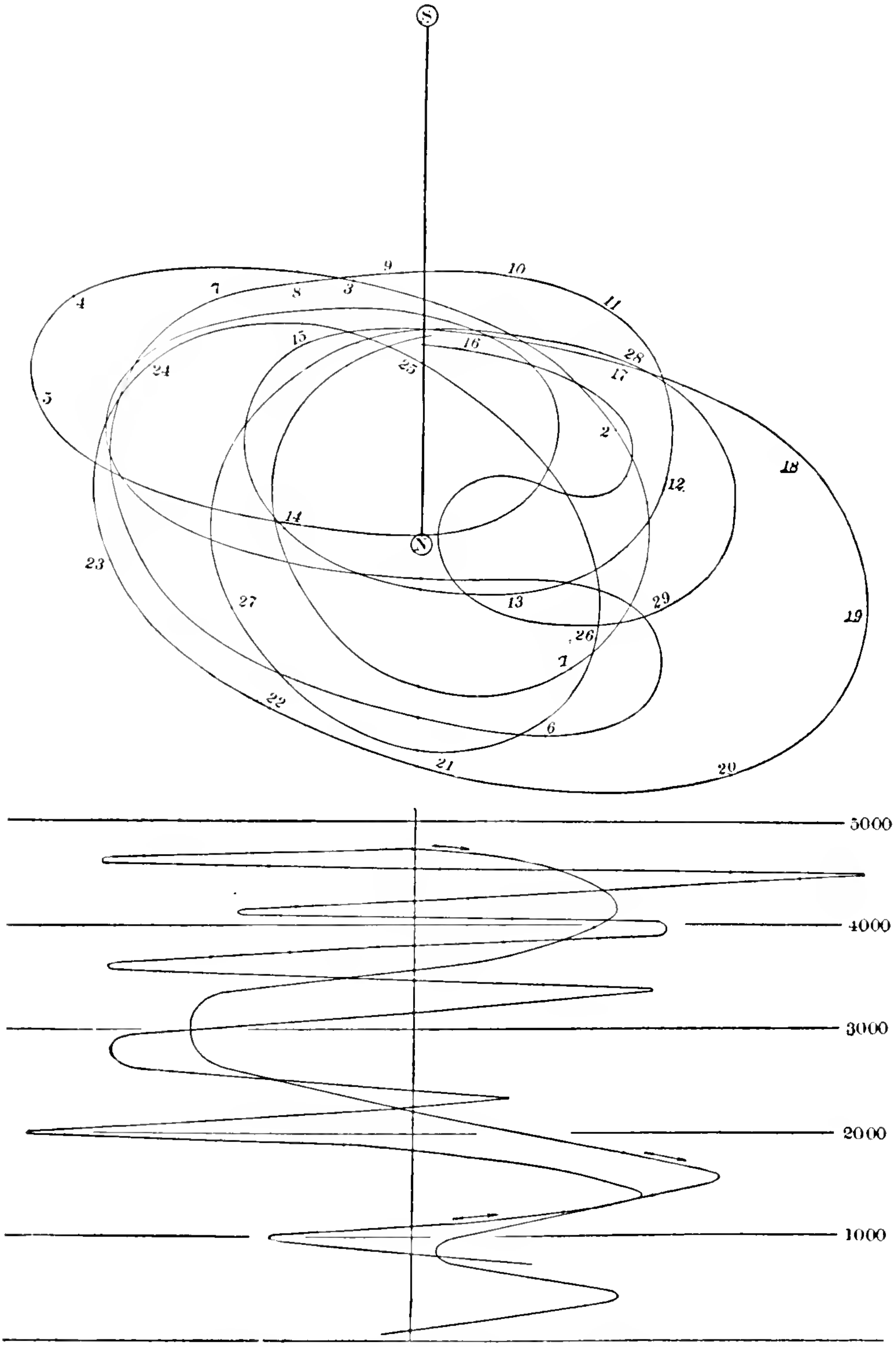

FIGURE 5. Spiral of Brookins, September 10, plotted from observations of Table III.

TABLE IV.

FLIGHT OF BROOKINS, SEPT. 8, 1910, WRIGHT BIPLANE. BASE LINE, 6236 FEET. COURSE 13 FEET ABOVE MEAN LOW WATER.

	Quincy Station. Height above Course 128 ft.				Milton Station. Height above Course 71 ft.			
No.	Time.	Vert. Angle.	Hor. Angle.	Altitude.	Time.	Vert. Angle.	Hor. Angle.	Altitude.
1	$5^h\ 38^m\ 41^s$	2° 29′	73° 2′	774 ft.	$5^h\ 38^m\ 41^s$	2° 48′	82° 26′	774 ft.
2	39 55	3 42	76 25	973	39 54	[3 55]	76 0	967 [1]
3	41 1	4 21	84 35	1156	41 1	4 19	69 46	1154
4	42 9	4 13	75 17	1319	42 12	4 32	82 14	1322
5	43 37	5 23	77 49	1506	43 36	5 36	77 34	1506
6	48 2	5 26	73 30	1499	48 0	5 54	81 11	1516 [2]
7	49 44	7 11	81 2	1732	49 46	7 8	71 19	1732
8	50 59	8 31	76 4	1888	51 1	8 40	73 22	1885
9	[52] 13	5 48	80 35	1505 [3]	52 7	5 52	73 17	1506
10	54 28	6 10	80 53	1782	54 27	6 16	75 51	1783
11	55 35	7 3	77 3	1880	55 35	7 17	77 30	1879
12	56 28	8 1	78 7	1959	56 26	.....	74 22	.....
13	57 19	9 22	79 26	2068	57 16	9 15	70 34	2068
14	58 8	10 41	76 10	2148	58 6	10 39	70 32	2145
15	59 35	8 56	76 18	2254	59 35	9 12	77 13	2255
16	6 0 23	9 17	86 3	2363	6 0 24	8 53	68 52	2365
17	1 32	10 36	95 34	2456	1 31	9 22	58 59	2454
18	2 33	12 27	100 24	2528	2 31	10 21	52 31	2532
19	5 11	[17 42]	86 51	2766 [4]	5 6	14 56	54 59	2759
20	6 28	[16 38]	69 35	2886 [4]	6 27	17 4	70 47	2884
21	7 36	14 31	60 20	2992	7 35	16 52	85 28	2994
22	8 51	12 10	55 16	3102	8 51	14 50	98 9	3104
23	9 41	11 12	62 2	3130	9 41	.....	93 44	.....
24	11 56	13 35	87 15	3237	11 54	12 44	[66 23]	3240 [5]
25	12 56	11 46	98 4	3237	12 55	12 42	55 57	3247
26	16 21	22 19	125 42	3419	16 16	14 44	30 49	3413
27	17 33	26 23	111 3	3598	17 33	.....	36 44	.....
28	18 46	23 32	90 3	3565	18 46	19 5	51 39	3552
29	20 14	18 17	75 54	3647	20 4	18 6	70 35	3651
30	22 36	14 52	86 33	3708	22 36	14 6	68 3	3715
31	23 45	15 21	78 25	3791	23 46	15 23	71 47	3799
32	24 51	15 28	71 28	3831	24 51	16 21	81 7	3837
33	26 23	12 59	91 41	3170	26 26	11 51	63 20	3168

[1] Vert. angle has been increased 1° for Station M.

[2] Marked worthless by observer at M. Clouds between 5 and 6.

[3] Time at Station Q has been decreased by 1^m.

[4] 5° has been added to each of the vertical angles.

[5] 10° has been added to Hor. Angle at Station M (spiral suggested this change and sextant also at $6^h\ 12^m\ 0^s$ confirms it).

tected in the whole series; it was not indicated by comparison with the Quincy values, as there is close agreement with either value of the horizontal angle, but the spiral showed that the horizontal angle must be in error by about 10°, and a sextant observation at almost the same instant corroborates the value of the height given in the table.

TABLE V.

Flight of Grahame-White, Sept. 12, 1910. Farman Biplane, Base Line 6236 feet, Course 13 feet above Mean Low Water.

	Quincy Station. Height above Course 128 ft.				Milton Station. Height above Course 71 ft.			
No.	Time.	Vert. Angle.	Hor. Angle.	Altitude.	Time.	Vert. Angle.	Hor. Angle.	Altitude.
1	5h 13m 15s	2° 25′	79° 51′	792 ft.	5h 13m 15s	2° 37′	77° 23′	796 ft.
2	5 16 12	4 17	64 6	1114	5 16 13	5 2	87 39	1115
3	5 16 52	4 51	70 36	1163	5 16 51	5 21	79 14	1167
4	5 17 44	4 42	83 22	1206	5 17 42	4 42	70 4	1210
5	5 18 30	4 11	86 3	1301	5 18 30	4 12	72 13	1307
6	5 19 24	3 59	78 23	1336	5 19 18	4 13	80 50	1340
7	5 20 19	4 22	70 23	1369	5 20 18	[4][1] 51	87 5	1372
8	5 21 2	4 51	65 34	1501	5 21 2	5 38	91 47	1525
9	5 21 43	5 27	62 51	1538	5 21 44	6 22	92 13	1540
10	5 22 22	6 13	61 14	1582	5 22 21	7 21	90 55	1581
11	5 23 10	7 14	66 6	1673	5 23 9	8 9	81 49	1682
12	5 23 55	8 4	78 33	1687	5 23 54	8 1	[69][2]24	1693
13	5 25 23	6 13	86 14	1813	5 25 21	6 6	71 19	1811
14	5 26 20	6 5	77 20	1873	5 26 19	6 21	80 36	1873
15	5 26 52	5 56	72 6	1854	5 26 50	6 26	85 54	1857
16	5 27 28	6 9	67 14	1851	5 27 25	6 58	89 49	1873
17	5 28 3	6 40	63 29	1910	5 28 2	7 40	92 24	1909
18	5 28 55	8 0	63 51	1981	5 28 55	9 10	87 56	1981
19	5 29 31	8 54	71 59	2020	5 29 30	9 29	77 44	2029
20	5 30 17	8 32	83 49	2111	5 30 18	8 20	69 53	2121
21	5 31 8	7 17	78 35	2104	5 31 8	7 31	78 10	2114
22	5 31 43	7 12	72 23	2093	......	7 42	84 7	2086
23	5 32 20	6 7	67 47	1687	5 32 20	6 50	86 52	1687
24	5 33 14	3 27	66 5	859	5 33 14	4 0	83 12	851

[1] Vert. angle at Milton recorded 5° 51′.

[2] Hor. angle recorded at Milton was 79° 24′. Spiral proves it to be 69° 24′ and sextant observation at almost same instant corroborates this.

It has been thought worth while to give these observations in detail for those especially interested in the problem. It is evident that there is much information in the tables and curves to which we have not referred; for example, rate of ascent per minute, gradient with and against the wind, etc. The reader who wishes to study them more minutely may therefore wish to plot them on a scale sufficiently large for his purpose. To make use of the sextant as well as the transit observations in plotting the spirals, it is necessary to know the relative position of the two bases. The north end of the field base is distant 15,000 feet and 14,700 feet from Q and M respectively. The south end of the field base is 10,056 feet from Q and 11,005 feet from M.

In regard to these tables we notice that there is apparently a small systematic difference between heights as observed at Q and M. This was at first suspected to be due to error in level of the two stations, but was not the same at all times. It was not due to difference in time of observation at the two stations, for although the setting at Milton was always a fraction of a second later, this could only give rise to a difference of about one foot at most. It may have been partly due to difference in levelling of instruments, and perhaps partly to neglect of refraction and curvature of the earth in the computation.

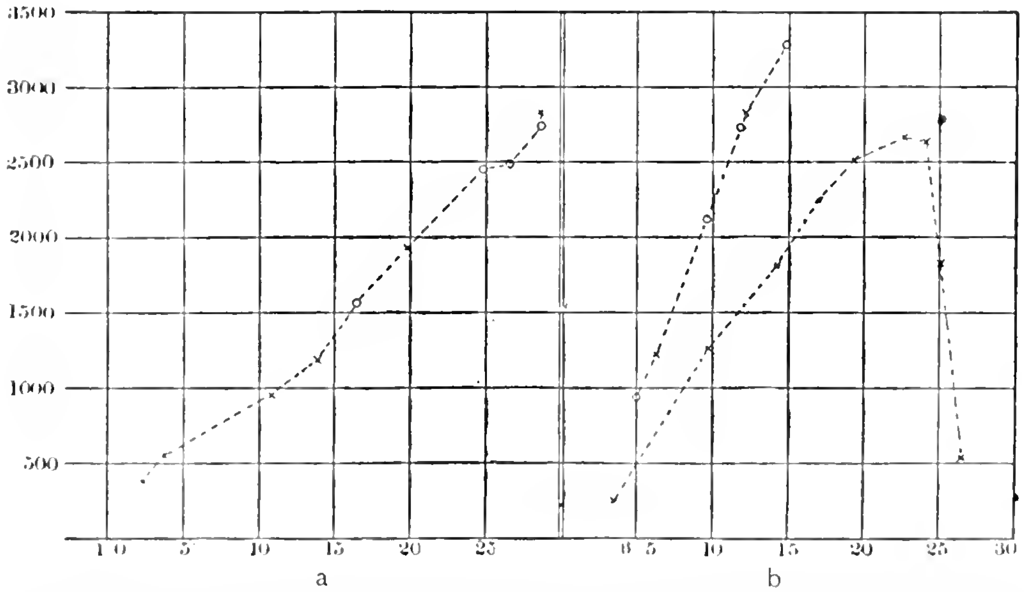

FIGURE 6. Time-altitude curve. (Left) flight of Johnstone, September 7 (Wright biplane); (right) flight of Grahame-White (Blériot monoplane), and flight of Brookins (Wright biplane).

The time-altitude curves have been plotted for all the flights of the meet which have any special interest. Those of Brookins, Johnstone, and Grahame-White on September 7 are plotted in Figure 6. They show the typical rate of ascent of the Wright biplane, about 100 feet per minute, in direct comparison with the Blériot which was in the air at the same time and rising more than 200 feet per minute.

Figure 4, plotted from Table III, represents the highest flight of the meet, that of Brookins on September 10, at an average rate of about 100 feet per minute. From $5^h\ 43^m$ to $5^h\ 57^m$ the transits were temporarily assigned to Grahame-White in a Farman biplane, who was far off the course to the southeast and could not be frequently observed by the sextants, while the latter instruments were sufficient for the observations of Brookins, who was describing large but regular circles above the field. At $5^h\ 52^m$ Grahame-White was cut off from view at Milton by a large tree which lay farther off the course than it was supposed that any aviator would go in an altitude attempt, and the transits were turned back upon Brookins.

The single sextant observation of Grahame-White's descent, however, combined with the fact that his usual rate on the beginning of the downward spiral was at least 800 feet per minute, enables us to fill out the dotted part of the curve, and conclude that he reached a height of approximately 2200 feet. A comparison of all the curves shows that if the highest point of the ascent is not actually observed by the transits, it may always be closely fixed by the intersection of the upper portions of the curves of ascent and descent.

The spiral of Brookins in this flight is shown in Figure 5. In the long interval between points 5 and 6, when the transits were turned upon Grahame-White, the general curve of the spiral, however, is plainly shown by the sextant observations, although the aviator changed the direction in which he was circling the course, apparently in order to make his crossings against the wind.

Figure 7 shows the time-altitude curve of Brookins on September 8, when he was lost to sight in a light cloud for five minutes at an altitude of 1500 feet, climbed another 500 feet and disappeared a second time, when he stopped his engine, descending to the 1500 foot level again out of the cloud, and then taking a somewhat different line of flight, ascended without further difficulties to a height of nearly 4000 feet. The conditions were such that the early part of the spiral was not well determined, and it does not seem worth while to reproduce it here. The main features are shown on the ground plan which is shown on the map of Plate 1. The very discordant sextant observations at $5^h\ 19^m$ and $5^h\ 22^m$, shown in Figure 7, are unexplained. The former was made with the machine about 1000 feet south of the southern station, nearly overhead, and moving in a course nearly parallel to the line, so that the vertical angle was changing very rapidly, and the observation difficult.

No such cause can be assigned for the second error, and it is perhaps more probable that both were caused by some accidental disturbance of the vertical plane of the sextant which affected the two observations alike. No other discrepancy approaching this in amount occurred in in the whole course of the observations.

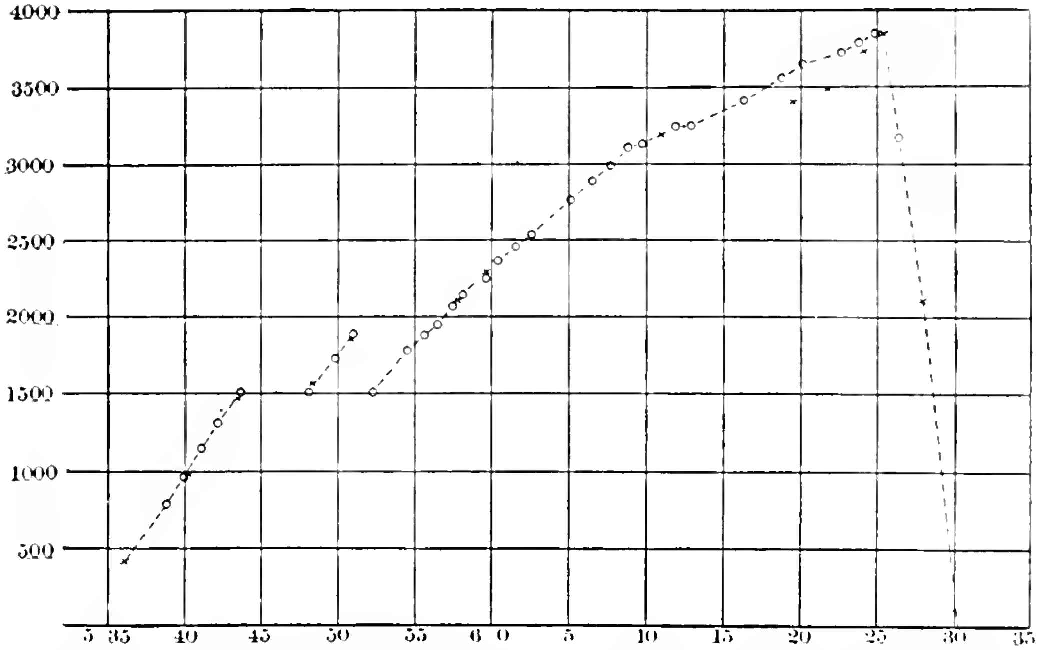

FIGURE 7. Time-altitude curve: Brookins (Wright biplane), September 8.

It remains to make grateful acknowledgment of the skill of the observers and of the interest of many others, without which this work would have been impossible; especially of the assistance of Mr. William Hunt in the observations and reductions, and in drawing the curves which illustrate this paper.

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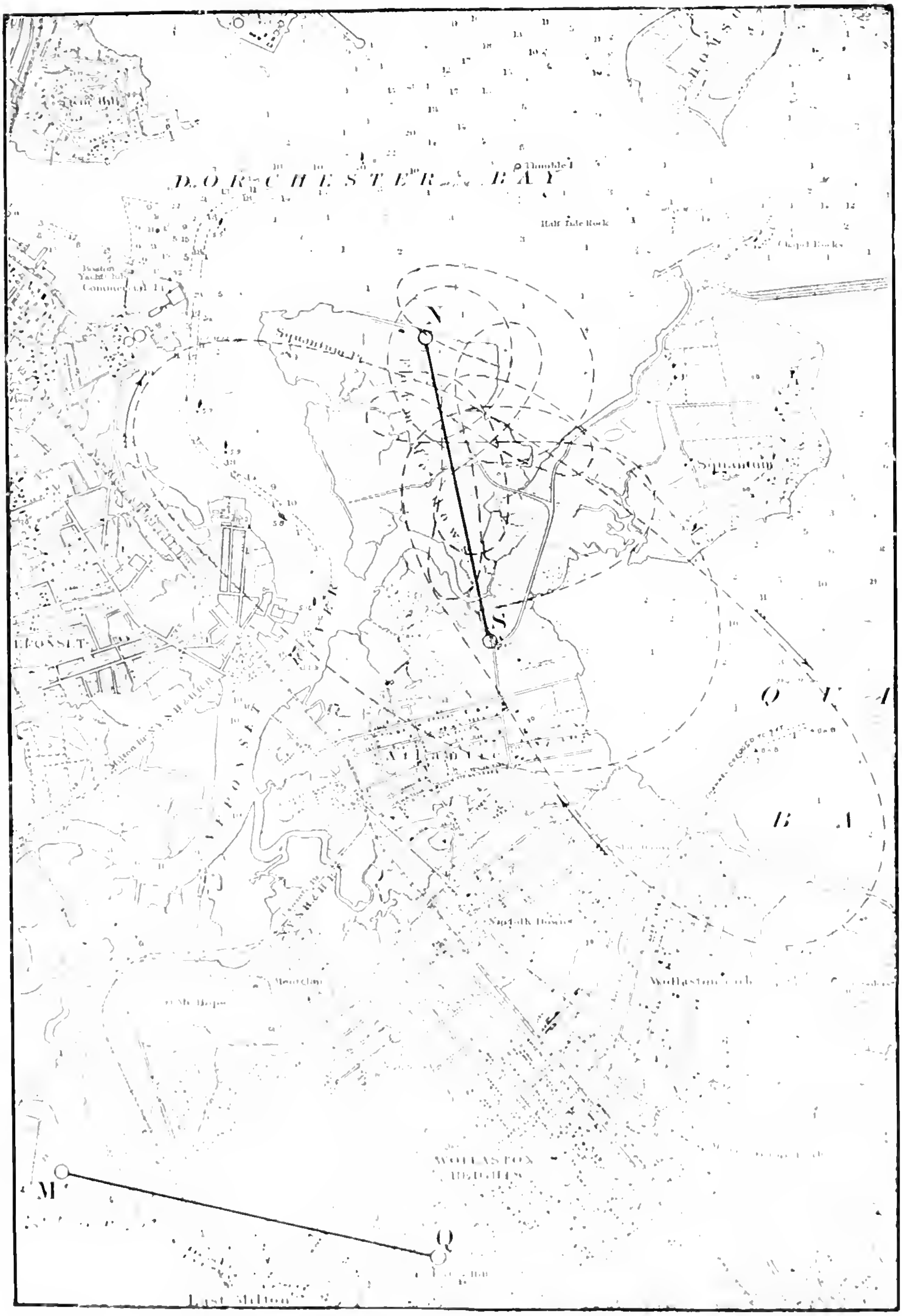
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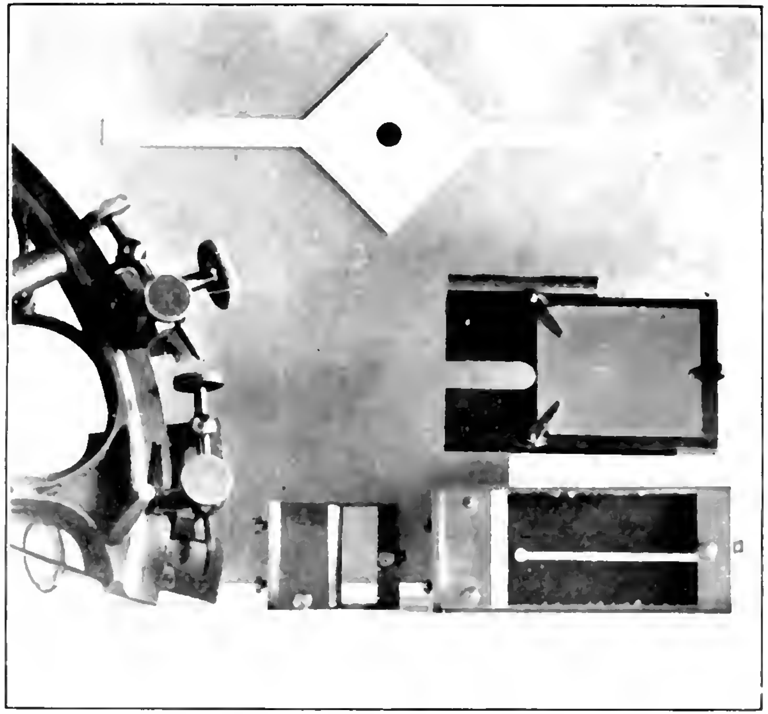

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 3. — June, 1911.

THE NATURE OF VOLCANIC ACTION.

By Reginald A. Daly.

With Five Plates.

THE NATURE OF VOLCANIC ACTION.

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Presented April 12, 1911. Received February 23, 1911.

Contents.

The Problem.

Volcanic action is the working of the extrusive mechanism which brings to the earth's surface rock-matter or free gas, initially at the temperature of incandescence. The mechanism involves the localization, opening, and shaping of the vent; the persistence of a vent as an open channel during seconds, days, years, centuries, or milleniums; the conditions for lava outflow, for gas and vapor outflow, and for the separation of gas or vapor from lava; the conditions leading to the periodicity of eruption at central vents; and those leading to chemical variations in the erupted magma.

Since the days of the Greek philosophers thousands of memoirs have touched upon this complex problem of terrestrial dynamics, but geologists are still looking for a generally acceptable solution. Within the last ten or twelve years the variety of new suggestions affecting the very core of volcanic theory has been, perhaps, as great as that of any previous decade. In the varying chemical affinities of water and silica for the bases of rock-matter at different temperatures, Arrhenius finds an essential condition of all vulcanism. He therefore attempts to support the time-honored hypothesis that the vapor of meteoric or marine water absorbed in plutonic magma is the prime motor in eruptions.[1] On the other hand, Brun holds that water is quite unessential to eruption of the first order, and he believes he can prove his thesis by actual analysis of the volcanic emanations.[2] Again, Chamberlin explains vulcanism as due to the extrusion of magmatic tongues, which, by tidal stresses, are slowly kneaded out of the deep interior of the otherwise solid earth.[3] In entire contrast to that hypothesis, Dutton has come to the belief that the indications are that most of the volcanic eruptions originate at depths between one mile and two and a half miles.[4]

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[1] S. Arrhenius, Geol. Fören. i Stockholm Förhandl., **22**, 395–419 (1900).

[2] A. Brun, Archives des sciences physiques et naturelles, Geneva, février, 1909; février, 1908; novembre, 1906. Le Globe, octobre, 1907.

[3] T. C. Chamberlin and R. D. Salisbury, Geology, **1**, 632 (1906), and **2**, 104 (1906).

[4] C. E. Dutton, Volcanos and Radioactivity, 1906, p. 5 (Paper read before the National Academy of Sciences, April 17, 1906), published at Englewood, N. J.

Without further noting the divergences of recent views, it is clear that volcanic theory is in a disorganized state.

There is one patent reason for this conflict of opinion. The Vesuvian "steam-engine" and the geyser-like Stromboli have dominated European thought. Though living in a wilderness of waters, the brilliant Englishman in Hawaii, W. L. Green, concluded that water is not an essential agent in vulcanism, for he had lived many years meditating on the dry, or nearly dry, emanation from Kilauea.[5] Arrhenius, a physical chemist; Moissan, a synthetic chemist; Brun, an analytic chemist; Mallet, a civil engineer; von Buch, a Wernerian geologist; von Humboldt, a Wernerian who traveled greatly; Scrope, who built his philosophy on observations in the limited European field: Stübel, a specialist in the giant volcanoes of Ecuador; Tschermak, a mineralogist; Daubrée, an experimental geologist; Dutton, master of geological reconnaissance — each of these, and every other leader in volcanic study has been forced to think in terms of his intellectual environment. Each investigator has approached the many-sided problem with special training and experience, and many vulcanologists have shared the racial subjectivity which finds explosions, earth-shaking, and other surface events humanly so important as largely to control inductions on the theoretical side. During the last half-century the discovery and study of thousands of plutonic igneous masses have promoted the view that vulcanism is a subsidiary effect of intrusion. This thesis is emphasized and illustrated in the following pages, wherein the attempt is made to show its agreement with the essential facts known about volcanoes, ancient and modern.

A general working theory of vulcanism is here outlined. It has taken its full form directly as a result of the writer's studies in the Hawaiian Islands during 1909, but many of the chief conclusions are founded on his field-work in plutonic geology as well as in the geology of many ancient volcanic formations. The effort has been made to cover the more important literature of vulcanism, and as yet no facts therein stated seem to the writer to be irreconcilable with the theory, which, on the other hand, finds strong support in the great body of recorded facts. Many of the essential points in the following argu-

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[5] "Water in a rainy district gets to the hot rocks in all sorts of ways, about which there need be little mystery. All this steam seems to have no further connection with the forces concerned in the action of the lavas in Kilauea, than the vapors which arise from the body of a hard-worked horse, when a shower of rain has fallen on him, have with the force he exerts in drawing his load." — W. L. Green, Vestiges of the Molten Globe, Part II., p. 82, Honolulu, 1887.

ment are by no means new. The principal reason for adding this paper to the already overburdened literature on volcanoes is that it attempts to coördinate the accepted principles of vulcanology with each other and with the truths of plutonic geology. Whether or not the actual result is to meet with favor among geologists, the writer feels certain that the synthetic ideal in vulcanological study has not been actively pursued in anything like its just measure. That this pursuit necessarily involves some speculation concerning the earth's interior is not a valid objection to the undertaking. The earth's interior is no more invisible than is the interior of a molecule. The sanction for modern chemistry has become as strong as it is because philosophical chemists have speculated about the invisible, intangible, and unweighable. Similarly, to be more productive than it is, geology must become more speculative. In this there is danger if the hypothesis is founded only on the facts met with in the individual worker's experience; there is little danger, but great promise of fruit, if the speculation is synthetic and regards all the published facts.

During the preparation of this paper the writer has been greatly aided by discussion of many points with his colleagues, Professor W. C. Bray, T. A. Jaggar, Jr., G. N. Lewis, and A. A. Noyes of the Massachusetts Institute of Technology, and also with Professor H. N. Davis, Professor L. S. Marks and Dr. P. W. Bridgman of Harvard University, and Professor A. C. Lane of Tufts College. To these gentlemen the writer's sincere thanks are due; he alone, however, must bear the responsibility for the form and substance of the paper. He wishes further to express special thanks to the Director and chemists of the United States Geological Survey, who have supplied two of the chemical analyses noted in the text; to Mr. H. E. Wilson, of Hilea, Hawaii, who has furnished one of the photographs here reproduced; and to Mr. Walter E. Wall, Government Surveyor of Hawaii, who has extended many courtesies to the writer, and gave him permission to copy many manuscript maps used in the assembling of some of the facts on which this paper is based.

ABYSSAL INJECTION.

Surveys on each of the continental plateaus have already shown that the average rock of the plateau's basement (pre-Cambrian terrane) is, chemically speaking, of granitic composition, with a silica-percentage not far from 70. Notwithstanding the vast erosions of many geological periods, this terrane is, in places, known to extend downward several kilometers even at the present time, and it is a reasonable inference, contradicted by no fact yet discovered, that the acid complex has, generally, a minimum depth of many kilometers. Upon its back each of these acid continental plateaus carries a sedimentary pellicle, locally increased to the imposing thickness of geosynclinal prisms. (See Figure I.)

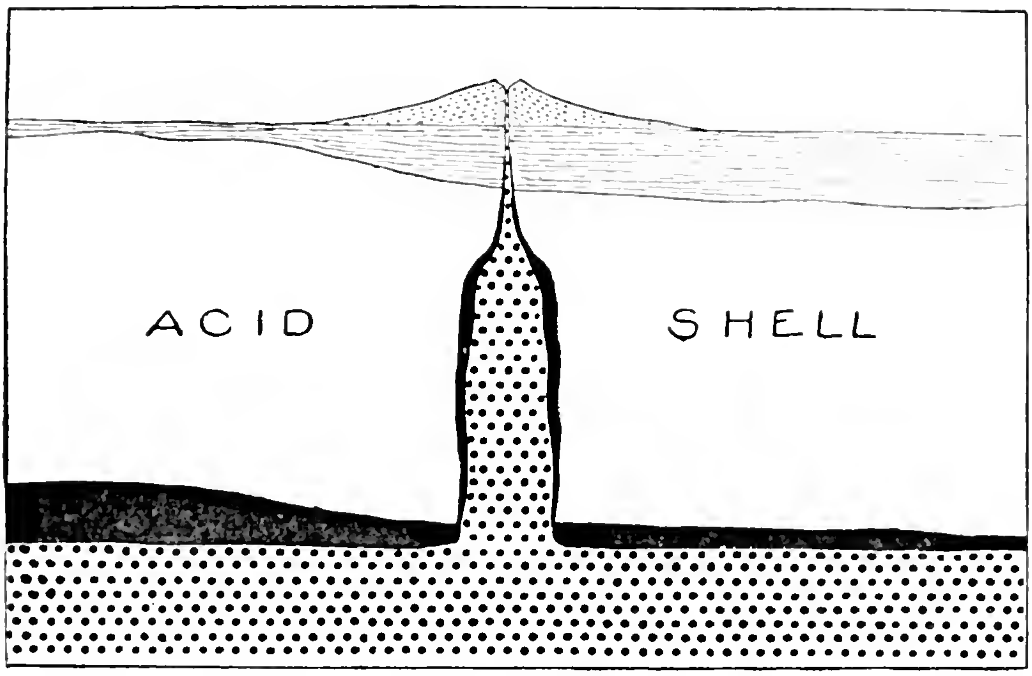

FIGURE 1. Diagrammatic section of the earth-shells, showing abyssal injection and accompanying central eruption. The broken lines below the cone represent a geosynclinal prism merging into sediments of more usual thickness. Solid black represents solidified matter of the basaltic substratum, the broad horizontal band indicating the part of the substratum crystallized since an early pre-Cambrian period. Heavy dots represent fluid matter of the substratum, in position after the abyssal injection has partly crystallized (along its walls). Scale given by height of cone, assumed as projecting 5 kilometers above the plain of sediments.

Most volcanic rock is of basaltic or andesitic composition, and it is clear that such material has not been derived from the mere liquefaction of the basement terrane, or of the sedimentary veneer, or of both together. The great bulk of the world's lava is *exotic*. It has *penetrated* the basement terrane and the sedimentary shell without absorbing these in large proportion. We thus seem driven to believe in *abyssal fissures*, opened in the earth's outermost shells for the passage of the molten rock.

By analogy such abyssal injection may be assumed as the preliminary stage of Pacific vulcanism, although there is much to be said for the view that the primary acid earth-shell is lacking, or else is very thin, over most of the area covered by that ocean. For example, geodetic results seem to suggest that the Pacific sediments rest, more or less directly, on a terrane whose average density is nearer the density of crystallized basalt than that of granite or common gneiss.

In the case of the greater lava-fields, the abyssal fissures have been prolonged, as true fissures, to the surface; there a leading condition of extrusion is probably the simple hydrostatic adjustment of magma to a breaking earth-crust. Most central eruptions have occurred in localities where emitting fissures are not visible. In emphasizing this fact some geologists have been disposed to deny that fissuring of the crust is a prerequisite of vulcanism. Their reasoning is strong so far as the actual opening of many vents is concerned, and one result has been to sharpen the eyes of vulcanologists as to field relations. But we may agree with Supan that "one should not throw out the baby with his bath-water." Though a vent, for the last few hundreds or thousands of meters, may have been opened by explosion or by other means than simple fissuring, a fair study of geological maps shows the existence of strong abyssal fissures beneath most of the volcanic piles which are not visibly located on surface fissures. Obviously, an immediate tendency of volcanic action is to cover such feeding fissures. Yet their existence is to be inferred from the group alignment of the greater cones. Such is, of course, the traditional explanation of groups like those of the American Cordilleras, of the Hawaiian series, the Samoan series, or the Antillean series. Some clusters of vents show no definite alignment; instances like the "embryo" volcanoes of Suabia will be discussed on later pages.

We may, therefore, assume abyssal fissuring and magmatic injection to be the *essential preliminary* to vulcanism, as it is, indeed, to all igneous action. Probably most vulcanologists have made the same assumption, but the literature of vulcanism nowhere contains a full statement of some of the chief theoretical consequences of the assumption. Some authors, either expressly or tacitly, refuse to believe in the principle, but their arguments against it have never been sufficiently supported by the facts of structural and areal geology. The matter is so fundamental that it has here been duly stated; it may savor of a truism to many working geologists.

Conditions of Abyssal Injection.

The principle may be accepted, though the circumstances permitting of injection at depths of ten, twenty, or more kilometers are not yet completely understood. This much more difficult subject has been speculatively considered by the writer in a paper published in 1906.[6] Therein the general result of the work of Reade, Davison, Fisher, and G. H. Darwin, on the stresses produced in the earth through cooling, was assumed as true. A superficial shell of compression is separated from a much thicker underlying shell of tension, by a level of no strain. The tensions of the lower shell and the failure of complete "compressive extension" in that shell furnish the conditions favoring magmatic intrusion into the shell. The writer's earlier statement (page 204 of the paper referred to), that laterally-confined rock-matter grows vastly more rigid with increase of pressure, has been recently corroborated in striking fashion by Adams and Bridgman in their respective high-pressure experiments. Adams shows that, with lateral support at high pressure, the normally weak mineral, fluorite, became less plastic than hard steel at ordinary pressure.[7] P. W. Bridgman (verbal communication) has proved that under external hydrostatic pressure amounting to 24,000 atmospheres, the cavity of a sealed glass tube is not closed, even after prolonged application of such enormous force. In an actual test, a tube, having undergone a hydrostatic pressure of 24,000 atmospheres — corresponding to the weight of more than eighty kilometers of the earth's crust — for a period of three hours, was removed from the press and was found to have undergone no sensible change in size or form. These experiments seem to sustain the view that at least the upper, cooler part of the shell in which tension is developed on account of the cooling of the earth, is not kept fully and continuously condensed by the weight of the overlying shell. On the contrary, the shell of tension may be capable of considerable condensation, which awaits, as well as permits of, the periodic injection of liquid matter from the substratum. This is also the conclusion of Lane, expressed in his highly suggestive paper on the "Geologic Activity of the Earth's originally absorbed Gases," where he has considered the mechanics of abyssal fissuring.[8]

In general, the injections must find difficulty in passing beyond the level of no strain, which is only a few kilometers below the surface of the planet. In the cases where the magma does succeed in penetrating the shell of compression, volcanic action ensues.

Since the speculation is not vital to the argument of the present paper, it will not be further reviewed. It may be noted that the same

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[6] R. A. Daly, Abyssal Igneous Injection as a Causal Condition and as an Effect of Mountain-building. Amer. Jour. Science, **22**, 195-216 (1906).

[7] F. D. Adams, Jour. Geol., **18**, 500 (1910).

[8] A. C. Lane, Bull. Geol. Soc. America, **5**, 269 (1894).

general conception has been independently stated by H. J. Johnston-Lavis, one of the world's most experienced students of volcanoes. Only quite recently has the writer found that he had been anticipated by Johnston-Lavis in the root idea, as expressed in brief notes published in the Geological Magazine.[9] It is a source of genuine satisfaction to find a fellow adventurer in an almost pathless field of investigation, and, yet more, to find in that companion a distinguished specialist.

The Substratum.

Similarly, the writer has found that he has been anticipated in the view that the heat-bringer in all Paleozoic and later igneous action is a general basaltic substratum underlying the shell of tension.[10] The essential point was stated by Cotta on page 78 of his "Geologische Fragen," published in Freiberg in 1858, and by W. Lowthian Green on page 61 of his "Vestiges of the Molten Globe," Part II, published in

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[9] **17**, 246 and 344 (1890). A fuller statement by the same author appears in the Geological Magazine, **36**, 433 (1909).

[10] Cf. R. A. Daly, Amer. Jour. Science, **15**, 294 (1903).

The writer is clearly conscious that this assumption of an uncrystallized general substratum conflicts with the planetesimal hypothesis of the earth's origin, as stated by Chamberlin. Whatever be the mode of assemblage for the earth's materials originally, it is extremely difficult to accept the view that, when the planet approached its present size, it could have avoided a stage where it was molten all over the surface. Lunn's temperature-depth curve (Chamberlin and Salisbury's "Geology," 2d ed., **1**, 564, 1906) for the earth, computed on the accretion hypothesis, shows temperatures of from 10,000° to 20,000° C. in the interior. Since, on the hypothesis, the mode of accretion afforded a very heterogeneous mass at the beginning, there must have been a gravitative readjustment of the materials rendered fluid by the high temperature of the interior. The less dense matter, rising from great depth, would bring to the surface a large proportion of its enormous heat-content, ultimately fusing a surface shell of great depth. In other words, the earth-furnace imagined by Chamberlin and Lunn would melt its own walls.

Another serious objection to the hypothesis that the earth has been largely solid (crystalline) throughout its history is the fact that each of the planets, Jupiter, Saturn, Uranus, and Neptune, has a density appropriate to a gaseous condition and to very high temperature even in the surface shell. Again, if the moon were never fluid at the surface, its matter has been fluid very close to that surface; every square meter of its visible surface seems to have witnessed igneous action. So far, the published statement of the planetesimal hypothesis has not discussed the earth's history in terms of the facts known about its fellow members in the solar system. Since both the gas-nebula and planetesimal-nebula hypotheses seem to demand an incandescent, molten stage for the earth, the present writer is inclined to doubt that the geologist, for most of his thinking, needs a decision as to the truth of either hypothesis. That is a matter for cosmogony and astrophysics.

Honolulu in 1887. Each of these books first became accessible to the writer in 1909. It is certainly a pity that the second part of Green's work is not more generally known. The book is almost as remarkable a contribution to the philosophy of vulcanism as Part I, on the Tetrahedral Theory of the Earth, is important in cosmogonic philosophy. With the advance of geologic exploration, the arguments for a universal basaltic substratum are to-day more convincing than ever. For the sake of brevity these arguments will not here be fully presented, though some of them are mentioned in the sequel.

It will further be assumed that the known temperature gradient may roughly indicate the depth (estimated at 40 kilometers) at which the basaltic substratum is actually or potentially fluid. Many writers have independently arrived at nearly equivalent estimates for this depth. At such depth the internal friction may be so increased by the pressure that the substratum almost perfectly resists deformation by the quickly acting tidal forces.[11] This assumption in no way excludes the possibility that the substratum basalt is a true, non-crystalline fluid, and that a powerful force, slowly applied (on the principle of stress differences), could force this highly viscous fluid into the solid crust. As the fluid rises, its viscosity must fall directly with the lessened pressure, from a possible initial value of perhaps many millions of millions of times that of water to that of less than fifty times the viscosity of water, when the fluid reaches the earth's surface.[12]

Some Direct Consequences of Abyssal Injection.

The estimate of 40 kilometers for the average depth of the surface of the substratum may be wide of the mark, but it will serve as the numerical basis for a statement of certain immediate effects of injection.[13]

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[11] Herglotz has recently concluded that a planet stratified according to density must resist tidal deformation better than would the homogeneous planet assumed by Lord Kelvin. G. Herglotz, Zeit. für Math. u. Phys. **52**, 275 (1905).

[12] Becker computes the viscosity of a Hawaiian lava flow (which was by no means the most fluid already observed) as no more than sixty times that of water. G. F. Becker, Amer. Jour. of Science, **3**, 29 (1897).

[13] Perhaps the surface of the substratum is as deep within the earth as the limiting depth of isostatic compensation. In the second of his notable memoirs concerning the figure of the earth and isostasy, Hayford states that the most probable value of this limiting depth, for the United States and adjacent areas, is 122 kilometers, if it be assumed that the isostatic compensation is uniformly distributed with respect to depth. See page 77 of his "Supplementary Investigation in 1909 of the Figure of the Earth and Isos-

First, basaltic magma, rising from such depth nearly to the earth's surface, must undergo an average expansion ranging between 1.5 and 6 per cent.[14] A small part of this expansional energy may be directly available for opening fissures in the shell of compression, with consequent extrusion at the surface or development of laccolithic or other bodies within that shell.

Secondly, some superheat might be expected in each thick abyssal injection, at levels where the pressure is much less than the 11,000 atmospheres of the original substratum level. The conditions for the superheat have been briefly discussed in a previous paper.[15] Superheat in large abyssal injections means power of assimilating the wall rocks either marginally, or through magmatic stoping (forming syntectic magmas); the batholithic type of intrusion results. Thin abyssal injections, rapidly chilled, are relatively or absolutely incapable of such solution of foreign material; those injections form the other great class, typified by ordinary dikes. Each of these types is capable of developing offshoots of the laccolithic, chonolithic, or sheet order, so that satellitic injections of primary basalt or of syntectic matter are formed. This simple but necessary division into assimilating and non-assimilating injections is of first-class importance in volcanic theory, and underlies the reasoning of the present paper.

Thirdly, magma which has been forced from the substratum level to levels where the pressure is 10,000 atmospheres less, must have completely altered conditions of equilibrium for the juvenile gases. These include hydrogen, sulphur gas, carbon monoxide, carbon dioxide, chlorine, nitrogen, and other gases, elementary or in combination. The theory of physical chemistry indicates that the dissolved volatile constituents must, in such a case, slowly diffuse upward, in order to reestablish equilibrium. There is thus a tendency to saturate and then supersaturate the upper part of the magma with juvenile gases; if by the mere change of pressure the magma is supersaturated with one or more of the gases, bubbles must form and these must slowly rise. If

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tasy," Coast and Geodetic Survey, Washington, 1910. If the top of the liquid (non-crystallized) basaltic substratum were at a depth as great as 122 kilometers, this change in premises would make no essential difference in the argument of the present paper. It may be noted that John Milne (Nature, **86**, 124 (1911)), using Rizzo's results in studying the velocity of the earthquake waves which were recently so disastrous at Messina, has estimated the thickness of the earth's "crust" to be 44 kilometers.

[14] See Amer. Jour. Science, **22**, 201 (1906).

[15] Amer. Jour. Science, **26**, 33 (1908). Cf. J. Joly, Radioactivity and Geology, London, 1909, pp. 103–109, where there is an important discussion of one phase of this subject.

the injected body is tightly roofed, the gases continue to rise until the growing gas-tension at the upper levels stops diffusion.

GENETIC CLASSIFICATION OF VOLCANIC GASES.

It will conduce to clearness if a brief statement is here made as to the absolute necessity of distinguishing the different classes of volatile materials which are associated with igneous activity. These fluids are either *magmatic* or *phreatic*.[16] Phreatic fluids are of atmospheric or oceanic origin, and include *vadose* waters, and also those which Lane has called *connate* (contemporaneous) waters, because trapped in sediments at the time of their deposition. As indicated by Suess, explosions due to the heating of phreatic fluids by intrusive magma have occurred without the ejection of true lava, either fluent or pyroclastic.

Magmatic fluids are those actually dissolved in magma or emanating therefrom. Those of primary origin and reaching the earth's surface for the first time are of the *juvenile* class. The magmatic fluids of secondary origin, that is, those absorbed from country-rock formations, have been called *resurgent*.[17] Resurgent fluids may enter the magma either as constituents of assimilated country-rock or by independent solution.

Although only magmatic fluids are important in the present connection, it is useful to review, in tabular form, the whole group of gases and vapors which are engaged in volcanic and subvolcanic activities.

Magmatic fluids (volcanic; internal).	Juvenile	Emanations directly from abyssal injection.
		Emanations from primary solid abyssal country-rock.
	Resurgent	Vadose and connate fluids absorbed in the syntectic process.
		Vadose fluids absorbed independently of rock assimilation.
Phreatic fluids (subvolcanic; external)		Vadose.
		Connate.

The resurgent fluids may possibly do something toward keeping a vent open, but their volatilization means the partial lowering of temperature in the magma, so that their abundance in a conduit implies

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[16] Cf. E. Suess, Das Antlitz der Erde, Bd. 3, 2te Hälfte, Wien and Leipzig, 1909, p. 655.

[17] R. A. Daly, Amer. Journ. Science, **26**, 48 (1908).

a certain "damping of the fires" already accomplished. In basaltic volcanoes assimilation of the normal, acid crust-rocks has evidently not been important; at such vents the juvenile emanations are clearly in control from beginning to end of each volcano's history. This statement does not conflict with the fact that resurgent water, either vadose or connate with sediments, is often responsible for the explosions at basaltic and other volcanoes. The clearing-out of the explosion funnel, which is always shallow and superficial, is not so vital to continued activity as the preservation of fluidity in the magma of the conduit.

Phases of Volcanic Action.

According to the views expressed in modern text-books of geology, the emission of incandescent matter at the earth's surface takes place either in the form of fissure eruptions or in the form of central eruptions. The writer believes that a third method should be entertained as a possibility, namely, by the partial or complete foundering of batholithic roofs. The relation of each of these three phases to abyssal and satellitic injection may now be sketched.

Fissure Eruptions (Massive Eruptions, Plateau Eruptions).

The regional or greater lava-floods known to have emanated from simple fissures in their underlying terranes range in date from the pre-Cambrian to the present. Without exception they are, chemically, of basaltic composition. As we have seen, such magma must be exotic. It is a type of lava (extrusive magma) to which a secondary origin cannot be theoretically attributed. Its abundance, its occurrence in every continental and oceanic area, and its field relations to the other chemical types of magma, all point to the derivation of the plateau basalt from a general substratum. Each flow thus represents an effusion from an abyssally injected body which has not been modified by assimilation of the earth's acid shell or of the sedimentary veneer. But the very low original slopes of the flows (very often inclined at less than one degree to the horizontal plane) and their correlative great lengths, show that the basalt of fissure eruptions is notably superheated. Such temperature is appropriate to assimilation.

That solution of pre-Cambrian gneisses or of other rocks has generally not taken place in sensible amount during fissure eruption must have either of two meanings. It may mean that the various abyssal injections underlying such a lava-field are narrow, with widths to be measured in meters or tens of meters, but not in thousands of meters; or the failure to assimilate may be due to special rapidity of injection with simultaneous extrusion, for solution of foreign rock must take considerable time. The observed average size of the feeding channels (dikes) in the great lava-fields of the western United States, of Northwestern Europe, of India, and elsewhere, corresponds with the former conclusion. The Icelandic flow of 1783 and the nature of the individual basaltic flows in every prehistoric lava-field, show or suggest that each extrusion has been rapid. The controlling condition for the lack of assimilation is probably the narrowness of the abyssal injections, at least in the part traversing the sedimentary and acid shells of the earth.

The effusion of a basaltic flood is usually ascribed to the mere squeezing out of the magma from beneath a cracked and sinking earth-crust. Yet some force may also be available from the expansion of the substratum material as it rises to levels of enormously lessened pressure. This expansion is of two kinds; — that of the lava regarded as bubble-free, and that of the gases separated from it in bubble form. If the expansive energy of the liquid proper is not all expended in driving asunder the walls of the injected body, some of that great force is available for extrusion. As magma nears the surface, the separation of the dissolved gas must still further increase the volume and tend to cause outflow at the surface. The relative importance of these three conditions for extrusion is by no means apparent, though the writer believes that the expansional energy of the injected *liquid* should have more attention than it has had in general treatises on igneous action.

The fact that the great bulk of visible igneous rock is intrusive, and the related fact that most of the larger Paleozoic and later injections have not extended to the surface, suggest that the upper part of the earth's crust has long been comparatively difficult of penetration by abyssal magma. It seems fair to hold that a leading cause of this relative impenetrability is the state of compression in the outermost shell of the crust. This compressive stress is relieved by an orogenic paroxysm. After each paroxysm, tensions in the same shell are produced by the cooling of the rocks which had been heated by shearing. For a double reason, therefore, fissure eruptions should be more numerous and of greater volume in periods subsequent to strong mountain-building. This expectation is fairly matched by the facts of geological history, as shown in the accompanying table.

Locality.	Date of Fissure Eruption.	Preceding Orogenic Period.
Lake Superior District.	Keweenawan.	Close of the Animikie.
Rocky Mts. at 49th Parallel.	Middle Cambrian (?)	Early Middle Cambrian (?)

Locality.	Date of Fissure Eruption.	Preceding Orogenic Period.
British Islands.	Carboniferous.	Devonian.
Appalachian Mts.	Triassic.	Close of Paleozoic.
Deccan, India.	Cretaceous (or early Tertiary ?).	Late Triassic (also later?).
Great Rift, Africa.	Cretaceous (Kaptian series).	" " " "
Washington State.	Eocene (Teanaway basalt).	Close of Laramie.
N. W. Scotland.	Oligocene (Lower Miocene).	?
Iceland.	Miocene.	?
Washington State.	Miocene (Yakima basalt).	Close of Eocene.
Great Rift, Africa.	Miocene (?)	Tertiary (Alps, etc.).
Great Basin, U. S. A.	Pliocene.	Miocene.
Snake River, Idaho.	Pliocene.	Late Miocene.
Hauran, Syria.	Pliocene.	Tertiary.
Iceland.	Pleistocene and Recent.	Tertiary.

Eruption through Local Foundering.

Narrow abyssal injections, like the average dike located near the earth's surface, will not be expected to show evidences of extensive assimilation of wall-rock, except at levels deeper than those which can be exposed by crustal deformation and erosion. If the width of the injection falls below a certain critical value, the magma is chilled too rapidly to permit of marginal solution or of stoping. If the width exceeds that critical value, the molten or magmatic period is prolonged and absorption of the country-rock by both methods may become important. Other conditions being alike, the critical width where the injection cuts the gneissic pre-Cambrian shell is doubtless somewhat greater than it is where the injection cuts the more hydrous, average sedimentary terrane. But in all cases, the minimum width for abyssal injections which have absorbed large masses of foreign rock, is to be measured in hundreds of meters, if not in kilometers. Abyssal injections of greater volume are believed by the writer to work their way upward, for hundreds or thousands of meters, by absorption of the country-rock. The molar-contact absorption may be directly solutional, or directly mechanical, i. e., by stoping (followed by solution of the sunken blocks in depth). The evidence for assimilation, either marginal or abyssal, is generally masked by that drastic differentiation which is to be expected in large bodies of syntectic magma. This, in brief, seems to be the essence of batholithic intrusion. A batholith is an abyssal injection originally endowed with sufficient thermal energy (size) to enlarge its chamber through incorporating roof and wall rocks. The lower and greater part of its chamber is formed by simple dike-like injection along a widening abyssal fissure. The upper part, which is generally the only part exposed by erosion, has been opened by the activity of the magma itself. The average batholith, at exposed levels, is granitic because granite represents the stable and least dense differentiate of the average syntectic.

The integrity of the batholith's roof is evidently threatened in two ways. It is thinned during the process of absorption of the roof-rock by the molten magma. The latter might work its way to the surface through piecemeal stoping, which might continue until a large area of the batholithic roof has disappeared. On the other hand, it is also possible that part or all of the roof should, under special conditions, founder *en masse* in the less dense magma. In either case true volcanic action is produced. Such wholesale or piecemeal foundering would not fairly be called simple fissure eruption, though it might be accompanied by lava floods emitted from fractures in the roof-rock surrounding the foundered area. The level surface of the lava in the area of foundering would, in form, resemble a plateau (fissure) eruption, but the lava would here be generally liparitic rather than basaltic, as in the great majority of plateau eruptions. Moreover, the liparite would form a continuous mass merging downwards into granite, and thus not a series of superposed distinct flows. According to the topography, the lava of the foundered area might flood valleys outside that area. If the hydrostatic adjustment were accomplished in stages, it would cause successive, superposed flows in the valleys. (See Figure 2.)

Needless to say, the field evidences do not favor the idea of foundering in the case of many, perhaps most, Paleozoic and later batholiths. These bodies must be regarded as truly plutonic, according to the orthodox creed. Yet it is expedient to entertain the hypothesis in explanation of the field relations of some pre-Cambrian batholiths as well as those of a few younger masses.

In the first place, the evidence of local foundering in the past is in special danger of being obliterated. The glassy or scoriaceous phase of the "batholith" will necessarily be eroded away before the granitic phase can be exposed. The liparitic phase need extend to a depth of no more than a few hundred meters, where it would rapidly merge into the holocrystalline phase. Therefore, comparatively little time would be required to remove the original surface phase. The geologist studying the erosion surface might have no inkling that the "batholith" had not been completely covered by a roof of country-rock. The former existence of a roof cannot be assumed simply because a "batholith" has a holocrystalline structure.

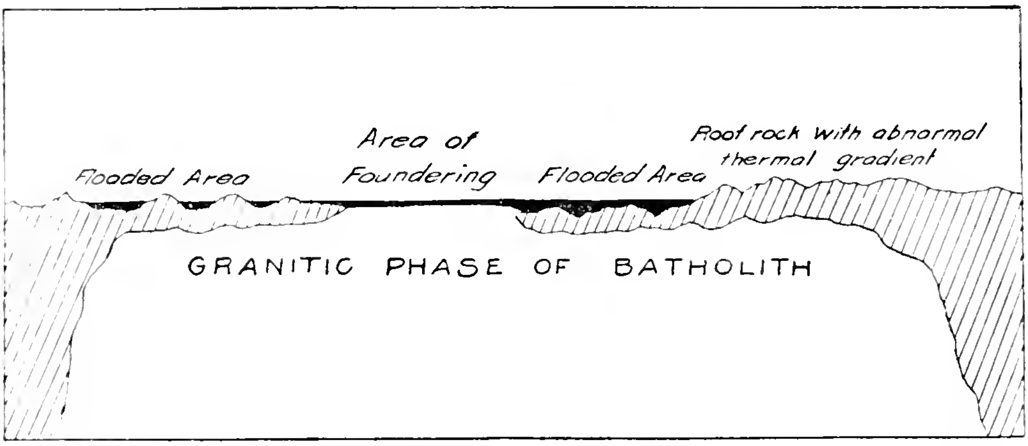

FIGURE 2. Ideal section of a district of batholithic foundering. Length of section assumed, for example, as 60 kilometers.

Blue Hills, Massachusetts.

The relations of the granite, quartz porphyry, and aporhyolite of the Blue Hills complex, near Boston, Massachusetts, to each other and to the Cambrian slate which forms the country-rock of the intrusive, suggest at least that the batholithic roof was very thin. Crosby describes two large areas of the aporhyolite (felsite) with the characters of both intrusive and effusive magma. He favors the view that these bodies are very thick surface flows of the ordinary type, though he states the alternative view that the aporhyolite represents the intrusive, latest phase of the batholithic magma.[18] The present writer believes that, in this case, the hypothesis of partial roof-foundering is worthy of a competitive place in a full discussion. The belief is founded on actual acquaintance with only a limited part of the observable field relations, and it is offered merely as a preliminary suggestion.

Glen Coe, Scotland.

The noteworthy paper of Clough, Maufe, and Bailey on "The Cauldron-subsidence of Glen Coe," illustrates a case where part of a

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[18] W. O. Crosby, The Blue Hills Complex. Occasional Papers of the Boston Society of Natural History, **4**, 385 (1900).

batholith's roof has sunk along peripheral faults. As the sinking progressed, the magma was squeezed up, following the faults on nearly every side of the sunken area. If the faulting had progressed still further, it seems inevitable that foundering would have occurred. In fact, the authors give a synthetic diagram which implies foundering on an enormous scale, though in no instance is the sinking crust-block shown as having extended to the earth's surface.[19]

Yellowstone National Park.

The possibility that foundering has played a part in comparatively recent vulcanism, first became clear to the writer on a journey in the Yellowstone Park. (See Figure 3.) The great rhyolite plateau, the largest known on the earth, is cut by canyons reaching 600 meters in depth. The canyon-walls of the Madison and Bechler rivers show that, for nearly or quite this depth and for very great areas, the rhyolite is massive and is not divisible into a number of distinct flows, as is characteristic of fissure eruptions and central eruptions. The rhyolite extends downward, below the river-levels, to unknown depths.[20] Does it merge, directly beneath, into the true granite of a batholith?

Part I of the government survey Monograph is, unfortunately, not yet published, and Part II states the field relations of the rhyolite in too little detail that one can now assemble the facts bearing on this problem. A few points may be noted to indicate the general need of including foundering among the multiple hypotheses relative to the mode of extrusion represented in the rhyolite plateau.

1. Few geologists will doubt that this lava is the effusive equivalent of a salic granite. The enormous volume of the rhyolite implies a plutonic feeder of batholithic proportions, especially if we grant that all Tertiary granite (or rhyolite) is a direct or indirect product of assimilation. The solution of enough of the pre-Cambrian terrane and of the locally thin, overlying sediments to yield, after differentiation, these thousands of cubic kilometers of rhyolite, could only take place in a very large plutonic chamber. General and independent theory suggests, therefore, that a portion of the Yellowstone Park area is underlain by a granite batholith, which, like the rhyolite, is of Pliocene age, and is one of the youngest batholiths on record.

2. The scale of the extrusion, its topography, and topographic rela-

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[19] C. T. Clough, H. B. Maufe, and E. B. Bailey, Quart. Journ. Geol. Soc., **65**, 670 (1909).

[20] J. P. Iddings, Monograph 32, Part 2, U. S. Geol. Survey, 1899, pp. 366 and 375.

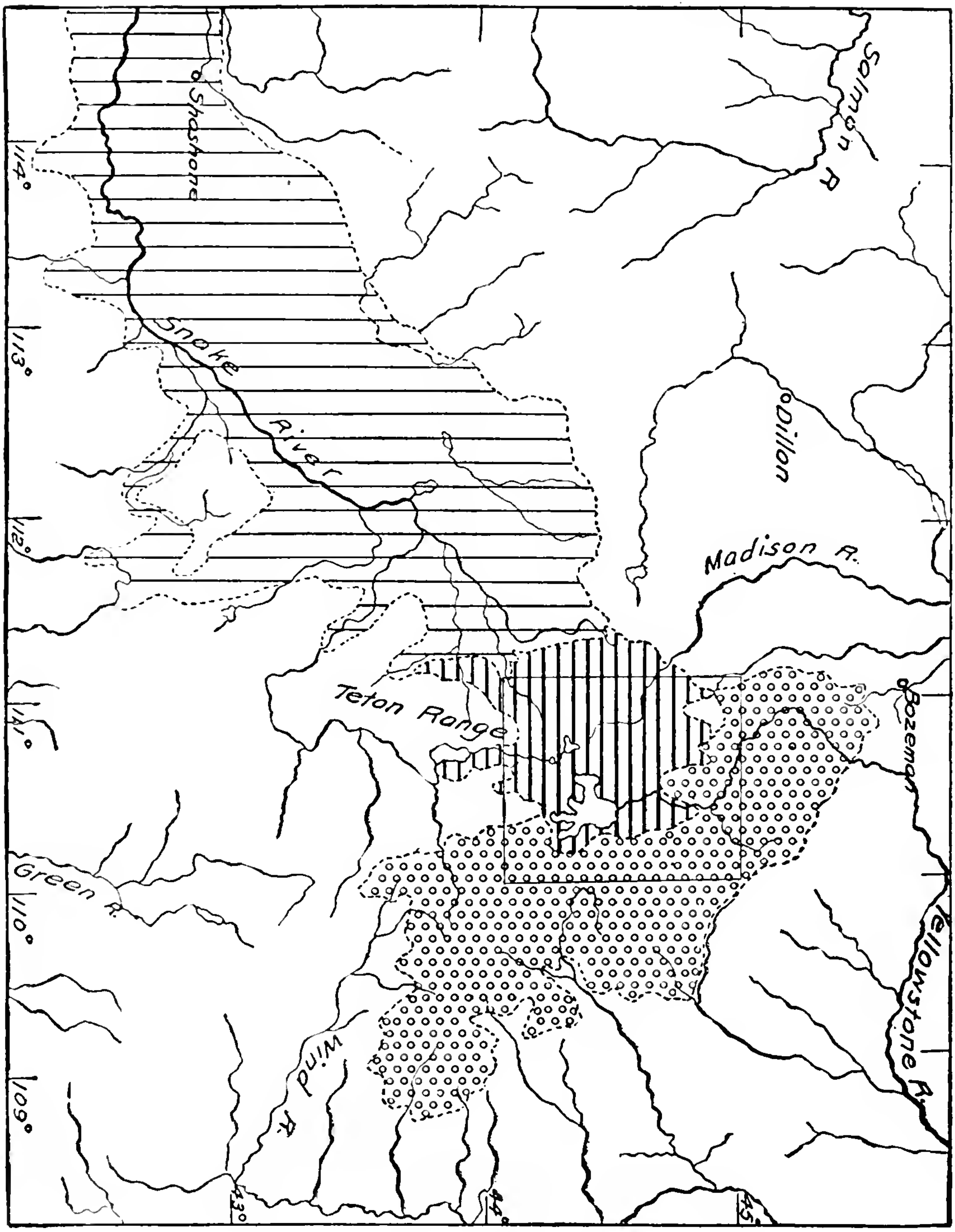

FIGURE 3. Sketch map of region embracing the Yellowstone Park (shown by rectangle on the 110th meridian); after Iddings. Small circles represent andesitic pyroclastics and flows of Eocene and Miocene age (central eruptions). Horizontal lines (map in usual orientation) represent Pliocene rhyolite of the Park (eruption chiefly by foundering). Vertical lines represent the Pliocene Snake River basalt (fissure eruption).

tions, and the relative insignificance of pyroclastic phases, are all opposed to the view that the rhyolite issued from one or more vents of the ordinary central-eruption kind. The unprecedented thickness of the lava in a single, extended mass — more than 600 meters thick for hundreds, if not thousands, of square kilometers together — is quite unparalleled in masses known to have been emitted during true fissure eruption. Moreover, Iddings points out that rhyolite dikes (feeding fissures) are almost entirely lacking in the Park.[21] The superposition of distinct rhyolite flows in the regions surrounding the main rhyolite body may be explained as due to successive outflows from the area of foundering. Thus, so far as the facts of the field declare against the central-eruption and fissure-eruption hypotheses, they appear to favor some other explanation. As yet the writer has conceived no other except that of foundering.

3. The geysers of the Park are practically confined to the area covered by the Pliocene rhyolite. In a similar way the other two great geyser-fields of the world, in Iceland and New Zealand, are located in regions where magma of liparitic (granitic) composition has been poured out at the earth's surface. The "fossil" geysers, described by Frech in the Kremnitz district of Hungary, are confined to areas of highly acid lavas.[22] Following the general argument outlined above, the liparitic lava in each of these four districts has been differentiated from one or more relatively and absolutely *large* magma chambers, i. e., in abyssal injections big enough to assimilate acid rocks in notable amount.

According to Holmes, the Yellowstone geysers were in operation long before the Pleistocene period and have been active ever since.[23] By an ingenious method Schlundt and Moore have calculated that about 20,000 years have elapsed since the Glacial period in the Park.[24] This figure agrees well with other recent estimates of post-Glacial time. Twenty thousand years is clearly much less than the total time during which the geyser activity has been sustained in the Park. Competent observers agree that the geyser waters are wholly or chiefly of meteoric origin. The thermal energy required to superheat this cold water to explosion-points during so many millenniums must be enormous. Though the spring waters are radioactive, the heat set free by radioactivity is not to be considered as of any direct importance in the

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[21] Monograph 32, Part 2, U. S. Geol. Survey, 1899, p. 381.

[22] F. Frech, Aus der Natur, Vol. 1, Heft 8, 1905.

[23] W. H. Holmes, 12th Ann. Report, U. S. Geol. and Geog. Survey of the Territories, Part 2, 1883, p. 29.

[24] H. Schlundt and R. B. Moore, Bull. 395, U. S. Geol. Survey, 1909, p. 31.

problem. The thermal energy is clearly derived from magma. The small amount of water ejected in the average geyser eruption, when compared with the observed diameter of the geyser's throat below its funnel, shows that the level of superheating is, on the average, not more than a few hundred meters below the surface. The heat can hardly be regarded as that residual from a Pliocene lava-flow even 600 meters thick. The specific heat of water is from three to five times greater than that of rock-matter between the temperatures of 100°C. and 1000°C.

Allowing for radiation above and conduction below the lava flow; considering also that the rhyolite was erupted tens of thousands of years ago, that the rhyolite is comparatively permeable for the chilling rain-water, and that the visible abstraction of heat from the rhyolite by the springs is continuous and rapid, — one must doubt the hypothesis that the original heat of even such a thick flow can be responsible for the present activity of the geysers. The hypothesis suffers, too, from the difficulty that it does not explain the high temperatures of the Mammoth Springs. These emerge from a Mesozoic terrane which lost its rhyolite cover (a sheet formed by lateral outflow from the main area of extrusion) in pre-Glacial times. The same point may be urged in the case of other hot springs, such as those in the bottom of the Grand Canyon of the Yellowstone. At each of these localities the heat is passing upwards through the relatively thin roof, composed of the country-rock of the batholith.

It would, therefore, seem just to refer the geyser temperatures to one or more great subterranean masses (batholiths) extending, nearly or quite continuously, 120 kilometers from north to south and 30 to 50 kilometers from east to west. Heat will pass upward from such a batholith either by simple conduction through the roof-rock or by gaseous transfer. The analyses of the spring-waters suggest that some magmatic gas has been added to the ascending meteoric water, which may have attained its high temperature to a certain extent from the hot gas.[25] But this cause seems quantitatively insufficient to keep the geysers working at their observed speed, and simple conduction through the rock is more likely to be the essential cause.

In whichever way the heat is applied to the water, it seems clear that the actual batholith must be at or near the surface in each geyser area. The shallowness of the zone of superheating shows a very steep

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[25] The peculiarly intense alteration of the rhyolite is, in part, explicable on the assumption that the magmatic gases (specially abundant in the upper part of every batholith) have slowly passed out through the rhyolite shell after that shell had solidified.

thermal gradient. That fact is inconsistent with the assumption of a thick roof over the granite batholith, and it must be remembered that the batholith has been cooling for a length of time sufficient to permit of the excavation of 600-meter canyons in massive rhyolite.

A brief study of the geysers thus lends much probability to these conclusions: first, that over thousands of square kilometers, the batholithic roof was extremely thin when the rhyolite plateau was formed; and secondly, that this thin roof was, in places, swallowed up. Briefly put, the rhyolite of the plateau is locally bottomless, in the sense that it passes downward into a typical granite batholith. The formation of the rhyolite plateau means a kind of vulcanism which evidently needs to be distinguished from fissure eruption and from ordinary crater eruption.

Central Eruptions.

The larger part of volcanic literature deals with the activities at cone and crater. Extensive and intensive as these studies have been, the number of memoirs treating of *all* the essential problems of central eruptions is very small. Yet every general theory of volcanic action must undergo the test of such a thorough questionnaire. This applies to the hypothesis that all vulcanism is a result of the abyssal injection of primary basalt. The following argument will be clearer if a preliminary list of the specific problems relating to central eruptions be reviewed. The list includes: —

1. The localization and opening of the vent.
2. The persistence of a principal vent for many thousands of years.
3. The intermittent character of the eruptivity, including (*a*) the alternation of active and dormant phases, and (*b*) the pulsatory or geyser-like quality of eruption during the active stage.
4. The origin of the heat which, by radiation in active craters, is lost in stupendous quantities.
5. The normal evolution of a vent as illustrated in (*a*) explosiveness, and (*b*) the nature of the lava emitted.
6. The mechanism of lava outflow at central vents.

These tests of our hypothesis will be briefly considered, nearly in the order given.

Opening and Localization of the Vent.

Enlarged fissures. — The events of 1783 at the famous Laki fissure of Iceland illustrate the close relation between some central eruptions and the pronounced fracturing of the surface rocks of the earth. For much or all of its length the master crack was doubtless connected with a typical, narrow, abyssal injection. Many hills of the cone-and-crater type were built along the fissure, which emitted floods of basalt on the greatest scale recorded by man. Escape of lava from the abyssal injection was evidently much easier at some points along the visible fissure than at others. The case is analogous to the formation of the "Dewey craters" (cinder-cones) on the Mauna Loa lateral fissure opened in 1899, and of scores of similar accumulations on the flanks of Mauna Loa, Etna, etc. Dutton[26] gives this explanation for some of the necks occurring in the well known Mount Taylor district of New Mexico. In all such instances certain *points* in the fissure-lines are favored in the eruptivity, while the remainder of each fissure was either never opened clear to the surface, or else was rapidly sealed up by congealing lava.

The continuance of eruption at any point depends on victory in the *struggle with cold.* That victory in its turn depends in part on a sufficient width of vent to permit of a column of lava which is not chilled too greatly by conduction into the wall-rock. Since erupting fissures are never more than a few meters in width at the surface, it seems necessary to postulate a widening of each fissure where it carries cone and crater of prolonged activity. The widening may be conceived to depend on four different factors: solution and mechanical removal of wall-rock by emanating lavas; melting and explosive abrasion of the wall-rock by magmatic gas emitted *through* the lava column. It is not important here to decide on the relative efficiency of these processes in merely enlarging the original fissure to full vent size. Their relative efficiency becomes of fundamental significance in the problem of the persistence of eruptivity at a central vent. In the following discussion of this topic it is concluded that the vent is kept hot, and therefore active, because of the emanation of free juvenile gas rising from great depth — a process which may be styled "gas-fluxing." Since a great enlargement of an original fissure, below the bottom of any possible explosion funnel, demands much time, it would follow that most of the enlargement is due to gas-fluxing. Gaseous explosion and erosion of the walls by emanating lava might be more effective in the widening of smaller and more short-lived vents.

It is an easy step from the observed case where central eruptions are developed on fissures of lava-flooding, to the case of the formation of central vents on surface fissures from which no true fissure-eruption has ever taken place. Such a crack may be too narrow to permit the extrusion of gas-free lava, which, through quick chilling, seals the fissure, and yet the crack may be wide enough to allow passage of the

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[26] Sixth Annual Report of the United States Geological Survey, 1885, p. 172.

juvenile gases from an underlying abyssal injection. Entering the crack under pressure and therefore at high temperature, these gases must tend to enlarge it by slow fusion of the wall-rock. The process may or may not be supplemented by the opening of an explosion funnel at the surface. As the vent is enlarged by gas-fluxing the magma rises within it, and, kept fluid by the emanating gas, permits of further upward blowpiping.

This mechanism implies that the original surface fissure may not be discernible by the geologist. It may correspond to no vertical or horizontal displacement, and at the surface itself be no wider than an ordinary master joint or fault fracture. Enlarging slowly downward, such a fissure might be charged with accumulating gases so far as ultimately to cause an explosion. Since the gases must tend to accumulate about one or more points along the fissure, the explosion form will be that of a vertical tube surmounted by a funnel. The resulting vent is a *diatreme*, the formation of which was so successfully imitated by Daubrée. This type of diatremes is, then, located on a surface fissure, which may or may not be continuous with the abyssal fissure of the primary injection. These considerations show the difficulty of disproving the existence of through-going crustal fissures beneath central vents.

Diatremes. — Daubrée's experiments suggest, however, that some volcanic diatremes may be formed in homogeneous, unfissured rock, and a second type, a pure explosion form, should be recognized in a full classification of vents.

A diatreme of either kind may be enlarged by the continued passage of the blowpiping gases, by the mechanical erosion of the walls by outflowing lava, or by the piecemeal stoping of the walls by the lava column.

Plutonic Cupolas. — Lastly, a complete genetic scheme should recognize a process of vent-opening which is neither explosion, nor the enlargement of through-going fissures. Most of the greater abyssal injections are strictly intrusive and do not occasion the outflow of magma at the earth's surface. Those of batholithic size show, in the field, clear evidence of having actually worked their way up the last few hundred meters or last few kilometers, before the respective magmas have solidified. The process is one of absorption of the roof-rock, and is clearly distinct from that of mere injection, either abyssal or satellitic. Both stoping and marginal assimilation are most rapid at the hottest parts of the contact between magma and country-rock. At the roof, the juvenile gases tend to accumulate in any cupola-like irregularities in the roof. These gases rise from the interior of the magma, perhaps from great depth. Because of the pressure reigning even at the roof of the plutonic body, the gases must have high temperature, which increases as the gas-tension increases. The total mass of the gas accumulated at a cupola at any one time may be small, but it may serve to determine a more rapid incorporation of the roof-rock at the cupola than in the area of roof surrounding the cupola. It is obvious also that some roof-rocks are more easily absorbed by a given magma than are other rocks.

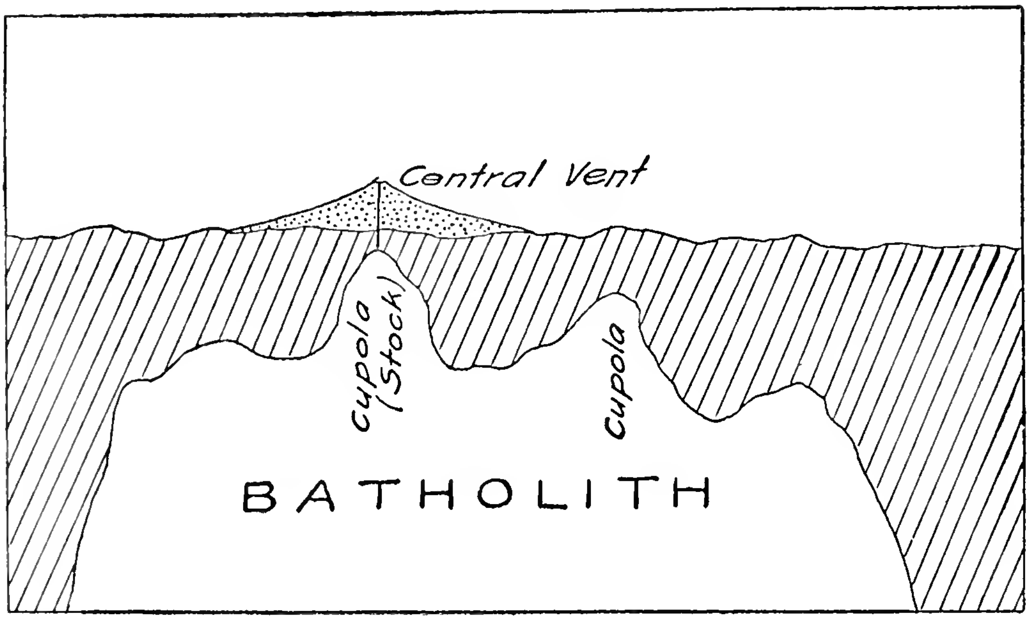

FIGURE 4. Ideal section showing formation of volcanic vent through the differential rise of assimilating magma.

The rise of batholithic magma is, therefore, differential. Partly because of gas control its attack on the roof is most efficient at *points*, rather than along lines or in large areas. (Figure 4.) This deduction seems well matched by the field fact that round intrusive bosses or small stocks are characteristic cupola forms on large batholiths. Some of these bosses have been proved to have very steep contact-surfaces and, in shape, as in their cross-cutting relations, closely simulate volcanic necks. It is evident that every such cupola increases as well as localizes the danger of true volcanic action. Blowpiping fusion or pure explosion may destroy the relatively thin roof above the cupola. The resulting vent is, then, of composite origin. Its upper part is like the two simple types of central vents already described. Its lower part is neither diatreme nor blowpiped hole, but represents the work of all the agencies of magmatic assimilation in depth. This composite type of vent illustrates the close connection between volcanic and plutonic geology.

The original location of each first-rank vent is thus explained by the roof-topography of the underlying magma chamber. Some one of the cupola-like offshoots of the fluid magma, where it penetrates the solid rock above, must become a place for the accumulation of the rising gases. A vent once formed at the top of the cupola, it must tend to persist as a vent throughout the period of magmatic fluidity. Other vents from the same chamber may be opened, but must have shorter lives, because of the drawing away of the juvenile gases toward the more favored vent. (See Figure 7.)

Continuance of Activity at Central Vents: Analysis of Conditions at Kilauea.

Left to itself, the lava column of a vent must soon freeze and activity must cease. Long-continued activity is conditional on victory in the struggle with cold. How is the victory attained? How is the heat of the underlying magma chamber transferred to the narrow vent? Hawaiian vents supply data on this fundamental question. Though Kilauea may be the vent of a satellitic injection (see p. 109), the mechanism is doubtless the same as for a vent over a main abyssal injection.

Rate of Heat-loss through Conduction into the Walls. — It is possible to obtain a rough idea of the enormous rate at which heat is given out, by conduction and radiation, at Kilauea. (Plate I.) Actual calculation will show that radiation is much more responsible for the loss of heat than is conduction into the wall-rocks of the vent. To make this point clear it will be assumed that the cross-section of the conduit is throughout as large as the area of the lava lake, though very probably the lake represents a strongly flaring part of the lava column. (See Figure 6.) The conditions of the lake in 1909, when it was studied by the writer, are assumed. The area of the lake (and therewith the cross-section of the lava column) is considered as circular, with radius of 100 meters. This is more than the superficial extent of the lake in 1909 but less than its average extent since 1820. The cylindrical pipe with the uniform cross-section is assumed to extend to a depth of two kilometers, where it opens out into the great feeding chamber.

Let the temperature of the magma be assumed as 1200° C.; and let the average original temperature of the rocks now forming the conduit walls be assumed as 40° C. Two hundred and fifty years after the conduit was first opened and henceforth occupied by lava at the uniform temperature of 1200° C., the rate of flow of heat through the walls would be nearly uniform; and 12 meters from the contact of the molten lava the temperature of the wall-rock would be about 1115° C.[27] This estimate is based on the assumption that the diffusivity for heat in rock at high temperature has the value given by Kelvin. That value is certainly too high, but the temperature stated for a point 12 meters from the contact would in any case be reached after some centuries following the establishment of the lava column. An idea of the heat loss by conduction may now be obtained. The equation for heat flow is :

$$Q = k \cdot A \cdot \frac{T - T_1}{x} \cdot t,$$

where k is the coefficient of conductivity, A the area of the surface traversed, x the thickness of the plate traversed, t the time, T and T_1 the steady temperatures of the two sides of the plate. In this case we may use C. G. S. units, with k 0.005 (certainly too high a value for these temperatures), t one second. x 1200, and A $2 \pi r \times 200{,}000$. We have

$$Q = .005 \times 2 \times 3.14+ \times 10{,}000 \times 200{,}000 \times \frac{1200 - 1115}{1200} \times 1$$

$$= \text{approximately } 4{,}450{,}000 \text{ gram calories.}$$

The result expresses the approximate amount of heat lost by conduction into the wall-rock during each second.

Rate of Heat Loss through Radiation at the Crater. — Siegl has recently supplied a datum required for estimating the heat lost by radiation from the surface of the lava lake. The general equation is

$$\log S = \log c + \epsilon \log T,$$

in which S represents the number of calories radiated per second, T is the absolute temperature stated in degrees centigrade, and c and ϵ are constants. For basalt Siegl has found that $c = (10)^{-12} \times 0.589$, and $\epsilon = 4.083$.[28] His experiments show that the equation holds for basalt up to 472° absolute. It is very probable that it may be applied, with relatively small, or at least non-significant, error, to basalt at the higher temperatures and under the conditions of radiation represented at Kilauea. Such extrapolation gives the following results :

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[27] R. A. Daly, Amer. Jour. Science, **26**, 23 (1908).

[28] K. Siegl, Sitzungsber. Akad. Wissen. Wien, Math.-Naturw. Klasse, Bd. 116, 1203 (1907).

$t°$ C.	$T°$ abs.	S.
450	723	0.277
727	1000	1.044
1000	1273	2.800
1200	1473	5.082

In 1909 the present writer used a Féry pyrometer to determine the average temperature of the non-incandescent scum which regularly covered at least two thirds of the lava lake. The average temperature for this part was estimated to be about 450° C.; the corresponding heat loss is computed to be 0.277 cal. per square centimeter per second.

At the best points of observation in 1909, the area of the hottest lava was not large enough to cover the "black spot" of the pyrometer for a time long enough to give a reading for its full temperature. It was clear, however, from the behavior of the galvanometer needle during the brief exposures of the very hot lava in the "Old Faithful fountains," that its temperature was well above 1000° C. From the color the temperature of the hottest lava visible in the lake was estimated to be somewhat over 1200° C. The third of the lake relatively free from scum was estimated to have an average temperature of 1000° C., corresponding to a heat loss of 2.8 calories per square centimeter per second.

With radius of 100 meters the circular lake would lose in heat about 375,000,000 calories per second. The actual lake of 1909 probably lost more than 230,000,000 calories per second.

We may conclude that heat was then being lost by radiation more than fifty times faster than by conduction into the walls of the Kilauean pipe, if it be assumed as two kilometers deep. It would seem that radiation at the crater must be the dominant one of these two phases of heat loss in any strongly active volcano.

Methods of Heat Transfer. — The upward transfer of heat into a volcanic pipe might conceivably take place in five different ways: (1) by explosive removal of material from the upper part of the vent, followed by uprise of magma from the still fluid chamber; (2) by simple overflow of magma at the lip of the crater; (3) by thermal convection in the lava column; (4) by a process which may be called, for convenience, "two-phase convection"; and (5) by the passage of free juvenile gas *through* the lava column, thus bringing abyssal heat to the upper part of the vent.

The first and second processes have obviously played no essential rôles in keeping up the heat supply in Kilauea since 1823, when detailed records of its activity began.

Mere thermal convection can hardly be regarded as an essential factor in postponing the solidification of a lava column. In this matter the analogy with water heated from below should be applied only with due attention to quantitative values. The degree of superheat in the actual well-established vents is not indefinitely high; it is doubtless no more than 200° or 300° C. If convection be lively enough to keep the column molten, the maximum thermal-density differences within the vent itself should certainly be less than those corresponding to a difference of 100°. A temperature change of 100° C. means a density change in magma of less than one half of one per cent.[29] The density change in water as it passes from 4° C. to 100° C., or vice versa, is about 4.3 per cent. With a density difference about one tenth that of water in the same temperature interval, and with that difference distributed through kilometers of depth instead of through decimeters, as in the ordinary convective experiment with water, the convective potential in the lava column is evidently of a very low order. Moreover, the speed of the convection depends on the viscosity of the magma, which through chilling and through pressure is doubtless, on the average, hundreds or thousands of times more viscous than water. It follows that in resistance to be overcome, as in working potential, heat convection must be incomparably less rapid in a volcanic conduit than in artificially heated water.

For example, let us suppose that at the depth of two kilometers the conduit passes into the feeding magma chamber; that there the temperature is 1300° C., while the temperature at the surface is 1200° C.; that the average kinetic viscosity of the conduit lava is as low as that of a liquid 100 times more viscous than water; that the thermal convection in the conduit is to be compared in rapidity with that obtaining in water heated from 4° to 100° in a wide tube one meter high. The maximum convective gradient for the water system may be expressed as

$$\frac{4.3 \text{ (per cent expansion)}}{1 \text{ (meter, thickness)}} = 4.3$$

The gradient in the lava column is approximately

$$\frac{0.5 \text{ (per cent expansion)}}{2000 \text{ (meters)}} = .00025.$$

The maximum speed of convection in the water of the imagined experiment is, then, $\left(\frac{4.3}{.00025} \times 100 = \right)$ 1,720,000 or more times greater than that of the lava in the conduit.

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[29] According to Barus, as quoted in Amer. Jour. Science, **26**, 26 (1908).

It seems certain that such slow transfer of magma could not keep the temperature of surface lava of the lake at anything like the observed point. On the average, every square centimeter of the lake's surface in 1909 radiated about one calory per second or 86 400 cals. per day. Taking .35 as the mean specific heat of basalt (1200°–1300°), this implies a daily heat loss corresponding to a temperature fall of 100° C. in a vertical column of lava more than 2400 meters deep, and one square centimeter in area at its upper surface. Evidently, other and much more effective agencies must be at work to keep Kilauea active, year in and year out.

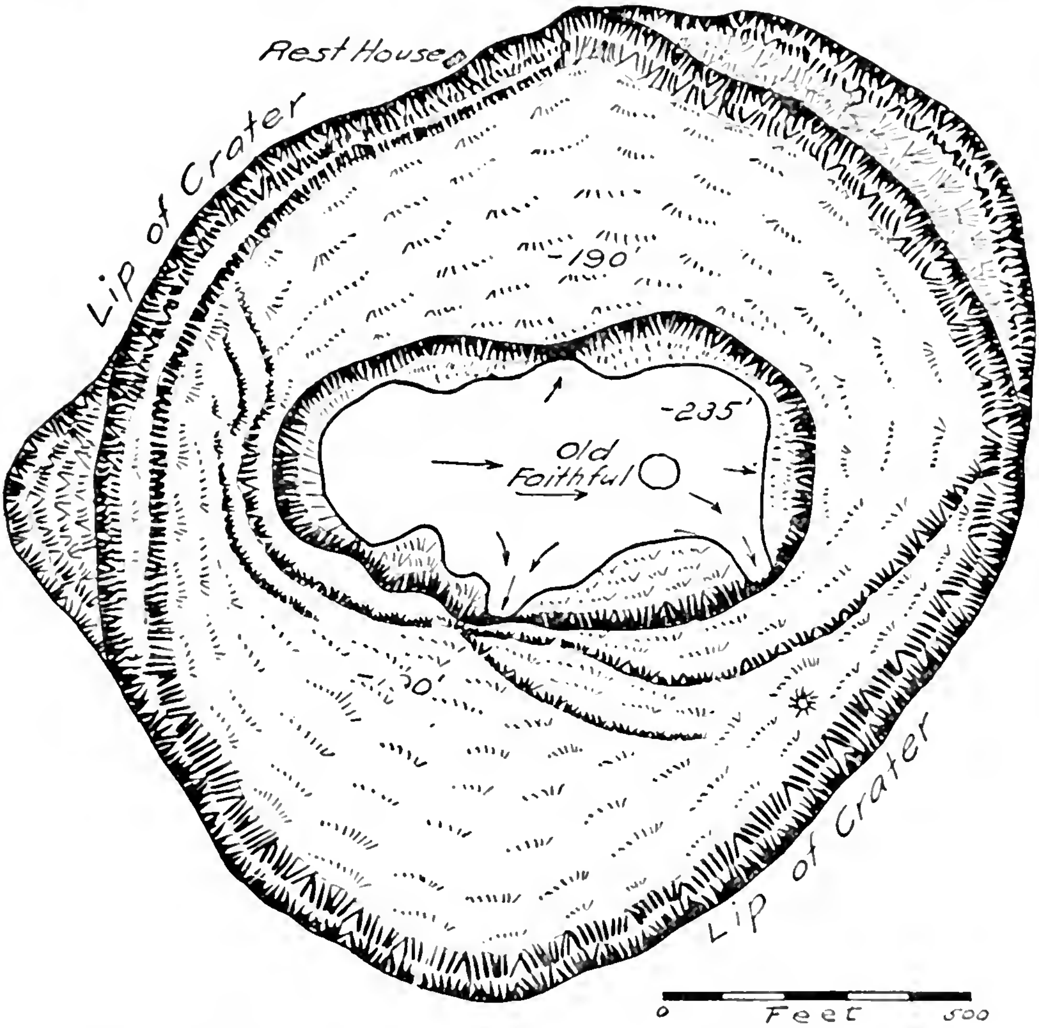

FIGURE 5. Sketch map (after J. M. Lydgate) of Halemaumau in July, 1909. Arrows indicate the general trend of currents in the lava lake during that month. The positions of "Old Faithful" and of the more important caves eroded by the liquid lava in the "Black Ledge" are shown. Figures show depths below the "Rest House."

Two-phase Convection. — However, there is a different and very powerful kind of convection constantly illustrated in Halemaumau when that lake is in full activity. (Figure 5.) The persistent streaming of the lava into the caves, characteristically developed at the shore cliffs of the lake, is evidently due to surface gradients. In general, the "scum" stands higher in the central part of the lake than it does in the caves and in the channels leading to the caves. The "scum" or thin crust of the lake prevents or retards the escape of the magmatic gases, which accumulate beneath it and form a kind of froth, or emulsion of lava and gas, of relatively low density. The tendency is, thus, to raise the crust in one or more areas. In each cave, because of reflection from its roof, and perhaps also because of special heating through actual combustion of sulphur, hydrogen, and other gases, the crust is rapidly and completely fused. The escape of the gases is there facilitated and the surface of the lava is correspondingly lowered. The surface slopes are, therefore, steepest in the channels leading to the caves, and streaming at the rate of two to five kilometers an hour may be observed in the channels. Elsewhere the surface slopes are lower and streaming is less rapid. The caves are not outletting tunnels, as so often stated, but each is closed at a distance of a few meters from its entrance. The lava which has streamed into the cave must return to the main part of the lake. Only one way of return is possible, that by a backward sub-surface current. Having lost its dilating gas and grown rapidly denser, the heavy lava sinks and flows toward the center of the lake. Similarly, the ever-changing surface slopes in other parts of the lake compel vertical currents and vortices of the most complex design. (Figure 6.) This type of magmatic movement may be called "two-phase convection."[30] It depends on the presence of a liquid "phase" and a gas "phase" in the lava.

If vesiculation of the liquid magma is possible in great depth, two-phase convection may cause a relatively speedy transfer of hot magma to the surface. How effective this process can be is worthy of somewhat detailed statement. The imposing change in magmatic density, which is effected by very slight increase in vesiculation, will first be indicated. The speed at which individual bubbles rise will then be estimated, and, finally, a rough quantitative idea of the convection enforced by the development of gas bubbles in depth will be obtained.

The specimens of Hawaiian pahoehoe lava collected by the writer

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[30] The term "two-phase," so convenient in describing this type of convection, was suggested to the writer by Dr. W. C. Bray, of the Massachusetts Institute of Technology.

contain, on the average, at least 200 vesicles per cubic centimeter of the lava. The vesicles of the surface layers are roughly spherical and average no more than 2 mm. in diameter, though, of course, the range of diameters is very great. For convenience, let a spherical mass of hydrogen, having the radius of 1 mm. at one atmosphere of pressure and at 1200° C., be called the "standard bubble" for basalt. Extrapolating on Amagat's pressure-volume curves for hydrogen at 1200 C., the volumes and radii for the standard bubble at high pressures may be calculated within a margin of error which is probably very small. Examples are shown in the following table :

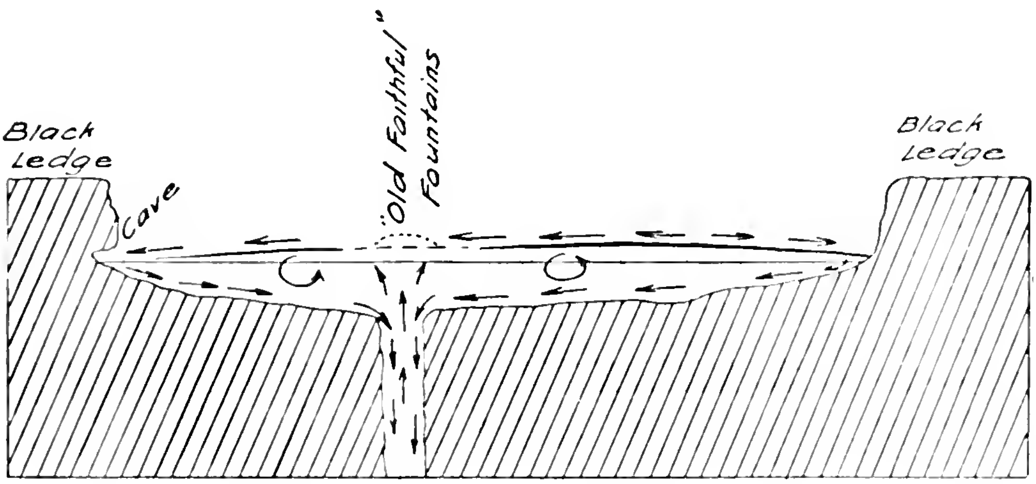

FIGURE 6. Diagrammatic section of Halemaumau, illustrating two-phase convection, erosion of caves, and vortical action. The lava "scum" is represented by the heavy black line at the lake surface. Length of section about 300 meters. Vertical scale specially exaggerated in drawing the "scum" line.

Approximate depths in magmatic column (meters).	Pressure in atmospheres.	Volume (cm.^{3}).	Radius (cm.).
730	200	0.0000115	0.030
3650	1000	.0000025	.018
7300	2000	.0000014	.015

Gas-free basalt at 1200°C. and one atmosphere has a specific gravity of about 2.75. On account of the slight compressibility of rock-matter, that value may be assumed as typical for gas free basaltic magma at pressures up to several thousand atmospheres. If such magma become charged with 200 standard bubbles per cubic centimeter, at 200, 1000, and 2000 atmospheres, the specific gravity falls to the following approximate values (Col. 1) :

Pressure.	Specific Gravity. 1.	 2.
200	2.688	2.7495
1000	2.736	2.74975
2000	2.742	2.74997

A single standard bubble replacing the liquid in each cubic centimeter of gas-free basalt would lower the specific gravity to the amounts shown, again approximately, in Col. 2.

This last table illustrates possible ranges of buoyancies induced by vesiculation at the three depths chosen. The actual buoyancy attained may often be much higher. It will be seen that the buoyancy produced by only a small extra vesiculation of a local mass of magma must occasion a rapid uprise of that mass.

The bubbles themselves, as independent bodies, must rise with comparative slowness. The experiments of H. S. Allen have shown that small spherical bubbles, rising in a liquid, attain their terminal velocity according to the formula previously deduced by Stokes for the rise of light solid spheres of very small radius.[31]

Let r represent the radius of a bubble; d', its density; d, the density of the surrounding magma; v, the coefficient of viscosity of the magma; g, the acceleration of gravity; and x, the terminal velocity of the rising bubble, that is, the velocity when the motion is steady. The Stokes formula applies if the product dxr is small compared with v. This is clearly true for the standard bubble in liquid basalt with the viscosities appropriate to pressures of 200 to 2000 atmospheres. We have, then,

$$x = \tfrac{2}{9}\, gr^2 \left(\frac{d - d'}{v}\right).$$

Computing the values of x when the magmatic viscosity is assumed to be constant and only 100 times that of water at 15° C. (0.0115) or 1.15 in C. G. S. units, we have, at the three illustrative pressures:

Depth (meters).	Pressure (ats.).	Terminal Velocity (x). Cm. per Second.	 Meters per Hour.
730	200	0.47	16.9
3650	1000	.17	6.1
7300	2000	.12	4.2

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[31] H. S. Allen, Phil. Mag., **50**, 323 and 519 (1900). G. G. Stokes, Cambridge Phil. Trans., **9** (2), 8 (1850).

Since experiment shows that the viscosity of a liquid rises rapidly with pressure, it is instructive to assume higher values of c for the greater pressures. If c be taken again arbitrarily as 500 and 10,000 times that of water for magma under the pressures of 1000 atmospheres and 2000 atmospheres, respectively, we have for x these values :

Pressure (ats.).	Viscosity.[1]	Terminal Velocity (x). Cm. per Second.	Terminal Velocity (x). Meters per Hour.
200	1.15	0.47	16.9
1000	5.75	.034	1.2
2000	115.00	.0012	.04

In all cases smaller bubbles would rise more slowly, x varying directly as the square of the radius.

Two important conclusions may be drawn from these computations. Gas bubbles of the "standard" mass or of smaller mass must rise from the deeper levels of an abyssal injection with extreme slowness. In view of the high magmatic viscosity and great pressure in depth, it is conceivable that it may take thousands of years for a "standard" bubble to rise from a depth of, say, ten kilometers to the earth's surface. This suggests one reason why gaseous emanation is so prolonged at central vents.

Secondly, from the slowness with which bubbles rise, it is clear that a swarm of bubbles, which for any reason have been aggregated locally in special abundance, would be dispersed into the surrounding, less vesiculated magma with great slowness. The local mass of magma thus specially vesiculated would be less dense than the average magma and, as a unit, would rise toward the crater. It now remains to indicate that a very moderate amount of extra vesiculation must cause such a two-phase mass to rise with comparatively great velocity.

Of course, this case has not been investigated experimentally ; an indirect method must be used in its discussion and the result can at present hardly be other than qualitative.

Once again to make the mental picture clearer, it is well to assume certain conditions arbitrarily. As an example, let the swarm-filled mass be spherical ; let the reigning pressures and magmatic viscosity be as in the foregoing cases ; let the surrounding magma have a density of 2.75 ; and let the extra vesiculation be to the extent of 50 "standard" bubbles per cubic centimeter on the average. The corresponding densities of the sphere are shown in the second column of the following table :

Pressure (ats.).	Sp. Gr.	$d-d'$.	v (assumed).	R (cm.).
200	2.734	0.016	1.15	0.52
1000	2.746	.004	5.75	2.40
2000	2.748	.002	115.00	22.25

For solid spheres rising in the magma we may compute the "critical radius" (R), that is, the radius of the largest sphere which would obey the law of the Stokes formula. The values for R, as stated in the fifth column, have been found with the help of Allen's formula : [32]

$$R^3 = \frac{9 v^2}{2 gd (d - d')}.$$

The terminal velocities of the solid spheres having the critical radii would be, for the corresponding values of R, v, and $(d-d')$, as follows :

$d-d'$.	v.	R (cm.).	Terminal Velocity.	
			Cm. per Sec.	Meters per Hour.
0.016	1.15	0.52	0.82	29.5
0.004	5.75	2.40	.87	31.4
0.002	115.00	22.25	1.88	67.6

The figures show that even for small solid spheres the velocities are considerable. With increase of radius the terminal velocities would at first increase very fast, and then more slowly. However, since the resistance to the motion would, for large spheres, vary with the square of the velocity, neither the Stokes formula nor any other yet developed can declare the actual velocity for large solid spheres moving in the magma.

Nevertheless, Allen's formula for large spheres is of distinct help in guiding one to a proper appreciation of the case. It reads :

$$V^2 = \frac{1}{k} \cdot \frac{4\pi}{3} \cdot gr \cdot \frac{d - d'}{d},$$

where k is a constant for a given liquid-solid system.[33] It follows that the terminal velocity here varies directly as the square root of the radius and as the square root of the difference of the two densities. Referring to the table showing terminal velocities for solid spheres with critical radii, it seems clear that, in any of the three cases, spheres of

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[32] H. S. Allen, Phil. Mag., **50**, 324 (1900).

[33] H. S. Allen, Phil. Mag., **50**, 532 (1900).

corresponding density and of radii of 10 or more meters would rise at the rate of at least 10 centimeters per second or 360 meters per hour.

This analogy of solid spheres seems to afford some help in our imagining the course of a specially vesiculated mass of liquid magma. The rough quantitative estimate just made for large solid spheres cannot be directly applied to this case. On account of the possibility of internal movements in the rising mass of liquid magma, its speed of uprise will not be quite the same as that of a solid mass of the same shape, size, and density. Yet the correction to be applied is probably small.

As such a mass approaches the surface, through a column of rapidly decreasing viscosity and with a constant increase of buoyancy because of expansion of the contained bubbles, the velocity must greatly increase. However much a given mass of magma might lose buoyancy through the loss of its larger, more swiftly rising bubbles, the total effect must be to generate a powerful upward current in the magmatic column.

In spite of the lack of the necessary, full experimental data, our general conclusion seems to be as follows. Experiment does show that the rise of individual gas bubbles in magma will be very slow. Neither experiment nor theory can as yet declare the actual speed of the rise of a mass of specially vesiculated magma, but the analogy of solid spheres moving under gravity in a liquid enforces the belief that the more buoyant magma will move rapidly if its volume is of the order of thousands of cubic meters. Assuming such differential vesiculation in great depth, and assuming also a mechanism by which the gas of risen magma is dissipated (as in a volcanic vent), two-phase convection must stir the magma column to great depth and with considerable rapidity. Such a process must be incomparably more rapid than that of thermal convection under volcanic conditions. The transfer of heat may readily be conceived as able to supply the radiation loss in the crater for long periods of time.

The basal assumption, that vesiculation occurs at great depth in a volcanic conduit, is necessarily difficult to test by the facts of field geology. During its solidification an intrusive body is likely to be cleansed of its bubbles, which rise, and the gas so collected at the roof is slowly dissipated into the country-rock. This may be the explanation of the lack of vesiculation in most dikes, sheets, laccoliths, and batholiths. In general, the rock of a lava neck may be similarly freed from bubbles during the relatively long period of crystallization. Nevertheless, cases are not wanting where bubbles are known to have been trapped in basalt at depths greater than 300 meters. The basalt of the West Maui neck, illustrated in Figure 10, is charged with many minute vesicles at a depth at least 300 meters below the original top of this lava column. Ransome (in Bulletin 303 of the United States Geological Survey, 1907, p. 68) states that the bottom of a single 320-meter flow of basalt at Eldorado Canyon, Nevada, is vesicular. These and other known examples seem to strengthen the belief that bubbles may form in magma at the depth of several kilometers.

It is important to note that two-phase convection has two distinct, though related causes. Principal stress has hitherto been laid on differential vesiculation in depth, whereby a mass of magma becomes more buoyant than the enclosing magma and rises. Just as inevitably, the magma which is freed of gas at the crater, must sink and stir the column to great depth. Even if the column is not vesiculated at all, this second mode of convection is likely to be effective in the vertical transfer of the magma. As a rule, the density of a liquid is lowered by the absorption of hydrogen, nitrogen, oxygen, or other relatively light gas. This is very probably true of natural mixtures of juvenile gases when dissolved in magma. As these gases stream or diffuse from all azimuths in the feeding chamber toward the base of the narrow conduit, they are there concentrated. Thus, the magma *in* the conduit, at its lower levels, attains a density less than that of the average magma of the feeding chamber, and, a fortiori, less than that of the gas-freed magma descending from the crater level. This is another kind of density convection depending on the relative concentration of juvenile gas. For lack of experimental data, it is now impossible to estimate the efficiency of this species of convection. It may be a powerful ally of two-phase convection proper. For example, it is conceivable that the upward movement of magma is *begun* in the conduit because of the concentration of gas in solution and not in bubble phase. Then, as the magma rises to levels of smaller pressure, the gas begins to separate out in bubbles and enforces true two-phase convection of ever-increasing speed. In view of these various modes of gas-control, the vertical stirring of the magma column may, perhaps, be more safely described as, in general, a gas-concentration convection. Yet, the actually observed fact is that, at the crater, the gaseous phase does separate, in bubble form, from the liquid phase, and the writer has preferred to emphasize this empirical fact in adopting the name "two-phase convection."

Lava Fountains. — Herein the writer believes that we have an essential part of the explanation of "Old Faithful," the site of the greater periodic "fountains" of Kilauea. (Plate II. B.) That circular area, about twenty meters in 1909, has represented the true axis of the lava column for many years, and seems to have been the main source of magmatic heat throughout the known history of Kilauea. In 1909, at average intervals of about thirty-five seconds, the surface of the lava lake in this area was domed up to maximum heights of a few meters. These fountains are not due to the rise and explosion of great gas bubbles, the collapse of which could have been readily observed. No appreciable amount of gas or vapor was given off at the moment of doming or immediately afterwards. The outbursts are best explained, in part, on the principle illustrated in the upspringing of a log of light wood freed at the bottom of a lake. Through its momentum the log may jump clear out of the lake. In part, the outbursts of "Old Faithful" are due to true explosive dilation of the gas bubbles in the "log." The latter process is doubtless the chief cause of the smaller "fountains" playing over the surface of Halemaumau, and of those which played over the surface of Dana Lake or New Lake twenty-five years ago. The draining of each of these two lakes has shown that it was saucer-shaped and very shallow over most of its area, and the writer believes this is true of Halemaumau to-day. (Compare Plate III.) The depth is generally much too small to allow of such momentum in magmatic "logs" that they might leap to the heights actually observed.

The site of "Old Faithful" is, thus, the place where the juvenile gases rise from the depths in two-phase mixture with liquid lava. With the collapse of each dome, the gas-charged magma finds its level and runs under the semi-solid or solid "scum" on the lake surface. (Figure 6.) There the gas is slowly freed and accumulates beneath the "scum" until the tension produces a true explosion, that is, one of the many smaller "fountains" so constantly appearing on the lake.

The incessant streaming in Halemaumau, the nature of the "Old Faithful fountains," and the ceaseless vortical motion in the lake, as well as the similar phenomena in the active Mokuaweoweo, are so many direct evidences of two phase convection, which calculation shows must be rapid, provided slight variations in vesicularity occur in the depths of the lava column. Though it is not possible to prove absolutely that the Kilauean column is vesiculated in depth, it certainly is so at the surface to a remarkable degree. At many points, the lower part of the wall of Halemaumau was found, in 1909, to be covered with thin coatings of black glass which represented splashes of lava from the adjacent lake. This lava almost instantly "froze" to the wall. In every case it was extremely porous, so as to be quite spongy in appearance. The vesiculation was almost if not quite complete before the "splash" struck the wall, and it is simplest to suppose that the surface lava of the lake is a froth. There is no known reason why vesiculation should be the rule at one atmosphere of pressure and non-existent at one hundred or one thousand atmospheres; it is all a question of the degree of saturation with gas. The two-phase convection hypothesis rests on this unproved assumption, but its merit is great, as it explains the essential facts of circulation in Halemaumau. The hypothesis also explains the periodicity of "Old Faithful." Throughout the years 1908 and 1909 its geyser-like uprush occurred, on the average, once every 35 seconds or thereabouts. This pulsatory effect is expected as a result of the mechanism of two-phase convection.

Cooling by Rising Juvenile Gas. — As a fifth hypothesis it might be conceived that the heat is kept up in the lake through the rise of bubbles of *free* juvenile gas from the magma chamber, the bubbles arriving at the surface with some excess of temperature above that required to give the lava of the lake its observed fluidity. But the feeble explosiveness of the emanating gas at Kilauea shows that any unit mass of it, arriving at the surface, is already nearly expanded to the volume appropriate to one atmosphere of pressure, and therefore that the gas is in nearly perfect thermal equilibrium with the enclosing lava at the surface. Such bubbles, as they rise and expand, must thereby tend to cool the magma.

The cooling effect is very great, as may be shown by the following calculation. In an adiabatic expansion of a perfect gas: let T' be the initial absolute temperature, and T the final absolute temperature; let p' be the initial pressure, and p the final pressure; and let $\gamma\,(= 1.4)$ be the ratio of the specific heat of the gas at constant pressure to its specific heat at constant volume. Then

$$\frac{T'}{T} = \left(\frac{p'}{p}\right)^{\gamma-1}.$$

At about 37 meters below the lake surface the pressure is 10 atmospheres. If the bubble, after expanding adiabatically, is to arrive at the surface at a temperature of 1200°C., it must have at the depth of 37 meters a temperature of about 3700°C. (assuming no dissociation of the gas). Evidently the free-moving gases have a cooling effect on the upper part of the lava column. That this effect is actually small is, of course, due to the small mass of gas emitted in a unit of time and to the fact that γ is much less than 1.4 for the actual (not "perfect") gases while rising through the deeper levels. Moreover, it has been noted that the rise of a bubble must be exceedingly slow if its mass is anything like that in the average vesicle of frozen lava. So slow is the transfer that the rapid heat wastage at Halemaumau cannot possibly be compensated by any residual superheat in the emanating gas.

On the other hand, the thermal conditions are different in craters floored with highly viscous lava. There the emanating gases commonly issue at pressures of more than one atmosphere, and they are thus kept hot and endowed with some fluxing power. The small blowholes in Kilauea, as in most other basaltic districts, have long been kept open through this action. It is quite possible that such hot-blasting is operative on a greater scale in larger openings like the crater of Stromboli. Yet even at Stromboli that cannot be the chief method of heat transfer from the depths, and again no other method than that of two-phase convection seems competent to keep the lower and greater part of the lava column fluid. At Kilauea, at the wonderful Mokuaweoweo (the vent of a main abyssal injection), at Matavanu in Savaii, we seem compelled to exclude all other agencies for heat transfer except this type of convection. The same explanation seems to apply also to Vesuvius and Stromboli, for their craters in times of strong activity have been observed at close quarters and, like Halemaumau, they show lava " fountains " and other features of this convection.

The Volcanic Furnace. — So far, no assumption has been made that the heat transferred to the top of the volcanic conduit is other than primary in origin, that is, heat due to the initial temperature of the parent abyssal injection. Such is the orthodox view of volcanic heat. The rough estimate made in the discussion of thermal convection suggests the difficulty of understanding how the mere primary heat suffices to explain the long life of many volcanoes.

It may well be questioned, however, that all the heat at a volcanic vent is primary.[34] That due to the radioactivity of magma during the fluid stage of an abyssal injection is too small in amount to affect the rate of heat loss to any sensible degree. More promising is the idea that heat-producing chemical reactions in the conduit may have powerful effect. Since the day when Sir Humphry Davy renounced his own explanation of magmatic heat as due to the oxidation of alkaline metals contacting with water, most volcanic theories have regarded magma as inert so far as exothermic reactions are concerned. On the other hand, recent studies of gaseous emanations from active volcanoes and from artificially heated rocks and meteorites clearly suggest the possibility of such reactions.

Analysis of any perfectly fresh igneous rock shows the presence of water to a considerable percentage by weight. This is true of intrusive gabbros and diabase as well as of basaltic lavas. Most of

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[34] Cf. G. Tschermak, Sitzungsber. Akad. Wiss. Wien, **75**, 162 (1877), where a brief statement is given, showing a clear anticipation of this hypothesis.

the non-hygroscopic water determined in the analysis of quite unaltered gabbro or basalt may be as much a primary constituent as the silica or the alumina. We must believe that hydrogen and oxygen, in the proportion characteristic of water, are present in primary basaltic magma. It does not follow that, under volcanic conditions, these elements will issue from the vent in combination as water. In his able monograph on "The Gases in Rocks," R. T. Chamberlin indicates the general reaction to be expected in the Kilauean or other basaltic magma chamber. He writes:

"The effect of pressure on chemical equilibrium is to favor the formation of that system which occupies the smaller volume, but if there is no change in volume, in passing from one system to the other, the increase of pressure presumably has no influence on equilibrium. In the reaction

$$3FeO + H_2O \leftrightarrows Fe_3O_4 + H_2$$

considered as a thermochemical equation, the number of gaseous molecules, and hence the volume of gas, always remains the same, so that it is not likely that this action will be influenced by change of pressure. A rise of temperature favors the formation of that system which absorbs heat when it is formed. A comparison of the amount of heat liberated by oxidizing three molecules of FeO to Fe_3O_4 and one molecule of H_2 to H_2O shows that, in the former case, 73,700 calories are evolved, and in the latter, 58,300; that is, $3FeO + H_2O \rightarrow Fe_3O_4 + H_2 + 15{,}400$ calories. As heat is evolved in this process, a rise of temperature would accelerate the reaction in this direction less than in the reverse. In other words, the higher the temperature, the more would the formation of ferrous oxide and water be favored as compared with the conditions at lower temperatures.

"Because of this, there is much reason to suppose that, at the depths where lavas originate, hydrogen and oxygen exist combined as water, since up to temperatures of 2000° C., the dissociation of water takes place only to a limited extent. If a state of equilibrium between hydrogen, water, and the iron compounds were established in the heated interior where a magma originated, as soon as it commenced its way upward and began to lose heat the condition of equilibrium would be destroyed. With the falling temperature the tendency to re-establish equilibrium would favor the formation of that system which was produced with the liberation of heat, *i. e.*, magnetic oxide and free hydrogen. In ascending lavas which are losing heat, the tendency, therefore, is to produce hydrogen and magnetite, or ferroso-ferric compounds. This is doubtless an important source for the hydrogen which is so copiously exhaled during a volcanic eruption. At the same time this process accounts for the widespread occurrence of magnetite in igneous rocks."[35]

The abundant animal life of Cambrian and later time implies that the earth's atmosphere has long had a very low content of carbon dioxide. The amount of this oxide which has been locked up in the carbonate rocks since the beginning of the Cambrian period is so enormous that most of it, or all of it, must be considered as of juvenile origin. Yet more clearly than in the case of water, carbon dioxide must be regarded as a primary constituent of earth magma. Under the same conditions as those described by Chamberlin, ferrous iron is oxidized to magnetite by carbon dioxide, yielding carbon monoxide and 6000 calories per gram molecule.

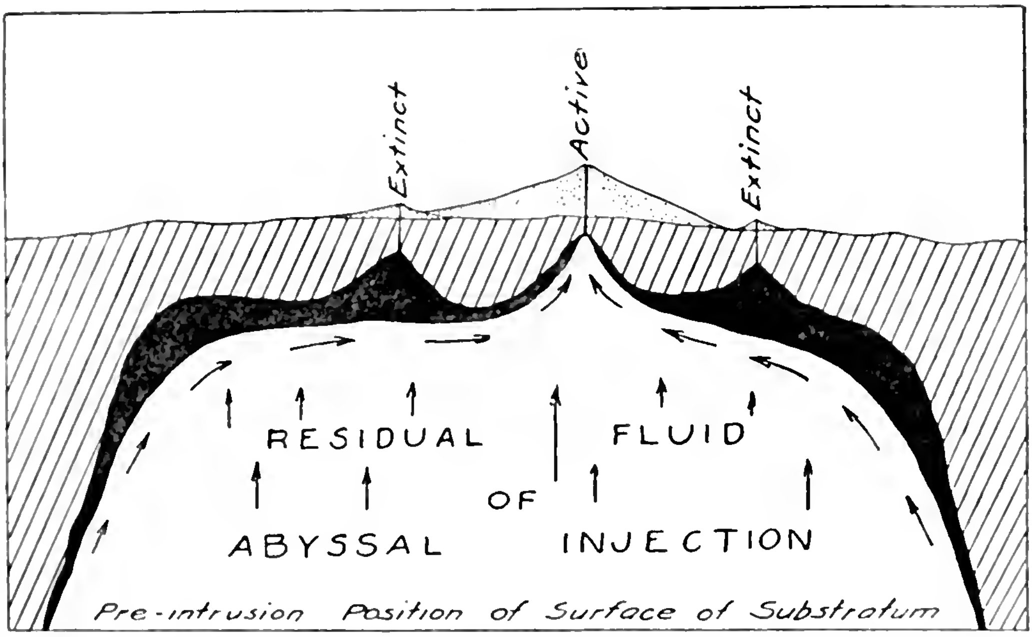

FIGURE 7. Ideal longitudinal section of an abyssal injection, showing the relation of vulcanism to the secular rise (arrows) of juvenile gas. The middle vent is active because it originates at the highest point (cupola) in the injected body. The other vents are extinct because of this advantage of the middle vent. Solid black represents the already crystallized material of the injection. Cross-lined area is the country-rock. Length of section about 100 kilometers.

The list of the juvenile gases and vapors also includes nitrogen, chlorine, sulphur, and hydrocarbons. These and other volatile sub-

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[35] R. T. Chamberlin, The Gases in Rocks, Publication No. 106, Carnegie Institution of Washington, 1908, p. 66.

stances, including hydrogen and carbon monoxide, stream from all azimuths in the magma chamber to the lower end of the conduit. The pipe has always a very much smaller cross-section than the feeding chamber, implying some concentration of the volatile matter. (Figures 7 and 8.) At conduit temperatures this ever-varying mixture of gases must, according to practically infinite probability, be in unstable chemical equililibrium; under the conditions new equilibria are attained with the evolution of heat.

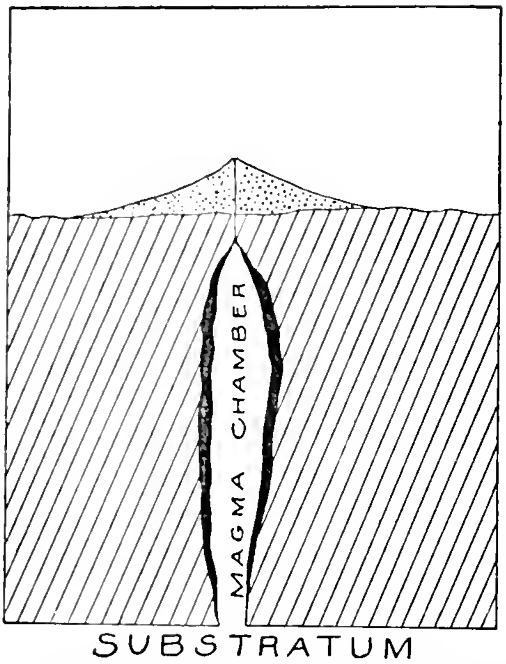

FIGURE 8. Ideal cross-section through middle cone shown in Figure 7, to same scale.

The relative proportions of each gas must, in general, be different from that in the primary magma before it was injected. Concentration of the gases means, according to the law of mass-action, the development of new compounds. As the pressure is less in the conduit than in the underlying chamber, the viscosity of the magma is less, the gas bubbles are larger, and the speed of possible reactions is thereby increased.

Of course, the actual amount of heat evolved during the chemical rearrangements in the conduit cannot be estimated, but a glance at the following tables (showing some examples) must assure one that the heat product from the complex system may be of a high order.[36]

HEATS OF FORMATION.

	Calories per Gram-molecule.		Calories per Gram-molecule.		Calories per Gram-molecule.
[HCl]	+22,000	[SO_2]	+71,080	[$CaCl_2$]	+190,300
[H_2O]	58,300	[CO_2]	96,960	[K_2Cl_2]	211,220
[H_2S]	5,400	[SO_3]	103,240	[Na_2Cl_2]	195,380
[H_3N]	11,890	[P_2O_5]	369,900	[$FeCl_2$]	82,050
[H_4C]	21,750	[FeS]	24,000		
[CO]	29,000	[CaF_2]	238,800		

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[36] The values for the heats of formation and reaction are taken from the works of Thomsen, Muir and Wilson, Nernst, and others. In some cases more recent experiments give slightly different values.

HEATS OF REACTION.

$CH_4 + 2O_2 = CO_2 + 2H_2O + 195{,}200$ cals.
$CO_2 + H_2 = CO + H_2O + 9{,}980$ cals.
$3FeO + H_2O = Fe_3O_4 + H_2 + 15{,}400$ cals.
$3FeO + CO_2 = Fe_3O_4 + CO + 6{,}000$ cals.
$NH_3 + HCl = NH_4Cl + 42{,}500$ cals.[37]
$CO + O = CO_2 + 68{,}040$ cals.

In addition, there is the possibility that a large supply of energy was potentialized at the high temperatures of the primitive earth and that this energy becomes converted into magmatic heat under the conditions of a volcanic vent. Becker has suggested this in the case of uranium.[38] Arrhenius has proposed the hypothesis that the heat of the sun is supplied principally through the break-up of endothermic compounds.[39] Warren has shown that, at high pressure and temperature, steam is partially converted into the strongly endothermic ozone and hydrogen peroxide.[40] Lines indicating cyanogen are found in the spectra of some stars and comets, and Arrhenius attributes the nitrogen of the air largely to the dissociation of volcanic cyanogen. In the formation of a gram-molecule of this gas, 65,700 calories are potentialized. The dissociation of chlorine involves the absorption of 113,000 calories.[41] Dissociation of other gaseous elements means heat absorption of the same order of magnitude. When ferric oxide and iron sulphide react to form ferrous oxide and sulphur dioxide, 80,640 calories are absorbed. When carbon and carbon dioxide react to produce carbon monoxide, 38,800 calories are absorbed. When steam and C react to form carbon monoxide and free hydrogen, 28,900 calories are absorbed.

In addition to the heat evolved by the dissociation of endothermic compounds, another source of great energy is to be found in the combination of the freed, "nascent" elements with other constituents of

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[37] Though ammonium chloride may not be able to form within the magma column of a volcanic conduit, it does form at the surface, where the loss of heat chiefly occurs. Similarly, ammonia may form from its elements in the relatively cool crust of the lava lake in a crater, also producing heat at the zone of radiation.

[38] G. F. Becker, Bull. Geol. Soc. America, **19**, 146 (1908). The final yield of radium is about 2,000 millions of calories per gram, or nearly 250,000 times the thermal value of a gram of carbon burnt in oxygen.

[39] S. Arrhenius, Worlds in the Making, New York, 91 (1908).

[40] H. N. Warren, Chem. News, **77**, 192 (1898). When one gram of oxygen is converted into one gram of ozone, 750 calories are absorbed.

[41] M. Pier, Zeit. für phys. Chemie, **62**, 385 (1908). Ekholm has suggested that the formation of "elements" may partly explain solar energy.

the magma. The powerful thermal effect of interaction between hydrogen or oxygen and the carbon or nitrogen atoms of cyanogen hardly needs quantitative statement to show its value.

In this connection it may be noted that the total melting heat of ordinary rock-matter (measured from 0°C.) is only 400 to 450 cals. per gram, and that the latent heat is only about 90 cals. per gram.

Such examples emphasize the value of the conception that abyssal injection, entailing a sharp change of pressure and a slower change of temperature in primary magma, may set free a vast amount of energy which is available for conserving the melting temperature in a lava conduit. Very great superheat is, however, prevented by two-phase convection, which tends to keep the volcanic furnace and the surface lava at nearly the same temperature.

The whole system, as imagined, is somewhat analogous to a modern hot-water plant with an almost perfectly lagged vertical pipe running up from the furnace. Or, again, the generation of heat in the conduit is analogous to that in the gas-mixture of a blowpipe. In the first case (two-phase convention) the rising gas is a passive agent in the upward transfer of heat; in the second case (chemical changes) the gas is a positive heater. For a double reason juvenile gas has fluxing power in the vent.

Summary on the Heat Problem of an Active Central Vent.— A volcano of the central-eruption type, like all others, depends on antecedent abyssal injection of magma into the earth's crust, furnishing a magma chamber whence the vent may draw its supply of energy.

Three possibilities are open: (1) The primary magma may have been initially saturated with juvenile gas at the original pressure of 10,000 atmospheres or more. (2) Only the upper part of the magma may be saturated with gas because of the change of pressure resulting from the injection. (3) Or the magma may not be saturated immediately after injection, even at the pressure of one atmosphere.

In the first case, bubbles must form throughout the chamber at all levels above the original depth of the magma. In the second case, bubbles must form at all levels above the lowest one where saturation has been developed by change of pressure. In the third case, bubbles will form only after other causes than mere change of pressure have operated. At least three such causes are conceivable. (a) The upper part of the magma chamber might become supersaturated through the upward molecular diffusion of gases, whereby these are concentrated. This is a reasonable expectation on the general principles of physical chemistry, though experimental or other proofs are lacking. (b) The slow crystallization of the magma might be accompanied by the ejection of gas, as it is actually seen to emanate during the crystallization of artificial slags. That process might cause local supersaturation in the still liquid magma, with the formation of bubbles. (c) Chemical reactions in the magma, such as the generation of hydrogen from dissolved primary water vapor — a reaction to be expected with a slight fall of temperature — might produce gases insoluble in the magma at the pressure reigning at the place of the reaction.

Among so many possibilities, it seems legitimate to assume the generation of free gas in the main magma chamber. Irrespective of their origin, the bubbles must rise with great slowness through the magma chamber, because, first, they are of small size; and, secondly, because the viscosity of magma under great pressures must be relatively high. Even in the case of supersaturation in all parts of the new abyssal injection, the entire freeing of the bubbles may occupy many thousands of years.

As the bubbles rise, the gas tends to be concentrated in the volcanic conduit. There the laws of mass-action and of the degradation of energy seem to enforce exothermic reactions of the gaseous constituents among themselves and with the elements of the liquid magma. It is most probable that the heat so generated is very great when compared to the mass of matter participating in the reactions. The conduit is thus a furnace where the potential energy of the accumulating gases is converted into heat energy.

Other sources of heat which aid in prolonging the activity of the volcano are: (a) the conversion of the potential energy of the liquid components of the magmatic system when thrown out of chemical equilibrium by the change of pressure and subsequent lowering of temperature; (b) the liberation of latent heat in the slow crystallization at the walls of the magma chamber; and (c) some degree of initial superheat in the magma, perhaps of the order of 100° or 200° Centigrade.

Since the loss of heat at an active vent is chiefly due to radiation at the crater, the continuance of activity is controlled by the efficiency of the mechanism by which the heat of the main chamber and the heat chemically generated in the conduit are transferred to the earth's surface. Field observations at Kilauea and elsewhere, along with a priori deductions, have suggested the general dominance of two-phase convection (or, more generally, convection due to systematic, local changes in gas-concentration) in making this transfer.

Juvenile gas is thus conceived to act in a two-fold capacity — as a positive heater and as the agent enforcing convection. Its net effect is to keep fluid the top part of the lava column during the volcano's activity. The conception as a whole may therefore be called the *gas-fluxing* hypothesis. For vents occupied by highly fluid lava this hypothesis as just stated seems to suffice. For craters floored with more viscous lava, the emanating gas issues under more or less high pressure and may function as a melting blast, making more perfect the analogy with an artificial blowpipe.

Revival of Activity at the End of a Dormant Period.

One of the leading problems in vulcanism relates to the periodicity of central eruptions. This also seems to find explanation on the gas-fluxing hypothesis. We have seen that the accumulation of gas bubbles in the conduit must be a very slow process. So long as the vent is open, the escape of the gas from the magma is specially facilitated. That is true, not because the pressure on the main part of the lava column is less than in times of dormancy, but because of the rapid freeing of gas into the open air, with the consequent rapid production of heavy, gas-freed lava which sinks and thus hastens the two-phase convection. The tendency is, therefore, sooner or later to exhaust the gas concentrated at the lower end of the conduit. With sufficient removal of the heat-producing and heat-transferring agent, the forces of cold temporarily win in the never-ceasing struggle and the lava solidifies at the surface; a plug of greater or less thickness is formed. The crater may become temporarily so dead that even solfataric action ceases and a forest may flourish within the crater, as has been the case with Vesuvius.

On account of the small horizontal dimensions of the average vent, the consolidation of such a lava plug may be completed in a few years. This new rock is characteristically tough; when cooled, it is the strongest rock in the average volcanic cone. In the text-books on dynamical geology and in special vulcanological memoirs, the removal of the plug is usually stated to be due to simple explosion of the gases accumulating below it. Yet it is obvious that in the normal cone, which is largely built of loose ash deposits of very low tensile strength, the weakest place in the pile is on its flank and not at the main central plug. By the orthodox view, therefore, the new crater, the main one for the succeeding period of activity, should have a different location from that of the earlier main crater. The fact is, that, in very many cases, the main vent is located at the same place through the many different periods of activity of the greater cones. The beautiful symmetry of a Fujiyama or of a Mayon is the result. The removal of the plug at the close of a dormant period is clearly not the mere mechanical result of explosion. There must be a preliminary weakening of the plug, and apparently the only cause for that weakening is to be found in the fluxing by juvenile gas.

First we may consider the case where the terrestrial forces keep the liquid column supported in the conduit. With the formation of the plug, the loss of heat falls to a very low rate as compared with that ruling in the active period. Until the plug is removed, nearly all the loss is due to conduction and is very slow. Two-phase convection is slowed down, but the rise of bubbles does not cease nor does the volcanic furnace cease working, since a renewed concentration of juvenile gas is begun. To that positive source of heat in the conduit is to be added the heat developed by the compression of the gas as it accumulates beneath the plug and as it is squeezed by any upthrusting of the magmatic column due to crustal movement. Gradually the lowest part of the plug becomes liquefied, preferably along its vertical axis, where the heat inherited from the last active period preserves the line of maximum temperature in the whole upper part of the volcano. The reliquefied lava sinks into the column, dissolving some of the accumulating gas, so that heat of solution is probably to be added to the other supplies which tend to threaten the existence of the plug. Hence, at least three processes coöperate in fusing the plug; these are: heat of chemical reaction, heat of gas compression, and heat of gas solution. As the plug is thus weakened, the gas-tension increases and activity is renewed by one or more major explosions, shattering the remaining part of the plug. (Figure 9.)

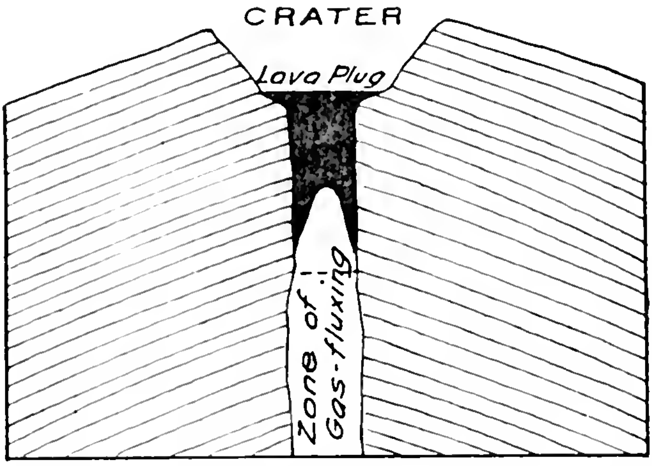

FIGURE 9. Section of upper part of a dormant cone, showing some progress in gas-fluxing. Broken line in middle of vent shows original depth of the solid plug.

Though full experimental data for the testing of these conclusions are not yet in hand, it is not difficult to see that the fluxing power of even small masses of juvenile gas is great under these conditions. If chemical reactions supply any large fraction of the heat lost by radiation in the active period, they must raise the temperature of the lava column under conditions of dormancy. This involves a slow melting of the country-rock, and especially the plug.

In most cases dormancy is ended by explosions so powerful as to show pressures under the plugs of even higher order than the pressures in the greatest modern cannon at the moment of discharge. These pressures run well over 2,000 atmospheres. If a given plug, when frozen to maximum thickness, is 1000 meters deep, the initial pressure on the gas first collecting beneath it would be about 270 atmospheres. Amagat's experiments furnish the data from which the temperature effect of the adiabatic compression of the typical gases, carbon dioxide and hydrogen, may be approximately computed.

At the request of the writer Professor H. N. Davis has kindly deduced the thermodynamic equation for these two cases. If T_0 is the initial temperature; T, the final temperature; p_0, the initial pressure; and p, the final pressure, we have

$$T = T_0 \left(\frac{p}{p_0}\right)^n,$$

in which n is an exponent approximately determined from Amagat's curves. If the initial temperature and pressure are, respectively, 1273°C. absolute and 270 atmospheres, and the final pressure is 2700 atmospheres, the average value of n for carbon dioxide is about 0.17; and, for hydrogen, n probably lies between 0.26 and 0.31. For carbon dioxide the computed value of T is 1880° absolute, and for hydrogen 2300° to 2600° absolute. This adiabatic compression of carbon dioxide would develop heat to the amount of about 200 calories per gram. Similar compression of pure hydrogen would develop an amount of heat ranging from 3000 to 4000 calories per gram. The compression of the gaseous mixture actually formed under volcanic plugs would produce heat to amounts intermediate between those calculated for carbon dioxide and for hydrogen. Since hydrogen is one of the most abundant constituents of the mixture, it is possible that adiabatic compression of the mixture, under the conditions above described, would produce at least 1000 calories per gram of gas. Since the latent heat of holocrystalline igneous rock is about 90 calories (Vogt), this heat of compression could fuse more than 10 grams of rock per gram of gas.

Calculation further shows that if the compression of a considerable volume of gas be isothermal, other conditions being as above assumed for the adiabatic compression, the heat produced is of the same large order of magnitude.

As the lower part of the plug is fused, the liquid sinks through the gas-rich part of the magma column, so that the fluxing gas is always in immediate contact with the solid rock. Since the solid plug retains a relatively high temperature inherited from the last active period, and since the vertical axis of the plug is the hottest part of the volcanic cone at all levels above the top of the lava column, it is clear that fluxing will be most rapid along the axis.

Again, a local development of heat is to be expected as the re-fused rock, which had been largely freed of gas in the last active period, begins to absorb the gases collecting in the conduit. Nothing is known as to the solution heat of any juvenile gas as it is absorbed in a natural magma. In each case it is practically certain to be positive and it may be important in amount. The data for the same gases when dissolved in water have some value in the way of analogy. The following table is taken from Thomsen's Thermochemistry:

Vapor or gas dissolved in water.	Heat of solution.	
	For 1 gram-mol.	For 1 gram.
NH_3	8,430 cals.	496 cals.
SO_2	7,700	120
Cl_2	4,870	69
CO_2	5,880	134
H_2S	4,560	134
HCl	17,315	475

When hydrogen dissolves in water, heat to the amount of about 800 cals. per gram of the gas is evolved.[42]

In this whole problem it must be remembered that hydrogen forms a relatively large part of juvenile gas-mixtures. This gas has the highest specific heat of all substances yet measured, and its heat of solution in water is also very high. Its efficiency in melting a volcanic plug may perhaps be greater than that of the other gases and vapors put together.

In view of all the conditions, it seems correct to hold that the accumulation of gas beneath a solid volcanic plug develops a special kind of local furnace. The energy here transformed into heat is both potential and mechanical. In part, it is heat of solution; in large part, it

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[42] G. N. Lewis, verbal communication.

may be due to chemical reactions; in part, it is due to the condensation of free gas constantly increasing in mass, within a closed chamber. The increase in mass is assumed to be due to the exclusion of gas in the crystallization at the walls of the abyssal injection, and perhaps to other molecular transformations within the magma chamber.

If the lava column is not kept supported, but withdraws for a time from the plug, the compression-melting of the plug must await sufficient accumulation of gas from beneath or the return of the fluid lava (because of general strains in the earth's crust or for other reasons) into the conduit. The mechanism is, however, the same as in the case just discussed, and the base of the plug is gradually melted.

The re-fused magma must become gradually more and more charged with gas. How much gas per unit weight of rock would be required to fuse an average plug is obviously now impossible to declare, but the maximum quantity of gas in solution may not need to be more than two or three per cent of the total weight of the magma in the actual conduit. The astounding explosive energy of newly awakened volcanoes, as shown in the vast heights to which fine ejecta are thrown and by the excessive comminution of the respective plugs, seem to indicate saturation of the magmas to an even higher degree. The "evisceration" of some cones has possibly been due to the concentration of juvenile gases beneath plugs not yet sufficiently fluxed to permit of a reopening of the former vents by more moderate explosions. In neither case, however, is it probable that pure explosion could restore activity to the dormant volcanoes. Here again, as in the continuance of activity after the vent is opened, the problem is one of heat supply.

Another cause for dormancy is to be found in the sudden emptying of a lava-filled conduit by escape through a lateral fissure, forming satellitic intrusion, or distant surface flow, or both at once. This is a common event at both Kilauea and Mauna Loa. A multiple effect is produced. A large volume of specially concentrated juvenile gas is taken out of the vent, just so far diminishing the motive power and heat supply in that vent. As observed at Kilauea, the level of the conduit lava may not be restored to its former height for months or years. During that time the upper part of the conduit wall is cooling, and, through decrepitation and initial weakness, large masses fall from the wall and choke the vent. A resumption of activity at the surface must be delayed by these processes.

In the present argument we need not dwell on the fact that, if the volcanic mechanism is nicely balanced, a minute effect, like tidal strain, may pull the trigger and renew activity, for which the essential conditions have been long preparing. However, it seems clear that cosmical stresses do not seriously deform an abyssal injection during its lifetime as the feeder of a central vent. During such a period, which may be thousands of years in length but seldom or never millions of years in length, crustal readjustments must be minute, for even the greatest lava flows that could have been thus squeezed out at central vents are always very small in relative measure. The last-mentioned fact and the persistent recurrence of eruption at the main vent appear to forbid the hypothesis that renewal of activity at central vents is due to *renewal* of injection along new abyssal fissures. It would be highly improbable that the vent of a second injection would coincide with that of the first injection; and on the other hand, the great crustal disturbance accompanying the second injection should normally cause first-class lava floods at the initial vent, instead of the comparatively insignificant flows actually observed at central vents. Difficult as the problem is, the change from dormancy to activity does not, in general, seem to call for anything so drastic as a strong deformation of the earth's crust in its entire thickness.

In conclusion, the gas-fluxing hypothesis appears to be worthy of a leading place among those which can be constructed to account for the stubborn persistence in the revival of activity at a vent like Mokuaweoweo, Vesuvius, or Etna.

Small Size of Central Vents.

The gas-fluxing hypothesis accounts for other general features of central eruptions. The small cross-sections of the vents at Kilauea, Hualalai, Mauna Loa, and even at Mokuaweoweo, as everywhere else in the world, are all of the order of size expected if the fluidity of each lava column is due to the slow passage of relatively minute masses of gas through those vents.

The writer is not able to agree with J. D. Dana, that the conduits beneath Kilauea and Mauna Loa are nearly equivalent in horizontal section to the great sinks ("calderas") in which the lava lakes are situated. Each of those sinks measures roughly five kilometers by three kilometers. The periodic rise and fall of the floor of the Kilauean sink (the only one carefully studied) can be explained on the assumption that its conduit has a much smaller cross-section. The "New Lake" after five years of activity, was emptied in 1886, and was proved to have had a depth of only a few meters. It was a saucer-shaped sheet of lava resting on solid rock. (Compare Plate III.) When the present Halemaumau is emptied, the lava runs out through a very narrow hole apparently less than thirty meters wide, and leaves a broad, funnel-shaped cavity. The action is like that of water running out of a domestic sink with centrally placed discharge; in both cases vertical motion is observed in the rapidly escaping liquid.[43] Similarly, the vast Kilauean lake of 1820 to 1860 is best interpreted as a true lake with solid floor, except for the narrow pipe which has always supplied the heat at this volcano. That pipe is probably the same pipe into which Halemaumau at times discharges its lava and from which the gas issues, to make the fountains of "Old Faithful." All the Kilauean lakes have represented *overflows* from that vent or from a few, more temporary, narrow pipes. The fluidity of the lake has, in each case, been preserved for years by the process above outlined for the existing lake.

Whatever adverse criticism of this conclusion regarding Kilauea may succeed, it is certain that the whole area of either of the Hawaiian sinks cannot be directly taken to represent the size of the conduits. The surface areas of other lava columns active in historic time are all very much smaller. It is doubtful that any one of them, just below the floor of the flaring crater, has been as much as one kilometer. J. D. Dana computed the volume of the 1852 floor from Mauna Loa, which appears to have emptied the conduit to a depth of 2,500 feet, as estimated from the difference of level of the summit lake and of the point of discharge. The result was 10,560,000,000 cubic feet.[44] This corresponds to the volume in a cylindrical conduit about 2,300 feet or 700 meters in diameter. Similar calculations from other lateral outflows seem to give a mean diameter for the conduit of the same order of magnitude. Such a lateral fissure once opened, it would seem highly probable that the conduit would be emptied almost entirely by the simple outflow of the lava through the fissure; discharge into "subterranean cavities," would be unlikely. Moreover, it is possible that some of the 1852 lava represents a temporary rise of magma in the conduit, so that only part of the estimated volume of the flow can be used in calculating the average diameter of the Mauna Loa conduit. Thus, the calculation made according to the method outlined, strengthens the suspicion that the lava column of the world's vastest volcano is but a comparatively narrow pipe, perhaps much less than 600 meters in average diameter.

All of the ancient central vents now exposed as "necks" after prolonged denudation, are relatively small. (Compare Figure 10.) The average diameter of the pipes recorded in geological literature is well under 500 meters. The largest of the hundreds of deeply eroded lava necks in the Mount Taylor region of New Mexico is said to be not more

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[43] C. H. Hitchcock, Hawaii and its Volcanoes, Honolulu, 1909, p. 254.

[44] J. D. Dana, Characteristics of Volcanoes, New York, 1891, p. 240.

than 450 meters in diameter. The size of the lava conduit is often not shown by the maps of many volcanic "necks." For example, the largest Scottish "necks" described by Geikie are chiefly composed of pyroclastic materials and may represent erosion sections through explosion funnels with their characteristic flare. Without even allowing for that uncertainty, the writer believes that the conduits of central eruptions, measured below the explosion zone, have an average diameter of much less than one kilometer. The term "conduit" here means, of course, the pipe above the primary abyssal injection. The main magma chamber may be indefinitely greater in horizontal section.

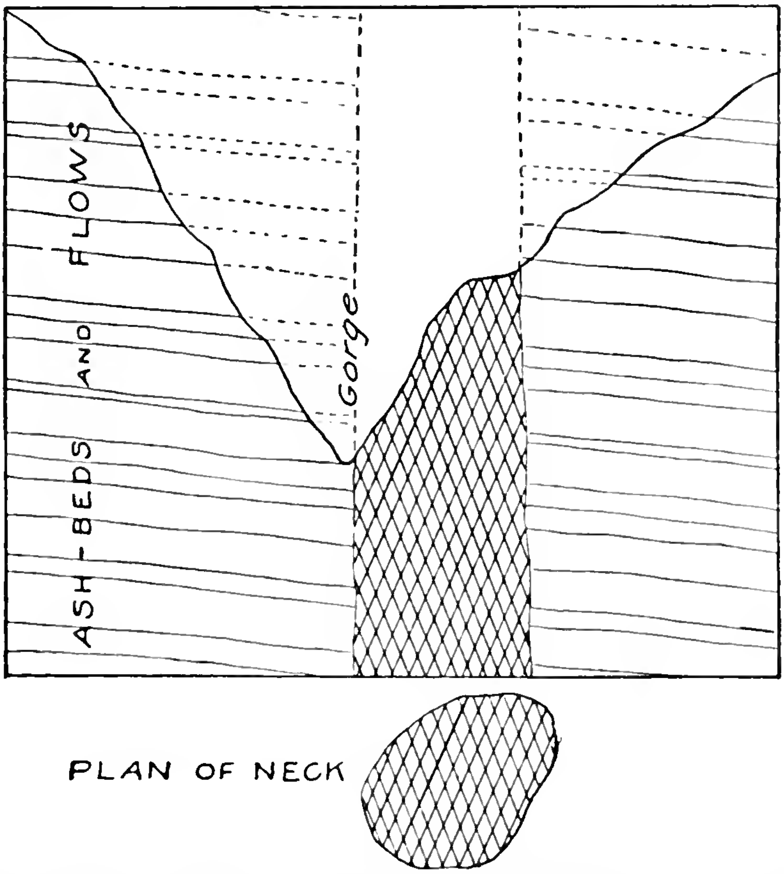

FIGURE 10. Section and ground plan of basalt-lava neck in a lateral gorge of the Iao valley in West Maui, illustrating the cylindrical form due to gas-fluxing. This was one of the subsidiary vents on the flanks of the great West Maui cone. There is no trace of faulting in the ash-and-flow series and it is possible that this neck represents the local enlargement (by gas-fluxing) of one of the dike fissures now visible in the canyon. Nearly natural scale; major diameter of the neck about 50 meters.

We may conclude that the conduits of central eruptions are always small and of the order of magnitude appropriate to the gas-fluxing hypothesis. On any other hypothesis it is hard to explain the fact that the pipes of moderately large cones are about as large as those of the very greatest cones. In all cases there seems to be a *limital size* and that is controlled by the available heat supply along the axis of the vent. The size is small because the (indirect) fusing power of emanating gas must be strictly limited. Moreover, the cylindrical shape of each typical pipe is a solutional or fluxing form. (Figure 10.)

Explosive types: Magmatic and Phreatic.

The foregoing genetic statement for the Hawaiian vents has been sketched in terms of a quite general process and it is necessary to glance at the relation of the hypothesis to the explosive type of central eruption.

Volatile matter occurring in the rocks of the contact-shell about any intrusive magma must show increased tension. If the intrusion is large and near enough to the earth's surface, this tension may lead to explosion in the roof of the igneous body. In case no incandescent matter is extruded, the explosion is not volcanic according to our definition of that term (p. 48). Following Suess, it may be called *phreatic.* A similar explosion may happen as a result of the slow conduction of heat from the conduit of a long dormant volcanic cone. Such a cone is normally porous. Rain-water, snow-water, or sea-water is trapped in the vesicular flows and loose tuffs, as these are in turn buried during the original growth of the cone. The circulation of vadose water is also facilitated by this special porosity.

The suggestion of Suess that the remarkable explosion at the famous Rieskessel was of phreatic origin has been supported by the detailed studies of Branco and others.[45] Purely geological studies had indicated the presence of a large laccolithic mass beneath the great Ries depression. That conclusion has been brilliantly supported by the magnetic studies of Haussmann in the region. The local disturbances of the needle in dip and azimuth can be explained, according to Haussmann, only by the assumption of one or more large subterranean bodies of basic rock.[46] In the Rieskessel itself the upper surface of the basic rock is calculated to be no more than two kilometers deep. Outside the depression, its average depth was estimated at five kilometers. Since the visible floor of the Ries is the granite of the " Grundgebirge,"

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[45] W. Branco, Abhand. kön. preuss. Akad. Wiss. Berlin, 1902, p. 14.

[46] K. Haussmann, Abhand. kön. preuss. Akad. Wiss. Berlin, 1904, Abt. IV, p. 137. Sauer has suggested that the liparite of the Kieskessel tuffs is due to the melting of the intruded granite by the basic magma. See W. Branco and F. Fraas, Abhand. kön. preuss. Akad. Wiss. Berlin, 1901, p. 54.

the basic mass or masses can only be interpreted as due to injection. Branco dates the intrusion of the Ries "laccolith" in the mid-Miocene. The overlying granite and its Mesozoic sedimentary veneer were domed by the injection and the top of the dome was largely destroyed by a phreatic explosion. It was followed by the appearance of a little liparitic tuff erupted at a few points in the newly formed basin, but the explosion itself was non-volcanic.

According to Sekiya and Kikuchi, the great explosion of 1888 at Bandai-San was absolutely unaccompanied by the extrusion of lava.[47] A priest living on the mountain survived the explosion. He reported the vapors surrounding him to have been respirable, and the Japanese geologists conclude from all available data that the catastrophe was a steam explosion. There were no signs that juvenile gases formed an important part of the volatile mixture. This "eruption" of Bandai-San seems, therefore, to be an excellent example of a phreatic explosion *on* a true volcanic cone.

Phreatic eruption means steam-explosion without magmatic extrusion. Kilauea represents magmatic extrusion without steam-explosion. Between these two extremes of terrestrial activity stands the type representing the vast majority of active and extinct central eruptions. In the non-volcanic or pseudo-volcanic activity of Bandai-San in 1888, as in a Kilauea or a Vesuvius, true igneous injection is a pre-requisite. The gases given off at Kilauea form a nearly pure juvenile mixture with characteristic high temperature. The gases given off at Vesuvius form a mixture of juvenile, resurgent, and vadose volatile matter. A type of the resurgent gas is the carbon dioxide set free in the demonstrable assimilation of Mesozoic limestone and dolomite in the Vesuvian lava column. The gas and vapor given off at Bandai-San in 1888 was apparently almost purely vadose or meteoric in origin.

True volcanoes of the central-eruption type must vary enormously in the relative and absolute proportions of juvenile, resurgent, and vadose fluids composing their emanations. As the resurgent and vadose fluids are volatilized, heat is lost and the viscosity of the lava column rises. Assimilation of foreign rock in depth must lower the temperature, and in the end, increase the viscosity and also the average violence of explosions. In addition, magmatic differentiation generally brings the more silicious and more viscous pole to the upper part of the lava column, and aids in the preparation of explosive conditions.

For these and other reasons, volcanoes of the central-eruption type

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[47] S. Sekiya and J. Kikuchi, Jour. Coll. Science, Tokio, 1889, p. 106.

have always had a great variety in dynamic habit and in the character of their ejectamenta. Yet, in every one of them, the essential problem is the same ; it refers to the mechanism by which heat is kept supplied to the narrow, thread-like vents for long periods. To that problem, the questions as to how sea-water or vadose water is absorbed by underground magma, as to the dominance or subdominance of steam-explosion at individual vents, and as to the physical differences in the emanating lavas, are subsidiary. The problem of the Hawaiian vents is, from this point of view, the problem of all vulcanism reduced to its lowest terms. Here the gas-fluxing hypothesis seems satisfactory. In most other volcanic regions, where thick sediments are cut by the feeding magma, or where heavy snows or rains wet the cones and, through seepage, cause steam-explosions, the control by juvenile gas may be obscured to the eye of the observer, but it still remains, in every case, the true cause of continued activity. Kilauea and Mokuaweoweo, like Matavanu and the vents in Réunion, teach us that steam-explosion is an adventitious feature of vulcanism. Except abyssal injection itself, the only indispensable process in central vents is *quiet exhalation.* Neither explosive drilling of the vent, nor ejection of lava, nor the contacting of meteoric or marine water with hot lava is indispensable. Each of these three processes is an expected effect of the slow emanation of juvenile gas from main abyssal injections or from their satellitic offshoots.

Magmatic Differentiation at Central Vents.

The chemical variation exhibited in the lavas or pyroclastic materials successively ejected at the normal vent offers a problem of special importance. Volume for volume, this variability is much more striking than it is in the average large intrusive body — stock, batholith, laccolith, or sheet. At present many petrologists favor the pure-differentiation theory, which regards the splitting magma as primary, and finds no place for notable assimilation of wall-rocks by the primary magma. The writer believes that this question can only be cleared up by an attentive study of the world's plutonic masses, and that, in the nature of the case, its answer is not to be found at central vents. Field and chemical relations point indubitably to the fact that wholesale assimilation has occurred in the subjacent bodies classed as stocks and batholiths. Because of assimilation these masses generally have not the basaltic composition of the primary abyssal injection. The visible granite, diorite, or syenite represents the frozen top of an abyssal injection which is there a more or less differentiated syntectic. The lower part of each injection, approaching the substratum level, is probably basaltic and little modified in composition from its original condition. The syntectic-differentiation theory is so strong that the writer is disposed to prophesy its ultimate victory in the competition among explanations of the igneous magmas and rocks.

Since the lava column of every volcanic vent is an offshoot from an abyssal injection, the lava may represent either the primary basalt, or one of its differentiates, or syntectic material, or a differentiate from syntectic material. The rapid chemical variations in the extrusive magma at the average central vent shows that the conditions are here specially favorable for differentiation. Two of these conditions are implied in the essential mechanism of central eruption. The upward passage of juvenile and resurgent gases in great relative abundance, lowers the "point" of solidification of the magma, increases the fluidity, and probably in still other ways aids in magmatic splitting. Secondly, the alternation of active and dormant periods means that the top of the lava column passes repeatedly through the narrow range of temperature (just above the crystallization point), where differentiation is most likely to take place.[48] High superheat is opposed to magmatic splitting.

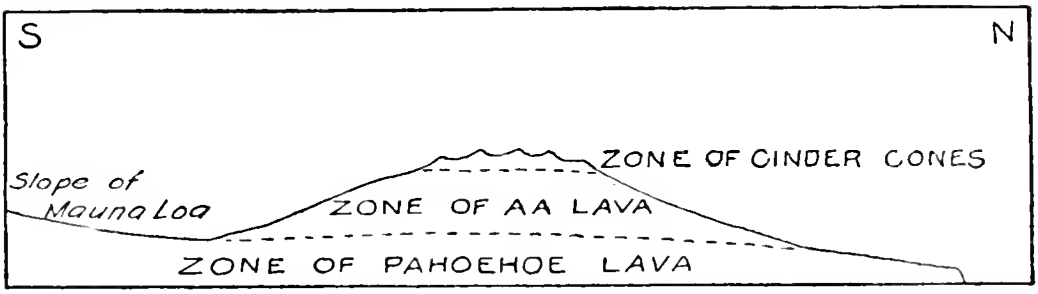

FIGURE 11. Diagrammatic projection of Mauna Kea, illustrating the field character of the rocks encountered in climbing from sea-level to the summit at 4213 meters above sea. Length of section 55 kilometers. Vertical scale twice the natural.

Each of these conditions affects only a small volume of magma at any one time; if lava representing either pole of the differentiation is alone extruded, the volume of that flow must be relatively small. New magma rises in the vent. It may be mixed with that representing the other pole of the differentiation just accomplished. The mixture may be extruded, or it may itself be differentiated before the next outflow. Through absorption of foreign rock the new lava may have a composition unlike that originally differentiated.

It seems inevitable, therefore, that, at the restless volcanic vent, the ever changing conditions must make a cone which is chemically heter-

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[48] Intrusive masses normally pass through this temperature range only once before solidification.

ogeneous to an extent not matched in the usual plutonic mass. Standard examples have been described at Electric Peak and Sepulchre Mountain in the Yellowstone Park; at the Lipari Island vents; at Tonopah, Nevada; at the Kaiserstuhl in Baden, etc.

The extinct Mauna Kea in Hawaii (alt. 4213 meters) affords a good illustration of a lava column which has not contacted with important sedimentary masses. In this case magmatic differentiation seems to have played the most important rôle, though its heavy winter snow-cap may have furnished a special condition for explosiveness in the last stage of the cone's activity. (Figure 11.) The broad base of this volcano, visible in the long sea-cliff on the north side of the island, is essentially composed of olivine basalt of the fluent pahoehoe type. From about the 1500-meter contour to the 3500-meter contour, the slopes are chiefly underlain by flows of a much less femic basalt, with some interbedded ash and breccia. Above the 3500-meter contour the mass is very largely pyroclastic, and the leading petrographic types are trachydolerite and andesitic basalt or basic augite andesite. (Plate IV, B.) The following analyses show the march of the differentiation:

	1	2	3
SiO_2	49.19	49.73	50.92
TiO_2	1.72	3.05	2.55
Al_2O_3	14.02	16.39	17.59
Fe_2O_3	5.62	7.58	3.80
FeO	8.68	3.98	6.69
MnO	.54	.23	.20
MgO	6.42	4.06	3.90
CaO	9.10	7.17	6.97
Na_2O	3.24	4.12	4.28
K_2O	1.04	1.93	1.86
H_2O-	.74	.81	.35
H_2O+		.54	.79
P_2O_5	.28	.84	.40
CO_2		None	None
NiO		.04	"
Cr_2O_3		None	"
BaO		.03	
SrO		None	
ZrO_2		.03	
S		None	
SO_3		"	
	100.59	100.53	100.30
Sp.gr.	——	2.911	2.761

1. Average analysis of twenty olivine basalts from Hawaii, representing closely the composition of the basement of Mauna Kea.

2. Andesitic basalt, flow at 11,000-foot contour, Mauna Kea.

3. Trachydolerite, flow at 13,000-foot contour, Mauna Kea.

Analyses 2 and 3 by G. Steiger in the laboratory of the United States Geological Survey.

Progress in Explosiveness at the Greater Vents.

The explosive effect at central vents is a function of the magmatic viscosity and of gas tension, which means gas concentration.

Though the presence of much gas tends to lower the viscosity, temperature is obviously in dominant control over that property of magma. The initial store of heat in the abyssal injection is normally lost through radiation in the crater, through conduction at the roof and walls of the whole magma chamber, through assimilation of country-rock, and possibly through the absorption of vadose water. As the whole mass cools, the juvenile gas emanates with ever lowering temperature and the lava of the volcanic conduit must have a slow decrease of average temperature.

Magmatic differentiation must tend to affect the viscosity of the upper zone of lava, the exploding zone, in the same sense. The more acid differentiate usually rises toward the top of the vent. Though differentiation may be roughly cyclical, the successive splitting tends to make a secular increase of acidity in the upper zone of the conduit magma. Hence, irrespective of temperature, there is an increase of viscosity in the magma zone where explosions originate. The case of Mauna Kea, just described, is an example of the partial control by magmatic differentiation over explosiveness. As the viscosity rises, the escape of magmatic gases is more difficult; the resulting tension is periodically relieved by explosions. Here also the action is cyclical, but there is, on the average, a slow increase in the amount of gas trapped before each explosion.

Again, the amount of volatile matter entering the magma column, either through assimilation of sediments or through the direct absorption of meteoric water, tends to increase with process of time. And, with the growth of a great, generally porous cone, the chance for phreatic explosion at or near the crater is favored.

All of these factors *work together* to produce maximum explosiveness at central vents which are long-lived because fed from great abyssal injections. The maximum normally appears in an advanced stage in the evolution of a first-class volcanic cone, though necessarily some time before complete extinction. Short-lived vents, opened above satellitic and therefore relatively small injections, will, of course, have no such tendency to great systematic change in explosiveness.

Lava Outflow at Central Vents.

A noteworthy feature of all central eruptions is the relatively insignificant size of their individual lava flows. Thoroddsen has estimated the volume of the celebrated fissure eruption of Skaptar Jökull in Iceland at 12,320 millions of cubic meters. He gives the volume of one prehistoric flow as 43,160 millions of cubic meters; of a second, 500,000 millions of cubic meters. In striking contrast are the following examples of the larger recorded flows at volcanic cones.

Locality.		Date.	Volume in millions of cubic meters.	Authority.
Semeroe, Java		1885	300	De Lapparent.
Etna		1669	980	von Waltershausen.
"		1852	420	"
"		1865	92	"
"		1879	57	"
Mauna Loa,	Hawaii	1852	299	J. D. Dana.
"	"	1855	455	C. H. Hitchcock.
"	"	1880–1	413	" "
"	"	1907	153	E. D. Baldwin.

Geological investigation shows that the flows from the central vents of Paleozoic and later periods have been of the same order of magnitude as the flows of the human period. With very few exceptions or none at all, these larger flows have issued from lateral fissures in the cones, and a large part of the volume of each flow is readily explained as the lava drained out, hydrostatically, from the upper part of each conduit. Without recorded exception all overflows at the main craters are incomparably smaller than those noted in the foregoing table. Therefore, the ascensive force in central conduits is either slight, or, if powerful, is applied for short periods.

The smallness of individual overflows clearly suggests that the magma chambers which continue to feed central vents are very seldom deformed by important movements of the earth's crust. If the magma in the chamber were diastrophically pinched, we should expect, at times, relatively enormous lava-floods from central vents. Some authors hold, on the contrary, that the growth of a great cone sometimes occasions subsidence, so that crustal movement may be a consequence rather than a direct cause of lava overflow at central vents.

Without entering further into this subject, it will here suffice to mention the principal causes for lava outflow as deduced from the abyssal-injection premise. These are:

1. Very minute deformation of the feeding magma chamber.
2. The effervescence of lava, due to the periodic accumulation of magmatic gases in the vent. These gases may be juvenile or resurgent.
3. The assimilation of country-rock in depth, leading, probably, to increase of volume.
4. The increase of volume through heating in the conduit "furnace" — a process specially like to occur during the dormant period when the vent is temporarily plugged.

These causes may co-operate, but at basaltic volcanoes the third is clearly subordinate.

The Two Types of Lava Flows.

A preliminary study of the Hawaiian lavas, with respect to their field habit, has led the writer to suspect significant gas-control even in this detail of vulcanism. On the average the vesiculation of pahoehoe or ropy lava was found to be more evenly developed than in the aa or block lava. The contrast is illustrated in Plate V. The rather uniformly disseminated vesicles of pahoehoe are of relatively small and relatively uniform size, and tend to have spherical form. The irregularly distributed vesicles of aa lava are generally larger, though more variable in size; much fewer in number, and of less total volume per unit volume of rock; and more irregular in shape. These facts indicate a more uniform distribution of gas in the pahoehoe than in the aa type. The aa vesicle, which is often thousands of times bigger than the average pahoehoe vesicle, has undoubtedly grown through the coalescence of many bubbles of gas. Such growth must in very high degree (see page 78) favor the escape of the gas into the air, and we may regard these large vesicles as representing so much gas trapped in the freezing lava. Before solidification had set in, gas must have escaped from every aa flow in large volume. In fact, observers of the two types in actual movement agree that the gas emanation from flowing aa lava is much more abundant than that from flowing pahoehoe.[49]

The difference of field habit in fluent lava and block lava is thus explained, with some show of probability, by the relative abundance of

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[49] Cf. J. D. Dana, Characteristics of Volcanoes, New York, 1891, p. 212. Judge Hitchcock describes a typical Hawaiian aa flow as advancing "with no explosions, but a tremendous roaring, like ten thousand blast-furnaces all at work at once."

volatile matter and, still more, by the evenness of its distribution. For both reasons pahoehoe lava is certain to be less viscous than is aa lava, other conditions being the same; the pahoehoe moves, as it were, on molecular and vesicular "ball-bearings."

The fact that many flows, from the very points of emission, are altogether of the one type, while others are throughout of the other type, shows that the differences of gas-distribution are developed in the vent. The problem as to exactly what circumstances there control the gas-distribution has not yet been solved. Slight differences in temperature, or differences in the advance toward solidification (with gas expulsion) may be the effective cause. The writer has observed a tendency for the phenocrysts of aa lava to be of larger average size than those in pahoehoe lava which gives practically the same oxide proportions in ordinary chemical analysis (volatile matter other than water neglected); but he is as yet not prepared to regard this as an established rule.

Vulcanism Originating in Satellitic Injections.

We have so far considered central vents as, in general, direct offshoots of main abyssal injections. The latter have been described: as dike-like, though often of great widths; as extending upwards from the primary substratum, nearly or quite to the earth's surface for some such vertical distance as forty kilometers. Batholiths have been interpreted as chemically modified abyssal injections of the primary basalt. Plutonic stocks and bosses represent cupolas in batholithic roofs. Stocks, bosses, and batholiths compose the group of "subjacent" intrusive bodies.[50] Laccoliths, sheets, and ordinary dikes are individualized bodies, satellitic with respect to their feeding abyssal injections, and like the latter, owe their intrusion to a simple parting of the invaded rock-formations. Irregular bodies intruded in the same fashion have been called "chonoliths"; they form a fourth class of "satellitic injections."[51]

All satellitic injections soon lose thermal and hydrostatic connection with their respective abyssal injections. All laccoliths and chonoliths, like most sheets and some dikes, have solid floors during most of their magmatic activity. If a satellitic injection is of large size, its content of heat energy and of gas may suffice to open one or more vents to the earth's surface, according to the methods already described. Volcanic action is thus initiated which differs in some respects from that due to direct emanations from a main abyssal injection.

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[50] R. A. Daly, Journal of Geology, **13**, 508 (1905).

[51] Cf. Journal of Geology, **13**, 498 (1905).

The importance of this fact is manifold. Its recognition aids in our understanding: the short life of many volcanoes of the central type; the lack of lava flows at many of them; the independent activity of neighboring vents; the chemical dissimilarity of the lavas from neighboring vents; the quite common clustering of many small vents in a region which shows no trace, or but few traces, of the alignment of its volcanoes; and the frequent evidence of surface deformation in such regions. The evidences for this type of vulcanism are indirect, but they are numerous; taken together, they form a combination of no mean strength.

In the first place, an excellent analogy to the vents from satellitic injections can be observed in nature. The blow-holes and driblet cones formed on the surface of the deep lava flows of Etna, Réunion, Hawaii, Savaii, etc., are continued in their brief activity because of the thermo-gaseous energy of lava quite removed from the parent vent. The blow-holes occasionally opened in the dome-shaped "bulges" or "tumuli" formed on the pahoehoe of Hawaii or Réunion are particularly instructive, for such tumuli, when just formed, represent small laccoliths of still fluid lava capped by recently frozen lava-crust.

To the weight of analogy is to be added that of a priori reasoning. According to almost any of the extant theories of igneous action, vulcanism originating in magmatic satellites should be *expected*. Many satellitic injections of great size have been exposed by erosion; it would be a matter for distinct surprise if none of them ever perforated its roof.

Field observation must naturally make the compelling test of the principle. Have we any active example? Can we find traces of it in denuded regions where erosion enables us to study the anatomy of volcanoes? Each method of applying the field test has its own difficulty. In the first case the satellitic injection is inaccessible and can only be located through inference; in the second case it is but rarely that denudation could expose the injected mass without destroying the conduit above. Yet the writer believes that the field inferences seem to support the principle.

The case of Kilanea, as an illustration, will be presented in some detail; the conception was first clearly attained by the writer during his field-work at that volcano in 1909.

Kilauea, the Vent of a Satellitic Injection. — A glance at the government map of the island of Hawaii shows the reader that the contour lines are peculiarly shaped in the southeast quarter of the island. (Figure 12.) From a low depression a few kilometers west of Kilauea to Cape Kumukahi, a distance of fifty kilometers, the lines are rather

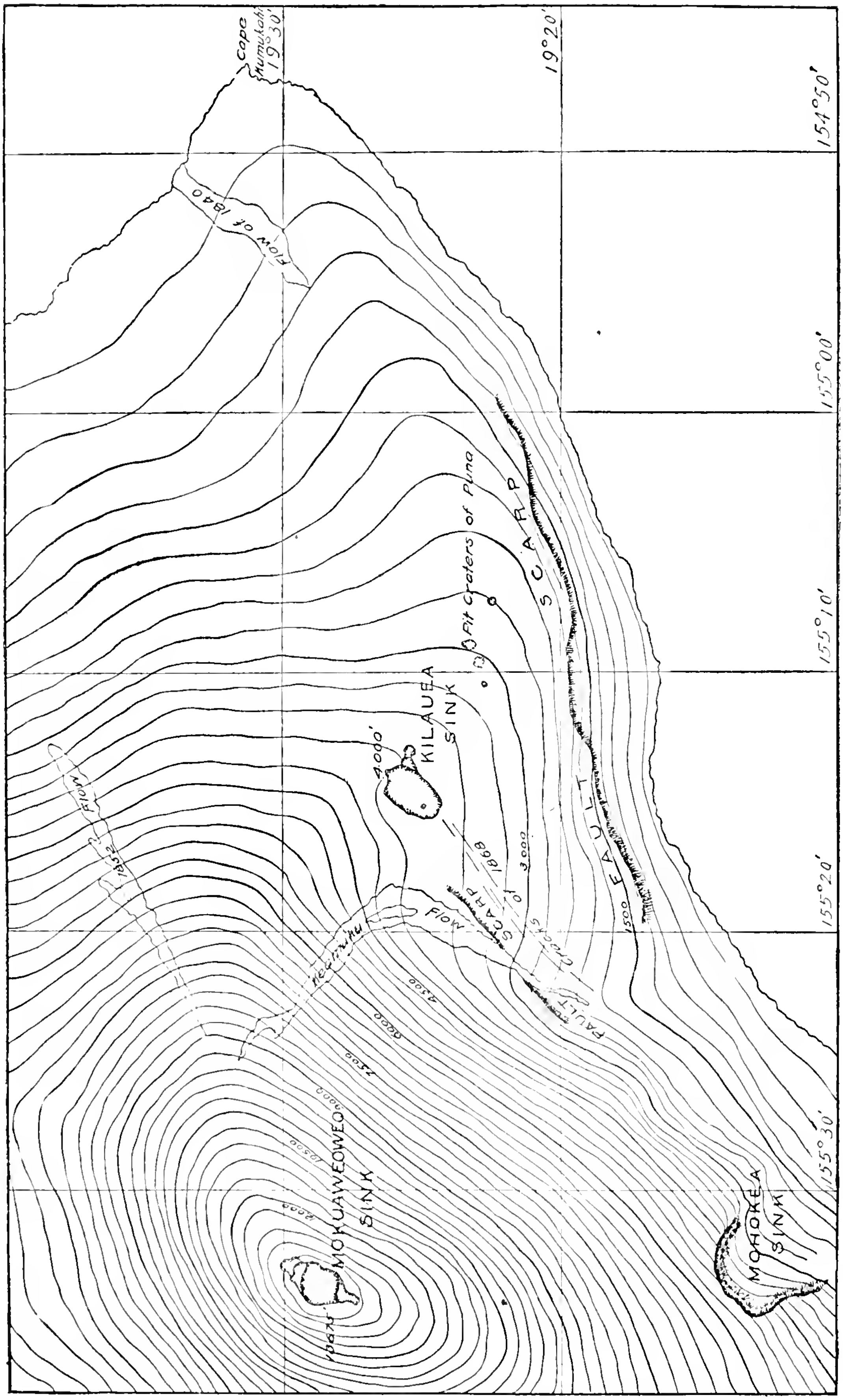

FIGURE 12. Redrawn Government map of southeastern Hawaii. Heights in feet.

strongly convex to the eastward. They there portray a long arch-shaped spur running out from Mauna Loa. From sea-level at the cape, the crest-line of the spur rises at the average rate of about twenty meters per kilometer, or 1 in 50. At Kilauea the spur is plateau-like, and immediately to the westward of the Kilauean "sink" there is a faint downward slope to the west. This arrangement of slopes does not mean that Kilauea is a crater surrounding a cone. It is rather a large pit or "sink" in the side of Mauna Loa (Plate II, A). Along the Kau coast, southwest of Kilauea, the Mauna Loa slope varies from 1 in 10 to 1 in 15, averaging about 1 in 12.

The broad spur is capable of two interpretations. It has either been built up by the specially prolonged extrusion of lava in this region, or it is due to local deformation of the general Mauna Loa slope, as if by deep-seated intrusion of the laccolithic type.

There is no sign that Kilauea has ever overflowed the outer walls of its great sink. The writer tried, in the field, to answer that question definitely by plotting the attitudes of the festoons of "ropes" on the pahoehoe flows forming the surrounding surface, but was defeated, through the failure to find a sufficient amount of that surface not covered by ash deposits. In any case, however, the general topography shows that no significant part of the spur could have been built up by overflows from this vent. Lava seems never to have issued from most of the many pit-craters situated on the back of the spur, and the total effect of activity of that kind at the other craters in the whole Puna district may have been a vanishing quantity so far as the development of the arch is concerned.

On the other hand, it is evident that lava flows from the upper slopes of Mauna Loa could not have constructed the spur in its present form. Such flows as do run down the southeast flank of the main volcano are deflected by the arch and run either northeastwardly toward Hilo, or southwardly into southern Kau. Finally, the spur does not appear to owe its principal volume to a succession of fissure eruptions along its axis. The flow of 1840 may be an exception tending to prove the rule. It represented a subterranean discharge of the magma chamber of which Kilauea is still the active vent. The formation of that chamber is really the point at issue. The injection of its magma might have followed or directly caused the formation of the spur; in either case extrusion of lava from the chamber is a wholly subsidiary and unessential fact. Further field work is necessary to determine how far the surface of the spur has been raised by local eruptions like that of 1840.

The alternative explanation of the spur-arch regards it as a mass of

Mauna Loa lava uplifted by a geologically recent intrusion of magma which is still fluid. The form of the arch suggests a laccolithic body. Though there is, perhaps, no possibility of proving it, this hypothesis has high value in giving a new explanation for the general independence in the activity of Mokuaweoweo and Halemaumau. The feeding channels of a typical laccolith are always narrow. They must freeze quickly and the satellitic injection loses hydrostatic connection with its parent abyssal injection. The latter may most simply be regarded as that underlying Mokuaweoweo now and during the building of most or all of the island of Hawaii. In other words, the postulated laccolith is an offshoot from the main Pacific fissure which located the Hawaiian archipelago. (Figure 13.)

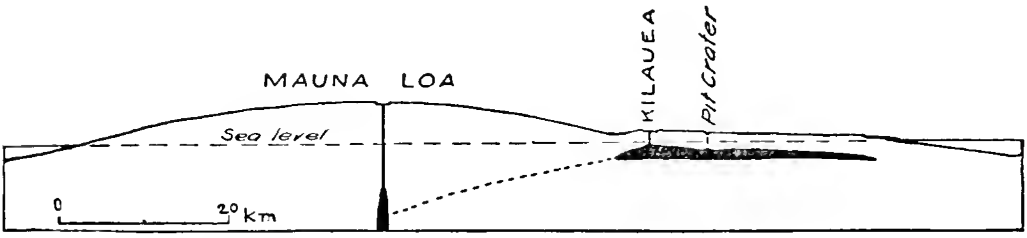

FIGURE 13. Diagrammatic section to illustrate the hypothesis that the Kilauean vent is fed from a large, still partly fluid laccolith injected into the side of Mauna Loa. The broken line represents the now sealed channel through which the laccolithic magma was injected; its course merely conjectural. Natural scale.

The remaining evidences favoring this hypothesis may be briefly listed.

1. The many pit-craters in the eastern Kau district and in the Puna district, including Kilauea, Kilauea Iki, Keanakakoi, Mokaopuohi, etc., are almost unique features in the whole island. (Plate IV, A.) Some of the pits on Hualalai are of similar form and their mode of origin may possibly be connected with another satellitic injection beneath that western cone. The pit-craters of Kau and Puna are not arranged in lines, as if located on master fissures, but are irregularly grouped in clusters. The field evidences show that most, perhaps all, of them have not been opened by explosion, and also that most of them have not emitted lava. The extinct ones, like the active Halemaumau, have been kept open by fusing gases. Their lives have been brief, because dependent upon temporary concentration of juvenile gases at the various points. In origin they are analogous to the clustered blow-holes on the crust of the Kilauean lake between 1820 and 1840.

2. The Kilauean records show that, from 1820 to 1911, that crater

has been decreasing in its activity with fair regularity. The very rapid rate of decline suggests a relatively small feeding chamber.

3. The imperfect observations so far made seem to show that the lava fountains of Mokuaweoweo more nearly approach brilliant-white heat than do those of Kilauea in the hottest state of its present eruption. The difference of temperature may be as much as 200° C.[52] Assuming that the magma of the Kilauean laccolith originally had the higher of these temperatures, the cooling would be of the order expected if the laccolith were of good size and not more than a few thousand years old.

If the average slope of Mauna Loa, before the laccolith was injected, was one in twelve, as now in southern Kau (obviously an uncertain assumption), a minimum estimate of the volume of the laccolith may be made. The top of the broad arch just east of Kilauea must have been raised at least 1000 meters, which is, therefore, the minimum thickness of the laccolith in that large area. The average thickness, as shown by the surface deformation, would be at least 500 meters and the area at least 500 square kilometers. The corresponding volume of the laccolith is 250 cubic kilometers. A body of magma of that size and endowed originally with the high temperature demonstrated at Mokuaweoweo, might, in part, remain fluid for 2000 years. There is nothing to indicate that Kilauea is so old.

Clearly little stress is due any such computation of the size. It can give only an order of magnitude. The magmatic body may be much larger, and it may have a form not ideally laccolithic.

4. Kilauea is the largest, the last, and most persistent of all the pit-craters for some good reason. The shape of the arch on which it stands suggests that it overlies the highest point in the roof of the laccolith, where the fluxing gases would naturally accumulate in largest quantity and where they would finally tend to emanate from the magma chamber. The smaller, extinct craters may easily represent so many points where irregularities in the roof, lower down, temporarily caused local accumulations of the gases.

5. Like the pit-craters, important systems of earthquake cracks like those of 1868 southwest of Kilauea, are concentrated in the Kau-Puna

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[52] Quite recently Dr. Tempest Anderson has recorded that, even in daylight, the lava of the active Matavanu lava lake in Samoa was, at the time of his visit in 1909, of brilliant-white incandescence (Quart. Jour. Geol. Soc. London, **66**, 627 and 632, 1910). This indicates a temperature little, if anything, short of 1400° C. The color of the hottest lava at the "Old Faithful" fountains of Kilauea of the same year was, in the daytime, a bright orange, corresponding to a temperature not far from 1200° C. The intensity of the heat at Matavanu has been, for years, of the order represented in the great eruptions of Mauna Loa.

region of the island. (Figure 14.) This fact is explicable on the laccolithic hypothesis for the origin of Kilauea, since the roof of such a body must evidently be in danger of fissuring and of moderate dislocation.

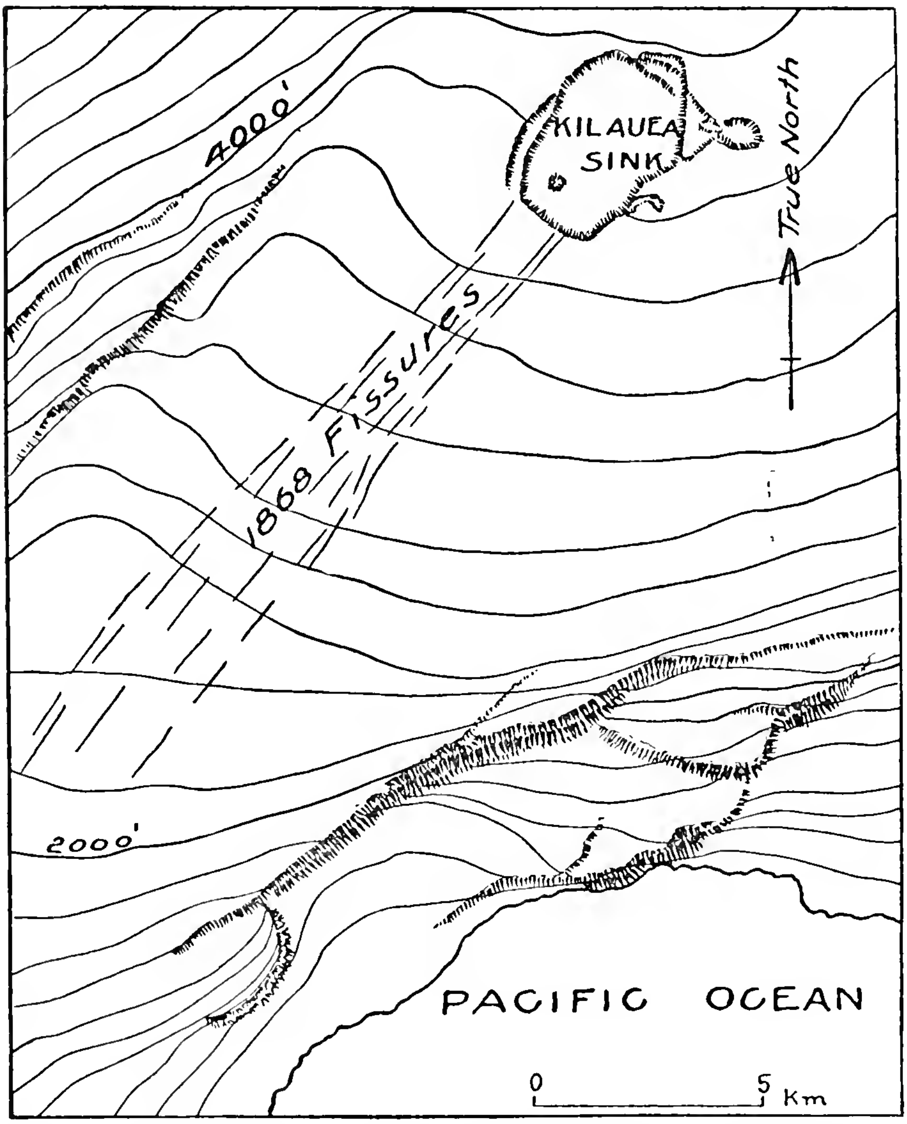

Figure 14. Redraft of the Government MS. map (1907) of part of southern Hawaii, showing fault-scarps and "earthquake" fissures. The long scarp in the south ranges up to 500 meters in height. Contour interval, 200 feet.

6. An obvious test of the hypothesis consists in the search for direct evidences of uplift in the laccolithic area. No notices of strongly elevated shore-lines in this region have been published. In view of the considerable number of good observers who have traversed this part of

the coastal belt, it is probable that neither old strands nor coral deposits are here to be found at any notable heights above sea-level. However, that fact, however fully demonstrated, could not invalidate the laccolithic hypothesis. Highly fluid laccoliths like that at Shonkin Sag do not disturb the strata into which they are thrust, to a greater distance from the edge of each laccolith than that equal to one-twentieth or one-tenth of the laccolith's horizontal diameter. Even for more viscous intrusions, like that at the classic Mt. Hillers in the Henry Mountains, this distance is less than one-fifth of the diameter. There is no sure reason for thinking that the edge of the Kilauea laccolith was near enough to the seashore of the pre-intrusion period to displace the coast-line materially. It is also important to observe that a fault runs roughly parallel to the longer axis of the great arch for a distance of about thirty-five kilometers. It is located from three to five kilometers inside the shore-line. Its downthrow throughout is on the seaward side, and the amount of throw varies from about 100 meters to 500 meters or more. (See Figures 12 and 14.)

The maximum displacement is registered in a remarkable cliff south of Kilauea. (Figure 14.) This greatest of all the pure fault-scarps in the island finds its own explanation, if we correlate the displacement with the upthrust incidental to the laccolithic injection.

7. The generally accepted hypothesis that Kilauea is a primary vent like Mokuaweoweo, entirely fails to explain the fact that we have no certain trace of a lava outflow over the wall of Kilauea. It places no difficulty in the way of the hypothesis here outlined.

8. Nevertheless, it is significant that, while Kilauea is less violent in its eruption than Mokuaweoweo, the lower vent is the more continuously active. The latter contrast finds simple explanation on the laccolithic hypothesis, which implies that the magma chamber of Kilauea, below the cylindrical vent, is much nearer the earth's surface than is the vaster magma chamber feeding the long pipe of Mokuaweoweo. The longer pipe is evidently liable to the more ready discharge by eruption through lateral fissures, and the space voided by such a discharge must, on the average, be greater than that voided in a discharge of Kilauea. A minute subsidence of the laccolith's nearly flat roof after a major discharge at Kilauea would be much more rapid than a similar settling of the thick roof over the main, probably narrower and more fissure-like chamber beneath Mokuaweoweo.

9. Finally, the laccolith has been imagined with the help of an actual example. Under the Uwekahuna triangulation station in the wall of the Kilauean sink, the writer found a small, but typical laccolith which arches the basaltic flows above it, and rests on older flat-lying

flows. (Figure 15.) This body, shown in complete section, is only about 150 meters long by 18 meters in thickness in the middle, thickest part. Its roof, still essentially unaffected by erosion, is little more than 140 meters thick. The rock of this small body is holocrystalline, wehrlitic in chemical composition, but having enough plagioclase to place it among the ultrabasic olivine gabbros. The body shows chilled contact phases and its injected origin cannot be questioned. We have here, barring volcanic perforation of the roof, a true homologue of the laccolith postulated to explain the peculiar history and relations of Kilauea.

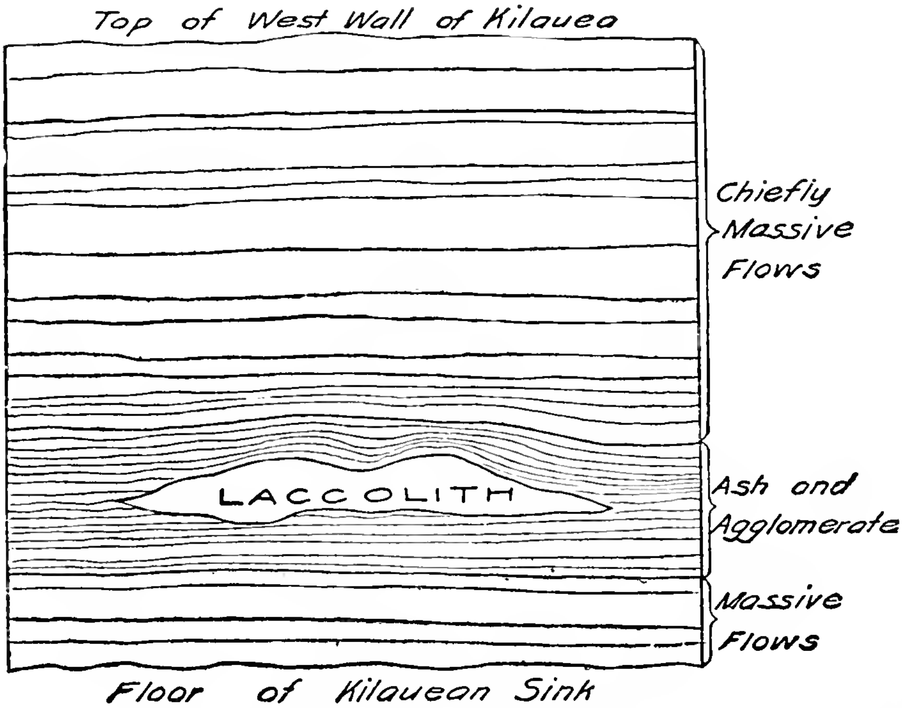

FIGURE 15. Diagrammatic view of wall of Kilauea at the Uwekahuna station, showing ultra-basic porphyritic gabbro injected into older volcanic layers. The "laccolith," arching the ash-beds above it, is about 150 meters in length. About natural scale.

In summary, we note the convergence of several independent lines of argument in favor of the suggested hypothesis. It seems justifiable to class Kilauea tentatively as the living vent of a still liquid satellitic injection. We may also conclude that it is unsafe to deny, simply because of the hydrostatic independence of the two active Hawaiian lava columns, that a primary fluid substratum of basaltic composition underlies the whole island.

An Icelandic Example. — Reck has suggested that the crater of the Hrossaborg in central Iceland is a gas-exploded opening (diatreme) in the roof of a laccolith. The injection is of comparatively late date, presumably Recent or Quaternary.[53]

We may now briefly note other probable examples of the opening of vents above satellitic injections. Testimony to its existence in former geological periods and in other regions tends to strengthen belief in the hypothesis as imagined in this Hawaiian study.

Tertiary and Older Vents from Satellitic Injections. Suabian and Scottish Examples. — As a result of his extraordinarily thorough study of the mid-Miocene eruptions in Suabia, Branco concluded that the Urach region is underlain by a "kuchenförmige Masse," or laccolith. In ground-plan its estimated diameters range between thirty and forty-five kilometers. Its position coincides with that of a very low, but broad doming of the Jurassic strata in the Bavarian Alb, as determined by Regelmann. Through secular erosion, the frontal escarpment of the Alb has retreated at least twenty-three kilometers since the volcanic epoch.

On the top of the Alb plateau are thirty-eight tuff vents; in the escarpment are thirty-five more, and in the "Vorland," or region traversed by the escarpment in its southward retreat, there are fifty-four tuff vents and five basaltic vents. No lava flows occurred on the Alb, and the few lava necks have become visible because of denudation in the "Vorland." Though the explosion funnels are still more or less intact on the Alb, the largest of them, the Randeck "Maar," does not exceed one kilometer in diameter. The average diameter of the 132 vents is far less. The evidence is clear as to the short life of each of these vents, which Branco has made the world type of "volcanic embryos." Their brief, almost wholly explosive activities, their distribution in a cluster without reference to master fractures, and the dome-like warping of the Jurassic beds in this region, all declare the justice of Branco's laccolithic hypothesis. Furthermore, his discussion of Mandelsloh's 340-meter boring at Neuffen shows that the temperature gradient in at least one part of the Urach region is abnormally high, about ten meters per degree Centigrade. Branco regards the abnormal gradient as due to the wave of heat still being conducted from the mid-Miocene injection. This suggestion is by no means extreme and it clearly tends to support his laccolithic hypothesis.[54] (See also p. 100.)

The peculiar abundance of small tuff-necks of Permian age in parts of Scotland is subject to a similar tentative explanation. Various memoirs of A. Geikie have made these vents famous as types of true

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[53] H. Reck, Monatsber. deut. geol. Ges. No. 4, 1910, p. 293.

[54] W. Branco, Schwaben's 125 Vulkan-Embryonen, Stuttgart, 1891. Cf. E. Suess, Das Antlitz der Erde, Bd. 3, 2te Hälfe, 1909, p. 655.

necks. In Fifeshire, eighty of them have been counted in an area measuring eighteen kilometers by ten kilometers. In western Ayrshire, sixty vents are found in an area measuring sixty by thirty kilometers, and, of those vents, twenty are necks occurring within an area of thirty-five square kilometers. In the great majority of cases, Geikie and his collaborators have been unable to find any connection between the positions of the necks and lines of dislocation. The Carboniferous strata have suffered sieve-like perforation like that of the Jurassic beds in Suabia. In each of the Scottish districts, the lower part of the very thick Carboniferous sedimentary series carries numerous thick sills of dolerite. These sills are mapped as chiefly Carboniferous in date, but Geikie thinks that some of the Fifeshire sills at least are Permian. The steady association of tuff-neck and sill in the Scottish shires scarcely looks accidental.

Gas emanations from the magma forming these actual intrusives or similar ones occurring in the underlying pre-Carboniferous formations, together with the possible emanation of gas from the heated country-rock, would seem to be competent to explain most of the tuff-necks. Explosive drilling (diatremes) and gas-fluxing might in turn dominate in the opening of the vents. The total activity must be small, because each gas-emitting or lava-emitting chamber was small.

The list of districts where the writer suspects secondary vulcanism includes also the area of necks in Noss Sound, Shetland.[55] These are small and the volcanic throats are filled with a coarse agglomerate of sandstone and shale. Peach and Horne infer that the vents never emitted any streams of lava.[56] The eruptivity is referred to the Lower Old Red Sandstone period. The date may be nearly the same as that of the injection or the thick sills and dikes which abound in the Noss Sound region.

A Necessary Division of Central Vents. — It is obviously difficult to devise field criteria which shall infallibly distinguish central eruptions respectively originating in main abyssal injections and in satellitic injections. Long and strong activity, large outflow of lava, and alignment in chains will generally characterize the central vents of abyssal injections. Brief activity, small output of lava, cluster grouping, and traces of surface deformation in the region are the expected features of the central vents of satellitic injections. As one or more of these features is absent or is obscured, the classification is hard to apply.

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[55] A. Geikie, Quart. Jour. Geol. Soc. London. Presidential Address, **48**, 95 (1892).

[56] B. N. Peach and J. Horne, Trans. Roy. Soc. Edinburgh, **32**, 359 (1884), and **28**, 418 (1878).

The chief object of the foregoing discussion has been, however, not to propose a division directly useful in field work, so much as to erect a fence over which speculation about the earth's interior cannot pass. The best way to check mischievous speculation is to advance beneficent speculation, founded on all the known facts. For example, the bold statement that there can be no magmatic substratum beneath a district bearing two simultaneously active lava columns of differing heights can no longer be made without an investigation of their nature as "principal" vents (abyssal injections) or "subordinate" vents (satellitic injections). The formal classification is of positive use in recognizing a mechanism by which the petrographic contrast of the lavas from neighboring vents may have originated. If two of these are opened above different satellitic injections, the chances are good that the magmatic histories of the injections will be different ; their emanating lavas would diverge in chemical type according to the progress respectively made in the formation of syntectic and differentiated magmas.

Some "subordinate" vents are monogenetic in Stübel's sense, and there are a few analogies between the system of vulcanism here suggested and that elaborated by the illustrious German. But the writer cannot agree with Stübel's principal conclusion as to the motor power in vulcanism, and entirely fails to find geologic or petrologic evidence for the existence of his "Panzerdecke."

GENERAL SUMMARY.

The general hypothesis briefly outlined in the present paper assumes, by sanction of the facts of general geology, that the earth is exteriorly composed of successive shells of density increasing with depth. Beneath the interrupted sedimentary shell is a continuous solid "granitic" shell, and still deeper, an *eruptible basaltic shell or substratum.* All igneous action, since an early pre-Cambrian period, is the result of the mechanical intrusion of the substratum basalt into the overlying shell. This fundamental process is specifically called "*abyssal injection.*" It is not a hypothetical process, but one which is clearly apparent in the chemistry and field relations of igneous rocks. The conditions leading to abyssal injection form a subject of great theoretical difficulty, but the discovery of the exact mechanism is not essential to the presented explanation of volcanoes. Nor is it necessary to decide on the degree of viscosity characterizing the basaltic substratum, although it is pointed out, once again, that the observed small amount of deformation of this planet under cosmical stresses does not prove that the substratum is crystallized. The central thesis of this paper is that all vulcanism is a consequence of abyssal injection, or in other words, that from the date of the oldest known pre-Cambrian lavas, every volcanic vent has been opened because of a preliminary *mechanical intrusion of molten basalt* into the *acid earth-shell.*

Emphasis is laid on the absolute necessity of classifying the gases and vapors which do important work at volcanic vents. These are either magmatic or phreatic in origin. The *magmatic* volatile fluids are subdivided into *juvenile* and "*resurgent*"; the *phreatic* fluids into *vadose* and *connate.* Each of these classes may be important in the dynamics of volcanic explosion; on the other hand, the juvenile magmatic gases are assuredly the most important in keeping a volcanic vent alive.

Besides fissure eruptions and central eruptions, the writer recognizes a class of vents not usually considered in treatises on vulcanism. This third kind of volcanic action may be called *foundering eruption;* the hypothesis is presented that some batholiths have swallowed up parts of their roofs, thus directly exposing a large area of each batholith to the sky.

This paper is chiefly concerned with the problem of central eruptions. They are of two main classes. In the "*principal*" class, each vent represents emanations from a main abyssal injection; in the other, "*subordinate,*" class, each vent originates over a magmatic body (laccolith, sheet, etc.) which is satellitic with respect to a main abyssal injection. Of these two classes, "principal" volcanoes must, on the average, be the more intense in activity, of longer life, more productive of lava-flows, and more clearly related to crustal fissures. The facts of the field suggest that Kilauea is a "subordinate" volcano. Tertiary and Paleozoic examples are probably represented in Suabia and Scotland. The localization of central vents and their very common alignment are explained by the principle of abyssal injection. Lack of alignment in a group of vents is suggestive of their "subordinate" origin. In the nature of the case, "subordinate" vents must, in their activities, show a high degree of *independence* of one another and of neighboring "principal" vents.

Continued eruption at a central vent is a heat problem. The primary heat of its abyssal injection is not the only source of thermal supply. A leading place in the theory should be kept for the supply due to chemical reactions among the primary constituents of the injected magma. Abyssal injection means an enormous change in the pressure conditions of the magma. As a result, the juvenile gases rise toward the top of the magma chamber. They are concentrated in the actual volcanic pipe and, according to the law of mass-action, exothermic reactions on a large scale are to be expected. The possibility that energy was potentialized in the primitive basaltic substratum by the formation of dissolved endothermic compounds, like cyanogen, ozone, hydrogen peroxide, etc., is indicated. In consequence of changes in pressure and temperature, due to injection, the dissociation of those compounds and the formation of new, stable compounds formed partly or wholly from their elements, give a double source of heat in the magmatic column. The heats of formation for the probable reactions are so great that small masses of juvenile gas might furnish a relatively large supply of heat. Though it is at present impossible to estimate the fraction of the total volcanic heat due to chemical reactions, a working philosophy of vulcanism should give due regard to the hypothesis that a central vent is a *true furnace.*

Using Siegl's recent results from experiments, the writer has calculated the approximate rate of heat loss through radiation at an active crater. The loss by radiation occurs, in general, at a much faster rate than the heat loss by conduction into the walls of the vent for a depth of many kilometers. The methods of the transfer of heat from the depths are discussed.

The principle of "*two-phase convection*" is concluded to be essential to the maintenance of prolonged activity at central vents. This conception is illustrated by the analogy of solid spheres moving, under gravity, in viscous fluids.

Explanation is offered for the dormancy and related periodicity of certain vents; for the typical shape of such a vent, and for its comparatively small size. These features, when coupled with long persistence in activity, are chiefly dependent on two-phase convection. Since the latter process is, in its turn, dependent on the rise of gases in the magma chamber, this general conception of central eruptions is called the *gas-fluxing hypothesis.*

The petrographic variety of lavas is to be largely explained on principles which have been demonstrated in plutonic geology. The lavas emitted at central vents may be: primary basalt; differentiates of pure primary basalt; syntectic magmas, i. e. those produced by the solution of foreign rock in primary basalt; or differentiates of syntectic magmas. The petrographic diversity in the lavas of neighboring volcanoes becomes better understood through the recognition of the two ("principal" and "subordinate") classes of central vents.

The explosiveness of volcanoes is a necessary step in the march of events following abyssal injection. The inciting cause is to be sought in the tension of resurgent gas as well as of juvenile gas. Progress in magmatic differentiation tends to favor explosiveness to an important degree. Magmatic and phreatic explosions must be distinguished if the tangle of vulcanological facts is to be unravelled. Though the rise of hot magma into rocks charged with vadose or connate water does often cause explosion, the steam-pressure produced by such volatilized water can no more be regarded as the cause of vulcanism than is the boiling of a kettle the cause of the heat in the stove. The formation of the magma column, extending through the earth's "granitic" and sedimentary shells to the surface, is the crucial problem. It is obviously a mere matter of detail whether or not the country-rocks at the upper end of the magmatic column are wet and therefore explosive.

The facts of volcanic geology seem, therefore, to co-operate with the facts of plutonic geology in showing that the essential process in igneous action on this planet is the rise of basaltic magma from the universal substratum along abyssal fissures in the earth's acid shell. The whole group of conceptions emphasized in this paper may be summarized in the name "*substratum-injection hypothesis.*"

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PLATE I.

A. Panoramic photograph of Halemaumau on January 13, 1910, with Mauna Loa in the background. The nearly circular lake was about 200 meters in diameter; its surface was estimated to be about 25 meters below the rim of the crater. Copyright by E. Moses, Hilo.

B. Panoramic photograph of Halemaumau on February 20, 1910. Lake level fallen about 30 meters below the surface of the "black ledge" in the foreground. Copyright by E. Moses, Hilo.

PLATE I, A.

PLATE I, B.

PLATE II.

A. Halemaumau, the crater in the Kilauean sink, taken from the Uwekahuna triangulation station by H. E. Wilson, Aug. 29, 1908. Diameter of crater about 500 meters.

B. The lava lake at Kilauea, taken at night (July, 1909) with an exposure of somewhat less than one quarter of a second, showing an outburst of "Old Faithful," an intensely luminous cave in the background, and a few of the brighter cracks in the "scum" on the lake.

PLATE II, B

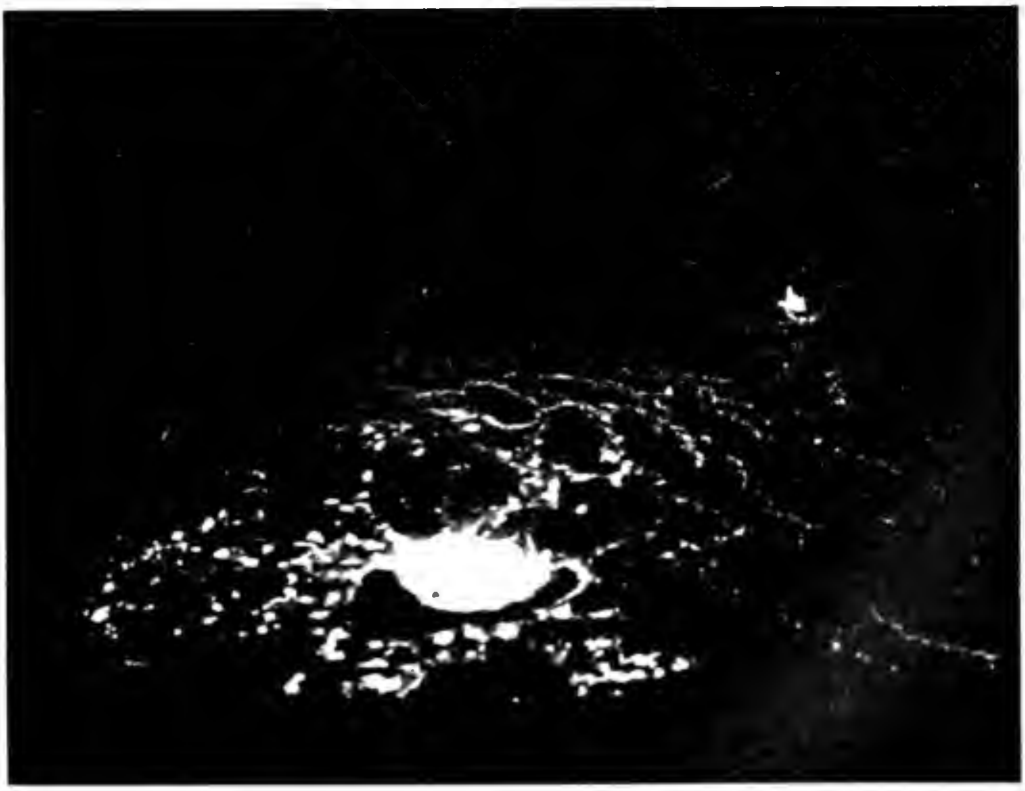

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PLATE III.

The largest of the Puna pit-craters in Hawaii. The plain is a frozen lava lake, the bottom of which is indicated by the inked line. Beneath that massive lava is old talus material, exposed in the fault-scarp of the foreground, which shows a maximum thickness of 60 meters for the lava prism. The conduit which fed this lake was probably at the deep hole overlooked by the fault cliff of the middle foreground. The lava plain is about one kilometer in length.

PLATE IV.

A. One of the small pit-craters of the Puna district of Hawaii. It is a pipe fluxed through the old, flat-lying lava of the Mauna Loa (fluent) type. The crater is about 175 meters in diameter.

B. Cinder cones from 100 to 200 meters or more in height, from summit of the highest cinder cone on Mauna Kea, looking northeast.

PLATE IV, A

PLATE IV, B

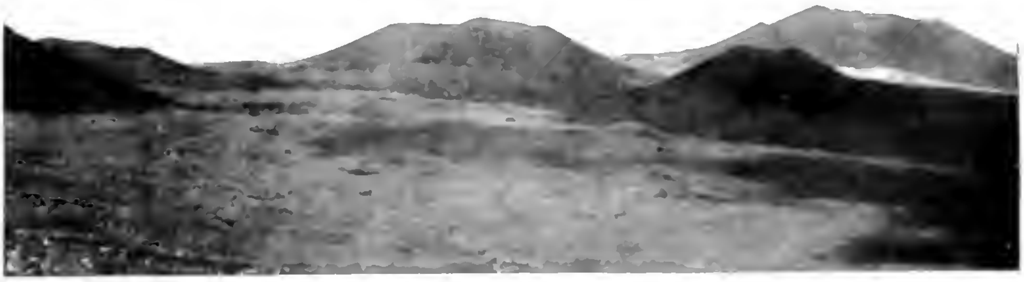


PLATE V.

A. Typical pahoehoe lava of Hawaii. About four-fifths natural size.

B. A common phase of the aa lava of Hawaii. About four-fifths natural size.

PLATE V, A

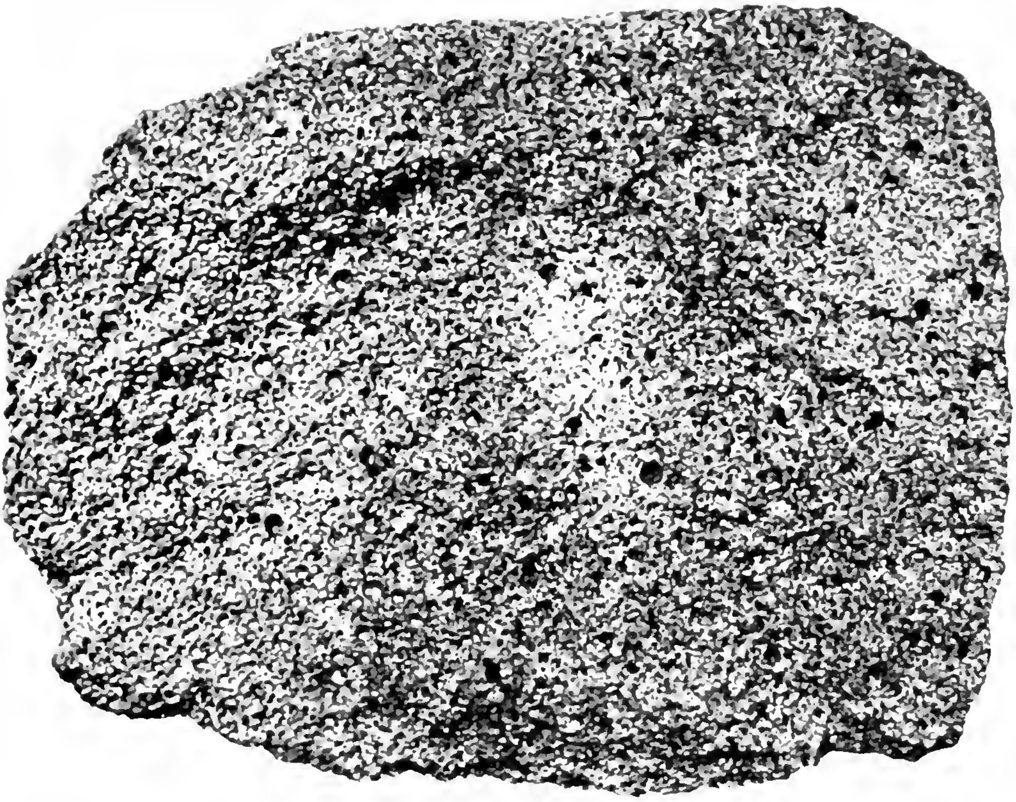
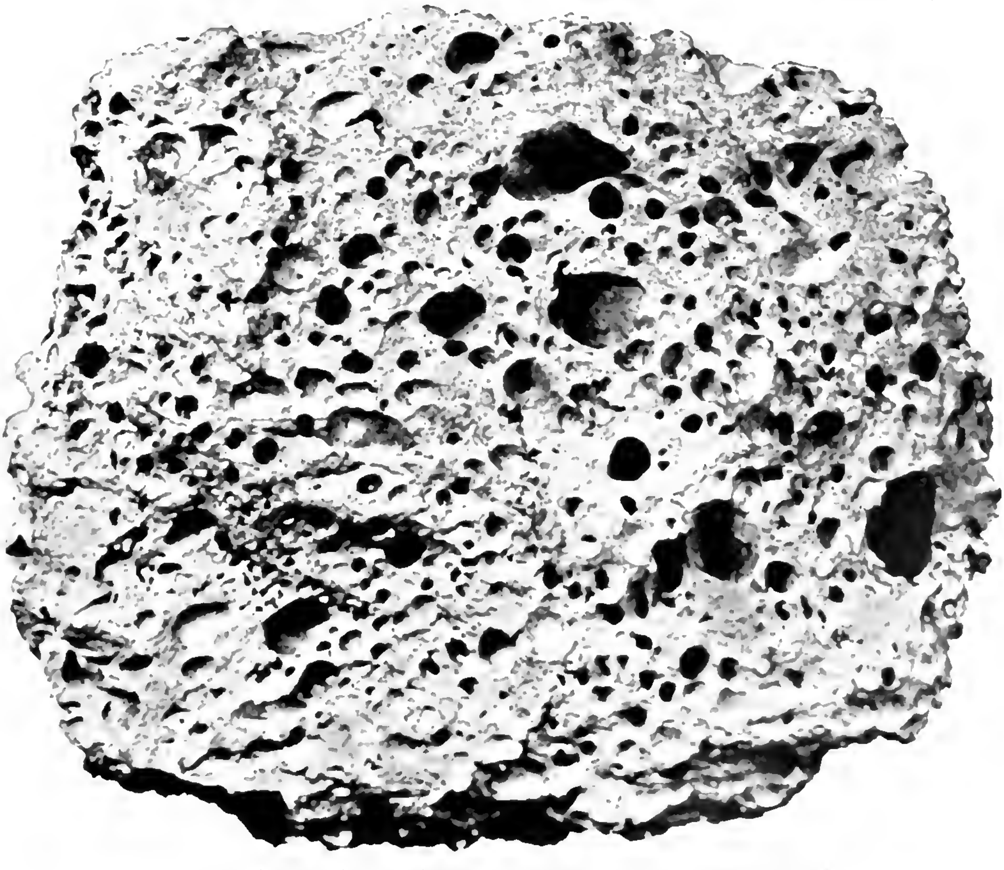


PLATE V, B



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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 4. — July, 1911.

THE PEGMATITES OF THE RIEBECKITE-AEGIRITE GRANITE OF QUINCY, MASS., U. S. A.; THEIR STRUCTURE, MINERALS, AND ORIGIN.

By Charles H. Warren and Charles Palache.

With Three Plates.

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Table of Contents.

Introductory.

The general geologic features of the area of riebeckite-aegirite rocks which have an extensive development a few miles south of Boston in the city of Quincy, and to the west of Quincy, in what is known as the Blue Hill reservation, have been brought most fully to the attention of geologists by Professor W. O. Crosby in a well-known memoir.[1] Taken as a whole the igneous rocks of this area form an intrusive mass of rudely elliptical outline measuring some 8 miles in length by 2 to 3 in breadth. They are intrusive into Cambrian strata and are quite certainly precarboniferous. They consist essentially of granite, extensive developments of granite-porphyry and quartz-alkali-feldspar-porphyry, the two last forming a cover over the granite; melano and leucocratic differentiation products; and large masses of apo-rhyolite, intrusive through the other rocks. On account of the economic importance of the Quincy granite it has received considerable attention from petrographers, and of it alone we have a somewhat full petrographical description.[2] Of the other rocks of the area, we have as yet

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[1] The Blue Hill Complex, Boston Soc. Nat. History, Occas. Papers, Vol. I.

[2] See particularly T. N. Dale, Bull. U. S. Geol. Sur., No. 354. Dr. Dale, besides giving a description of the granite, gives also the more important references to the literature of this region.

no adequate petrographical description; but work is now in progress which it is hoped may soon make good this deficiency.

Pegmatitic developments, so common in many granites, were almost unknown in the Quincy granite until some few years ago a mass of pegmatite was discovered in one of the quarries and later two other pegmatites were exposed in another quarry. These pegmatites possess so many features of unusual interest, structurally and mineralogically, both in themselves and in their relations to the enclosing granite, that it has been thought well to publish a detailed description of them; and with this task the present paper is concerned.

PART I. THE ENCLOSING GRANITE.

Before taking up the detailed description of the pegmatites it will be appropriate to give a very brief summary of the important characters of the enclosing granite. In texture it is equi-granular, hypautomorphic to xenomorphic and of medium to coarse grain. Mineralogically it consists of albite-microcline perthite, quartz, riebeckite with related alkali-hornblendes as yet not exactly determined, and aegirite, with zircon, ilmenite or magnetite, and fluorite as the chief accessories. The characteristics of the various minerals including their textural relations to each other, are quite similar to those of the main part of the pegmatites and it will be unnecessary to go into a detailed description of them here. It may be remarked that the rock shows evidence of having suffered from movements, the minerals being sometimes considerably disturbed or even crushed and recrystallized. The granite enclosing the Ballou and Fallon quarry pegmatites is practically identical with that in the adjoining Hardwick quarry of which Dr. H. S. Washington has given us a chemical analysis[3] which is here reproduced.

SiO_2	73.93
TiO_2	.18
Al_2O_3	12.29
Fe_2O_3	2.91
FeO	1.55
MnO	trace
MgO	.04
CaO	.31
Na_2O	4.66
K_2O	4.63
H_2O	.41
	100.91

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[3] Am. Jour. Sci., **6**, 181 (1898).

For a rock so high in silica the iron is notably high ; the alkalies are also high, particularly the soda, and account for the abundant soda-iron amphibole and pyroxene present in the rock. MgO and CaO are very low. At least one third of the lime is present as calcite.

Occurrences of Pegmatite in the Quincy-Blue Hill Area.

Up to the present time the following pegmatites have been noted in the area : 1st. Crossing the top of Rattlesnake Hill (east-central part of the area) in a nearly E. W. direction, is a narrow, dike-like vein of pegmatite. It has been traced for about 60 feet and varies from 8 to 10 inches in width. Structurally it is somewhat similar to the pegmatite pipes to be described beyond, having on both margins a zone of fine graphic-granite succeeded toward the center by rather coarse feldspar and quartz containing riebeckite. The center contains a few small crystal pockets and occasional masses of quartz. Another smaller and less regular vein of similar character occurs nearby.

2nd. On the low hill lying south of North Common Hill, Quincy, and just east of the railroad near Pine Hill on the top near its southern brow, are several veins and irregular spots of pegmatitic character. The granite near the top and on the steep southern slope of the hill is capped by a fine-grained granitic rock with a strong tendency toward a porphyritic texture. It dips gently to the south. It is in sharp contact with the granite and along the contact is frequently a rather abundant and coarse-grained development of riebeckite crystals. A few feet north, and underneath the contact in the granite, is an irregular streak of fine-grained granitic rock which contains streaks of much coarser quartz, feldspar, and riebeckite. Its width will average in the neighborhood of two feet and its length, while considerable, cannot be closely determined. While this may be a dike it may also be a detached piece of the overlying fine-grained rock. Its exact nature has not yet been determined. The granite in several places near the contact shows a local coarsening of the grain forming pegmatitic spots made conspicuous by presence of long black riebeckite crystals. Several vein or dike-like streaks of coarse texture also intersect the granite here. The smaller ones vary from one to about four inches in thickness, and are more or less irregular in course, and of only a few feet or yards in length. They consist essentially of feldspar, the usual microcline-microperthite albite, riebeckite, and quartz, and are for the most part considerably coarser in grain than the granite, but also contain a variable amount of fine granitic material. This sometimes forms a streak along the margin and again has an irregular distribution through the coarser material. The largest vein lies some ten yards north of the contact mentioned and has been traced for at least 75 yards in a nearly E. W. direction. The maximum width of this vein is about 12 inches. Along its strike, at least to the east, in which direction it is best exposed, it tapers to two or three inches in width. Its contacts are well defined, but are in the nature of a sudden coarsening of the granite. Its structure is symmetrical and indicates successive stages of formation. First come bands of coarse material 2 to 5 inches in width. This consists essentially of microperthite, albite, quartz, and riebeckite. The riebeckite is very conspicuous, suggesting tourmaline at first sight, and is the most abundant mineral present. While many of the riebeckite prisms are of small size, the average will measure from 1 to 1½ cm. thick and perhaps 5 cm. long. Many crystals are much larger, measuring 1 to 1½ cm. thick and 10 to 12 cm. long. There is a strong suggestion that there was originally an orientation of these normal to the walls, although they now lie at random and occasionally parallel to them. Although they frequently include feldspar grains, sometimes arranged symmetrically to their own structure, and are deeply indented (or corroded) about the margins, they nevertheless commonly show a fairly good crystal cross-section consisting of *m*, 110 and *b*, 010. They are commonly fractured and the fractures are filled with fine-grained quartz and feldspar. This band is succeeded by a narrow gray streak of much finer grained (1 to 2 mm.) which in turn is followed by a narrow (1–2 cm.) streak of a light brown color, of somewhat coarser grain than the preceding. In the gray streak the riebeckite crystals lie irregularly or, if anything, show a tendency to stand normal to the contact. In the central streak there is a marked orientation parallel to the contact. The microscope shows that this portion of the vein was probably undergoing movement during the process of crystallization. The larger grains are much disturbed in structure, broken, crushed, recrystallized particularly about the margins, and are surrounded by very fine material consisting largely of albite or quartz grains with shreds and particles of riebeckite. Fluorite, ilmenite (or magnetite) and zircon are accessories. There has been considerable kaolinization, and ferruginous decomposition products and carbonates are often present. Except for the tendency of the riebeckite to develop rough prismatic outlines in the prism zone, the minerals are xenomorphic. Aegirite is entirely wanting. It may be noted that the enclosing granite here shows very little aegirite.

These pegmatitic developments are entirely different in character from those to be described later and certainly have a somewhat different origin. While no positive conclusion has yet been reached regarding them, they are believed to be closely connected in their manner of origin with the seams and veinlets occurring elsewhere in the granite which are rich in riebeckite. The formation of these appears to be connected with a period of movement attended by fracturing of the granite and followed by a healing up of the fractures with granitic material. (See general discussion at the end of Part I.)

3rd. Three masses of pegmatite, pipe-like in form, one located in Ballou's and the other two in Fallon's quarry, both quarries being close together on the south central portion of North Common Hill, Quincy. These pipes are, up to date, the only important pegmatites of the Quincy area and are the special subject of this paper.

Occasional small patches of coarser texture than the granite occur in several places in the area. Quite recently several have been found a little to the east of the Ballou quarry and just west of the Hardwick quarry. They are interesting because of a considerable content of molybdenite segregated about their margins.

THE PEGMATITE OF THE BALLOU QUARRY, NORTH COMMON HILL, QUINCY.

The pegmatite in the Ballou quarry was first brought to the attention of mineralogists in 1895, at which time it was examined by Dr. Palache. In 1908 a short description of it was published by Dr. Dale (Bull. U. S. G. S., No. 453, p. 49). Several handsome specimens were cut from it and polished by Mr. F. Wesley Fuller of West Quincy, one of the finest, a complete section, now in the mineralogical collection of Harvard University, being reproduced in Plate **1**, Figure 12.

The pegmatite was encountered at a depth of something like 100 feet, and its downward extension, covered by slide material, still remains in the bottom of the quarry. Its position is nearly vertical. Some twenty feet of it have been removed, and while its depth is of course largely conjectural, it seems safe to assume that it is at least 40 or 50 feet. Its form is that of a pipe, in places nearly cylindrical and again rudely lenticular in cross-section with small, irregular branches. It is always concentric in structure and sometimes shows an indistinct radial arrangement of its minerals from the margin inward. Its three shells or zones, although quite irregular in outline and width and intimately blended where they pass into one another, are nevertheless fairly distinct; likewise the contact with the granite is blended although the change from one to the other is sudden. The outer zone is characterized by being considerably darker in color than the granite about it. It is much heavier on one side of the pipe than the other. Its width is here from 2 to 5 inches and it is marked toward the granite by a greater segregation of dark constituents, chiefly rather slender aegirite or riebeckite crystals. These are arranged to some extent parallel to the margin. The same sort of segregation marks also the inner margin. Between these, the rock in texture and composition resembles closely the granite except that the riebeckite and aegirite are considerably more abundant and the mineral grains are all of larger size. The proportion of aegirite to riebeckite is also greater than in the granite. On one side of the pipe the dark margin is less prominent, the whole zone having practically shrunk to an irregular streak of granitic material in which the dark constituents are very abundant, particularly aegirite.

As a rule the next zone is an irregular one, 1 to 2 inches wide, of fine graphic-granite, containing a few prisms of riebeckite and aegirite. It is the least clearly defined of the zones and passes almost imperceptibly into the main part of the pegmatite. In places the graphic-granite seems to be almost or quite wanting and its place is occupied either by the coarse pegmatite or by a fine-grained mixture of microperthite, quartz, aegirite and a little riebeckite. The main portion consists essentially of a pegmatite or coarse-grained, aegirite granite, carrying some riebeckite, abundant accessory zircon, fluorite, ilmenite, and smaller amounts of other minerals including parisite. The feldspars are an albite-microcline-microperthite of a pale greenish color except where reddish from iron stains. Toward the center where they are the largest, they measure as much as 2 by 2.5 cm. They contain aegirite and riebeckite microlites and black inclusions, also the minute cavities common to all the feldspar of the granite and pegmatites. The quartz, in amount the next mineral present, is without crystal form. Its grains are, except near the center, on the average smaller than the feldspar and of a grayish to white semi-translucent variety. Toward the center the quartz is coarser and more abundant, and at intervals along the length of the pipe, it forms masses two inches or more in thickness and several inches long. In fact the quartz forms a more or less well-defined central core. The aegirite, besides occurring in the form of many small, light-green grains and prisms, forms also abundant, large prismatic individuals of a more or less composite character. These frequently measure 1 cm. in width and 2 or 3 cm. in length, are dark green in color, and form a very striking characteristic of the polished specimens. Riebeckite forms occasional large crystals always more or less completely enclosed by a parallel growth of aegirite. Riebeckite is also usually intergrown in the aegirite crystals and commonly forms a sort of a central core in many of the crystals. These should in fact be properly termed aegirite-riebeckite crystals. They often contain granular masses of dark purple fluorite mixed with zircon, ilmenite, and quartz, besides decomposition products, chiefly ferruginous in character, which are apt to discolor that portion of the crystal in which they occur. With the coarser material of this zone is more or less fine-grained material. This corresponds to the more abundant fine material to be noted later in connection with the description of the Fallon quarry pegmatites, and consists largely of quartz, microcline, aegirite, zircon, fluorite, ilmenite, a few grains of a nearly colorless, isotropic mineral of very high refractive index thought to be beckelite (see later), besides various secondary products. The larger feldspar grains lying about these fine-grained, zircon-rich areas, are particularly apt to contain small, slender prismoid crystals of albite which are probably later crystallizations, and are connected with pneumatolitic processes. Parts of this fine-grained material are very rich in zircon, and ilmenite (and hematite ?). Alteration develops in this material (see later) a red or brownish-red stain which produces in the rock the appearance of metallic spots. Occasional crystals of zircon attain macroscopic size and are well developed crystallographically. Thin sections of these zircon-rich portions show an interesting relationship between the quartz and zircon. There is a marked tendency on the part of the zircon to form granular intergrowths with quartz. In some instances relatively large zircon grains showing simultaneous extinctions are found enclosed in a quartz grain. In most cases, however, both minerals are granular. The zircon tends to form closely packed aggregates; the grains may have a parallel orientation, although they are often separate and show a more or less well-defined crystal outline. The quartz also shows a tendency to a parallel arrangement of its grains. The quartz-zircon intergrowths are commonly bounded as a whole by a crystal outline, apparently that of a zircon crystal having a short prism with the unit pyramid termination. This outline is usually marked by a string of small zircon grains. The quartz surrounding these areas has frequently a distinct orientation of its crystals perpendicular to the boundaries of the area, a feature that, indeed, may be obscurely visible in the hand specimen. The areas often penetrate adjoining feldspar grains and are closely associated with aegirite. Fluorite, ilmenite, and ferruginous alteration products are also quite abundantly mixed with the zircon and quartz. These zircon-quartz groups evidently belong to the pneumatolitic period and represent, it is believed, zircon crystals which subsequent to their formation suffered more or less recrystallization, replacement by quartz, and perhaps granulation. Figure

14, Plate 2, is a microphotograph of some of these zircon-quartz groups.

Mr. Dale [4] states that these spots consist of magnetite, titanite, epidote, zircon, allanite, fluorite, aegirite and quartz. So far as the present investigation has shown the iron oxide is practically all ilmenite, nor has titanite or epidote been identified in the material at our disposal. Two or three minute, dark reddish grains with a highly resinous lustre have been noted macroscopically, and are not improbably allanite, though this has not been positively ascertained on account of the very meagre amount. Ilmenite and hematite besides the mode of occurrence noted, occur frequently in the form of tabular crystals lying along the sides, or between the cleavages of the feldspars and in the aegirite. The parisite has been observed to occur in crystals, a millimeter in diameter closely associated with aegirite crystals, quartz and fluorite, and clearly belongs, as in the other pegmatites, to the last stage of crystallization of the pipes, and is apparently pneumatolitic in origin. It may be noted that small amounts of galena, sphalerite, chalcopyrite, molybdenite occur in small grains here and there through the pegmatite. For other details relating to the minerals see the later description of the large pipe of the Fallon quarry and the special descriptions beyond.

The Fallon Quarry Pegmatites.

The first pegmatite discovered in the Fallon quarry outcropped at the surface on the south rim of the quarry, where a small remnant of it still remains. From this point the pegmatite, having a similar pipe-like form, and quite similar otherwise to the pegmatite in the Ballou quarry, dipped down into the granite to the north at an angle of about 45°. Following this course, it extended to a depth of about 75 feet (vert.) and then terminated. There is now no trace of it in the bottom of the quarry, but many fragments of it, still remaining on the dump, show clearly its structure and composition.

The second and far more interesting pegmatite follows the same general direction but appears to have flatter dip, and lies below and to the south of the first. The uppermost part yet exposed appears in the southern wall of the quarry about fifty feet below the surface. Here it resembles the first pipe except that it is larger. Along its downward extension, it increases in size, becomes rudely elliptical in cross-section, the major axis being vertical, and contains centrally toward its lower end a remarkable pocket. A few feet below the pocket the pegmatite terminates rather abruptly. Its total length as

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[4] Bull. U. S. Geol. Sur., No. 354, p. 50.

now exposed is about 20 feet. The indications are that it may extend upward into the granite toward the south for some distance.

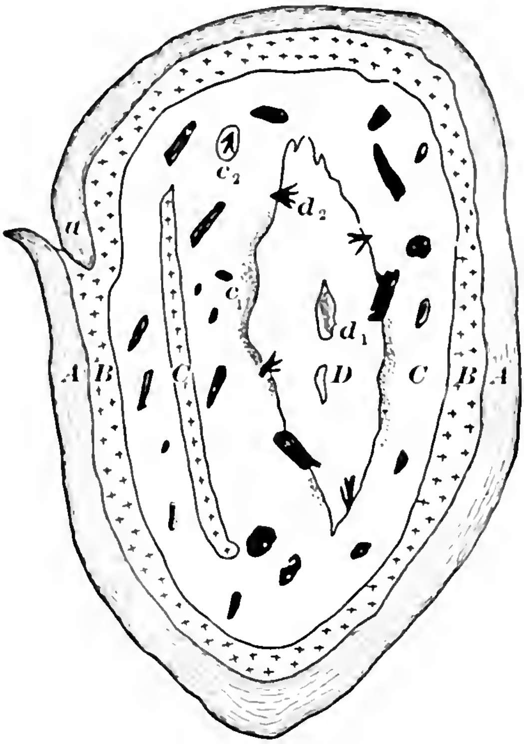

FIGURE 1.

Sketch of cross-section of upper portion of the large Fallon quarry pipe.

A, outer dark colored zone 2 to 5 inches wide, finer in grain than the granite, richer in dark silicates; both margins richer in dark silicates than the middle, and with an arrangement of minerals parallel to the margins. *a*, offset in the band.

B, zone of graphic-granite 2 to 4 inches wide. An intergrowth of microcline-albite microperthite (60 per cent) and quartz (30 per cent) with a few scattered prisms of riebeckite. Passes almost imperceptibly into the next zone.

C, principal zone of unequal, but prevailingly coarse-grained granite or pegmatite; contains a streak of graphic-granite (crossed) and numerous large crystals of riebeckite-aegirite. c_1, concentration of fine zircon, quartz, aegirite rich material next to quartz center. c_2, quartz bleb (2 or 3 inches) with penetrating aegirite prisms.

D, central mass of quartz, grayish-white and massive, penetrated by radiating aegirite groups and large aegirite-riebeckite crystals along margins (d_2) and containing centrally masses of sulphids with fluorite (d_1). One foot wide by two high, roughly.

Compare with Figure 13, Plate 1.

The concentric structure of this mass is marked as in the other pipes, but little if any radial structure can be seen. The section exposed in the quarry wall shows that in its general characteristics it is closely similar to the Ballou pipe. Figure 1 is a sketch of this section and with its legend will serve to give a general idea of the character and arrangement of its parts. It should be noted that the demarkation between the zones is not usually as sharp as those in the figure. Figure 13, Plate 1, a photograph, gives also an idea of its structure and appearance.

The dark marginal zone (A in the figure) is here somewhat finer in grain than the granite and much darker in color. There is a distinct arrangement of its minerals parallel to the margins which are also characterized by a greater abundance of dark silicates with which are numerous small grains of black oxides and chalcopyrite. The zone is particularly dark, fine grained, and sharply defined about the upper side of the pipe and in one place is sharply offset. Except in its finer grain, the parallel arrangement of its minerals and the greater proportion of dark minerals, particularly aegirite, which occurs to the exclusion of the riebeckite in some of the slides examined, the rock of this zone appears in thin section under the microscope to be much like the granite; the textural relations of the minerals are the same and their composition appears to be identical.

The zone of graphic-granite (B of Figure 1) seems to be practically continuous just inside the dark band above described and with a width of from 2 to 4 inches passes almost imperceptibly into the main zone of coarse granite or pegmatite within.

In the graphic-granite, individual cleavage surfaces of the feldspar will perhaps average two to three cm. on a side. Their long direction stands generally perpendicular to the margin. In this occurs, sometimes quite plentifully, riebeckite crystals somewhat intergrown with aegirite. The feldspar is a microcline-albite-microperthite. As determined by a Rosival measurement made on two extra-large thin sections it makes up approximately 60 per cent of the intergrowth. The albite appears to be slightly in excess of the microcline and always acts as the host. It strongly predominates about the margins of the crystals and quite generally forms practically the outside of the perthite crystals. The feldspar contains the same microliths of aegirite and riebeckite, the black specks and cavities, as do those of the granite. The contacts of the feldspars (largely the albite member) and the quartz are mutually indented and show what has been described by Pirsson[5] as the "interdentated" texture. Minute rounded grains of quartz are common just within the feldspar along the contacts, and suggest chains of tiny islands in appearance. The quartz contains

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[5] Am. J. Sci., **23**, 272, 1907.

minute black inclusions and fluid cavities often with moveable bubbles. The extinction of the quartz is usually quite uniform, there being little indication here of strains or crushing. The riebeckite forms rather flat, elongated prisms (1 to 5 mm. broad by 10 to 30 mm. long), but without terminations, the ends being always frayed or continued with aegirite. Aegirite with the exception of the growths on the riebeckite and the microlites in the feldspars is rather sparingly present in this graphic-granite zone.

The zone just described passes almost imperceptibly into the next and principal zone (C in Figure 1) whose leading characteristic is perhaps its irregularity of grain. Running through this material in a direction parallel to the outer margin is a narrow strip of graphic-granite (crossed in figure). It consists essentially of greenish-white crystals of albite-microcline-microperthite ; irregular grains of semi-transparent, grayish quartz, long black riebeckite prisms, often much intergrown and practically always surrounded and terminated on the ends by aegirite ; aegirite prisms and grains ; filling in the spaces between the larger grains is a considerable amount of fine-grained material. This may be light green in color when aegirite is abundant, but more commonly is brownish or brownish red. Occasional small crystal pockets occur in this zone, and in these parisite, fluorite, ilmenite, and secondary riebeckite have been noted. Parisite grains have also been found closely associated with aegirite and quartz, particularly near the quartz center. The fine material forms a more or less continuous network through the zone and in places forms patches of a centimeter or more across. Toward the central quartz zone the fine material seems to increase in amount and immediately about the quartz it constitutes almost a distinct zone itself.

Under the microscope the fine material is seen to consist of variable amounts of quartz, microcline with a little microperthite and albite, aegirite, zircon and ilmenite, magnetite (?), calcite and certain poorly defined decomposition products. The quartz and feldspar occupy spaces of about equal size, but under crossed nicols the feldspar breaks up into a mosaic of small equi-dimensional grains. The quartz shows an undulatory extinction. The aegirite is abundant in the shape of irregular grains lying for the most part in the quartz areas or between the quartz grains and the microcline. Many of the smaller grains lie grouped in such a manner as to suggest that they were once parts of a single crystal. Zircon is very abundant, particularly in quartz-rich portions of the fine material, and while some of the grains will measure 1 to 2 or perhaps 3 mm. on a side and exhibit well-developed short prisms capped by unit pyramids, the majority are small and appear at least in thin section to lack sharp crystalline form. The larger grains commonly show a fine zonal structure; the small ones are usually clustered, sometimes with parallel orientation and sometimes without, but in the latter case forming a mass often suggesting a larger crystal in outline as in the Ballou pegmatite. The zircon also lies almost wholly in the quartz or between it and the feldspar. Only a few grains have been noted in the microcline. Ilmenite and perhaps magnetite (?) are abundant with the zircon and by their alteration furnish the brownish or reddish-brown stain which often gives these colors the surrounding grains. Calcite is also present here, and is apt to be closely associated with the clusters of zircon, frequently embedding them. Closely associated with the calcite and the stained areas, sometimes quite abundantly, are several other products evidently secondary. One resembles chlorite. Another compact yellowish material has not been identified. The zones in the zircon crystals, particularly the outer zone, are often filled almost to opacity by a fine light brown to red, dusty product. In spots the smaller zircons are also more or less filled with it. What this product is has not been determined.

The feldspar of the coarser-grained portion is the same microcline-albite-microperthite as that in the granite. Its color is usually a pale greenish-white, although it is sometimes reddish from the alteration of small plates of ilmenite or hematite which occur along the cleavage planes. The crystals are rudely rectangular in outline but always with xenomorphic outlines towards the other minerals. In size they vary greatly, ranging from grains 3 or 4 mm. on a side to ones 1.5 by 2 cm., rarely larger. The average probably lies about midway between these figures. As in the granite, the albite strongly predominates about the outside of the grains. Smaller, relatively long and narrow shreds of albite lie in or along the margins and to some extent within the body of the crystals. The usual included microlites of aegirite and riebeckite as well as the minute black particles and cavities are present. A little kaolinization has taken place in portions of the pegmatite.

Aegirite and riebeckite are both abundant. Taking the zone as a whole the former is the most plentiful. The riebeckite forms elongate crystals ranging in size from small grains up to large and very conspicuous crystals, 1 to 2 cm. in diameter and 5 to even 15 cm. in length. The larger crystals are more abundant towards the center and may extend out into the quartz center. Although indented by the feldspar and often including grains of it, the riebeckite, especially in the larger crystals, shows a tendency to develop a crystal cross-section made up of the forms 110 and 010. Terminal planes are wholly wanting. Without exception the riebeckite is intergrown with aegirite. Commonly in parallel position, though again without definite orientation (c axis in common), the aegirite may occur quite at random in the body of the riebeckite, but it is most abundant about the outside, particularly on the ends, forming an almost or quite continuous shell about the riebeckite. Indeed the ends of the riebeckite crystals are usually continued as a solid mass of aegirite. The aegirite may almost wholly replace the other mineral, there being only a core or a few shreds of riebeckite visible. Besides this mode of occurrence the aegirite is found scattered throughout the coarser parts of the rock and as noted, abundantly in the finer material — and as inclusions in the feldspar. The habit of the aegirite is distinctly toward a delicate columnar structure parallel to the vertical axis, and when broken the fracture is usually splintery. Often there is a marked radial arrangement of the prisms or groups of prisms. This habit is especially common along the contact with the quartz center where clusters of some size occur, the tapering aegirites extending out into the quartz. Occasional separate crystals may be seen lying in the massive quartz 3 or 4 mm. in thickness and several centimeters long. In general throughout this zone the main part of the aegirite, although clearly more closely connected with the quartz in period of formation than with any other mineral, appears to have to some extent preceded it, since a tendency toward automorphic outlines is commonly observed with reference to the quartz. Its color is prevailingly grass-green.

A commonly noted feature of the aegirite-riebeckite crystals is the occurrence in their midst of spots consisting of dark purple fluorite grains, associated with ilmenite, zircon, calcite. These are often stained with ferruginous products.

The central quartz (D of figure) is massive in character, semi-translucent and of a grayish or grayish-white color. Like the rest of the quartz it contains minute inclusions and cavities often with bubbles. Masses of granular galena and sphalerite, one nearly as large as a man's fist, also similar sized pieces of a very dark purple fluorite occur in places through the center of the quartz. Some of these were associated with blue crocidolite like that found in the large pockets.

On the other and western side of the pipe, the succession of zones is essentially the same except that they are not quite so wide.

Through the lower and thicker part of the pegmatite containing the large central pocket the section differs somewhat from that given above, is less regular, and shows sudden changes in character difficult to describe. Going from east to west through its thickest part we meet

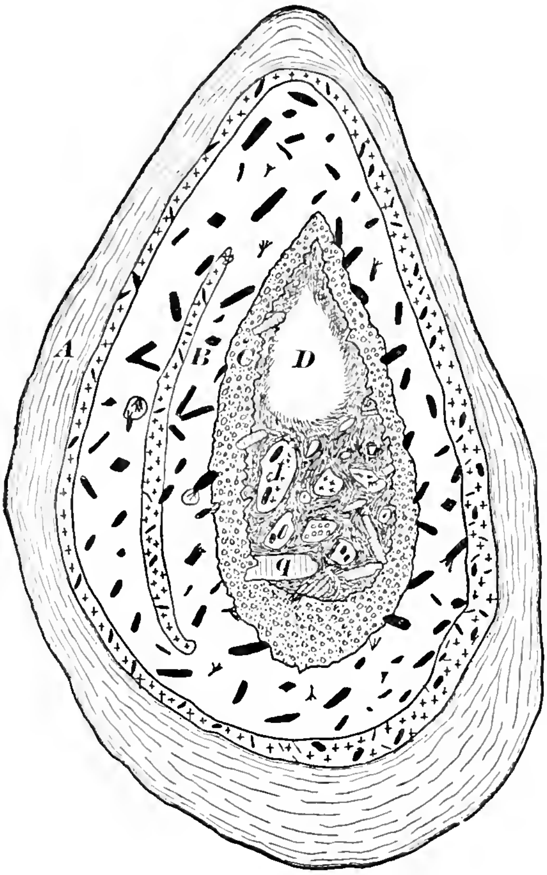

FIGURE 2.

Cross-section through the lower portion of the large Fallon quarry pipe at a point where the central pocket has its maximum development. The vertical dimension is about 10 ft., the horizontal about 6 ft.

A, dark marginal zone, similar in character to that described for Figure 1, but as a whole somewhat less sharply defined, and, in its lower portions, merging almost imperceptibly into the granite without.

B, main zone of the pipe showing a more or less well defined outer band of graphic-granite with streaks and patches of the same in other parts, but in the main consisting of an inequi-granular but prevailingly coarse mixture of microcline-albite microperthite, quartz, large, scattered aegirite-riebeckite crystals, aegirite, zircon, etc. Occasional quartz blebs and small crystal pockets are also present.

C, zone consisting of a porous, inequi-granular mixture of microcline and aegirite. This becomes exceedingly open in texture as the walls of the central pocket are approached and exhibits beautifully free crystallizations of aegirite and microcline on which are implanted crystals of parisite, octahedrite, and ilmenite.

D, microlitic cavity more or less completely filled with quartz crystals, free and attached, fluorite octahedra, fragments of all portions of the surrounding pegmatite, except the dark margin, and the whole embedded in a closely felted mass of beautifully fibrous, grayish-blue crocidolite.

first the dark marginal band (Zone A, Figure 2) here wider than further south, less sharply defined, coarser, and at the lower end merging almost imperceptibly into the surrounding granite.

As in the previous section this zone is succeeded by graphic-granite and uneven though rather coarse granite or pegmatite forming together a zone about 2 feet in width in its eastern and thickest portion, but much narrower on the western side as shown in the figure (B, Figure 2). It will be noted that in the figure a continuous band of graphic-granite (crossed) has been indicated just inside the dark margin; also another strip within the zone running parallel to the boundary. This misrepresents the actual facts to some extent. The graphic-granite is not, so near as could be told, entirely continuous, but is replaced at times, either by the coarse pegmatite, or by a finer, granular rock carrying rounded quartz grains and relatively long, slender riebeckite crystals. Occasionally streaks of large feldspar crystals lie in this latter material with an arrangement rudely parallel to the margins of the zone. These variations seemed particularly strong on the western side of the pipe, but the exact extent, however, of the graphic-granite, etc., was exceedingly difficult to trace accurately and no attempt to do so has been made in the figure. As elsewhere, the gradation of the graphic-granite into the main rock of the pipe is almost imperceptible. The texture and mineral composition of the main part of this zone is practically identical with that of zone B of Figure 1, previously described.

Along a somewhat irregular surface this zone changes rather abruptly both as to texture and mineral composition into the next zone (C of Figure 2). This latter varies considerably in thickness and consists of numerous, relatively large, rudely rectangular crystals of microcline (range of size, 4 or 5 mm. by 2 or 3 cm.) with xenomorphic borders, embedded in a groundmass consisting essentially of microcline and aegirite, quite fine in grain and highly porous in texture. In this groundmass the microcline usually predominates in amount although frequently the aegirite equals or exceeds it. Quartz, while present in the form of small grains in the groundmass, is hardly more than an accessory. As the walls of the central pocket are approached this rock becomes essentially a mass of rather loosely cohering, white or cream-colored microcline crystals and very abundant, dark green to almost black aegirite prisms and needles, the whole filled with small ramifying pockets into which the free ends of the crystals project. Although much of this material is rather course (centimeter) grained there is also a large amount of fine material. The feldspar crystals, although somewhat kaolinized in places, are as a whole remarkably fresh. Some crystals are deeply pitted by solvent action and where freely exposed, show a secondary growth of clear microcline substance. These later growths contain abundant inclusions of minute aegirite and riebeckite microliths, sometimes being literally crowded with them. The central part of the crystals appear to be rather freer from inclusions than the run of feldspar in the pegmatites. The aegirite occurs crowded in between the feldspars and projects in thickly clustered groups into the free spaces. Its crystals are of all sizes from mere slivers up to crystals 1 cm. broad, 4 cm. thick, and 3, 4 or 10 cm. long. The crystals show a strong tendency toward a composite subradial grouping and great irregularities of development. The larger crystals, to even a greater extent than the feldspar, show evidence of a strong solvent action, some of them being largely eaten away or completely honeycombed. Implanted on the surfaces of the feldspar and original aegirite crystallizations are many beautiful, light green patches of very minute, thickly clustered aegirite crystals of later growth. Occasional quartz crystals occur in the pockets or are embedded in the feldspar and aegirite near the walls of the main central pocket.

Implanted on the surfaces of the feldspar and aegirite, particularly in the pockets, are also: many slender, often richly terminated crystals of the rare mineral *parisite*, often including or closely associated with minute crystals of aegirite; small quartz crystals; minute, beautifully crystallized, black octahedrites, occurring as single crystals, in twinned couplets and in clusters; ilmenite, in the form of minute flat plates or in rosettes of black or grayish black color. Both the ilmenite and octahedrite are often abundant in the cavities formed by solution in the larger aegirite crystals. On the surfaces of the feldspar and closely associated with the parisite, there is sometimes to be seen a pale pink or buff coating of a material composed of tiny clusters of exceedingly minute, feebly translucent grains. The identity of this coating has not been determined, but it is thought to be zeolitic in character. Some of the aegirite and feldspar is also coated with a thin, blackish-red or brown film of iron and manganese oxides.

Inside the zone just described is a remarkable pocket (D in Figure 2) which is unquestionably miarolitic in character. Although a considerable portion had been removed when the pipe was first examined by the writers, the evidence collected shows that it was almost certainly a single continuous cavity of somewhat irregular contours with a maximum width of about 2 feet, narrowing upward along its strike and broader below than above. Its greatest depth vertically, as observed, was about 3 feet. It was continuous with the central mass of quartz exposed above in the quarry wall. It may be noted here, as indicated by the figure, that the position of the pocket is not exactly central since the zones on the eastern side are considerably thicker than those on the west which measure each only a few inches.

The Central Pocket. — The contents of the large central cavity were most unusual in character and consisted essentially of: quartz crystals of all sizes from exceedingly minute individuals up to great crystals, 10 cm. thick and 30 cm. long; rock fragments of all portions of the pegmatite except the dark marginal zone of sizes ranging from that of a walnut up to that of a man's head; fluorite octahedra, sometimes of large size; and a thickly felted mass of a delicate, grayish-blue crocidolite filled with minute hair-like crystals of riebeckite. The crocidolite embeds, more or less completely, the quartz and rock fragments.

Many of the quartz crystals, particularly the larger ones, were attached to the walls and included the microcline and aegirite crystals of the pocket lining. Others, and possibly the greater number, were wholly enclosed in, and enclose, the crocidolite, or were attached to the fragments. In fact, the crocidolite is literally crowded with quartz crystals, most of them quite small. Much of the quartz has been strongly attacked by solvent action, the crystals being deeply etched, pitted, and in some instances a good part of a crystal has been dissolved away. Some of the quartz is coated with the same black or brownish material noted on the aegirite crystals of the pocket lining. The minerals of the fragments show abundant evidence of solvent action and a later second growth. The riebeckite crystals in particular are often deeply honeycombed and in the cavities thus formed are later crystallizations of hair-like riebeckite, ilmenite, quartz, and fluorite. Some of the broken surfaces of the fragments have received a later growth of quartz parallel to the original quartz crystals of the fragment. The hair-like riebeckite, often suspending minute, pierced quartz crystals, frequently form beautiful clusters on the free surfaces of the fragments or in small cavities. Crystals of parisite are implanted in the same way on the fragments. Embedded in the crocidolite are casts of original fluorite octahedra sometimes partially filled with a mass of riebeckite fibers and crocidolite originally contained in the fluorite. The casts are generally discolored or partially filled by brown wax-like material. The large riebeckite crystals of the coarse granite or pegmatite bordering the upper portion of the central pocket also show strong corosion. Here the usual lining of microcline and aegirite appears to have been either very thin, or more probably was broken off, since many fragments of coarser pegmatite with aegirite and microcline crystals attached to one side are found among the fragments in the pocket.

Below and somewhat to the east of the central pocket (not shown in the figure) and apparently continuous with the aegirite-microcline rock surrounding the pocket, is a considerable mass of a fine-grained, light greenish-white rock of quite unusual character. The microscope resolves it into: quartz, microcline, and albite, a little microperthite, accessory zircon, ilmenite, calcite, fluorite, rarely parisite and probably the rare-earth silicate, *beckelite.* The albite forms perthitic intergrowths with the microcline only to a small extent, but occurs abundantly in the form of slender, simply twinned crystals elongated parallel to the edge 001 ∧ 010. In width they rarely exceed 0.06 mm., while the length varies from 4 to 20 times the width. These lie clustered around the microcline grains or between them and the quartz, often parallel to the margin and again projecting at random into them. They also occur quite thickly scattered through the microcline crystals, less commonly in the quartz. Their relation to the aegirite crystals is like that of plagioclase to augite in the diabases. Where the albite crystals lie together in parallel or sub-parallel position, their side lines are straight, but where they cross one another, or where they touch or penetrate microcline, quartz, or aegirite, the boundaries are sinuous and curiously irregular. The aegirite also includes, or is indented by the microcline.

The zircon is abundant for an accessory and lies mostly in the quartz. It exhibits much the same features as the zircon in the fine-grained portions of the main zone. The same is true of the calcite and ilmenite and the same alteration products are associated with them.

Associated with the zircon in the quartz is a small amount of a mineral whose properties are as follows: — color, pale yellow to almost colorless; habit, usually in rounded grains, but occasionally in sharp octahedra; cleavage, occasional, as prominent cracks, thought to be cubical; index of refraction, very high; isotropic. Unless this be some new species, its properties, as enumerated, point to its being the rare mineral, *beckelite*, a silicate of calcium and the cerium earths, discovered and described by J. Morozewiez from Balka Wali-Tarama, where it occurred in a dike-like apophysis of mariaupolite. The apophysis consisted of a sugar-grained groundmass of albite containing phenocrysts of nephelite and magnetite. (See Rosenbusch, Mikroscopische Physiographie, 1905 Ed., p. 395.) The occurrence of the parisite, also a calcium, cerium-earth mineral, in the pegmatite perhaps supports the identification of this mineral as beckelite.

An estimate of the percentages of the main constituents by the Rosival method, in this case only approximate, gave: quartz 26.1 per cent, microcline 22.5 per cent, albite 35.0 per cent, aegirite 14.2

per cent, remainder 2.2 per cent. This shows that the composition of this rock does not probably depart very far from that of the granite, although texturally so radically different. Figure 16 Plate III, is a microphotograph of a thin section of the rock and will illustrate its main features.

To what extent the texture of this rock may be original, and to what extent due to recrystallization under pneumatolitic conditions it is difficult to say. If original, we have a striking example of the strong contrasts of texture which may occur in a portion of a rock-magma rich in mineralizers, but not otherwise, so far as can be determined, very different in chemical composition. If a product of recrystallization, we see that there has been an almost complete separation of the potash and soda feldspars with the consequent destruction of the microperthite structure, as well as other minor changes.

CHEMICAL COMPOSITION, SEQUENCE OF CRYSTALLIZATION, ORIGIN.

Without an exact knowledge of the chemical composition of the pegmatites as a whole, a thing almost impossible to obtain, it is of course not possible to discuss with as much certainty as we could wish, the relationships that exist between the pegmatites and the granite. A careful consideration of the mineral composition of the two leads, however, to the conclusion that the pegmatites are decidedly richer than the granite in quartz, aegirite, zircon, fluorite, the rare earth mineral, parisite, and metallic sulphides. The central pocket in the Fallon quarry pipe, which was undoubtedly originally filled with water or water vapor, leads to the conclusion that the material from which the pegmatite formed was also richer in water or water vapor, a conclusion in keeping with the usual idea regarding pegmatites. Of the constituents present in the pegmatite in excessive amounts over those in the granite magma, the water or water vapor and the fluorine appear to be the only ones competent to have exerted an influence strong enough to have brought about any considerable variations in the texture of the two rocks. And after all it appears to be true in the present case, as has been suggested for other pegmatites,[6] that the main difference between the pegmatite and its granite is irregularity of texture in the former accompanied in part at least by a considerably greater coarseness of grain. In the present case there is also a remarkable zonal arrangement of parts as a further distinguishing mark.

The textural relations of the minerals in the pegmatites are, up to a certain point, identical with the granite, and show that a striking

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[6] Bastin, Jour. of Geol., vol. 18, No. 4, 1910.

characteristic of both is the great overlapping of the periods of crystallization of the minerals. In fact, if we take into consideration the small included crystals of aegirite and riebeckite in the feldspar and consider them as original crystallizations from the magma, we are forced to conclude that all of the minerals have been growing during the entire period of the solidification of the rock. This overlapping of the crystallization periods appears to be a characteristic of rocks of this type.[7] If, on the other hand, we disregard the small included aegirite, and riebeckites, it seems clear that the feldspar and riebeckite were first to individualize from the magma. If aegirite be an original mineral, and there appears no adequate reason to think otherwise, its period of growth must have begun well back in that of the original riebeckite and extended beyond it. In portions of the pegmatites and granite where aegirite predominates, or where riebeckite is wanting, the aegirite appears to some extent contemporaneous with the feldspar but the greater part is distinctly later. Throughout the granite and the massive parts of the pegmatites, the aegirite is closely associated with the development of the quartz as is also the zircon. It has been generally noted in riebeckite rocks that zircon has crystallized from first to last. In the present case, the mineral does occur in the feldspar and riebeckite, but the bulk of it is characteristically associated with the quartz, indicating a preference to a late development.

Murgoci, in discussing the origin of riebeckite, in the article previously alluded to, assigns a rôle of the utmost importance to mineralizers and variations of pressure as factors controlling the formation of riebeckite and aegirite in rocks of the Quincy type. He advances the idea that the question as to whether riebeckite or aegirite develops in a magma of this kind, depends entirely on variations in the pressure and the amount of mineralizers "(Fl, Na, Ti, Zr, etc.)" obtaining, or present at any given point in the crystallizing magma. Mineralizers are, doubtless, a leading characteristic of such magmas, and were certainly present in the Quincy-rock magma, but the evidence thus far available does not seem sufficient to guarantee to these mineralizers so critical a rôle. In fact the evidence gleaned from the present investigation, while it does not in any way deny to mineralizers an important rôle in the crystallization of the rock, seems to argue against the hypothesis referred to. The two minerals are not dimorphous, for they differ sharply in chemical composition. The aegirite for example, contains, 31.86 per cent of Fe_2O_3 and 0.87 per cent FeO ; the riebeckite

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[7] Murgoci, Am. Jour. Sci., **33**, 133 (1905).

contains 14.51 per cent of Fe_2O_3 and 21.43 per cent of FeO. Or the aegirite contains 22.98 per cent of iron, the riebeckite, 26.81 per cent, a difference of 3.83 per cent. There is an even greater difference in the soda content, not to mention minor differences. To convert one into the other calls upon the mineralizers and pressure, besides oxidizing or reducing a considerable amount of iron, to actually affect a considerable change in the chemical composition. It seems more reasonable to assume that the development of one or the other of these minerals depends primarily upon the relative concentrations at a given point of the various constituents which go to form the minerals.

The separation, whether by actual crystallization or by some process of molecular segregation prior to actual crystallization, of the feldspar and a part at least of the riebeckite from the magma, had the effect of greatly increasing the concentration of the more volatile or liquid constitutents, such as water, fluorine, also silica, the aegirite radical, zircon, etc., in the residual portions of the magma. The habit which the minerals crystallizing from such portions of the magma might or may have assumed, also the habit of the main part of the feldspar and riebeckite, has been somewhat modified by movements in the rock, either during the later stages of crystallization or subsequently, or both. This is indicated by the straining and granulation of the quartz; the deorientation of the portions of the feldspar, particularly the marginal portions; the development (recrystallization) of the smaller albite crystals about and between the larger grains; the frayed, granular, broken or otherwise irregular character of the last formed riebeckite and aegirite. Evidence of strong movements, accompanied by solvent and crystallizing action, are to be seen in the presence of the fragments in the large central pocket of the Fallon pipe, in the solution and recrystallization recorded there, and in the many seams, now sealed with relatively coarse riebeckite, feldspar, etc., which cross the granite in many places; also in the small quartz veins cutting the granite in some of the quarries. There is also abundant outside evidence that the granite has passed through profound periods of dynamic disturbance since intrusion. It was during some period or periods of movement, accompanied perhaps by an increase of temperature and possibly by a recurrence of pneumatolitic activity, that the development of the greater number of the minute cavities and the crystallizations of aegirite and riebeckite in the feldspar is thought to have taken place. Their location is generally in positions most favorable to the penetration of solutions, viz. — along the boundaries of twinning or perthite lamellae, or along cleavage directions. Other crystallizations of like origin but varying habit lie about the borders of the aegirite-riebeckite individuals, between the grains of broken quartz and in minute fracture zones. By admitting this mode of origin for these crystallizations we are at least relieved of the difficulty of explaining how the aegirite, with an undoubted tendency to develop in the main at a late period with or just preceding the quartz, should also have been the first secretion from the magma. It simplifies the sequence of crystallization. Future study of the porphyries, etc., associated with the granite will doubtless throw further light on this question.

The zonal structure of the pegmatites and the mineral composition of each shows that there was a progressive segregation of mineral-forming compounds. In each zone, however, we notice essentially the same sequence of crystallization as in the granite, as if such zone had to some extent at least crystallized as an individual unit.

Following out these considerations relative to the crystallization of the granite magma, etc., we may, perhaps, find a clue to the mode of the formation of the pegmatite masses. The earlier compounds which separated from the magma resulted in a gradual concentration of the more volatile and liquid constituents and of the elements or radicals which tend to accompany them. These, becoming segregated at certain points, determined by unknown local factors, tended to escape by rising through the surrounding material. In so doing they became elongated in form by reason of the drag exerted on their margins by the more viscous material enclosing them. Hence the pipe-like form. This idea of movement in the pegmatitic material finds support in the presence of the fluidal structure noted as characteristic of parts of the dark marginal zone. This structure also suggests that the band belongs perhaps as much to the granite as to the pegmatite proper, as does also its texture, mineral composition, and gradual merging into the granite through portions of its extent. The pipe in the Ballou quarry is far below even the present surface of the granite, nor is there any indication anywhere that these pegmatites ever succeeded in reaching the surface. They appear to have been imprisoned in the granite by its solidification.

While the exact process of formation of the zonal structure cannot be accounted for with certainty with our present knowledge of the factors determining rock differentiation and crystallization, the hypothesis which seems to the writers to be best in accord with the observed facts is as follows: — In the case of each pipe the entire mass of pegmatitic material from which they developed having segregated from the granite magma as above outlined, it retained by reason of its different composition (greater per cent of water, etc.) its liquidity and power for further differentiation, etc., and perhaps retained them even after the enclosing magma had solidified. Further differentiation into more or less clearly defined and well characterized zones then took place within this material, possibly by a process of fractional crystallization, although we are inclined to believe that the differentiation preceded actual crystallization and that each zone crystallized as an individual. This process resulted in still further concentration of the silica, water, fluorine, rare-earths, etc., toward the center of the mass resulting finally in the quartz centers, and, in the case of the large Fallon quarry pipe, of a free space or pocket filled with a watery solution.

It may be noted here that the graphic-granite zone with its 60 per cent feldspar and 40 per cent quartz seems to depart rather widely from the proportions of these minerals supposed by Vogt and others to be nearly constant and to represent a eutectic mixture. The graphic-granite does not, so far as we can see, correspond either in its mineral composition or in its structural relations to the rest of the pegmatite, to a eutectic mixture of the minerals of the pegmatite. In fact, not only in the present case, but in graphic-granites in general, there appear to the writers to be serious, if not fatal, objections to their being regarded as eutectic mixtures. The idea is at present little more than an interesting speculation suggested by a resemblance in the texture to that of known eutectics among metals and a crude approximation in a number of cases to a constancy in chemical composition.

At some time subsequent to the solidification of the pegmatite as a whole, but while there was still liquid in the pocket containing fluorine and some dissolved mineral matter, movements took place in the granite which were sufficient to fracture the pegmatite, fragments of which fell into the pocket. This was followed by the period of resolution and recrystallization already noted as occurring in the pocket and its lining and believed to have been contemporaneous with a similar process in the massive pegmatite and the granite as well.

It is possible that some portion of the crocidolite formation may have taken place at a later period perhaps even subsequent to the formation of the present system of joint cracks in the granite. As Dale has pointed out and others observed, the joint cracks are commonly filled with riebeckitic crystallizations, often crocidolitic in character.

PART II. SPECIAL NOTES ON THE MINERALS OF THE PEGMATITES.

Quartz. — Crystallized quartz is an abundant constituent of the central pocket of the Fallon pegmatite, individual crystals reaching a length of 30 cm. They are either smoky through included black needles of riebeckite, pale blue from inclusions of crocidolite, or quite colorless.

The smoky and blue crystals are invariably of simple quartz type, prism largely developed with positive and negative rhombohedrons; in the crocidolite the crystals are doubly terminated. Most of these crystals are deeply etched by solutions which have in some cases dissolved away the whole termination leaving a ragged pitted fragment; only occasionally has the etching been of a sort to leave solution planes and such as were seen were too rough to be measurable.

The colorless quartz crystals are of a later generation, are small and complexly developed, the following forms having been observed on the one crystal measured:

m$(10\bar{1}0)$, r$(10\bar{1}1)$, z$(01\bar{1}1)$, ⌈$(40\bar{4}1)$, e$(50\bar{5}1)$, s$(11\bar{2}1)$, x$(51\bar{6}1)$, u$(31\bar{4}1)$, $(21\bar{3}1)$, $(53\bar{8}3)$, $(8.5.\bar{13}.5)$, $(32\bar{5}2)$.

The crystal measured was a right-handed one; left-handed crystals were equally abundant and both types are commonly twinned on the "Dauphiné law."

One very interesting phase of the development of quartz crystals is seen on the surfaces of fractured masses of graphic-granite which have evidently remained after fracture in a solution capable of supplying silica. The quartz of the graphic-granite has grown outward into the surrounding free space, the crystals parallel over considerable areas and with good lustre and a smoky or bluish color but much etched. Some similar but less abundant growth of feldspar and riebeckite could also be observed on the same fragments. Almost always these fragments of regenerated pegmatite are cemented by finely felted crocidolite and the quartz is only revealed when the adhering fibres are removed by vigorous scrubbing with a stiff brush.

The quartz in the central portion and in the massive parts of the pegmatite all contains strings and sheets of inclusions other than riebeckite, etc. These are either minute black particles or cavities. In the more freely developed quartz crystals of the pocket the fluid cavities and black inclusions do not seem to be as abundant and often there are almost none at all. The cavities are exactly similar to those in the granite except that they probably reach a larger size on the average. In shape they are round, elliptical, pear-shaped or irregular; rarely they have been noted with a dihexahedral shape. The cavities commonly contain bubbles which can often be made to move from side to side by turning the stage of the microscope in an inclined position. The largest cavity noted measured 0.02 mm. and the bubble 0.005 mm. Many cavities may be seen from .001 to 0.010 mm. in diameter, while the bubbles will in general range from one fifth to one third of the diameter of their cavity. The cavities are often discolored with a ferruginous stain.

The quartz of the massive part of the pegmatites is relatively or wholly free from the minute microliths of aegirite and riebeckite so abundant in the feldspar. It appears to have been the last mineral to develop in the normal crystallization of the pegmatite as well as in the granite, and also to have been the last mineral to cease its growth in the secondary deposition which took place in the pocket.

The Feldspars. — *Microcline* in well formed crystals of orthoclase habit makes up the greater part of the porous material near the great central pocket. The crystals range from a diameter of two and a half cm. downwards to mere crystal specks; they are, however, very constant in habit presenting a remarkably cuboid form due to the dominant development of the base, clinopinacoid, and orthodome; prism and unit pyramid, the only other forms found, being very subordinate in size. The faces are smooth and give fairly good reflections of the goniometer signal. The albite twinning, shown by microscopic study to be universally present is not apparent on the exterior of the crystals: its presence makes the crystals sensibly monoclinic, however, and the measurements obtained approximate to those of orthoclase. Well formed Baveno twins are seen in a few specimens but most of the crystals are in clusters without apparent definite relation of the constituent individuals. The color of the microcline is white to pale ivory yellow. On faces of the prism, there is often a secondary coating of colorless glassy feldspar in parallel position to the main crystal which the microscope shows to be also microcline although its appearance strongly suggested the growths of albite so common on orthoclase from numerous localities.

Orientated sections, cut from the freely developed crystals of the pocket lining and from some of the larger crystals of zone C, show that the microcline is twinned after the albite law only and thus lacks the grating structure characteristic of microcline in general. In basal sections the twinning is seen to be very finely polysynthetic. The individual lamellae appear as short strips slightly elongated parallel to 010. Their boundaries are as a rule not sharp. The two sets of lamellae extinguish symmetrically on either side of the trace of the twinning plane at an angle of 16 degrees (average of 12 measurements). The clearer growths of later age are in parallel position to the older crystal and in them the twinning lamellae are often longer and more sharply defined. In the small microclines throughout the finer grained portions of the pipe the twinning is usually more sharply defined. The extinction in 010 sections was found from the average of ten measurements to be 5 degrees. Figure 17, Plate 3, is a microphotograph, in polarized light, of a basal section of one of the microcline crystals from the pocket, and Figure 16, Plate 3, one of an approximately basal section of a small microcline crystal in a thin section from some of the fine-grained portion of zone C. In these figures one set of lamellae are seen extinguished. Although there is some kaolinization, the crystals are as a whole quite fresh.

The microcline of the microperthite throughout the massive parts of the pegmatites, as well as in the enclosing granite, is also quite fresh. The relative amounts of microcline and albite appear to be fairly constant, the latter being slightly greater in amount particularly about the margins, and hence appears as the host. The microcline strips as seen in 010 sections appear as narrow bands with somewhat irregular outlines. They have the usual orientation, steeply inclined to the vertical axis, usually extend with fair continuity and variable width nearly across the width of the crystal, pinching out at or near the border. In basal sections they are commonly quite irregular in outline although they preserve in a general way a course across the crystal parallel to the ortho-axis. The twinning in the microcline, when present, is nearly always after the albite law only, "gitter" structure being rare. In many crystals the microcline strips show twinning throughout, in others a portion only of the strips show the twinning, while again a part of one strip will be twinned but not the remainder. There is a close similarity between the microperthite of the Quincy granite and its pegmatites and that of certain dike-rocks (aegirite-gorudite) from Norway. Brögger, Becke and Kloos [8] in writing of these dike-rocks from the neighborhood of Langesundfiord, Laurvik, Fredriksvarn, Lövö, etc., note that the predominant microperthite is a microcline — plagioclase intergrowth in which the microcline has the relations that orthoclase usually does. The microcline departs from the usual habit of granitic microcline in that the lack of the gitter-structure is altogether characteristic, the mineral being often untwinned, or again twinned after the albite law only. Microcline showing this particular habit of twinning has been termed moiré-microcline by Brögger to distinguish it from the more common "gitter-microcline." The general shape of the perthite lamellae and their manner of arrangement appears also to be much the same as in the Quincy rocks.

The *albite* throughout seems to have a composition not more basic than Ab_{95} An_5. Some measurements on the smaller separate individuals indicate that some of it may be nearer an albite oligoclase. The albite of the microperthite is characterized by its freshness and relative freedom from included black particles and cavities. As already noted

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[8] Zs. f. Kr., **16**, 54 et seq. (1890).

it usually strongly predominates about the outside of the grains, often forming the entire margin. It is generally very finely twinned, rather high magnifications being required for its clear definition. The twinning lamellae are usually broader and stronger in the marginal parts. The albite about the margins is often extended out into adjoining feldspar and quartz grains, and these parts are sometimes deorientated. Separate small crystals of albite, usually elongate in habit and finely twinned, are commonly found about the larger feldspar grains. These often penetrate into the adjoining crystals sometimes with sharp crystal terminations, particularly with reference to the quartz. With them are quartz and microcline and these smaller, interstitial grains in places form almost a groundmass for the larger crystals.

The peculiar relations of the albite to the microcline, quartz, and aegirite in the fine-grained rock lying below the central pocket in the Fallon pegmatite has already been described. It is especially noteworthy that albite is lacking in innermost portions of this pegmatite except in this fine-grained rock, and that here it is not in perthitic intergrowth except to a slight extent.

Inclusions in the Feldspar. — The feldspar of the pegmatite as well as the granite is remarkable for its inclusions. There appears to be a strong tendency toward regularity in their arrangement. Thus in sections they may be seen arranged roughly parallel to the twinning plane, the direction taken by the perthite strips, or to cleavage directions; again they appear to be wholly without definite arrangement. Aegirite and riebeckite microlites are both usually quite numerous, but their relative proportions vary considerably. It has often been observed that they are apt to be more abundant in the immediate neighborhood of large crystals of aegirite-riebeckite, and that they may in such cases even have an orientation exactly parallel to the large crystal. The riebeckite has the form of minute shreds or rods rarely exceeding 0.02 mm. in width and usually many times as long as wide. They sometimes form clusters. Strings of small crystals of riebeckite also occur along fractures in the feldspar. In optical character they correspond to riebeckite. Their prevailing color is a rather light to dark blue, often more or less smoky. The aegirite microlites vary much in size from grains whose dimensions are measured in thousandths to those measured by a few hundredths of a millimeter. Usually with a distinct elongation parallel to the vertical axis, they are often curiously irregular in habit. Sometimes particles of different sizes and shapes are arranged in strings following some definite direction through the feldspar. In color they are pale yellowish-green, or yellow to almost colorless when in very small grains. a is always parallel to the elongation and the extinction is very small. These have apparently been called epidote by Dale[9] and do suggest that mineral in appearance as does much of the coarser aegirite of the pegmatites. Epidote is, so far as observed, altogether wanting, a fact quite in keeping with the chemical character of the pegmatite.

The minute black particles, like occasional larger black grains, are probably mostly ilmenite or magnetite; some are hematite. They frequently give rise to slight reddish stains in their immediate surroundings. They are more common in the microcline than in the albite. Minute cavities are also abundant in the feldspar. These may be round, elliptical, almost rectangular, or amoeba-like in shape. Though sometimes partially filled with black, reddish or yellowish stains, they do not seem to have now any other filling.

Riebeckite. — Macroscopically the riebeckite is characterized by a black or bluish-black color, often rendered greenish by the associated aegirite. The crystals of riebeckite are prismatic, showing only outlines of the unit prism and occasionally a face of the clinopinacoid. Terminal faces were not observed. Measurements of the prismatic cleavage angle made on two fragments yielded identical values of 55° 5′, an angle considerably larger than that of common hornblende which is 55° 49′. A rather feeble tendency to part parallel to the base seems to be present. With the exception of the inclusions in the feldspar and some of the smaller crystals, the riebeckite is always intergrown with aegirite to a greater or less extent in the manner previously described. Where the riebeckite comes in contact with the feldspar and quartz, the two are always to some extent intergrown and as already noted small shreds or grains of riebeckite often lie near the contact sometimes with the same orientation as the larger grain. Again shreds grow out from the edge as if they were secondary growths. The riebeckite also usually contains abundant black particles and larger black oxide grains, presumably ilmenite. Occasional grains of feldspar, fluorite, and zircon are also included, and patches of carbonates, fluorite, ore grains, and zircon are often seen.

The deep color and strong absorption of the mineral makes the determination of its optical properties with any precision very difficult. This difficulty is increased by the fact that it has been found impossible after many trials to obtain entirely satisfactory sections of the mineral across the cleavage owing to its extreme brittleness. By the study of finely crushed material and thin sections the following characters have been made out:

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[9] Loc. cit., p. 49.

Ray near $c' = \mathfrak{a}$	Ray // to $b = \mathfrak{c}$	Ray near $a = \mathfrak{b}$
For sections 0.03 mm. or under, deep blue to bluish smoky green. For over 0.03 mm. nearly or quite black.	For 0.03 mm. thickness, very dark smoky green to almost black.	For thickness under 0.03 mm., yellow. For 0.03 and over, brownish yellow with a greenish shade.

Absorption $\mathfrak{a} < \mathfrak{c}$ much greater than $\mathfrak{b}$. For many sections intermediate in position between the front and side pinacoids, a peculiar dull, grayish blue (some might call this a drab or even see a violet tone of color) is seen. This is particularly true of thin cleavage fragments. In many sections parallel to the clinopinacoid it has been observed that the distribution of color is not uniform, the blue being seen in streaks parallel to the cleavage, or lying along lines crossing the cleavage, suggesting in appearance minute cracks along which there has been some slight chemical change. In such cases the remainder of the section had a dull green color. In the riebeckite from the pegmatites at least, such variation in color does not appear to be connected with any significant change in the chemical composition. Tests with the sensitive tint on very thin cleavage fragments show always a negative elongation. The extinction in 010 sections does not exceed 4 or 5 degrees, measured on the prismatic cleavage. Its accurate determination is rendered difficult by the strong natural color and strong dispersion of the mineral. A single section perpendicular to the prismatic axis was obtained sufficiently thin to yield, in convergent light, using a powerful illumination, a faint biaxial interference figure. The hyperbolae move well out of the field on rotation of the preparation, indicating a large axial angle. The axial plane bisects the acute angle of the cleavages. This is substantiated by the interference figure obtained from the 010 section which is clearly that of an obtuse bisectrix with the axial-plane lying parallel to the cleavage direction. The hyperbolae in figures from this section are faintly colored red and blue ; also interference brushes obtained from random sections are strongly colored red or blue indicating a strong dispersion, the exact character of which has not been made out. From the above it appears that the axial plane in this riebeckite lies *perpendicular to b*, 010, *an unusual relation for a hornblende*, while the acute bisectrix lies inclined by not over 4 or 5 degrees to c', and is negative. A determination of the index of refraction for the yellow ray $\mathfrak{b}$, by the immersion method, gave a value of 1.695 (sodium).

Chemical Composition. — Material for a chemical analysis was obtained from a single large crystal which appeared exceptionally free

TABLE I.

Nos.	1	2	3	4	5	6	7	8	9	10
Spec. Gr.	3.39	..	..	3.433	..	..	..	..	..	..
SiO_2	51.79	50.01	49.30	49.83	49.65	45.4	52.11	51.89	52.13	51.03
TiO_2	1.28	..	..	1.43	..	4.0	..	..	..	..
Al_2O_3	.68	..	..	.75[4]	1.34	..	1.01	..	..	..
Fe_2O_3	14.51	28.30	30.72	14.87	17.66	16.8	20.62	19.22	19.53	17.88
FeO	21.43	9.87	7.97	18.86	19.55	22.0	16.75	17.53	21.25	21.19
MnO	1.15	.63	..	1.75	..	..	..	..	..	..
CaO	1.28	1.32	2.75	..	3.16	4.2	..	.40	..	..
MgO	.10	.34	..	.41	..	0.6	1.77	2.43	.22	.09
Na_2O	6.15	8.79	By diff. 19.26	8.33[1]	7.61	6.7	(6.16)	7.71	6.26	6.41
K_2O	1.10	.72		1.44	..	..	..	.15	..	..
F	.20	..	..	..	..	..	..	..	..	..
$H_2O - 115°$ C.	.10	..	..	.20	..	..	..	..	..	..
$H_2O + 115°$ C.	1.30	..	..	..	1.67[2]	..	1.58	2.36[2]	3.95[2]	3.64[2]
Totals	101.26	99.98	..	97.87	100.64	99.7	..	101.69	99.74	100.24
Less 0 = 2 F	.09									
	101.17[3]									

[1] Including Li_2O.

[2] Total No. 5 and probably 8–9–10 are loss on ignition.

[3] The total is too high, a fault most difficult to avoid in the laboratory where it was made. In the summer when the windows have to be open the dust from innumerable trains and the street causes small increments, chiefly silica, to accumulate. — C. H. W.

[4] ZrO_2.

No. 1. Riebeckite, from pegmatite, Fallon Quarry, North Common Hill, Quincy, Mass., U. S. A. Analysis by Warren.

2. Riebeckite, Island of Socotra. Analysis by Sauer, Z. D. G. G., **40**, 138 (1888).

3. Riebeckite, Island of Socotra. Analysis by Sauer, ibid.

4. Riebeckite, Colorado, U. S. A. Analysis by Koenig, Zs. Kr., **1**, 430 (1877).

5. Riebeckite, Cape Ann, Massachusetts, U. S. A. Analysis by Dr. J. F. McGregory. Quoted by Rosenbusch, Mikr. Phys., p. 341, from private correspondence.

6. Riebeckite, Red Hill, New Hampshire, U. S. A. From Paisanite, Pirsson and Washington, Am. J. Sci., **33**, 439 (1907). Calculated from the rock analysis.

7. Crocidolite, South Africa. Analysis by Doelter, Zs. Kr., **4**, 40 (1879).

8. Crocidolite, South Africa. Analysis by Renard and Klement, Bull. Ac. Belg., **8**, 530.

9. Crocidolite, Cumberland, Rhode Island, U. S. A. Analysis by Chester and Cairns, Am. J. Sci., **34**, 108 (1887).

10. The Same as No. 8.

from impurities. This was broken up and carefully picked over by hand under a powerful glass. When examined under the microscope it appeared agreeably free from alteration and included grains, except some inevitable black dust and a few black oxide particles as well as a trace of aegirite and microcline. The average of closely agreeing duplicates is given in column 1, Table I. For comparison a number of analyses of riebeckite and crocidolite of similar composition from other localities are reproduced in columns 2–10. Several others have been omitted because their large content of MgO and CaO excludes them from a close comparison with the present type.

The Quincy mineral differs rather sharply from the Socotra variety in the relative proportions of ferric and ferrous iron, the latter being much higher in ferric and lower in ferrous oxide. The Colorado and Cape Ann varieties (this last is from an alkaline stock similar in many respects to the Quincy stock and distant from it some forty miles) are much closer in this respect, as is also that from Red Hill, although this contains a notable quantity of CaO. The crocidolite analyses (7–9) show a rather closer relationship to the Quincy mineral. The alkalies of the Socotra and Colorado minerals are also notably higher than those of the Quincy riebeckite which, however, is nearer to the values for these oxides in the case of the Cape Ann and Red Hill mineral and in all of the crocidolites. The water percentages are not satisfactory, and at least in the case of crocidolite undoubtedly represent in part hydroscopic water. Fluorine is probably present in all. With corrections made in the waters and fluorine the agreement in the analyses would probably be closer. For further comparison the molecular ratios derived from the above analyses are given in Table II.

TABLE II.

Nos.	1	2	3	4	5	6	7	8	9	10
SiO_2	0.863	0.833	0.822	0.830	0.820	0.756	0.868	0.865	0.869	0.850
Fe_2O_3 + a little Al_2O_3	0.097	.177	0.192	0.093	0.123	0.105	0.137	0.120	0.122	0.111
TiO_2	0.015	..	..	0.017	..	..	..	..	..	..
RO, chiefly FeO	0.337	0.176	0.168	0.278	0.326	0.391	0.262	0.296	0.299	0.300
Na_2O + a little K_2O	0.111	0.148	(0.150)[2]	0.149	0.123	0.108	(0.098)[2]	0.125	0.101	0.103
H_2O + F	0.082[1]	..	..	..	0.089[3]	..	0.083[3]	0.128[3]	0.217[3]	0.200

[1] H_2O above 115°. [2] By difference.

[3] Total, probably loss on ignition and therefore high.

If the TiO_2 is deducted, with a proportionate amount of FeO to form ilmenite, the ratios for the Quincy riebeckite (No. 1) may be apportioned as follows: — $Na_2Fe_2Si_4O_{12}$, 0.582; $R_4Si_4O_{12}$; 0.834; SiO_2 left, 0.058. This may also be expressed by the ratio, $SiO_2 : R_2O_3 : (RO + R_2O + H_2O + F) = 8 : 0.90 : 4.76$. The excess of silica is considerable. What the cause is, is not clear. It may be due to impurity of the material analyzed. The potash seems rather high and may be in error. The presence of even a little feldspar or quartz in the sample would easily produce the apparent excess of silica as calculated. In the cases of several of the other analyses it is necessary, in order to make them correspond to the metasilicate formulae, to assume the presence of a molecule, $R''Fe_2Si_4O_{12}$ on account of the excess of Fe_2O_3. In any case, the ratios lack sharpness and are far from satisfactory. It seems highly probable, however, that if the fluorine and water were correctly determined, and the precise rôle which they play known (whether they are a part of the chemical molecules or are merely held in solid solution or both), also probably some minor changes made in the figures for some of the other constituents, the molecular ratios of these amphiboles would show satisfactory agreement and the formulae would correspond quite closely to the simple metasilicate molecules. Table III shows the molecular ratios apportioned among the molecules mentioned above; also the percentages of the molecule $Na_2Fe_2Si_4O_{12}$ for each of the minerals whose analyses have been given.

TABLE III.

	1	2	3	4	5	6	7	8	9	10
$Na_2Fe_2Si_4O_{12}$	0.582	0.888	0.900	0.558	0.738	0.630	0.588	0.720	0.606	0.618
$RFe_2Si_4O_{12}$	..	0.174	0.252	..	..	..	0.234	..	0.126	0.048
$(R \cdot R_2)_4Si_4O_{12}$	0.834	0.294	0.252	0.668	0.838	0.785	0.612	0.858	0.812	0.984
Rem'nder SiO_2	0.058	0.022	0.072	0.134	0.087	..	0.014	0.044	0.025	0.086
Per cent of $Na_2Fe_2Si_4O_{12}$	42	68	69	43	57	44	45	55	47	47

The Quincy mineral (1), that from Colorado (4), from Cape Ann (5), from Red Hill (6), and one of the crocidolites (8) show perhaps the greatest similarity, although there is considerable divergence among even these. In every one but No. 6 there is an excess of SiO_2. The amount of the $Na_2Fe_2Si_4O_{12}$ radical varies from 69 per cent for the Socotra mineral to 42 per cent for the Quincy variety. Six numbers, 1, 4, 6, 7, 8, 9, fall below the average which is 51.7. Statements in the literature regarding the composition of riebeckite and crocidolite are to the effect that they consist essentially of the radical $Na_2Fe_2Si_4O_{12}$ with varying amounts of $R_4Si_4O_{12}$ and analogous molecules. While the former molecule is certainly essential, the above data indicate that we are not justified in considering it the predominant molecule.

Crocidolite and the Slender Blue or Black Amphibole Crystals of the Pocket. — As seen under the microscope the crocidolite appears as a tangled felt of the most exceedingly minute fibers, pale blue to almost colorless. **a** lies with the elongation, the extinction is apparently small, and the index of refraction for the ray vibrating perpendicular to their length seems to be the same, as near as can be told, as the yellow ray of the riebeckite. If the crocidolite be immersed in water the fibers straighten out in a most remarkable manner. The crocidolite is shot through and through with the slender black amphibole crystals and tiny quartz crystals. It is therefore impossible to get pure material for analysis. Some carefully picked material, freed from quartz, so far as possible, by hand, was analyzed for ferrous iron and was found to contain 17.8 FeO. This figure must be much under the true value, since considerable quartz weighed out with the crocidolite must have been dissolved during the decomposition with hydro-fluoric acid, and the content of hydroscopic water is undoubtedly large. Making allowances for these, the value for the ferrous iron is probably close to that found in the riebeckite.

The blue or black amphibole crystals occurring in the crocidolite, in pockets, and on exposed surfaces of the pegmatite fragments have the form of elongated, relatively flat prisms, deeply striated parallel to the elongation (parallel c′) but not so far as observed, terminated with definite planes.

The smallest of the crystals will measure in thickness but little more than the larger crocidolite fibers. The width may in general be said to run from 0.04 to 0.003 mm., although the larger crystals may sometimes be observed as wide as 1.5 mm. The thickness will vary from about one fourth to one tenth of the width. The majority of the crystals as they lie on the flat side are opaque except at the very edges. The pleochrism and absorption are the same as for the riebeckite and the index of refraction for the yellowish colored ray appears to be also the same.

Both the crocidolite and the minute prisms are believed to be near to or identical with the riebeckite in chemical composition.

Aegirite. — The aegirite of the central pocket is also prismatic in development, sometimes, and especially in the smaller crystals, showing distinct and measurable terminations. There is, however, even in the best crystals much facetting and curvature of part of the terminal planes, especially in those highly inclined to the vertical axis. The faces of the prism zone are generally plane and measurements of sufficient accuracy were obtained to make it clear that these crystals may be referred satisfactorily to the axial elements of aegirite as described by Brögger. As a rule the smaller the crystal the better the quality of its faces; the best ones were minute needles of clear green color. Larger crystals are dark green to blackish green in color and often occur in subparallel groups, sheafe or rosette forms; many show fractures more or less healed or extreme bending.

Twinning on the orthopinacoid is common in larger crystals but is invariably associated with rounding and irregularity of the terminal planes to a degree that entirely precludes measurement.

The basal plane was not observed. The form series as a whole is much more like that of augite than like that described as typical for either aegirite or acmite. None of the forms supposed by Brögger to be peculiar to those species were discovered. On this account and because several of the forms determined have not been recorded for aegirite, since, moreover, this aegirite is shown by the analysis to be nearer to the theoretical aegirite molecule $Na_2Fe_2Si_4O_{12}$ than any previously described, it was deemed advisable to calculate the angles of the forms found on the basis of the axial ratio derived from these measurements, and they are accordingly presented in the following table together with the observed angles.

The axial ratio calculated from fifty faces of six forms on eight crystals gives the values of the first line below, with which may be compared the ratios of aegirite and acmite as determined by Brögger.

	a		b		c	β
Aegirite, Quincy	1.1044	:	1	:	0.6043	72° 27′
Aegirite, Norway, Brögger	1.0975	:	1	:	0.6009	73 09
Acmite, " "	1.0996	:	1	:	0.6012	73 11

TABLE OF ANGLES OF AEGIRITE, QUINCY.

		$p_0 = .5572$		$q_0 = .5762$		$e = .3015$	$\mu = 72°27'$		
		Calculated.		Measured.		Limits.		No. of Faces.	Quality.
		φ	ρ	φ	ρ	φ	ρ		
a	100	90°00′	90°00′	89°57′	90°00′	89°37′ − 90°04′		5	poor
b	010	00 00	90 00	00 37	90 00			1	poor
m	110	43 35	90 00	43 33	90 00	43 00 − 43 55		27	good
f	310	70 42	90 00	70 26	90 00	69 56 − 70 56		5	poor
u	111	55 50	47 06	55 54	47 08	55 17 − 56 16	46°54′ − 47°31	11	good
s	$\bar{1}11$	−23 15	33 20	−23 40	33 24			1	fair
w	331	48 21	69 52	48 29	69 50	47 45 − 49 13	69 36 − 70 00	4	poor
λ	$\bar{3}31$	−37 47	66 27	−37 46	66 42			1	poor
δ	551	46 31	77 10	44 46	77 57	44 02 − 45 31	77 30 − 78 25	2	v. poor
τ	$\bar{1}12$	−5 32	16 53	− 5 51	16 50	5 16 − 6 19	16 40 − 16 57	5	good
s	$\bar{3}11$	−66 44	56 50	−66 40	56 45	66 37 − 66 44		2	v. poor
d	131	26 09	63 39	26 40	63 48	26 19 − 26 52	63 34 − 64 03	3	good

The forms w(331), (551), $(\bar{1}12)$, and d(131) are new to aegirite although all are known on augite. The habit of the Quincy aegirite crystal is shown by Figures 3 and 4.

The general mode of occurrence of aegirite in the massive parts of the pegmatites has been previously described and may be briefly summarized here as follows : — It is in almost constant association with the riebeckite, either intergrown with it in the body of the crystal, or more commonly about the margins, particularly the ends where it is usually very strongly developed. The vertical axis is commonly parallel to that of the riebeckite, though frequently there is no relation between the positions of the two. This relation to the riebeckite and its common occurrence with quartz indicates a strong preference for the late stages of crystallization. Its dominant habit is toward a decided prismatic elongation with a parallel or sub-parallel grouping of separate prisms, as has been noted with regard to crystals in the pockets. When in quartz good prismatic outlines are often noted, but terminations were rarely observed in the sections examined. Macroscopically, the color varies from a light, slightly yellowish green to dark, or even blackish green. In thin sections the color is seen to vary greatly even in a single and otherwise optically homogeneous fragment. The usual color is:

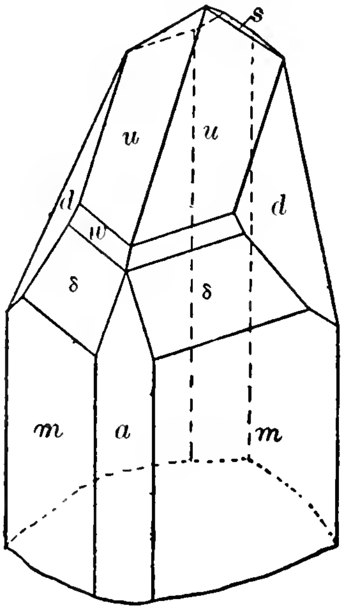

Figure 3.

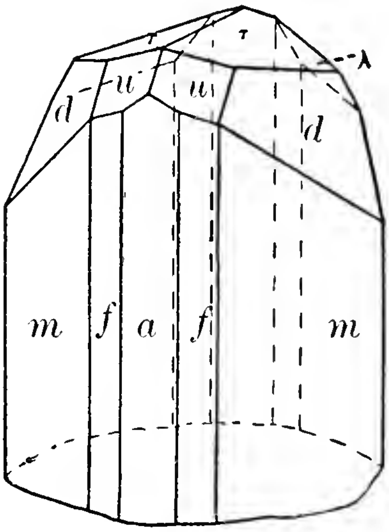

Figure 4.

a = Pale to deep green, sometimes with a slight bluish caste : rarely almost colorless, particularly in one part of a crystal.
b = Pale yellowish green to almost colorless.
c = Pale yellow to pale yellowish green : almost colorless.

In many crystals the whole or a part possess a brownish-yellow or even reddish-yellow color. This is often most pronounced about black oxide (ilmenite) grains and is believed to be due to a pigment stain of ferruginous character. There at least appears to be no regularity in the distribution of the brownish and reddish colorations. 𝔞 makes an angle of 6° with c′, and other optical properties are the usual ones for this mineral. Twins parallel to *a*, 100 are common. A careful examination of aegirite from various portions of the different pegmatites indicates that it is identical in chemical composition throughout.

Chemical Composition. — The almost universal contamination of the aegirite with other minerals made the obtaining of suitable material for chemical analysis very difficult. By means of magnetic and heavy solution separations combined with hand picking under the microscope about three grams of material was finally obtained which showed as impurities only a little ilmenite and a trace of octahedrite and quartz. The analysis made in duplicate averaged as follows :

Aegirite, Fallon Quarry, North Common Hill, Quincy, Mass., U. S. A. Analyst Warren.

	Per cent.	Molecular Ratios.	
SiO_2	51.73	0.862	0.862
TiO_2	0.64	0.008	0.008
Al_2O_3	1.91	0.018	0.217
Fe_2O_3	31.86	0.199	
FeO	0.87	0.012	
MnO	0.60	0.008	
CaO	0.87	0.015	0.226
MgO	0.14	0.003	
Na_2O	11.43	0.184	
K_2O	0.40	0.004	
H_2O	0.20		
F	none		
Total	100.65		

Specific gravity at 25° C. 3.499.

Although a portion of the TiO_2 was probably present as TiO_2 (octahedrite) most of it is combined with RO as ilmenite, and after deducting the TiO_2 and the proportionate amount of RO as ilmenite, the combined ratios are, $SiO_2 = 0.838$, $R_2O_3 = 0.217$, $RO + R_2O = 0.218$; or very nearly $SiO_2 : R_2O_3 : RO + R_2O = 4 : 1 : 1$. This is almost exactly the ratio of the compound $(R''_2R)\,Fe_2Si_4O_{12}$. So far as known to the writers the ferrous iron is lower in this aegirite than in any hitherto analyzed, and the composition approaches very closely to the theoretical composition of the compound $Na_2Fe_2Si_4O_{12}$ which is SiO_2 52 per cent Fe_2O_3 34.6 per cent, Na_2O 13.4 per cent.

Parisite. — The occurrence of the rare fluo-carbonate of calcium and the cerium earths, parisite, as a pneumatolitic mineral in the Quincy pegmatites is a new and interesting one. A closely related mineral, synchisite, associated with the barium-parisite, cordylite, has been described by Nordenskiold[10] and Flink;[11] it occurs at Narsasuk, Greenland, implanted on feldspar and aegirite or in cavities in pegmatite, an occurrence identical with that at Quincy.

Parisite has been found both in the Ballou pegmatite where it occurs only as grains in the massive rock, and in the Fallon pegmatite pipes where it is relatively abundant in all parts of the pipe where open spaces are present, implanted on the surfaces of the microcline and aegirite crystals. It also is found to some extent on the fragments in the central pocket. The crystals of parisite are generally sharply formed and of prismatic habit, ranging from extremely slender columns as much as one cm. long to short, stout, prismatic individuals scarcely longer than broad. The color is clear amber yellow in fresh crystals, dull yellow to brown and opaque when altered as it not unfrequently is. Such altered crystals show a perfect basal cleavage and pearly lustre on the base, both of which properties are entirely absent in fresh material. The same dependence of cleavage upon chemical alteration was found to exist upon parisite from Muso, the type locality, so that cleavage is undoubtedly a secondary property in this mineral.

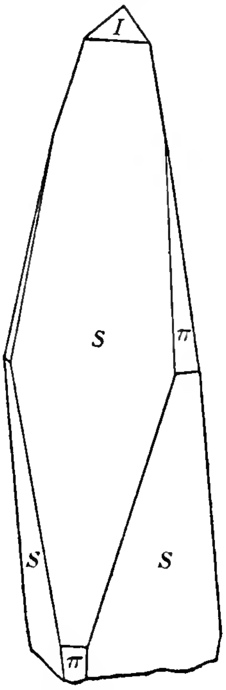

FIGURE 5.

The crystals are invariably striated horizontally and show infinite variety in the detail of individual development. They are either trigonal or hexagonal in cross-section; in the former case steep rhombohedrons being dominant, in the latter second-order pyramids. In neither case are actual prism planes more than rudimentary, the pseudoprisms being bounded by oscillatory combination of the steeply inclined rhombohedron or pyramid faces. The termination is generally a large and brilliant lustrous face of the pinacoid; sometimes, however, the relative size of this plane is much reduced by the presence of low rhombohedrons and second-order pyramids which either slightly truncate the edges between base and pseudoprism or may be developed

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[10] G. For. Forh., **16**, 338 (1894).

[11] Bull. G. Inst. Upsala, **5**, 81 (1901); Med. om. Gronland, **14**, 236 (1898).

to such a degree as to give a pointed trigonal or pyamidal termination. Many crystals were measured and a very complex form series was found to be present, full details of which are to be found elsewhere.[12] It may suffice to state here that parisite was found to be undoubtedly rhombohedral in symmetry and to be referable to axes having the ratio $a : c = 1 : 1.2912$. The forms of most prominent occurrence are the base and second-order prism, c(0001), a$(11\bar{2}0)$,

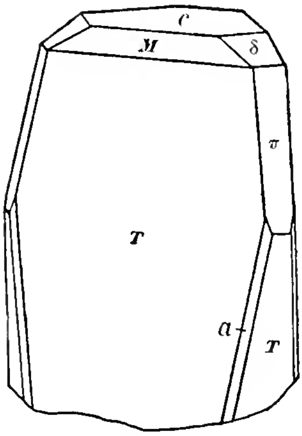

FIGURE 6.

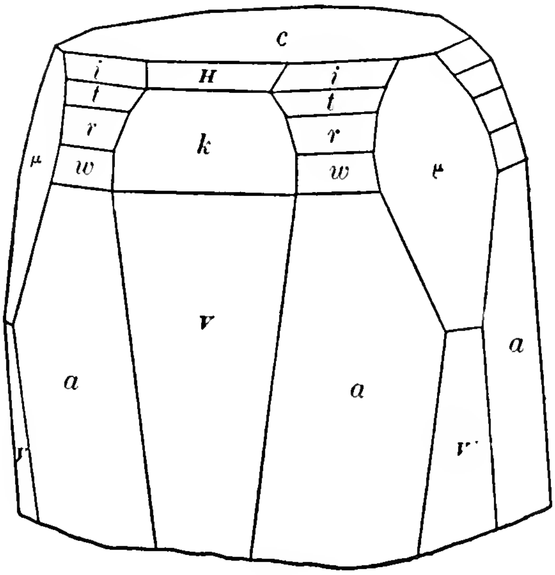

FIGURE 7.

second-order pyramids, $(11\bar{2}3)$, $(5.5.\overline{10}.12)$, $(44\bar{8}9)$, r$(22\bar{4}3)$, $(44\bar{8}3)$,
positive rhombohedrons, $(4.0.\bar{4}.15)$, $(20\bar{2}5)$, $(50\bar{5}4)$, k$(20\bar{2}1)$, s$(30\bar{3}1)$, $(10.0.\overline{10}.3)$, $(50\bar{5}1)$, $(60\bar{6}1)$,
negative rhombohedrons, $(0.3.\bar{3}.10)$, $(0.9.\bar{9}.25)$, $(02\bar{2}1)$, $(05\bar{5}2)$, $(03\bar{3}1)$, $(04\bar{4}1)$, $(06\bar{6}1)$,
scalenohedron $(4.2.\bar{6}.11)$.

Figures 5, 6, and 7 show typical combinations.

The relation of the position here adopted for the crystals of parisite to that formerly used (as in Dana, System, p. 290) may be stated thus: the former second-order pyramid series corresponds to the rhombohedrons of the new position; the former unit pyramid p$(10\bar{1}1)$ receives the new symbol p$(11\bar{2}1)$, the former second-order pyramid g$(11\bar{2}3)$ becomes the new positive unit rhombohedron g$(10\bar{1}1)$.

Optical Properties of Parisite. — As seen under the microscope, very small crystals or fragments are a very pale yellow to almost colorless and show a barely perceptible dichroism. For crystals ½ mm. thick the

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[12] Am. J. Sci., **31**, 533 (1911). Zeitschr. für Kryst., 49 (1911).

ω ray is bright yellow, often with a brownish tone; the ϵ ray is golden yellow. The absorption is $\omega > \epsilon$ slight. For crystals 1 mm. thick the dichroism and absorption is but slightly greater. Upon alteration the crystals become filled with a dusty product, are less transparent, and often exhibit a brownish or brownish-red stain of varying intensity.

The indices of refraction were determined by the immersion method using a barium-mercuric-iodide solution. The determinations were made on a number of perfectly clear, small crystals chosen on account of the uniform development of their prism zones; also upon one larger crystal (1½mm. in diam.) terminated by a perfect basal plane which made it possible to orientate the crystal and cut a section parallel to the prismatic axis. An attempt was made to measure the indices directly upon this crystal by means of the Abbe refractometer but without success owing to the small size of the section and its low degree of transparency. The fine striations parallel to the edge between the base and the prism stand out very sharply under the microscope and make it possible to orientate the crystals with great accuracy on the microscope stage. The values obtained with sodium light are given below, also those heretofore given for parisite as determined by Senarmont and those for synchisite according to Flink.

Parisite, Quincy. Warren.	Parisite, Muso. Senarmont.	Synchisite, Greenland. Flink.
$\epsilon = 1.757$	1.670	1.7701
$\omega = 1.676\ (\pm\ 0.002)$	1.569	1.6742
$\epsilon - \omega = 0.081$	0.103	0.0959

The Montana parisite, also crystals from Muso valley taken from the mineral collection of Harvard University were tested by the immersion method and their indices were found to correspond to the values given for the Quincy mineral. The older values given for the Muso mineral appear to be quite wrong. The ordinary rays for parisite and synchisite are almost identical. The extraordinary rays appear to differ by 0.0131. While the extraordinary ray for the Quincy mineral is probably not as accurately determined as the value for the ordinary, the error can hardly be as great as 0.0131, and the difference between the two minerals for this constant may be a real one.

Chemical Composition of Parisite. — About a kilo of fine-grained material recovered from the fragile lining of the central pockets was carefully washed and fractioned by means of screens, an electro magnet, and heavy solutions until a fraction was obtained weighing about ten grams and consisting largely of parisite mixed with more or less aegirite, octahedrite, feldspar, and quartz. From this about three grams of *clear* *yellow* or *amber* colored crystals were separated by hand-picking under a powerful lens. Aside from a slight stain in a few crystals the only impurities visible under the microscope were minute adhering grains of octahedrite and aegirite hardly amounting to more than a trace.

The result of the chemical analysis made on these crystals is as follows :

Parisite, Quincy, Mass.
Analysist Warren.

CO_2	24.16	SrO	tr.
Fluor.	6.56	Na_2O	.30
Ce_2O_3	30.94	K_2O	.20
$(La, Di)_2O_3$	27.31	H_2O	tr.
Yt_2O_3	tr.	Gangue	1.02
Fe_2O_3	.32		102.21
CaO	11.40	less O = 2F	2.76
		Total	99.45

Spec. G. 4.320

The molecular ratios derived from the above analysis are : — $CO_2 : F : R_2O_3 : CaO = 0.549 : 0.345 : 0.178 : 0.205$. This may be written, $CO_2 : F : R_3O_3 : CaO = 3 : 1.88 : 0.97 : 1.11$ which equals very nearly $3 : 2 : 1 : 1$. This ratio leads to the formula $(R''F)_2 Ca(CO_3)_3$, which is the same as that derived for the mineral by Penfield and Warren[13] from analyses of the mineral from the original locality, Muso valley, U. S. of Colombia and a locality in Ravalli Co., Montana. The chemical composition throughout of the Quincy mineral is very close to that of the parisite from the other localities mentioned. The formula also agrees with that derived for the barium-bearing mineral from Greenland. Synchisite, although identical with parisite in its crystallographic and essentially so in its optical constants and in the elements present, contains, according to the analysis of Flink, one more molecule of calcium carbonate, the formula for the synchisite being $(R''F)_2Ca_2(CO_3)_4$. It is true that the two minerals differ perhaps slightly in specific gravity and in the value for the extraordinary ray. The relationship deserves further investigation.

For a more complete discussion of the relationship of these minerals and the crystallography of the parisite, see a paper by Palache and Warren.[14]

Ilmenite. — Ilmenite occurs in moderate abundance in both the Ballou and Fallon pegmatites. It appears to have been of rather late

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[13] Am. J. Sci. **8**, 21 (1899).

[14] Zeits. f. Kryst., 49 (1911), and Am. J. Sci., **31**, 533 (1911).

formation and is particularly associated with aegirite, as embedded xenomorphic plates, and groups of tiny crystals implanted on crevices of fractured aegirite crystals (Ballou quarry), and as clusters of larger crystals upon the walls of cavities left by the destruction of such crystals by magmatic resorption (Fallon quarry). The crystals are small, not exceeding a diameter of 2 mm. and are always very thin tabular in habit. A dull black coating of manganese oxide commonly gives them a lustreless appearance, but in two specimens brilliant crystals were obtained which, despite minute size, gave good measurements on the goniometer. Octahedrite is almost always sparingly present with ilmenite.

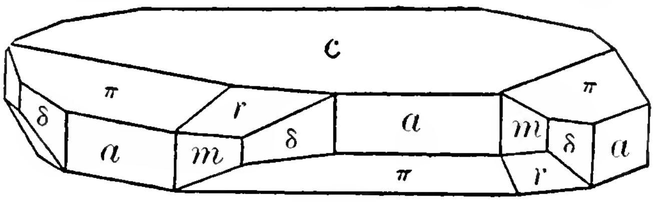

FIGURE 8.

The forms observed are as follows: c(0001), m$(10\bar{1}0)$, a$(11\bar{2}0)$, δ$(21\bar{3}0)$,* θ$(10\bar{1}9)$, u$(10\bar{1}4)$, ξ$(20\bar{2}5)$, r$(10\bar{1}1)$, f$(0.7.\bar{7}.20)$, e$(01\bar{1}2)$, Λ$(04\bar{4}5)$,* s$(02\bar{2}1)$, λ$(05\bar{5}2)$,* g$(0.3.\bar{3}.11)$,* k$(0.3.\bar{3}.10)$,* π$(11\bar{2}3)$, n$(22\bar{4}3)$. (* New forms.)

The crystals from Ballou quarry showed the forms c, m, a, δ, r, and π, the prism zone being well developed and the base large and very brilliant. The prism is new to ilmenite. Figure 8.

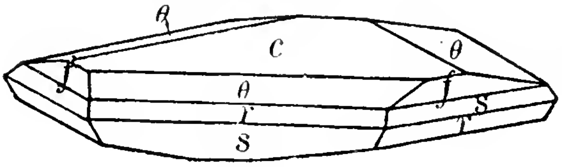

FIGURE 9.

Crystals from Fallon quarry are dominantly rhombohedral, prism faces being reduced to mere lines. The crystals measured showed the following combinations :

1. c, δ, r, f, e, s, n.
2. c, m, θ, ξ, r, k.
3. c, m, θ, r, u, e, k, π, n.
4. c, m, θ, r, n.
5. c, θ, ξ, r, e, g, Λ, λ, n.
6. c, m, θ, ξ, r, e, Λ, k, n.
7. c, u, r.

As shown in Figure 9, flat positive rhombohedrons are largely developed on these crystals, recalling the description of one (the common) phase of "Crichtonite" from Oisans by Descloizeaux.[15] That author considered the rhombohedrons which he measured, $(10\bar{1}5)$ and $(10\bar{1}9)$

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[15] Mineralogie, **2**, 222 (1893).

and $(1.0.\bar{1}.11)$ as negative but left the determination of sign doubtful. The second of these forms is common to all the crystals from Fallon quarry and is certainly positive, so both the others should be likewise so considered. Several negative rhombohedrons new to ilmenite were observed and are based on the following data :

	Form.	Calculated.		Measured.		No.	Face limits of ρ.
		φ	ρ	φ	ρ		
g	$(0.3.\bar{3}.11)$	30 00′	23° 34′	30 00′	23°46′	3	23° 28′ to 24° 05′
k	$(0.3.\bar{3}.10)$	"	25 37	"	25 34	1	
Λ	$(04\bar{4}5)$	"	51 59	"	51 57	2	51 53 to 52 00
λ	$(05\bar{5}2)$	30 00′	75 57	30 00′	76 06	1	
							Limits of φ
δ	$(21\bar{3}0)$	10 53	90 00	10 30	90 00	4	10° 36′ to 11° 34

The presence on one crystal of the form f, observed before only by Solly on a Binnenthal crystal, confirms this form. All the forms present gave angles agreeing very closely with the values calculated from the axial ratio of Koksharow as used by Dana.

Chemical tests on the ilmenite from both quarries revealed strong qualitative reactions for manganese ; an analysis would be interesting but it was not possible to separate enough of the fresh mineral for this purpose.

Octahedrite. — Octahedrite is found chiefly in the large central pocket of the Fallon pegmatite, generally in close association with aegirite and often formed posterior to the alteration of that mineral since it is not infrequently seen on the walls of hollow casts of aegirite crystals associated with fluorite and ilmenite. Isolated crystals were also found implanted on feldspar crystals. The crystals of octahedrite are small, of a deep black color and of very brilliant lustre. They show only the forms c(001), m(110), p(111), k(112), and z(113), the two last the least common. These crystals are marked by two peculiarities ; they are in large part of prismatic habit with the first-order prism dominant, a habit not before described for this mineral and causing the crystals to be at first mistaken for zircon ; and they occur in cruciform twin groups with the form (101) as twin plane. The twins are sometimes complete interpenetrations of two equal crystals as shown in the figure ; sometimes but one end of each is developed ; again a larger crystal has a much smaller one in twin relation to it. The groups are exquisitely sharp and leave no doubt as to the definiteness of the twinning since the two upper faces of the unit pyramid of each crystal and the two lower, parallel and opposite faces to these reflect the signal simultaneously in pairs; thus the faces of (101) which are in zone with these unit pyramid faces must be parallel to the twin plane.

This twin law has been observed but once before on this mineral, on crystals from the titaniferous calcite-quartz veins of Somerville, Mass.[16] There twins were extremely rare, while here they are sufficiently numerous to be considered characteristic for the locality. Combinations of prism and unit pyramid are far the most common among these crystals. A few, however, show the base as a tiny facet and in a few the flatter pyramids k or z replace the acute summit of the common form. Figures 10 and 11 illustrate the habit of the octahedrite crystals.

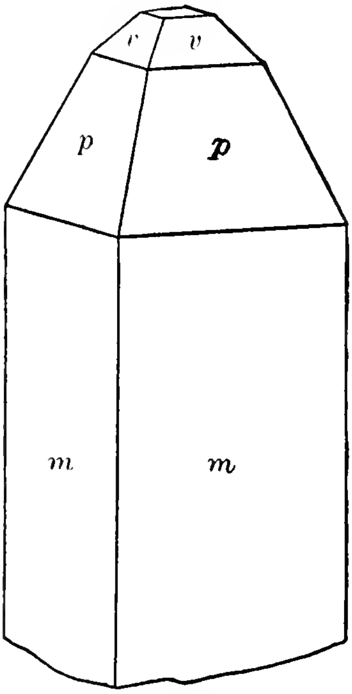

FIGURE 10.

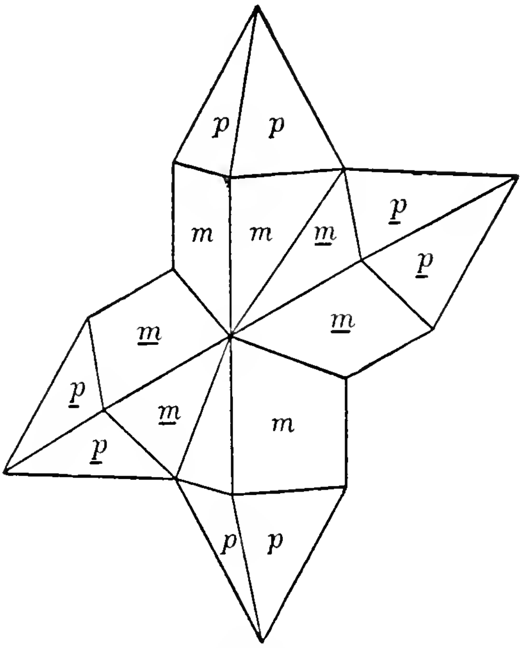

FIGURE 11.

Fluorite. — Mention has been made in preceding pages of the distribution of fluorite throughout all parts of the pegmatite masses. It is generally in small grains but near the central pocket, especially in that part where crocidolite was abundant the fluorite individuals were larger, one mass showing cleavage faces nine inches across having been found. Where wholly embedded in crocidolite the fluorite crystals are automorphic, octahedrons up to one inch in diameter thus occurring; they are dull and somewhat rounded, the color a deep purple like all the fluorite of this locality, but occasionally there is a surface layer of

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[16] On Octahedrite, Brookite, and Titanite from Somerville, Mass., C. Palache, Rosenbusch Festschrift, 1906, 311.

bluish green color due to included fibers of the blue crocidolite. The hollow casts left by the solution of such crystals have already been described.

In one or two cavities in the Fallon pegmatite there were seen tiny cubes of fluorite implanted on quartz, and in another such pocket, peculiar in containing also crystals of calcite, the cube was modified by two hexoctahedrons which appear to be new to fluorite. The measurements and derived symbols of these forms follow:

	Calculated.		Measured.		Limits.		No. of Readings.
	ϕ	ρ	ϕ	ρ	ϕ	ρ	
3.10.16	16°42′	33°07′	15°45′	33°20′			
3.16.10	10 38	58 26	10 36	58 33	10°30′ – 10°42′	58°30′ – 58°36′	2
10.16.3	32 00	80 58	32 04	81 05	31 52 – 32 16	80 50 – 81 20	4
259	21 48	30 54	21 01	31 15	20 45 – 21 18	31 11 – 31 19	2
295	12 32	61 32	12 32	61 25	12 27 – 12 37	61 23 – 61 26	2
592	29 03	79 00					

Calcite. — Certain small pockets in the Fallon pegmatite were filled by a final deposit of calcite. In one or two cases the calcite supplied was insufficient to wholly fill the open space and in these cavities calcite crystals were found showing the somewhat unusual combination of prism and base only, m($10\bar{1}0$) and c(0001).

Wulfenite. — Thin coatings of light yellow color as well as tiny crystals of Wulfenite were found on smoky quartz in the crocidolite pocket. The crystals are in part model-perfect combinations of first-order pyramid with third-order prism, n(111) and f(320), see Figure 6, p. 990, Dana, System, in part cube-like combinations of a prism and the base. The amount of wulfenite is very small and its presence is easily accounted for by the association in the same region of the pegmatite of molybdenite and galena.

EXPLANATION OF PLATES

PLATE I.

Figure 12. Section of Ballou Pipe.

The photograph shows a block cut from the pipe through its center about parallel to its axis (face marked A) and also across the axis (side marked B). The diameter is a little more than three feet. The concentration of dark silicates about the margin is very strong. The graphic-granite zone can hardly be distinguished from the main zone of pegmatite. The long dark prisms, more abundant toward the center, are of aegirite-riebeckite. The dark gray center is largely quartz. An indistinct radial structure may be seen.

Figure 13.

This is a part section across a portion of one of the Fallon quarry pipes. It was cut from a loose block and its exact location cannot be told. The height of the block is about three feet, but as the section is cut somewhat obliquely the actual width of the zones is less than that shown by the figure. D is a piece of the quartz center. C is the zone of coarse pegmatite with its large aegirite-riebeckite prisms. B shows the graphic-granite band, here very strongly developed. A is the marginal zone with a slight concentration of dark silicates along the inner margin. This band here is very similar to the granite and probably merges gradually into it.

Compare with Figure 1, page 133.

Fig. 1a.

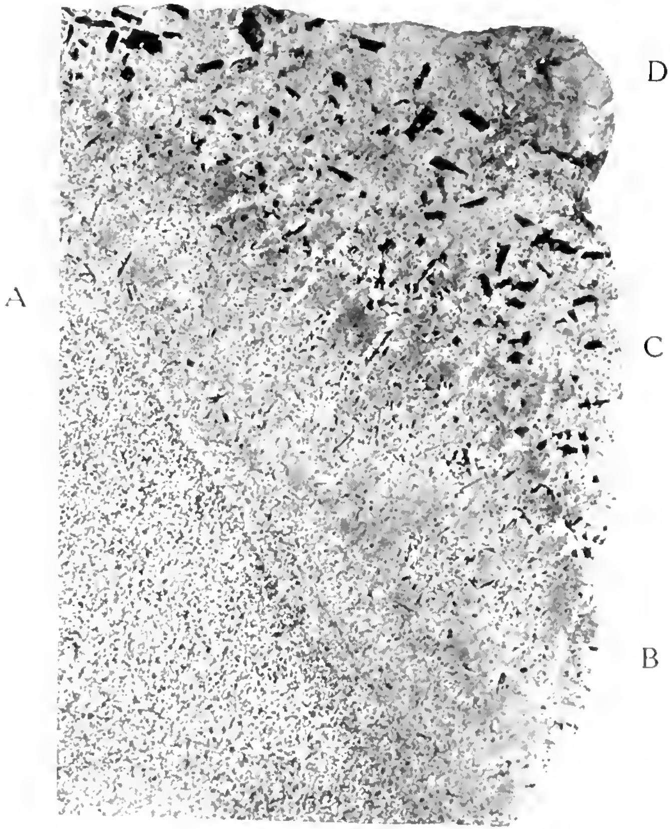

Fig. 1b.

EXPLANATION OF PLATES

PLATE II.

FIGURE 14.

Microphotograph of quartz-zircon groups in the fine-grained portions of the pegmatite pipe in the Ballou quarry. In the lower right-hand quadrant one of these aggregates is seen with a well developed crystal outline. In this, the dark areas are zircon, the white, quartz. The surrounding material is quartz. Other groups above and to the left.

Crossed-nicols. Magnification about 120 diameters.

FIGURE 15.

Microphotograph of fine-grained rock lying just below and slightly east of the large pocket in the Fallon quarry pegmatite. Shows small lath-shaped albite crystals scattered through, and lying about, microcline grains. The smooth areas are quartz. Just between the two lower quartz grains is one of aegirite, also penetrated by the albite.

Crossed-nicols. Magnification about 120 diameters.

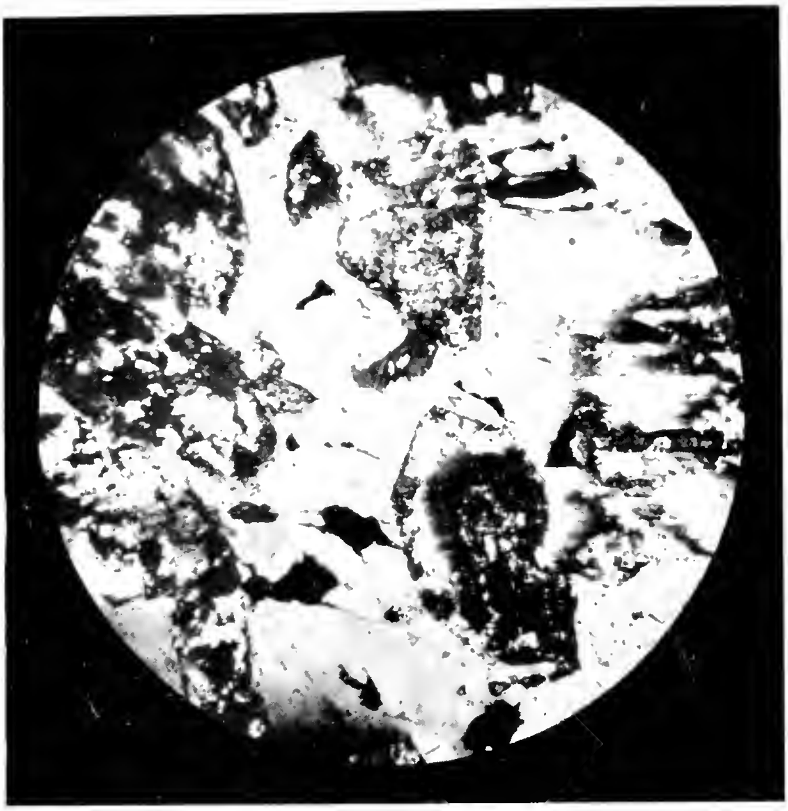

FIG. 14.

FIG. 15.

EXPLANATION OF PLATES.

PLATE III.

FIGURE 16.

Microphotograph of a small microcline crystal in the finer-grained portion of the main pegmatite zone. The section is approximately parallel to the base and shows twinning after the albite law only. One set of lamellae are in the position of extinction between crossed-nicols. Magnification about 150 diameters.

FIGURE 17.

Microphotograph of a basal section of microcline, cut from a freely developed crystal from the pocket. Shows twinning after the albite law only. One set of lamellae are shown in the position of extinction between crossed-nicols. Magnification about 350 diameters.

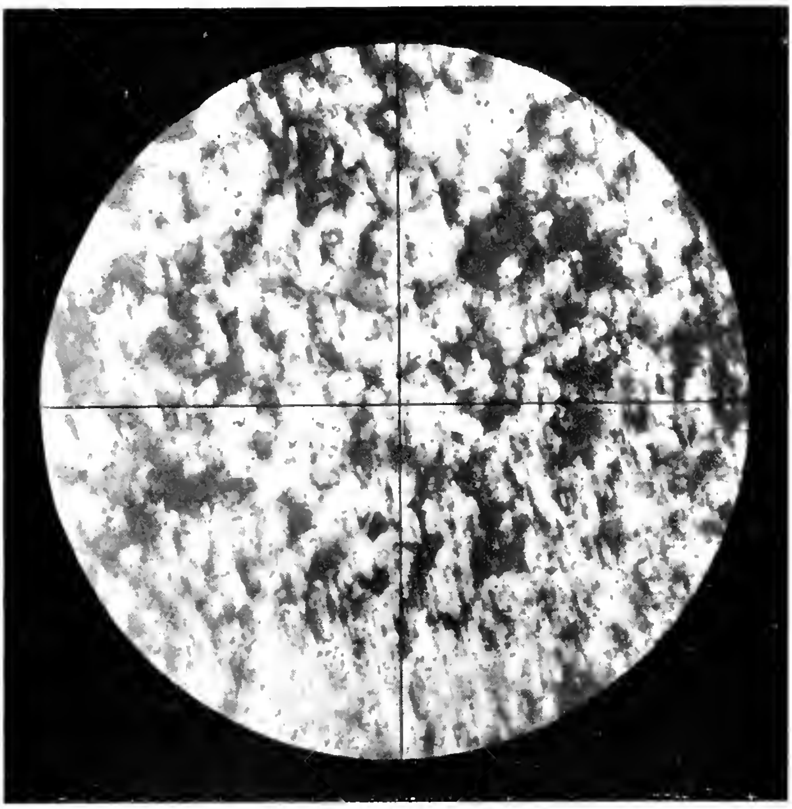

FIG. 16.

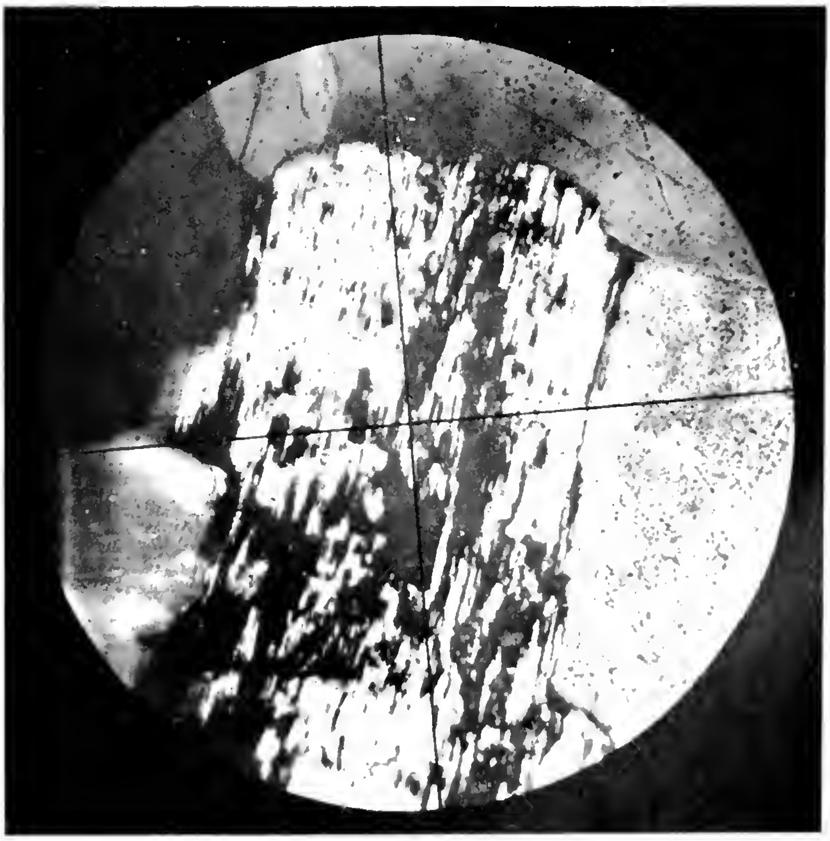

FIG. 17.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 5. — July, 1911.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE TRANSITION TEMPERATURES OF SODIUM CHROMATE AS CONVENIENT FIXED POINTS IN THERMOMETRY.

By Theodore W. Richards and George Leslie Kelley.

Investigations on Light and Heat published with Aid from the Rumford Fund.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE TRANSITION TEMPERATURES OF SODIUM CHROMATE AS CONVENIENT FIXED POINTS IN THERMOMETRY.

By Theodore William Richards and George Leslie Kelley.

Presented April 12, 1911. Received April 4, 1911

Introduction.

In previous papers[1] from this laboratory it has been shown that the transition temperature of a crystallized salt is in some cases so easily observed and so constantly maintained as to form a convenient fixed point of reference for the scale of temperature. The cases of sodium sulphate (32.383°) and bromide (50.674°) and manganese chloride (58.089°) have been studied in detail and found to be very satisfactory in these respects.

Among other substances suggested for this purpose, sodium chromate is especially inviting because two of its transition temperatures are near 20°, a temperature at which it is frequently desirable to verify thermometers.

The outcome of the work on this salt described in the present paper was entirely satisfactory, and gives promise of great practical usefulness to those who are interested in exact thermometric measurement. Nevertheless, the problem was not so simple as it had at first appeared. The wealth of variety exhibited by the hydrates proved at first to be an embarrassment of riches, and led to some preliminary confusion, which has been happily reduced to order. Moreover, the salt is some-

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[1] T. W. Richards, Am. J. Sci. (4), **6**, 201 (1898); Richards and Churchill, These Proceedings, **34**, 277 (1899); Richards and Wells, These Proceedings, **41**, 435 (1906); Ibid., **38**, 431 (1902); Richards and Wrede, These Proceedings, **43**, 343 (1907). These five papers are all to be found in full in the Zeitschr. für phys. Chem., the references being respectively **26**, 690 (1898); **28**, 313 (1899); **43**, 465 (1903); **61**, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin.

what less easy to purify than the sulphate, and when it is impure, a given percentage of impurity causes a larger error in the transition temperature than in the case of the sulphate. This is largely because the transition is from the dekahydrate to tetra- or hexahydrate, instead of to anhydrous salt, so that the amount of solution formed to dissolve the impurities is less, and therefore the concentration of the impurity in the solution is greater. Another difficulty arises from the fact that chromic acid is a weak acid, and hence its salts are easily capable of absorbing acid impurities. This was shown experimentally by passing pure carbon dioxide into the solution. Large volumes of the gas were absorbed, and the solution became perceptibly orange because of the formation of the dichromate. Boiling expels the gas but slowly, because the hydrolysis increases with rise of temperature. Indeed, a boiling solution of the purest salt is so much hydrolyzed as to be red in color and to react strongly with phenolphthalein. Probably the passing of pure air, or boiling at low temperature for a long time in a partial vacuum, would be needed to displace all of the carbon dioxide, and even this might not serve. Of course the solution of the salt absorbs hydrochloric acid and other strong acid vapors yet more easily; and even the dry salt, which is unaffected by carbon dioxide, is attacked by stronger substances.

Theoretically the tendency of the solution to hydrolyze offers no objection to the use of the salt as a means of fixing a definite point on the thermometer scale, because the Phase Rule, which determines the definiteness of the points, does not consider the state in which the substance exists in any of the phases. The feeble nature of chromic acid is annoying and objectionable only for the practical reason that it makes the preparation and preservation of the pure salt more difficult. When the salt has once been prepared in the pure state, it must be carefully guarded in order to preserve its purity.

These difficulties, however, all disappear when the experimenter is forewarned against them; for easily effected precautions are capable of surmounting them all.

Preparation of Pure Sodium Chromate.

Several methods of further purification of sodium chromate were tried. Crystallization as the dekahydrate is of no avail as a means of ridding the crystals of their most usual impurity, the sulphate, because this is isomorphous with the chromate. Indeed the sulphate tends into the crystals, leaving the mother liquor somewhat purer than before the crystallization. The tetrahydrate is but little more satisfactory as a means of accomplishing the purification; ten successive crystallizations having failed to yield a pure salt. Moreover, inconvenience arises from the fact that it is stable under the solution only between 26° and 62.8°, and because its solubility has only a comparatively small temperature coefficient, the yields are small.

Attempts to prepare the salt by recrystallizing chromic anhydride were likewise abandoned as unprofitable. The best chromic anhydride obtainable was found to contain much sulphate, which was very slow to leave during the particularly wasteful process of its crystallization. In one case twelve successive crystallizations of a kilogram of chromic anhydride gave only a few grams of product which still contained traces of sulphur. These unsuccessful methods are recounted only to save other experimenters the trouble of attempting the same processes.

Another method which is distinctly better than the preceding is perhaps worthy of more detailed discussion, although a still better and much simpler procedure was afterwards devised.

The sulphate can be quickly eliminated by relying upon the very different solubilities of silver chromate and sulphate. If a chromate is slowly precipitated by silver nitrate in dilute solution, using not quite enough of the precipitate to remove the chromate wholly from the solution, the precipitate contains very little sulphate. The chromate of silver is then thoroughly washed, and easily converted into sodium chromate by treatment with a solution of pure sodium chloride. The presence of an excess of precipitated silver chromate ensures the absence of all but the merest traces of chloride in the solution, if time has been allowed for the attainment of equilibrium. If greater purity is desired, the chromate may be reprecipitated by silver nitrate, and again treated with pure common salt. The very appreciable quantity of silver which the solution of sodium chromate still contains is easily precipitated by copper wire or gauze, and the cupric chromate, being easily soluble, is quickly eliminated upon crystallizing the sodium chromate as dekahydrate. It is idle to attempt to get rid of the silver chromate by crystallization, since its solubility is affected about as much proportionally by temperature as that of sodium chromate is. After the silver has been removed, five crystallizations were enough to remove all the copper and other impurities, and a specimen of sodium chromate was obtained which gave every evidence of being pure.

Yet another available method, the most satisfactory one of all, depends upon the fact that sodium bichromate may be easily and quickly freed from sulphate by recrystallization. The bichromate is very soluble, and possesses a moderately great change of solubility with the temperature; 100 parts of water dissolve 162 parts of the dry salt at 100° and 109 parts at 15°.[2] Since, however, the salt crystallizes with two molecules of water, the actual loss on crystallization is less than would appear from a superficial inspection of these figures. The weight of the crystals separated from a saturated solution between these two temperatures from 162 grams of anhydrous salt dissolved in 100 grams of water is easily calculated from the equation:

$$x + \frac{2H_2O}{Na_2Cr_2O_7}x + (162 - x)\frac{209}{109} = 262$$

when $x = 87$ grams. Thus more than half the salt is easily recovered from each crystallization, and if use is made of a wider range of temperature, permitted by the high saturated boiling point (139° with solubility 210 parts to 100 of water) a still larger yield may be obtained. Since the solubility diminishes but slightly below 15°, further cooling is not profitable. Thus the crystallization of this salt is convenient and efficient; and since sodium bichromate is not isomorphous with the corresponding salts either of potassium or of sulphuric acid (the most probable and insidious impurities) crystallization forms an admirable means of purification. The elimination of the sulphuric acid requires only three or four crystallizations if the crystals are separated centrifugally. A large excess of chromic acid causes unnecessary loss, because of the very great solubility of the trichromate,[3] but a small excess is convenient, because the elimination of the dark brownish tint of the trichromate from the mother liquor is a convenient guide as to the purity of the salt.

The crystallized, pure bichromate was treated with *somewhat less than the calculated amount* of pure sodium carbonate, and with the help of the excess of bichromate the carbon dioxide was easily removed by boiling the solution during an hour. From a neutral solution all the carbon dioxide cannot be expelled. The sodium carbonate for this purpose should be prepared by repeatedly crystallizing the purest soda of commerce in porcelain, or better in platinum dishes, until sulphates and chlorides are certainly absent.

The sodium chromate containing a small amount of sodium bichromate, prepared as described above, was neutralized with the help of phenolphthalein by means of a solution of pure sodium hydroxide, made from sodium by allowing this metal to stand in a platinum dish in a desiccator over a dilute solution of the hydroxide.

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[2] Stanley, Chem. News, **54**, 194 (1886).

[3] Ibid.

Some time was spent in determining the conditions under which phenolphthalein gives satisfactory results in the presence of pure sodium chromate. Schreinemakers[4] states that the chromate is neutral to phenolphthalein and recommends the use of this indicator in analyzing solutions of chromates for excess of either hydroxyl or chromate ion. In our experiments it appeared that the solubility of the indicator in very concentrated sodium chromate solutions is too small under ordinary conditions to permit of a visible reaction with the low concentration of ionized hydroxyl which must exist there. This is especially true when alcoholic phenolphthalein is dropped into a saturated solution of the chromate. In this case the indicator seems to be precipitated by the salt in such form as to dissolve only very slowly on subsequent dilution. This difficulty was avoided by diluting the indicator with pure water in the first place. On the other hand, a dilute solution of the salt is easily shown to be appreciably hydrolyzed, the color of phenolphthalein being distinctly visible superposed on the yellow of the salt. Increasing temperature of course causes increasing hydrolysis; in boiling solutions of the purest very concentrated sodium chromate the hydrolysis is sufficiently great to cause a distinctly reddish tint.

As an outcome of these experiments the neutralization was conducted in concentrated solutions of sodium chromate at room temperature, the indicator in dilute solution being added to the separate test portions. To the main solution sodium hydroxide was added until the phenolphthalein just began to show its color in the separate test, and then sodium dichromate until the color just disappeared. This solution may have contained a constant and very slight excess of dichromate, but this substance is easily removed by subsequent crystallization, being heteromorphous as regards sodium chromate.

The neutral salt prepared in this way may be further purified by crystallizing either as the dekahydrate, hexahydrate, or tetrahydrate. The first named phase, $Na_2CrO_4 \cdot 10H_2O$ is to be preferred on account of economy of material, except as a means of eliminating sodium sulphate.

To crystallize the salt with four molecules of water the temperature of the solution must be kept above 26°; but at 20° 100 parts of water dissolve 86 parts of sodium chromate, whereas at 0°C. 100 parts of water dissolve only about 32 parts of sodium chromate in equilibrium with dekahydrate; hence arises one reason for the greater economy in crystallizing the dekahydrate at the lower temperatures. Moreover, a greater rate of purification from every common impurity except sodium

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[4] Zeitschr. f. Phys. Chem., **55**, 72 (1906).

sulphate is possible by this method than from the other hydrates. Six or seven crystallizations as the tetrahydrate give only the same degree of purity as three or four crystallizations as the dekahydrate.

The dekahydrates of sodium sulphate and chromate are isomorphous, as already stated; hence the sulphate must be previously removed by crystallizing the dichromate in the manner already described.

Crystallization of the pure chromate is best carried out at 5° in platinum vessels; and centrifugal drainage, as usual, greatly increases its efficiency as a means of purification. After three or sometimes four crystallizations the sodium chromate was found to give a transition temperature which could not be raised by further crystallization. This is, of course, the criterion to be used in deciding how long to continue the purifying operations. The difficulties attending the purification of this substance are no greater than those attending the purification of sodium sulphate, provided that isomorphous substances are absent. The mother liquors may be made to yield at least two more crops of crystals; their evaporation for this purpose is free from danger only when the platinum vessels employed are so constructed as to prevent the entrance of carbon dioxide. The yield of pure sodium chromate may be nearly fifty per cent of the amount corresponding to the pure sodium bichromate employed. Pure sodium chromate must be preserved in a desiccator, containing a small amount of a solution of sodium hydroxide solution to absorb carbon dioxide. If the salt is to be kept for any length of time it should be placed in platinum vessels. The tetrahydrate is the most convenient form in which to preserve the salt for long periods, as it is permanent under usual conditions.

The Hydrates of Sodium Chromate.

The dekahydrate, $Na_2CrO_4 \cdot 10H_2O$, isomorphous with common Glauber's salt, is so well known that description is unnecessary. It is easily obtained in large crystals by inoculating a cold supersaturated solution of the former salt with a crystal of the latter. In order to avoid the suspicion of contamination with sulphate, inoculation was carried out successively on several watch glasses, the first being touched with sulphate, the second with chromate taken from the opposite side of the first, and so on, the bulk of the material being inoculated with pure chromate from the last watch glass. Whenever the temperature of the laboratory rose above 20° this procedure was necessary, because at this temperature all of the chromate in the laboratory suffered change into the tetra- or hexahydrate, and so none remained wherewith to start the crystallization of a new specimen. Like sodium sulphate, the chromate has a wide range of metastability of supersaturation, and like it, the chromate is efflorescent in the dry air of the steam-heated [5] laboratory. In order to make sure of the composition of the salt, a specimen which had been dried as much as possible without visible efflorescence was analyzed. 0.8316 gram of the salt lost on dehydration 0.4358 gram of water, or 52.43 per cent. The theoretical percentage is 52.70, hence there can be no doubt as to the formula $Na_2CrO_4 \cdot 10H_2O$.[6]

The hexahydrate, $Na_2CrO_4 \cdot 6H_2O$ has only a very small range of stability, as will be seen from an examination of the diagram on page 178. The preparation of this hydrate was first described by Salkowski.[7] At temperatures below 19.53°, especially in contact with its solution, it tends to pass into the dekahydrate modification, and above 26°, into tetrahydrate. Inasmuch as the temperatures within which it is stable are those most frequently found in the laboratory, it is the phase most frequently met with. When the dekahydrate warms to 19.53° or the tetrahydrate cools to 26° particles of hexahydrate in the atmosphere induce the crystallization of this form so readily that it is often difficult to prevent the appearance of this phase. In two analyses, 1.4152 grams and 1.7786 grams of the salt lost respectively 0.5705 gram and 0.7122 gram of water on drying at 180° to constant weight. These results correspond to 40.3 and 39.4 per cent of water respectively, and since the first sample was somewhat moist and the second was slightly effloresced, there can be no doubt that the substance was really $Na_2CrO_4 \cdot 6H_2O$, a salt possessing theoretically 40.0 per cent of water. The material gives a transition point at about 25.9° (hydrogen scale), being converted into tetrahydrate at that temperature.

The tetrahydrate, $Na_2CrO_4 \cdot 4H_2O$, is stable in contact with its solution only at temperatures above 26° and below 62.8° ±. Even in the dry air of a steam-heated room it shows no evidence of efflorescence ; therefore its aqueous vapor tension must be very low. This hydrate is formed when a hot concentrated solution of sodium chromate is allowed to cool to a temperature above 26°, and the needle-shaped crystals melt at about 62.8°. Occasionally other crystals of a hydrate or anhydride separate from the solution above 62.8°. Because the hydration of the latter crystals at low temperatures is slow, enough water should be added to a very hot solution to keep the salt dissolved until the temperature 62.8°

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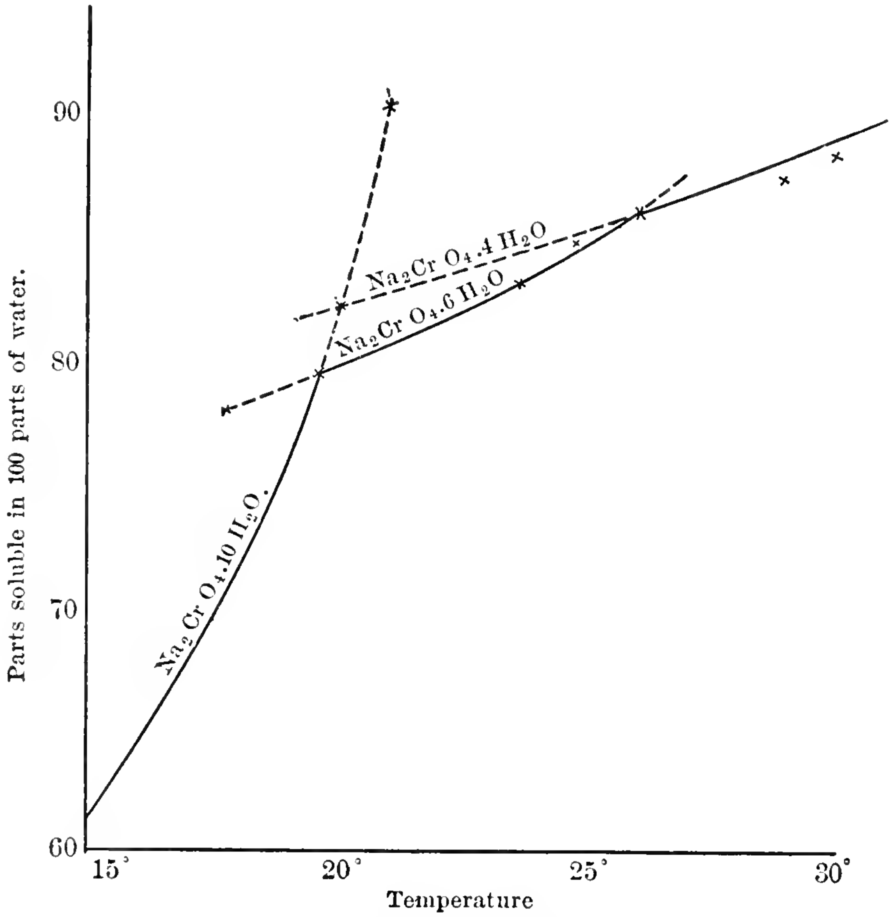
[5] Kopp's ascribing deliquescence to the salt must have been due to his working in a very moist atmosphere.

[6] These analyses, as well as those of the hexa- and tetrahydrate given further on, were kindly made by J. B. Churchill under the direction of one of us.

[7] Salkowski, Ber., **34**, 1947 (1901). The salt had been made and analyzed previously by Richards and Churchill, but no description had been published.

has been reached by the cooling material. Two analysis of the tetrahydrate showed 30.74 and 30.76 per cent of water, sufficiently close to the theoretical value 30.72. On cooling a solution saturated at 63°, it frequently happens that no crystals appear, although upon adding a crystal of the tetrahydrate crystallization at once occurs.



In the accompanying figure the solubilities [8] of sodium chromate in contact with its various hydrates have been plotted for temperatures in the neighborhood of room temperature. Evidently three transitions are possible within a small range. The dekahydrate undergoes transition to the hexahydrate and solution at 19.53°, or into tetrahydrate and solution at 19.99°,[9] depending on which of these last-named hydrates is present. A similar transition from hexahydrate to tetrahydrate and solution occurs at 25.9° ±.

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[8] Mylius and Funk, Ber. d. ch. Ges., **33**, 3689 (1901); also Salkowski, ibid., **34**, 1948 (1901). These are recorded in Landolt and Börnstein Tabellen (1905), page 557.

[9] This is probably the point found by J. L. R. Morgan as approximately 19.92°, Zeit. anorg. Chem., **55**, 263 (1907).

To bring about the transition at 19.90°, it is necessary to superheat the dekahydrate past the lower transition point, 19.53°. Not many other instances of this sort have been carefully studied. Walker and Fyffe[10] have examined the solubility of $Ba(C_2H_3O_2)_2 \cdot 3H_2O$ (which undergoes a transition into the monohydrate and solution at 24.7°) as far as 26.1°, 1.4° above its transition point; and the solubility of *a* $Ni(IO_3)_2 \cdot 2H_2O$ has been studied by Meusser[11] up to 50°, 13° above the temperature of its transition into the anhydride and solution.[12]

The addition of a foreign substance not isomorphous with the dekahydrate lowers the transition point as usual.[13] The addition of sodium chloride was found some time since by C. A. Bigelow and one of us to lower the transition temperatures (19.53) about the expected amount. This result was not published at the time, but has since been confirmed by J. L. R. Morgan.[14]

A much more interesting effect is observed with isomorphous hydrates. For example, successive additions of sodium sulphate to the solution of chromate gave successive *elevations* of the transition temperature, even when the crystals contained no sodium sulphate.[15] These elevations were roughly proportional to the amount added. The experiments were not carried on with a view to determining the limits of this change, but an elevation of about 4° was found in some instances. The temperatures at first obtained were variable; but on vigorously stirring in an environment 0.5° warmer than the mixed hydrates, equilibrium was apparently reached after five minutes, and often remained undisturbed for fifteen minutes or longer. This raising of the transition point involves an interesting extension of the range of stability of the dekahydrate.

So far as we can find this phenomenon of the raising of the transition temperature of hydrated crystals by the presence of isomorphous hydrated crystals is here described for the first time. It deserves and shall receive here in the near future more thorough investigation.

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[10] Walker and Fyffe, Journal Chem. Soc., **83**, 180 (1903).

[11] Meusser, Berichte, **34**, 2440 (1901).

[12] See also Berthoud, Sur l'impossibilité de surchauffer un solide. Journal de chim. Phys., **8**, 377 (1910).

[13] Löwenherz, Zeit. phys. Chem., **4**, 349 (1889).

[14] Morgan, Zeit. anorg. Chem., **55**, 263 (1907); **56**, 168 (1907).

[15] This fact was first observed by Churchill and one of us about ten years ago, but has not been published until now. The value 19.6° (which made no pretensions to great accuracy) assigned to the lowest transition point of sodium chromate at that time was undoubtedly too high from this cause, because the salt was made from ordinary chromic anhydride. These Proceedings, **34**, 277 (1899).

The relative composition of crystals and mother liquor was evidently worthy of study. A solution of sodium chromate containing a considerable amount of sodium sulphate was cooled to 10° to crystallize. The crystals were drained in a centrifuge, washed with a little cold water, and again centrifuged. 7.05 grams of this solution contained 0.432 gram of sodium sulphate and 1.707 grams of the chromate, whereas 2.25 grams of the hydrated crystals contained 0.425 gram of the sulphate and 0.515 gram of the chromate. The solubility of the chromate at 10° is roughly speaking 50 parts in 100 of water and of the sulphate 9 parts in 100 of water. The distribution of the dissolved substances between their solution and mixed crystals is thus seen to be in the same sense as their respective solubilities at the temperature of crystallization. The sulphate decidedly tends towards the crystals, the chromate towards the mother liquors.

As has been elsewhere pointed out, Salkowski was the first to observe that the curve of solubility of the hexahydrate cuts those of the deka- and tetrahydrates at about 19.5° and 26° respectively. Mylius and Funk [16] earlier observed that the transition from the dekahydrate to the anhydride is accomplished through the intermediate tetrahydrate, which is stable between 20° and 65°. Salkowski,[17] commenting upon their work in view of his later discovery of the hexahydrate, says that this statement must be extended to include the hexahydrate for its few degrees of stability. The statement of Salkowski must now be extended to include the fact that the transition from dekahydrate to the anhydride may be through the hexa- and tetrahydrates, or in the absence of the hexahydrate, this transition may be through the tetrahydrate alone, as originally stated by Mylius and Funk.

We have confirmed the statement of Salkowski that the temperature of the transition from the hexahydrate to the tetrahydrate is in the neighborhood of 26°, but owing to lack of time we have been unable to determine this point with exactness.

The exact determination of the two lower transition points, for use in precise thermometry, will now be described.

The Apparatus.

The apparatus employed was like that employed in determining the transition temperature of sodium sulphate.[18] It was essentially similar

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[16] Abhandlung der Physik. Techn. Reichsanstalt, III, 449 (1900).

[17] Loc. cit.; this fact had also been observed but not published by Richards and Churchill before that time.

[18] Richards and Wells, Zeit. phys. Chem., **43**, 465 (1903); These Proceedings, **38**, 43 (1902).

to Beckmann's well-known freezing point apparatus, consisting of two large test-tubes, one within the other, immersed for nine-tenths of their length in a roomy, transparent water bath. The inner test-tube, which contained the mixed hydrate, was 3.3 cm. wide and 16 cm. long (internal measurements) and had a capacity of 120 cc. The outer tube was large enough to allow a small air space between the two vessels at every point except the top, where the inner vessel was insulated from the outer one by a narrow rubber ring. This ring held the inner tube in place, preventing heat conductance through the glass to the material, and excluded the outer air from the space between the two tubes. Thus all the heat obtained by the melting material came to it from the outer bath through the confined air-jacket, which is an absolutely necessary provision if accuracy is sought.

The inner large test-tube containing the sodium chromate was closed at the top by a rubber stopper, carefully freed from loosely adhering matter which might contaminate the materials. It was pierced by two holes, through which short glass tubes were passed. One of these tubes was of the same length as the thickness of the stopper, and served to hold the stirrer; while the other reached 0.7 cm. above the stopper and below to within 1 cm. of the sodium chromate, and served to admit and support the thermometer. To the upper end of the latter tube a short length of stout rubber tubing was attached, the object of which was to hold the thermometer in place at any desired level. A water jacket around the thermometer is necessary only when the temperature of the room is several degrees distant from 20° ; because a correction for the protruding column can be applied with sufficient accuracy when the temperature difference is small.

The stirrer was made of a piece of platinum wire 15 cm. in length, at one end bent into the shape of a ring, at the other end sealed into a glass tube which served as a handle.

The thermometers were three in number. The first, an excellent Beckmann thermometer, the scale of which was divided into hundredths of a degree, was used for the preliminary experiments, where the constancy of the transition temperature of successive fractions was the main issue. Two Baudin thermometers, 15200 and 15276, standardized with the greatest care at the Bureau International des Poids et Mesures, were used in the final determination of the points on the hydrogen scale. These thermometers have been previously described;[19] their scales are divided into tenths of a degree, and readings within 0.001° were made by means of a Geneva cathetometer, observing the marks not

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[19] Richards and Wells, These Proceedings, **38**, 43 (1902); Zeit. phys. Chem., **43**, 465 (1902).

only in the usual way, but also through the glass behind the mercury. The freezing-points were taken both before and not long after the transition temperatures, and during the intervening time the instruments were carefully protected from large temperature changes.

The Temperature of the Transition from $Na_2CrO_4 \cdot 10H_2O$ to $Na_2CrO_4 \cdot 6H_2O$.

When moist crystals of the dekahydrate are melted without the addition of the solid hexahydrate, the temperatures obtained are variable and generally low. This is undoubtedly due to the fact that the water of crystallization, together with the water adhering to the crystals, is enough to dissolve the sodic chromate completely, thus preventing the formation of solid hexahydrate.

In order to avoid this difficulty, it was found best to heat about one fifth of the moist hexahydrate in a quartz or platinum vessel to 60°, thus driving off perhaps a third of the water of crystallization. The cooled product yielded solid $Na_2CrO_4 \cdot 4H_2O$ and its solution. This was added to the remainder of the $Na_2CrO_4 \cdot 10H_2O$, after which the whole mass was warmed to 28°C. in the test-tube in which the determination was to be made. The proportion of $Na_2CrO_4 \cdot 4H_2O$ to $Na_2CrO_4 \cdot 10H_2O$ should be such that at this temperature the whole is in solution. The solution was then cooled by dipping the test-tube into a beaker containing water at 20°. When the temperature of the solution had fallen to 25°, a crystal of $Na_2CrO_4 \cdot 6H_2O$ was added; it produced copious crystallization. On further cooling to 19° or slightly lower a crystal of dekahydrate was added, and still more heat was taken from the mixture, with stirring, until the mixture of the two solid phases and solution of sodium chromate was plastic.

The temperature of the water bath was kept one or two tenths of a degree higher than the equilibrium point (19.5°) and the room temperature also was kept not far away. This latter condition was not very essential, because with one of our thermometers the stem exposure was 6.5° and with the other only 0.5°.

In a preliminary set of readings, corrected in the usual way for calibration, for internal and external pressure, for error in the fundamental interval, for the corrected ice-point, for the exposed column, and to the hydrogen scale, the following values were found : —

Preliminary determination by thermometer	15200	19.518°
" " "	15276	19.525°
		19.522°

The Beckmann thermometer in this mixture indicated 0.580°. Upon crystallizing the material once more, and separating the mother liquor by centrifugal action, the crystals still gave exactly the same transition point, 0.580°, — the atmospheric pressure having remained essentially constant. Therefore it was clear that the material was as pure as it could be obtained by crystallization, and the final estimation was made.

The individual readings were corrected for stem exposure, and all averaged to give the observed value used in calculating the temperature referred to the hydrogen scale. The ice-points, which are the most uncertain part of this determination, were taken as the averages of four separate fairly concordant sets of readings, two of which were made some time before the determinations, and two immediately afterwards. As the thermometers are old and well seasoned, this procedure seemed likely to furnish the best result.

Thermometer 15200,		
Reading in salt (cor.)	19.804°	In ice + .201°
Correction, calibration	− .026	+ .002
" internal pressure	+ .027	+ .009
	19.805°	+ .212°
Corrected reading in ice	− .212	
	19.593°	
Correction, fundamental int.	+ .014	
	19.607°	
Correction to hydrogen scale	− .084	
	19.523°	
Thermometer 15276		
Reading in salt (cor.)	19.750°	In ice .143°
Cor. calibration	− .025	− .001
" internal pressure	+ .039	+ .012
	19.764°	+ .154°
Corrected reading in ice	− .154	
	19.610°	
Cor. fundamental interval	+ .001	
	19.611°	
Cor. to hydrogen scale	− .084	
	19.527°	
Total average of two final readings	19.525 ± 0.002°	

The average of the two preliminary readings was 19.522° + .004°, a result as near as could be expected to the final value, considering the range of error of each. The value of 19.525°, the result of the final determination above, may be accepted for the present as the most probable figure.[20]

The Temperature of the Transition from $Na_2CrO_4.10H_2O$ to $Na_2CrO_4.4H_2O$.

This mixture of hydrates is somewhat more difficult to prepare than the mixture of deka- and hexahydrates. From a study of the diagram on page 178 it appears that the tetrahydrate is metastable with respect to the hexahydrate between the temperatures 19.53° and 25.9±. The difficulty is to exclude the hexahydrate during the cooling of the tetrahydrate and solution from 26° to 19.99°, the transition point of the deka- to the tetrahydrate.[21] Even after the dekahydrate has appeared, and has in part relieved the supersaturation, care must be taken to exclude the intermediate hydrate. At 19.99° both dekahydrate and tetrahydrate are metastable with respect to the hexahydrate. If to a mixture of the two former a crystal of the latter be added, a depression and irregularity in the temperature occurs, and the temperature gradually falls to that of the lower transition point.[21]

The mixture of hydrates is prepared (within the test-tube in which the transition temperature is to be determined) by a method closely resembling that described for preparing the mixture of dekahydrate and hexahydrate. To the dekahydrate is added such a quantity of tetrahydrate that nearly all the solid will be in solution at 28°. By heating the mixture to this temperature, one may feel certain that none of the hexahydrate is present. The tube is then closed by a clean stopper through which the handle of a stirrer passes. The stopper serves to protect the contents from accidental inoculation by hexahydrate. When the solution has been cooled to about 19°, it is inoculated with some freshly prepared dekahydrate, which must be free from hexahydrate. Further gradual subtraction of heat, with constant stirring, gives a mixture of the desired plastic consistency.

The material used in the preliminary determination of this transition point was the same as that used in the preliminary determination of

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[20] Over one third of an atmosphere's pressure is necessary to alter this temperature by as much as 0.001°. (See Tammann, "Krys. und Schmelzen," 262 (Leipzig, 1903).)

[21] Gernez's supposed disintegration of $Na_2CrO_4.4H_2O$ in the presence of the $10H_2O$ salt (Compt. Rend., **149**, 77 (1910), would not affect this point, if, as Gernez reasonably supposes, this disintegration is due simply to the formation of the dekahydrate from included water within the salt, and not to the formation of a hydrate with less than $4H_2O$.

the equilibrium temperature of the mixed deka- and hexahydrates. With the Beckmann thermometer the new point was 1.039°. On the Baudin thermometers all individual readings were corrected for stem exposure and averaged as before.

Preliminary reading by Thermometer	15200	19.984°
" "	15276	19.990°
The average		19.987°

The material used in the final observations was the same as that used for the previous final work, after conversion into a mixture of deka- and tetrahydrate. With the Beckmann thermometer it gave the transition point 1.039, the same as that given by the salt used in the preliminary tests just recorded.

Final Determination I.

Thermometer 15200			
Reading in salt (cor.)	20.269°	In ice	.201°
Cor. calibration	− .028		+ .002
Cor. internal pressure	+ .027		+ .009
	20.268°		.212°
Corrected reading in ice	− .212		
	20.056°		
Cor. fundamental interval	+ .014		
	20.070°		
Correction to hydrogen scale	− .085		
	19.985°		

Final Determination II.

Thermometer 15276			
Reading in salt (cor.)	20.209°	In ice	.143°
Cor. calibration	— .022		− .001
Cor. internal pressure	+ .039		+ .012
	20.226°		0.154°
Corrected reading in ice	− ·154		
	20.072°		
Cor. fundamental interval	+ .001		
	20.073°		
Cor. to hydrogen scale	− .085		
	19.988°		
Total average of two final readings	19.987° ± 0.002		

It is interesting to note that the difference between the two transition temperatures is given as almost exactly the same quantity by the final readings of the two thermometers.

Difference by thermometer	15200	= 0.462°
" "	15276	= 0.461°

This of course gives a means of calibrating the Beckmann thermometer, which gave 0.459° for the interval — evidently the marks were a trifle too far apart on the latter instrument.

The close parallelism of the results with the two Baudin thermometers seems to indicate that the most probable cause of error in such work is not due to mistake in observing either of the transition temperatures, but rather to the difficulty of determining the ice-point. There can be no question that either of the sodium chromate equilibrium-temperatures is a far better means of fixing the scale of a thermometer to be used near room temperature than is the freezing point of water.

The Temperature of the Transition from $Na_2CrO_4 \cdot 6H_2O$ to $Na_2CrO_4 \cdot 4H_2O$.

The material used in this determination was sodium chromate obtained from the mother liquors of previous preparations, purified by recrystallization as dekahydrate until the temperature of transition from the dekahydrate to the hexahydrate as shown by the Beckmann thermometer was 0.580. A supersaturated solution of this pure salt at 25° was inoculated with hexahydrate and further cooled with stirring to 18°, the dekahydrate being scrupulously excluded. The plentiful crystals of hexahydrate were then centrifuged to remove the excess of mother liquor, and in order to make certain that none of the dekahydrate was present, the crystals were allowed to stand in a bath at 25° for an hour. No change occurred in the appearance of the material. Just before taking the transition temperature a few crystals of the tetrahydrate were added.

Whether on account of the interference of other unknown hydrates, or of the comparatively small heat of this transition, or of the unavoidable haste in which the experiments had to be conducted, much less constant results were obtained in this case than in the preceding. It appeared that the equilibrium temperature of the hexa- and tetrahydrates was not far from 25.90° on the hydrogen scale; but this figure is subject to further revision.

This point is worthy of further investigation, for it is exceedingly convenient, taken together with the other points given by this same salt, as a means of calibrating a Beckmann thermometer. The interval between the dekahydrate-tetrahydrate point (19.987) and the higher transition temperature is almost 6°, the usual length of a Beckmann thermometer. By adding a degree to the scale, which could easily be done in future, the lowest transition temperature of sodium chromate also could be brought within the scope of the instrument. To be able to verify a thermometer over its whole length, and at the same time to evaluate accurately the interval 0.462 on one part of the scale, all with the single purified salt, is indeed a highly desirable circumstance.

Of course the determination of the several points as given in this paper must be looked upon as merely preliminary, because time permitted the study of these temperatures on only two thermometers. The average of the readings of many thermometers should ultimately be taken. Nevertheless we believe that the averages given in this paper are sufficiently exact to be a great boon to those desiring to verify thermometers about the temperature of the room.

It is a pleasure to acknowledge the usefulness of a grant made many years ago by the Rumford Fund, of the American Academy of Arts and Sciences, for this purpose. Much of the material used in the investigation was purchased with its aid.

SUMMARY.

1. The great advantage of sodium chromate as a means of verifying thermometers at three fixed temperatures in the neighborhood of 20° is emphasized.

2. A method for the easy preparation of pure sodium chromate has been elaborated.

3. The existence of three hydrates of sodium chromate; namely, the deka-, hexa- and tetrahydrates has been confirmed.

4. The accurate estimation of the point of conversion of each of these hydrates into each of the other two has been shown to be easily feasible.

5. The addition of heteromorphous substances lowers the transition points as usual.

6. The addition of sodium sulphate (which gives an isomorphous dekahydrate) raises the temperature of the dekahydrate-hexahydrate equilibrium. This is perhaps the first observation of this type of phenomenon.

7. The temperature of the dekahydrate-hexahydrate transition is found to be approximately 19.525°, on the international hydrogen scale.

8. The temperature of the dekahydrate-tetrahydrate transition is found to be approximately 19.987°, on this scale.

9. The temperature of the hexahydrate-tetrahydrate transition is found to be approximately 25.90°, on this scale.

10. All these points, especially the last, are to receive further investigation at Harvard in the near future.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 6. — July, 1911.

CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

New Series. — No. XXXIX.

By B. L. Robinson.

I. On the Classification of certain *Eupatorieae.*
II. Revision of the Genus *Barroetea.*
III. On some hitherto undescribed or misplaced *Compositae.*

CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.—NEW SERIES, NO. XXXIX.

By B. L. Robinson.

Presented March 8, 1911. Received May 4, 1911.

I. ON THE CLASSIFICATION OF CERTAIN EUPATORIEAE

Ageratum Gaumeri, sp. nov., annuum erectum 4 dm. vel ultra altitudine copiose ramosum modice pubescens; caule tereti gracili medulloso; ramis oppositis adscendentibus foliosis; foliis ovatis acuminatis crebre et regulariter crenato-serratis tenuibus 3.5–6 cm. longis 2.5–4 cm. latis utrinque viridibus basi integris rotundatis vix ad insertionem petioli acuminatis, petiolo 1.5–2.2 cm. longo; inflorescentia perlaxa in ramulis singulis racemiformi, pedicellis 2–4 (usque ad 6) cm. longis unicapitulatis cum bracteolis 1–4 filiformibus minimis munitis; capitulis oblate subsphaericis 7–9 mm. diametro; involucri squamis linearibus attenuatis costatis glabriusculis subaequalibus; disco conico; corollis limbum versus caeruleis; styli ramis longe exsertis pulcherrime caeruleis; achaeniis nigrescentibus 5-angulatis vix in angulis obscure hispidulis 1.2 mm. longis; pappi squamis 5, aliis saepissime brevioribus muticis, aliis in aristam longam desinentibus et achaeniam longitudine subaequantibus.—*Ageratum intermedium* Millsp. Field. Col. Mus. Pub. Bot. Ser. iii. 90 (1904), not Hemsl.—Izamal, Yucatan, *Dr. G. F. Gaumer*, no. 395 (type, in Gray Herb.). From the species here described *A. intermedium* Hemsl. differs in having stems of a decidedly firmer texture, presumably perennial and of a more spreading habit. The leaves are smaller and the heads are borne in rather compact 2–5-headed long-peduncled cymes. Finally the pappus is much shorter. From the common and somewhat variable annual species *A. conyzoides* L., the plant here described differs much in habit, in its more finely serrate leaves, greater smoothness, and especially in its loose open inflorescence, which on the individual branches becomes somewhat racemiform.

Ageratum Peckii, sp. nov., annuum erectum fastigiatim ramosum 5 dm. altum foliosissimum glabrum; radice fibrosa; caule subtereti basin versus crassiusculo nodoso, internodiis inferioribus brevibus, superioribus gradatim longioribus gracilioribus atropurpureis folia longitudine superantibus; foliis lineari-oblongis integris 2.5–4.5 cm. longis 2.5–6 mm. latis obtusiusculis vel vix acutis basi subsessilibus vel petioliforme angustatis; cymis inaequaliter trichotomis, ramis lateralibus quam terminali multo longioribus usque ad 8 cm. longitudine; cymulis parvis 1–2.5 cm. diametro 3–7-capitulatis; bracteis subulatis; pedicellis 2–10 mm. longis bracteolatis; capitulis 3.5–4 mm. diametro; involucri squamis ca. 20 glabris anguste lanceolati-linearibus acutissimis plerumque 2-costatis; corollis glabris purpureis; achaeniis nigris acute 5-angulatis 1 mm. longis glabris; pappi squamis 5 lanceolatis scariosis apice setiferis 2 mm. longis. — British Honduras, in sandy open ground, on pine ridge near Manatee Lagoon, 25 July, 1905, *Prof. Morton E. Peck*, no. 80 (type, in Gray Herb.). A very distinct annual species with glabrous narrow entire leaves, commonly proliferous in the axils.

Ageratum radicans, sp. nov., glabrum prostratum ramosum ad nodos et etiam hinc inde inter eos radicans; caule teretiusculo brunneo vel stramineo-brunneo; internodiis 3–8 cm. longis; foliis oppositis anguste elliptico-oblongis integerrimis glabris 3-nerviis supra viridibus et cum nerviis impressis subtus pallidioribus impunctatis 4–8 cm. longis 5–15 mm. latis apice obtusiusculis basi petioliforme angustatis; inflorescentiis longe pedunculatis contractis cymosis paucicapitulatis; capitulis breviter pedicellatis 8–10 mm. diametro; involucri squamis anguste lanceolatis acutissimis plerumque 2-costatis subaequalibus (paucis exterioribus parvis exceptis) maturitate patentibus; flosculis glabris; corollis limbum versus purpurascentibus; achaeniis acute 5-angulatis ca. 1.2 mm. longis; pappi squamis 5 albis plus minusve erosis vel laceratis apice cum seta munitis ca. 2.2 mm. longis. — British Honduras, in fresh water pond near Manatee Lagoon, 4 August, 1905, *Prof. Morton E. Peck*, no. 99 (type, in Gray Herb.). This species, in technical characters exceedingly near *A. Peckii*, differs much in its prostrate and repent habit, its very much larger leaves, and slightly larger heads, flowers, and achenes.

Podophania dissecta (Hook. & Arn.), comb. nov. *Phania? dissecta* Hook. & Arn. Bot. Beech. 433 (1841). *Eupatorium dissectum* (Hook. & Arn.) Benth. Bot. Sulph. 113 (1844). *Podophania Ghiesbreghtiana* Baill. Bull. Soc. Linn. Par. i. 268 (1880). Repeated efforts to discover any distinctions between the types of Hooker & Arnott and of Baillon have failed to disclose any difference, the floral characters, foliage, and even pubescence appearing to be identical.

HOFMEISTERIA FASCICULATA (Benth.) Walp., var. **pubescens** (Wats.), comb. nov. *H. pubescens* Wats. Proc. Am. Acad. xxiv. 54 (1889). The glandular pubescence, although, when copious, as in the original specimen upon which Dr. Watson founded his species, becoming a striking feature, seems to be accompanied by no other differential character and is, as shown by later collections, by no means constant.

Trichogonia capitata (Rusby), comb. nov. *Eupatorium capitatum* Rusby, Bull. N. Y. Bot. Gard. iv. 380 (1907). An examination of a cotype of this species (*Bang*, no. 2114) in the Gray Herbarium shows not only that it has the general habit and foliage as in *Trichogonia*, but possesses the plumose pappus characteristic of that genus, to which accordingly it should be referred.

EUPATORIUM BETONICIFOLIUM Mill., var. **integrifolium** (Gray), comb. nov. *E. Hartwegi* Benth. Pl. Hartw. 19 (1839). *Coelestinia Hartwegi* (Benth.) Walp. Rep. ii. 545 (1843). *Conoclinium betonicum* DC., var. ? *integrifolium* Gray, Pl. Wright. i. 88 (1852). *Eupatorium betonicum* (DC.) Hemsl., var. *subintegrum* Gray, Syn. Fl. i. pt. 2, 102 (1884). *Conoclinium integrifolium* (Gray) Small, Fl. S. E. U. S. 1170, 1338 (1903). *Eupatorium betonicum*, var. *intregrifolium* (Gray) Small, ll. cc.

EUPATORIUM COELESTINUM L., var. SALINUM Griseb. Cat. Pl. Cub. 146 (1866). This plant (Wright's no. 2811 from Cuba) though a marked form is described somewhat misleadingly thus: "forma foliis acute dentatis." The teeth of the leaves are in fact by no means acute, being in most instances actually rounded at the tip; but what furnishes the really striking difference between this form and the typical *E. coelestinum* is the fact that the leaves are considerably more deeply and somewhat doubly toothed. The blades also are of a more deltoid outline.

Eupatorium frustratum, sp. nov., perenne 3–9 dm. altum a basi paulo lignescenti ramosum, radice fibrosa, ramis teretibus striatis viridibus patente vel crispe puberulis adscendentibus, internodiis longiusculis folia multo superantibus; foliis oppositis petiolatis ovatis (vel eis ramulorum lanceolato-ovatis) 3-nerviis crenato-serratis obtusiusculis 1.5–3.2 cm. longis 0.8–2.2 cm. latis utrinque breviter pubescentibus; inflorescentia iterum atque iterum cymoso-furcata, axe principali in capitulo quasi abortive terminante (unde nomen); capitulis ovoideo-cylindricis 1 cm. longis 5 mm. diametro, involucri squamis multiseriatim imbricatis arcte appressis viridi-striatis apice rotundatis valde deciduis, receptaculo elevato crassiusculo cylindrico 1.5 mm. alto minute papilloso; flosculis caeruleis; achaeniis olivaceis minute in faciebus sursum strigillosis. — *Ooclinium rigidum* Chapm. Bot. Gaz. iii. 6 (1878), not DC. *Eupatorium heteroclinium* Gray, Syn. Fl. i. pt. 2, 95 (1884), not Griseb. *Osmia heteroclina* Small, Fl. S. E. U. S. 1164 (1903), excl. syn. — South Florida: coral soil, Lignum Vitae Key, *A. H. Curtiss*, no. 1195* (type, in Gray Herb.); Key West, *Blodgett*; Jew Fish Key, *Chapman*; rich thicket, Key Largo, June, 1880, *A. H. Curtiss*, no. 171; Upper Metacumbe, 11 April, 1892, *J. H. Simpson*, no. 565. This species, long identified with the Jamaican *E. heteroclinium* Griseb., differs in having decidedly smaller heads, shorter leaves of a more deltoid contour, more obtuse involucral scales, olivaceous instead of dark violet-brown achenes which are strigillose instead of smooth on their faces, and in other minor characters. Were these plants of Florida and Jamaica really identical, it would certainly be strange that their range did not include Cuba.

EUPATORIUM GLABRATUM HBK. Nov. Gen. et Spec. iv. 127 (1820). To the synonymy of this species should be added *E. xalapense* HBK. l. c. 128 (1820), and *E. gonocladum* DC. Prod. v. 171 (1836). The greater part of recently collected material of this affinity has been referred to *E. glabratum*, while *E. xalapense* and *E. gonocladum* have remained obscure. After examining at the herbarium of the Museum of Natural History in Paris original material of *E. glabratum* and *E. xalapense*, and at the De Candollean herbarium in Geneva the exceedingly fragmentary type of *E. gonocladum*, the writer has failed to detect any significant difference. Of the two earlier names, the more commonly used *E. glabratum* happily has priority of position.

Eupatorium iodostylum, sp. nov., fruticosum; ramis teretibus flexuosis brunneo-griseis plus minusve striatulis glabratis; ramulis foliosis crispe vel patente purpureo-puberulis, pilis sub lente moniliformibus; foliis oppositis oblongo-lanceolatis undulate et subremote serratis tenuibus basi anguste acuminatis ad apicem verum subobtusum gradatim angustatis 10–16 cm. longis 3–3.6 cm. latis utrinque sparse obscureque pubescentibus penninerviis supra austere viridibus subtus vix pallidioribus; petiolo 1.8–2.8 cm. longo patente pubescenti; corymbis terminalibus erectis pedunculatis alternirameis multicapitulatis 6–10 cm. diametro convexis vel planiusculis; bracteis linearibus 1–2 cm. longis; ramulis inflorescentiae crispe purpurascenti-puberulis; pedicellis anthesi 5 fructu saepius ad 10 mm. longitudine; capitulis 26–34-floris graciliter campanulatis anthesi ca. 11 mm. altis 7–9 mm. diametro; involucri squamis ca. triseriatis linearibus ciliolatis laxe imbricatis, exterioribus herbaceis attenuatis 4–8 mm. longis, interioribus ca. 1 cm. longis perangustis tenuibus subscariosis acutis striatulis; corollis graciliter tubulosis 5–6 mm. longis apicem versus pulcherrime roseo-purpureis a basi ad apicem levissime ampliatis, faucibus nullis, limbi dentibus 5 deltoideis 0.8 mm. longis, antheris distinctis anguste oblongis apice appendiculatis basi integris; styli ramis longe exsertis filiformibus laete violaceis; achaeniis 3 mm. longis argute 5-costato-angulatis glabris basin versus attenuatis; pappi setis gracillimis albis 25-30 corollam subaequantibus. — Limestone rocks, Trinidad Mountains, Santa Clara, Cuba, Arroyo Cimarron, altitude 470 m., *N. L. & E. G. Britton*, 5 March, 1910 (type, in Gray Herb.).

Eupatorium (§ **Imbricata**) **pluriseriatum,** sp. nov., fruticosum inflorescentia excepta glaberrimum; ramis arcuatis pallide griseo-brunnescentibus subteretibus lucidulis; ramulis purpurascentibus striatulis; foliis oppositis graciliter petiolatis ovatis firmiusculis longe falcatim attenuato-acuminatis denticulatis 9–12 cm. longis 4.5–5.5 cm. latis utrinque laete viridibus basi rotundatis sed ad insertionem petioli ca. 2.7 cm. longi in eo plus minusve acuminato-decurrentibus; panicula corymbosa oppositiramea multicapitulata densiuscula, axe et ramulis puberulis; capitulis (infeliciter immaturis) cylindraceis ca. 8 mm. altis 4 mm. diametro 7–10-floris breviter pedicellatis vel in apicibus ramulorum subsessilibus et fasciculatim aggregatis; involucri squamis valde inaequalibus multiseriatim imbricatis glabris subscariosis viridi-striatulis fimbriati-ciliolatis, apice rotundatis, margine saepius brunnescentibus quasi ustis, a receptaculo cylindrico truncato caducis; corollis glabris graciliter tubulosis quam achaenis etiam glabris multo longioribus; pappi setis tenuibus corollas subaequantibus sursum minute scabratis. — On bank; Aguacate, altitude 750–850 m., Trinidad Mountains, Santa Clara, Cuba, 10–11 March, 1910, *N. L. Britton & Percy Wilson*, no. 5407 (type, in Gray Herb.).

Eupatorium urticaefolium Reichard, var. **tomentellum,** var. nov., formae typicae habitu statura foliis etc. simile; caule ab apice usque infra mediam partem dense breviterque crispe griseo-tomentello; foliis plerumque subtus tomentellis. — Madison, Wisconsin, 28 August, 1893, *Judge J. R. Churchill* (type); Mt. Carmel, Illinois, 1875, *Dr. D. Schneck* (Gray Herb.); edge of maple forest, Marquette, Michigan, 12 August, 1901, *Bronson Barlow* (Gray Herb.). This variety differs from *E. urticaefolium*, var. *villicaule* Fernald of the middle Atlantic States in having a very much shorter closer non-viscid indumentum.

Mikania cristata, sp. nov., robusta scandens; caulibus angulato-striatis puberulo-tomentellis, internodiis usque ad 1.7 dm. longis; foliis oppositis longe petiolatis late ovatis profunde cordatis acuminatis firmiusculis integriusculis utrinque breviter velutino-tomentosis a basi 3–5(–9)-nerviis; petiolis robustis recurvatis tortis anguineis ca. 5 cm. longis basin versus crassioribus, eis ejusdem jugi membrana stipulari margine appendicibus caudiformibus conspicue cristata connexis; capitulis 4-floris corymbosis ca. 9 mm. longis breviter pedicillatis, corymbis oppositis pedunculatis ca. 1 dm. diametro, pedunculis (4–6 cm. longis) et inflorescentiae ramulis valde compressis; involucri squamis oblongis obtusiusculis ca. 6 mm. longis, exterioribus dorso puberulis; corollae tubo cylindrico curvato glabro 3 mm. longo, faucibus nullis, limbi dentibus 5 oblongo-linearibus patentibus 1.8 mm. longis obtusiusculis; achaeniis glabris 5-costato-angulatis deorsum attenuatis 3.6 mm. longis; pappi setis ca. 50 rufis 4.5 mm. longis laevibus. — Bushy places, La Palma, Costa Rica, September, 1898, altitude 1459 m., *Ad. Tonduz*, no. 12,583 (type, in U. S. Nat. Mus., fragm. in Gray Herb.). A species well marked by the conspicuously crested stipular appendages.

Mikania hexagona sp. nov., fruticosa robusta scandens; caulibus lignosis tortis acute et subalato-hexagonis atrobrunneis cavis 1 cm. diametro, internodiis longissimis (3 dm. et ultra); ramis oppositis alato-hexagonis praecipue in angulis tomentellis; foliis late ovatis acuminatis integris 1 dm. longis 7 cm. latis basi rotundatis in petiolum 2.5 cm. longum plus minusve cuneatum decurrentibus paulo supra basin 7-nervatis utrinque scabro-puberulis viridibus infra paulo pallidioribus, superioribus et floralibus multo minoribus subsessilibus; inflorescentiis composite corymbosis ca. 2 dm. diametro densiusculis; bracteis herbaceis ovato-lanceolatis acuminatis tenuibus, ultimis involucri squamas saepe aequantibus dorso obscure puberlis; pedicellis gracilibus 3–5 mm. longis; involucri squamis anguste lanceolato-oblongis acuminatis tenuibus pallide viridibus glabriusculis; corollis 5 mm. longis glabris, tubo proprio 2.5 mm. longo gracili firmiusculo, faucibus bene distinctis campanulatis vix 1 mm. altis, dentibus limbi oblongis crispis ca. 2 mm. longis saepe conniventibus; achaeniis 5-angulatis ca. 4 mm. longis deorsum decrescentibus; pappi setis ca. 70 ca. 5 mm. longis rufescentibus; styli ramis filiformibus nec clavellatis 4 mm. longis. — Near Tovar, Venezuela, 1854–55, altitude 1700 m., *A. Fendler*, no. 626 (type, in Gray Herb.). A species seemingly well marked by its very robust hexagonal stem with acute narrowly wing-margined angles.

Mikania leucophylla (Rusby), comb. nov. *Willoughbya leucophylla* Rusby, Bull. N. Y. Bot. Gard. iv. 382 (1907).

Mikania longiflora (Rusby), comb. nov. *Willoughbya longiflora* Rusby, Bull. N. Y. Bot. Gard. iv. 382 (1907).

MIKANIA MYRICAEFOLIA (Bojer) DC. Prod. v. 188 (1836). *Trixis myricaefolia* Bojer in litt. ex DC. l. c. Examination of the type of this plant of Madagascar, kindly permitted by Mr. Casimir de Candolle, showed that it has alternate thickish leaves narrowed at the base to short but slender petioles, heads (all in bud) nearly cylindrical, involucral scales 6 to 7, and florets 10 to 11. Although from the very immature heads it is impossible to ascertain satisfactorily the style characters or other details regarding the florets, it is nevertheless certain from the number of involucral scales and of the florets in the head that the plant is not a *Mikania*, nor from its habit and alternate leaves does it seem likely that it belongs in the tribe of the *Eupatorieae*.

Mikania paezensis, sp. nov., scandens; caule et ramulis striatis a tomento brevi fusco vel atropurpureo etiam fere nigrescenti tectis; foliis longiuscule petiolatis oppositis ovatis acutis crenato-denticulatis supra bullato-rugosis pubescentibus subtus pallidioribus tomentosis basi sinu patenti cordatis ca. 4.5 cm. longis ca. 3.5 cm. latis; petiolo tomentoso 3–3.5 cm. longo; corymbis ad 7 cm. longe pedunculatis 6–10 cm. diametro planiusculis tomentellis, bracteis foliaceis reductis 0.8–1.6 cm. longis ovatis petiolatis, pedicellis gracilibus 4–6 mm. longis; capitulis ca. 12 mm. longis; involucri squamis lanceolato-oblongis acutiusculis dorso fusco-tomentellis 8–9 mm. longis; corollis 5–6 mm. longis, tubo gracili, faucibus campanulatis, limbi dentibus 5 latissime triangularibus erectiusculis apicem versus tomentellis; achaeniis 5 mm. longis atrobrunneis glabris deorsum decrescentibus argute 5-costato-angulatis; costis albidis minutissime scabratis. — Las Escaleretas, Moras Valley, Rio Paez basin, Tierra Adentro, State of Cauca, Colombia, altitude 2500–3000 m., February, 1906, *Pittier*, no. 1336 (type, in U. S. Nat. Mus., fragm. in Gray Herb.). Notwithstanding its constantly 5-angled achenes this species seems to be suspiciously near the plant described below as *Kanimia violascens*. The two differ sufficiently in leaf-form, indumentum, length of peduncles, size of heads, etc., to be satisfactory as species, but in placing them in different genera (though their technical characters appear to require it) there seems to be some artificiality.

MIKANIA PARVIFLORA (Aubl.) Karst. Deutsche Fl. 1061 (1883); Urb. ex Hieron. in Engl. Bot. Jahrb. xxviii. 579 (1901). *Eupatorium parviflorum* Aubl. Fl. Guian. ii. 797, t. 315 (1775). — To the synonymy of this widely distributed and moderately variable species should be added, in the opinion of the writer, the following: *Mikania olivacea* Klatt, Bull. Soc. Bot. Belg. xxxi. 195 (1892); Rob. & Greenm. Proc. Am. Acad. xxxii. 12 (1896), and *Willoughbya Hieronymi* Rusby, Bull. N. Y. Bot. Gard. iv. 383 (1907). As thus interpreted, this species ranges from Costa Rica to Guiana and Bolivia.

Mikania sulcata (Hook. & Arn.), comb. nov. *Eupatorium sulcatum* Hook. & Arn. Comp. Bot. Mag. i. 243 (1835). *Mikania penstemonoides* DC. Prod. v. 189 (1836). *M. pentstemonoides* Bak. in Mart. Fl. Bras. vi. pt. 2, 221 (1876).

Mikania sulcata (Hook. & Arn.) Robinson, var. **ambigua** (DC.), comb. nov. *M. ambigua* DC. Prod. v. 187 (1836). *M. pentstemonoides*, var. *ambigua* (DC.) Bak. in Mart. Fl. Bras. vi. pt. 2, 221 (1876).

Mikania ternata (Vell.), comb. nov. *Cacalia ternata* Vell. Fl. Flum. (text) 336 (1825), viii. t. 56 (1827). *Mikania dentata* Spreng. Syst. iii. 422 (1826) presumably, but scarcely of Schlecht. Linnaea, xi. 12 (1837), which notwithstanding the sign of affirmation employed by Schlechtendal can from character hardly have related to the plant described by Sprengel. *M. apiifolia* DC. Prod. v. 202 (1836).

Kanimia corymbiifolia, sp. nov., herbacea perennis erecta rigidula glaberrima 6–7 dm. alta usque ad inflorescentiam corymbosam simplici, internodiis infimis brevibus (2–15 mm. solum longis), supremis usque ad 6 cm. longitudine; foliis oppositis erectis appressis linearibus crassiusculis rigidulis integerrimis 3-nerviis obtusis sessilibus 4–7 cm. longis 1–3 mm. latis superioribus gradatim minoribus; inflorescentia trichotoma 3–11 cm. lata planiuscula 4–20-capitulata; bracteis anguste linearibus plus minusve alternis 8–12 mm. longis; capitulis (quoque cum bracteola unica arcte suffulto) 1.3 cm. altis 4-floris erectis; involucri squamis ovato-oblongis crassiusculis acutiusculis 2–3 mm. latis; corollis 7 mm. longis, tubo gracili 3 mm. longo, faucibus brevissimis, limbi dentibus lineari-oblongis; achaeniis immaturis 4.5 mm. longis summa parte 10-costato-angulatis; pappi setis ca. 44 rufis 6 mm. longis scabridis. — Moist meadows near a brook in the Serradão near Cuyabá, Mattogrosso, Brazil, February, 1889, *R. Pilger*, no. 220 of Dr. Hermann Meyer's second Brazilian journey. Type in the herbarium of the Royal Botanical Gardens, Berlin; fragments and tracing in the Gray Herbarium. A species markedly distinct in habit from its congeners, resembling in its thickish firm ribbed narrow leaves some species of the African genus *Corymbium.*

Kanimia violascens, sp. nov., scandens ubique a hirsutia densa sordida violascenti tecta; caule flexuoso torto multi-angulato, internodiis 6–9 cm. longis; foliis oppositis petiolatis ovalibus grosse crenatis profunde cum sinu angusto cordatis ca. 4 cm. longis ca. 3.5 cm. latis apice rotundatis crassiusculis bullato-rugosis; petiolo 1.5–2 cm. longo; corymbis trichotomis axillaribus erectis ad 2 cm. longe pedunculatis cum bracteis foliaceis suborbicularibus munitis; bracteolis parvis ovalibus; pedicellis 4–8 mm. longis; capitulis 1.2–1.5 cm. altis 4-floris; involucri squamis oblongis apicem versus carinatis plus minusve attenuatis sordide villoso-tomentosis ca. 9 mm. longis; corollis 7 mm. longis, tubo gracili glabro 4 mm. longo, faucibus campanulatis glabris; dentibus limbi 5 deltoideis erectiusculis apicem versus hispidulis; achaeniis 5.5 mm. longis nigris basin versus decrescentibus, costis plerumque 7–8 (rariter in eodem capitulo achaenio uno vel altero 5-costato) albidis minutissime scabridis, pappi setis ca. 75 rufidulis corollam aequantibus; styli ramis gracillimis filiformibus longe exsertis et recurvatis antheris linearibus apice cum appendice ovata obtusa scariosa munitis. — Alto del Tabano among the Andes of the southern Cordillera of Colombia, altitude about 3500 m., 4 May, 1876, *E. André*, no. 3123 (type, in Gray Herb.).

Brickellia amplexicaulis, sp. nov., herbacea vel fruticulosa 1.3–1.8 dm. alta; caulibus teretibus medullosis saepe purpureis copiose et patente glandulari-pubescentibus; foliis oppositis oblongis vel saepius ovato-oblongis crenato-serratis vel -dentatis basi arcte sessilibus late cordato-amplexicaulibus ad apicem obtusiusculum angustatis 8–13 cm. longis 2.5–5.8 cm. latis utrinque pubescentibus subtus paulo pallidioribus saepe indumento densiori tectis pinnativenatis et a loco 1–1.5 cm. supra basin 3-nerviis; inflorescentia elongata laxe paniculata folioso-bracteata; pedicellis ad 5 cm. longis filiformibus patente adscendentibus; capitulis 1.2–1.5 mm. altis ca. 13-floris; involucri squamis angustis tenuibus attenuatis valde inaequalibus viridibus vel saepe purpurascentibus vel etiam atropurpureis saltim exterioribus patente ciliolatis; corollis 9 mm. longis gracillimis exacte tubulatis glabris, faucibus nullis, limbi dentibus brevissimis erectis; styli ramis erectis nigrescentibus modice clavellatis; achaeniis breviter sed dense hirsutulis; pappi setis 50–60 laete albis quam corolla distincte brevioribus. — *B. Wislizeni* var. Gray, Pl. Wright. ii. 71 (1853). *B. Wislizeni*, var. *paniculata* Gray acc. to Pringle, Pl. Mex. (1885), nomen nudum. — SONORA: near Santa Cruz, 1851, *Charles Wright*, no. 1136 (type, in Gray Herb.); Huchuerachi, 4 December, 1890, *Hartman*, no. 325; Oakridge Pass, *Hartman*, no. 333. CHIHUAHUA: rocky hills near the city of Chihuahua, 8 October, 1885, *Pringle*, no. 609; Sierra en Media, 28 September, 1899, *E. W. Nelson*, nos. 6475 and 6491; near Batopilas, 3–4 October, 1898, *E. A. Goldman*, no. 204. SINALOA: Cerro Colorado, 3 November, 1904, *Brandegee*. — This species, though somewhat variable in the breadth and toothing of the leaves, seems to be constant and readily recognizable as to essentials. It is readily distinguished from *B. Wislizeni* by its smaller decidedly fewer-flowered heads, looser inflorescence, and larger leaves.

Var. **lanceolata** (Gray), comb. nov., foliis quam eis formae typicae multo angustioribus lanceolato-oblongis minus amplexicaulibus ca. 6 cm. longis 1.2–1.5 cm. latis. — *B. Wislizeni* Gray, var. *lanceolata* Gray, Syn. Fl. i. pt. 2, 107 (1884). — San Francisco Mountains, near Clifton, Arizona, 1 November, 1880, *E. L. Greene* (type, in Gray Herb.).

Brickellia brasiliensis (Spreng.), comb. nov. *Eupatorium brasiliense* Spreng. Syst. iii. 417 (1826); DC. Prod. v. 182. *Clavigera pinifolia* Gardn. in Hook. Lond. Jour. Bot. v. 461 (1846). *Brickellia pinifolia* Gray, Pl. Wright. i. 84 (1852); Bak. in Mart. Fl. Bras. vi. pt.

2, 372 (excl. syn. *Carphephorus coridifolius* DC., which is clearly distinct). *Mikania ericoides* Mart. ex Bak. l. c. (1876).

Brickellia coridifolia (DC.), comb. nov. *Carphephorus coridifolius* DC. Prod. vii. 267 (1838). This species, resting solely upon the original material collected on the Serro do Frio, Minas Geraës, Brazil, in 1833, *Vautier*, no. 314, was placed by DeCandolle in the genus *Carphephorus* doubtless because he found the receptacle chaffy at least to some extent. Dissection of a head from a cotype in the Gray Herbarium shows the receptacle to be chiefly free from chaff. At only one point two narrow scales, like the inner ones of the involucre, were crowded in among the flowers, and formed, as it were, a sort of re-entrant part of the involucre. In all other respects the plant agrees technically with *Brickellia*. Mr. J. G. Baker, in treating the *Eupatorieae* for the Flora Brasiliensis, doubtfully reduces the species to a synonym of *Brickellia pinifolia* (Gardn.) Gray — a species above reduced to *B. brasiliensis* (Spreng.) Robinson — but the plant, when compared with *B. brasiliensis* is obviously distinct. The involucral scales for instance are very different, being in *C. cordifolius* nearly twice as long as in *B. brasiliensis*. They are furthermore much more attenuate, distinctly 3-ribbed, and dorsally glandular-puberulent, while in *B. brasiliensis* they are glabrous and minutely many-striate. In involucre the plant agrees much better with *Brickellia* than with the North American genus *Carphephorus*. Moreover, the limb of the corolla is very short as in *Brickellia* instead of being rather deeply cleft as in *Carphephorus*. The affinities of the species appear to be with *B. brasiliensis*, though without doubt the plant is specifically distinct. The species being little known it seems worth while to put on record the traits brought out by recent examination. Capitulis 8-floris turbinato-campanulatis 1.2 cm. altis ca. 1 cm. diametro; involucri squamis lanceolatis vel anguste oblongis acutis dorso convexis tomentellis striatulis ca. 3-seriatis valde inaequalibus; receptaculo parvo plano cum paleis paucissimis marginalibus irregulariter munito; pappi setis ca. 30 barbellatis corollas aequantibus; corollis 7–8 mm. longis vix sursum ampliatis, dentibus limbi 5, 0.5 mm. longis; styli ramis clavellatis; antheris anguste oblongis vix connatis apice breviter et late appendiculatis basi integris; achaeniis immaturis 2 mm. longis papillosis deorsum decrescentibus 5-costato-angulatis cum nerviis obscuris intermediis.

BRICKELLIA DIFFUSA (Vahl) Gray, Pl. Wright. i. 86 (1852). *Eupatorum diffusum* Vahl, Symb. Bot. iii. 94 (1794). To the synonymy of this species should be added *Eupatorium trichosanthum* A. Rich. Fl. Cub. Fanerog. ii. 41 (1853), the type of which was recently examined by the writer in the herbarium of the Museum of Natural History at Paris.

BRICKELLIA SCOPARIA (DC.) Gray, var. **subauriculata,** var. nov., foliis basin versus paulo ampliatis ad 7 mm. latitudine subauriculatis, auriculis brevissimis rotundatis, margine revolutis. — Hills of Zacatecas, Mexico, 25 October, 1888, *Pringle*, no. 1766 (type, in Gray Herb.); also en route from San Luis Potosi to Tampico, December, 1878, to February, 1879, *Palmer*, no. 1077. The hitherto unpublished herbarium name of this variety has been on some plant-labels attributed to Dr. Gray, but this seems to have been an error. So far as can be ascertained from the material and records at the Gray Herbarium, Dr. Gray regarded Palmer's no. 1077 as typical *B. corymbosa*, and the Pringle plant was not collected until after Dr. Gray's death. Under these circumstances it seems undesirable, as it is unnecessary, to employ a parenthetical authority in this case.

Kuhnia adenolepis, sp. nov., perennis, caulibus saepe 2 gracilibus e caudice lignescenti oriuntibus erectis summa parte minutissime puberulis 6–8 dm. altis teretibus obscure striatulis purpureis; foliis alternis, infimis ante anthesin delapsis, intermediis anguste lanceolatis integerrimis longe attenuatis 6–7 cm. longis 7 mm. latis saepe falcatis patentibus utrinque viridibus glabris puncticulatis basi 3-nerviis; foliis superioribus gradatim minoribus, eis ramorum floriferum parvis linearibus; capitulis paucis 2–3 in ramis gracilibus elongatis bractiferis solitariis terminalibus erectis vel leviter nutantibus 12–13 mm. diametro 18 mm. altis ca. 10–12-floris; involucri squamis viridibus albido-striatis multiseriatim imbricatis, saltim exterioribus cum glandulis nigrescentibus subsessilibus eleganter ciliolatis; corollis gracilibus apicem versus atropurpurascentibus, dentibus limbi brevissimis suberectis; styli ramis nigrescentibus clavellatis conspicue exsertis; pappi setis valde plumosis leviter fulvescentibus. — Chapala Mountains, near Guadalajara, Mexico, 13 December, 1889, *C. G. Pringle*, no. 2933 (type, in Gray Herb.). A species of graceful habit and seemingly unique in its curiously glandular-ciliolate involucral bracts.

LIATRIS TENUIFOLIA Nutt., var. **laevigata** (Nutt.), comb. nov., quam forma typica conspicue robustior; foliis 4–8 mm. latis coriaceis; capitulis saepe sed non semper paulo majoribus etiam ad 9 mm. longitudine.— *L. laevigata* Nutt. Trans. Am. Phil. Soc. vii. 285 (1840). *L. tenuifolia* Nutt. *β* Torr. & Gray, Fl. ii. 70 (1841). *Lacinaria laevigata* (Nutt.) Small, Fl. S. E. U. S. 1175 (1903). *Laciniaria laevigata* (Nutt.) Small, l. c. 1339.—To this variety may be referred Mr. Nash's nos. 1669 and 2599 from Eustis, Florida, while Prof. Hitchcock's no. 154 from Marco, Florida, represents a transition to the more slender typical form. It is believed that few persons will be disposed to follow the older authors in uniting without distinction of name plants so conspicuously different in their foliage as *L. tenuifolia* and *L. laevigata*, yet on the other hand intergradation seems to be demonstrated and there are no differences of much taxonomic significance. To maintain the larger plant as a distinct species on the sole ground of its greater robustness, seems as undesirable as to suppress it altogether.

II. REVISION OF THE GENUS BARROETEA.

BARROETEA Gray. (Clarissimo *G. Barroeta* doctori medicinae et professori scholae metallorum ad oppidum mexicanum San Luis Potosi dictum institutae ob amicitiam suam cum collectoribus botanicis doctoribus Parryo et Palmero petito eorum dedicata.) — Capitula mediocria 17–35-flora; involucri campanulati vel turbinati squamis valde inaequalibus appresse imbricatis tenuibus costato-lineatis saepius attenuatis raro obtusis vel apice rotundatis mucronulatisque; receptaculo plano nudo. Corollae tubulatae glabrae pallidae ad insertionem filamentorum plus minusve constrictae, faucibus vix ullis, limbo breviter 5-dentato. Antherae distinctae vel levissime connatae, apice in appendicem latam obtusissimam productae, basi rotundatae integrae. Styli rami clavellati vel apud speciem unicam valde sursum incrassati, paulo exserti. Achaenia valde obcompressa anguste oblonga, margine sursum scabrata vel ciliolata, in facie exteriori vel uninervia vel conspicue unicostata, in facie interiori 2–3-nervia vel -costata. — Proc. Am. Acad. xv. 29 (1879), xvii. 206 (1882); Hemsl. Biol. Cent.-Am. Bot. ii. 102 (1881); Hoffm. in Engl. & Prantl, Nat. Pflanzenf. iv. Abt. 5, 142 (1890). *Barroetia* Hook. f. & Jacks. Ind. Kew. i. 276 (1893); Dalla Torre & Harms, Gen. Siphon. 528 (1905). — Herbae graciles annuae vel perennes nonnunquam basi paulo lignescentes saepius ramosae foliosae crispe puberulae vel tomentellae rarius glanduliferae. Folia vel omnia opposita vel superiora alterna ovata petiolata vel sessilia crenati- vel argute serrati-dentata, apice et dentibus saltim posticis in appendices setiformes desinentibus. Capitula saepius in panicula laxiuscula foliaceo-bracteata disposita.

Genus Brickelliae arcte affine et eae habitu, involucro, etc. simillimum differt dentibus foliorum setiferis et praesertim achaeniis valde obcompressis 5–6-costatis.

Species hucusque cognitae 7 omnes mexicanae praecipue montanae et calciphilae locos umbrosos praeferentes, una (n. 1) excepta inter se arctissime affines characteribus quamquam saepe obviis tamen incertis et minus constantibus diagnoscendae.

Clavis specierum.

a. Pubescentia pedicelli glandulifera. Corolla achaenio distincte brevior. 1. *B. glutinosa.*
a. Pubescentia pedicelli non glandulifera. Corolla achaenium subaequans vel eo longior, *b.*
  b. Folia arcte sessilia, *c.*
    c. Capitula nutantia, involucri squamis subscariosis exterioribus cum ceteris contiguis . . . . 2. *B. Pavonii.*
    c. Capitula erecta, involucri squamis majus herbaceis exterioribus subremotis . . . . 3. *B. sessilifolia.*
  b. Folia saltim caulina petiolata, *d.*
    d. Achaenia obscure in faciebus nervata, *e.*
      e. Folia argute et grosse dentata, dentibus omnibus longiuscule setigeris. Capitula 17–23-flora . . . . 4. *B. setosa.*
      e. Folia crenato-dentata, dentibus breviter setigeris vel setis ad apicem et dentes 1–3 posticos restrictis. Capitula 30–35-flora. 5. *B. subuligera.*
    d. Achaenia prominule et conspicue in faciebus 1–3-costata, *f.*
      f. Inflorescentiae saltim secundariae conspicue dichotomae capitula saepe in dichotomis gerentes; pedicelli capitula longitudine aequantes vel superantes . . . . 6. *B. laxiflora.*
      f. Capitula subsessilia in ramis elongatis paniculae. 7. *B. brevipes.*

1. B. GLUTINOSA Brandegee, annua subsimplex vel pauciramea 1–2 dm. alta undique breviter denseque glandulo-puberula; caule subtereti purpurascenti; foliis ovatis duplice crenato-serratis omnino esetosis tenuibus utrinque viridibus subtus vix pallidioribus supra minute papillosis subtus resinoso-atomiferis 1–2 cm. longis 8–15 mm. latis basi subtruncatis vel subcordatis, petiolis 1–1.5 cm. longis; capitulis 1–5 in pedunculis axillaribus 4–50 mm. longis erectis vel leviter nutantibus ca. 25-floris; involucri campanulati 9 mm. alti squamis obtusis mucronulatisque oblongo-lanceolatis atropurpureis; corollis 3–6 mm. longis sursum in fauces subdistinctos ampliatis; styli ramis sursum valde incrassatis; achaeniis 4 mm. longis griseis vix costatis scabridis, pappi setis laete albis sursum scabridis achaenio brevioribus. — Zoe, v. 262 (1908). — In umbrosis montium Cerros dictorum prope San Luis Tultitlanpa, Puebla, Mexico, *Purpus*, n. 2625. Species generis ob staturam minorem, indumentum purpureum glanduliferum, capitula pauca, styli ramos apice crassissimos distinctissima.

2. B. PAVONII Gray, herbacea ramosa; foliis ovatis basi subcordatis vel subtruncatis tenuibus subduplice crenato-serratis ca. 3 cm. longis 2 cm. latis utrinque pubescentibus supra viridibus subtus pallidioribus, apice et dentibus paucis posticis setuliferis; capitulis laxe paniculatis 9 mm. altis ca. 15-floris in apice pedicelli gracilis 1 cm. longi nutantibus; involucri squamis anguste lanceolato-linearibus acutis subglabris

margine tenuissimis scariosis; corolla achaenium subaequanti; costis achaenii nigrescentis sursum hispidulis, intervallis glabris. — Proc. Am. Acad. xvii. 206 (1882). *Eupatorium setiferum* et *E. cuspidatum* herb. Pavonii ex Grayo, l. c. — Mexico, hb. Pav. nunc hb. Boiss. Species ut videtur nunquam iterum lecta.

3. B. SESSILIFOLIA Greenman, caule erecto tereti crispe pubescenti 6 dm. alto superne oppositirameo; foliis arcte sessilibus late ovatis basi subtruncatis duplice serratis acutis supra laete viridibus subtus paulo pallidioribus 2.5–4.5 cm. longis 1.4–3.5 cm. latis utrinque pubescentibus, dentibus apiceque setuliferis; panicula diffusa; capitulis graciliter et longiuscule pedicellatis ca. 17-floris; involucri squamis anguste lanceolatis attenuatis viridibus albicostatis, margine scariosa; corolla 4.8 mm. longa ad insertionem filamentorum obscure constricta, superne non ampliata; styli ramis leviter clavellatis; achaeniis nigrescentibus 3.5 mm. longis in facie interiori 1- obverse plerumque 3-costatis. — Proc. Am. Acad. xl. 35 (1904). — In collibus calcareis prope pagum Yautepec, Morelos, Mexico, *Pringle*, n. 9865; in rupibus calcareis convallis praeruptae Iguala, Guerrero, altitudine 915 m., *Pringle*, n. 10,322; et prope urbem Acapulco, *Palmer*, n. 625 (expeditionis Oct. 1894–Mar. 1895 factae).

4. B. SETOSA Gray, herba a basi decumbenti suberecta gracilis ca. 6 dm. alta; caule tereti rubescenti minute crispeque puberulo oppositirameo; foliis ovatis argute serrato-dentatis 1.2–3 cm. longis 8–15 mm. latis membranaceis utrinque viridibus tenuiter puberulis, petiolis 4 mm. longis; capitulis ca. 20-floris in axillis foliorum superiorum pedicellatis vel numerosioribus et in panicula plus minusve diffusa dispositis; involucri squamis anguste oblongo-lanceolatis attenuatis saepe purpurascentibus; corolla et pappi setis achaenium superantibus; achaeniis facie interiori planiusculis obscure 1-nervatis dorso 2-nervatis. — Proc. Am. Acad. xv. 29 (1879); Hemsl. Biol. Cent.-Am. Bot. ii. 102 (1881). *Barroetia setosa* (Gray) Hook. f. & Jacks. Ind. Kew. i. 276 (1895). — San Luis Potosi, altitudine 1830–2440 m., *Parry & Palmer*, n. 353; in collibus calcareis prope pagum Cardenas, San Luis Potosi, *Pringle*, nn. 3319, 3320.

5. B. SUBULIGERA (Schauer) Gray, perennis saepe basi suffrutescens; caulibus 1 vel saepe pluribus teretibus suberectis laxe ramosis fere a basi foliatis 4–8 dm. altis crispe tomentellis vel puberulis; foliis deltoideo-ovatis crenato-serratis utrinque pubescentibus vel puberulis 1–3 cm. longis 9–18 mm. latis, apice saepe obtusiusculo et dentibus saltim 1–3 posticis vel saepe omnibus cum setis munitis; capitulis ca. 30-floris 1 cm. altis; involucri squamis linearibus vel lineari-lanceolatis attenuatis plerumque viridibus; corollis gracilibus 5.5–7 mm. longis ad

insertionem filamentorum constrictis, faucibus vix ullis, limbi dentibus brevissimis; achaeniis 3–3.8 mm. longis, faciebus planiusculis vix nervatis. — Proc. Am. Acad. xv. 29 (1879); Hemsl. Biol. Cent.-Am. Bot. ii. 102 (1881). *Bulbostylis subuligera* Schauer, Linnaea, xix. 718 (1847). *Eupatorium ? subuligerum* (Schauer) Gray, Pl. Wright. i. 86 (1852) ex Hemsl. l. c. sed combinatio a Grayo non expressim facta est. *Barroetia subuligera* (Schauer) Hook. f. & Jacks. Ind. Kew. i. 276 (1895). — In reipublicae mexicanae late distributa. HIDALGO: ad Zimapan, *Aschenborn*, n. 260 (specimen typicum, hb. Berol., fragmentis a cl. Eichlero benevolente missis in hb. Grayano etiam conservatis). CHIHUAHUA: in montibus Santa Eulalia, *Pringle*, n. 346; in convalle praerupta Bachimba, *Pringle*, n. 111. COAHUILA: ad Soledad, *Palmer*, n. 452 (anno 1880); prope Torreon, *Palmer*, n. 483 (anno 1898). ZACATECAS: prope Arroyo Cedros, *Kirkwood*, n. 35. DURANGO: ad Mapimi, *Palmer*, n. 519 (anno 1898).

Var. LATISQUAMA Greenman, foliis majoribus usque ad 5 cm. longis 3.5 cm. latis; capitulis paulo majoribus 30–35-floris; involucri squamis anguste lanceolati-oblongis purpurascentibus obtusis vel apice rotundatis et mucronulatis. — Proc. Am. Acad. xl. 35 (1904). — In collibus prope Etzatlan, Jalisco, *Pringle*, n. 8773.

6. B. LAXIFLORA Brandegee, annua crispe puberula diffuse oppositiramea, ramis patente adscendentibus gracilibus; foliis late ovatis vel deltoideo-ovatis tenuibus grosse crenatis vel plus minusve argute dentatis utrinque tenuiter pubescentibus vel glabriusculis basi truncatis vel late cordatis ad insertionem petioli saepe breviter cuneatis apice saepe obtuso et dentibus plerisque posticis cum setis munitis; foliis caulinis 4–6 cm. longis 3–5 cm. latis graciliter ad 2.5 cm. longe petiolatis, ramealibus multo minoribus nunc ovato-oblongis nunc triangulari-lanceolatis 3–5 mm. longe petiolatis; capitulis graciliter saepius longiuscule pedicellatis 9 mm. altis 4.5 mm. diametro ca. 23-floris; involucri squamis anguste lanceolatis vel linearibus attenuatis viridibus albo-striatis, interioribus ad 7 mm. longitudine; corollis achaenia longitudine subaequantibus tubulosis sine faucibus ullis distinctis; achaeniis in facie interiori 1-costatis in facie exteriori 2-costatis in costis et etiam saepe inter eas sursum hispidulis. — Univ. Calif. Publ. Bot. iv. 93 (1910). — PUEBLA: Coxcatlan, *Purpus*, n. 4128. OAXACA: in convalle praerupta Tomellin dicta, altitudine 915 m., *Pringle*, n. 5968; Cuicatlan, altitudine 550–600 m., *Pringle*, n. 5799, *E. W. Nelson*, n. 1868. SINALOA: prope Culiacan, *Schaffner*, *Brandegee.* ALAMOS: *Palmer*, n. 677 (anno 1890).

7. **B. brevipes,** sp. nov., oppositiramea; caule tereti purpurascenti crispe pubescenti, internodiis folia multo superantibus; ramis elon-

gatis plus minusve flexuosis; foliis triangulari-ovatis late cordatis crenato-serratis apice et dentibus 1–3 latere utroque basin versus setigeris supra viridibus sparse pubescentibus subtus paulo pallidioribus in venis villosulis, caulinis ca. 3 cm. longis 2.5 cm. latis graciliter (praecipue inferioribus) petiolatis, ramealibus 1–2.5 cm. longis subsessillibus; capitulis ca. 18–21-floris numerosis brevissime pedicellatis vel subsessilibus in ramis paniculae longis flexuosis spiciformibus bracteatis interrupte dispositis; involucri squamis viridibus albo-costatis lanceolato-linearibus valde inaequalibus vix subuligeris, interioribus ca. 1 cm. longis; corollis gracillime tubulosis 4.3 mm. longis; achaeniis atrobrunneis valde compressis lineari-oblongis 3.6 mm. longis; pappi setis ca. 18 albis corollas aequantibus. — OAXACA: secundum viam ad Cuicatlan altitudine 2075–2380 m., 3 Oct. 1894, *E. W. Nelson*, n. 1520 (specimen typicum in herb. Grayano conservatum). Species capitulis subsessilibus facile diagnoscenda.

III. ON SOME HITHERTO UNDESCRIBED OR MISPLACED COMPOSITAE.

Microglossa mespilifolia (Less.), comb. nov, *Aster mespilifolius* Less. Syn. Comp. 180 (1832). *Nidorella mespilifolia* (Less.) DC. Prod. v. 321 (1836). *Microglossa mespiloides* Benth. & Hook. f. Gen. ii. 282 (1873), without express combination and with obvious clerical error as to the specific name; Hook. f. & Jacks. Ind. Kew. ii. 229 (1895).

Psiadia Boivini (Klatt), comb. nov. *Pluchea Boivini* Klatt, Ann. Sci. Nat. ser. 5, xviii. 369 (1873). As suspected by Cordemoy, Fl. de l'Ile de la Reunion, 526 (1895), this species proves on examination of Dr. Klatt's type (now in the Gray Herbarium) to have the characters of a *Psiadia* and not of a *Pluchea*. The anthers, for instance, are entire and rounded at the base and not caudate. Whether or not Cordemoy's *Psiadia Frappieri* may prove a synonym is a point which cannot be determined from description alone. In any event, however, the earlier specific name of Klatt would have to prevail.

Pluchea rubelliflora (F. v. Muell.), comb. nov. *Eyrea rubelliflora* F. v. Muell. Linnaea, xxv. 403 (1852–53). *Pluchea Eyrea* F. v. Muell. Rep. Babb. Exp. 11, 12 (1858); Benth. Fl. Austral. iii. 528 (1866). — The restoration of von Mueller's earlier specific name becomes necessary under the International Rules of Nomenclature.

Rutidosis multiflora (Nees), comb. nov. *Styloncerus multiflorus* Nees in Lehm. Pl. Preiss. ii. 244 (1846–47). *Pumilo argyrolepis* Schlecht. Linnaea, xxi. 448 (1848). *Actinopappus perpusillus* Hook. f.

and *A. Drummondii* Gray in Hook. Jour. Bot. and Kew. Misc. iv. 226 (1852). *Pumilo Preissii* Sonder, Linnaea, xxv. 487 (1852–53). *Rutidosis Pumilo* Benth. Fl. Austral. iii. 595 (1866). It is obvious that Bentham's specific name Pumilo, though long current, cannot stand under the International Rules, since it is antedated by several other names. Of the various designations under which the plant has been described, Nees's *Styloncerus multiflorus* bears the earliest date. It was published in the second fascicle of the second volume of Lehmann's Plantae Preissianae, and the preface of this volume, which included three fascicles, was dated November, 1847. Meisner under date of July, 1848, speaks (Flora, 1848, p. 496) of the second and third fascicles of the second volume of Lehmann's work as just issued, an expression, which at least so far as it concerns the second fascicle presumably means sometime during the spring or early summer of 1848. Schlechtendal's *Pumilo argyrolepis* was also published in 1848, a circumstance raising no small doubt as to the relative priority of these names. Yet it is to be noted that on a preceding page of his paper (Linnaea, xxi. 444) Schlechtendal refers to an article in the issue of the Botanische Zeitung, dated 26 May, 1848, proving that Schlechtendal's own publication must have been distinctly later. Indeed, it is shown therein that in the meantime added plants had been found by one of his correspondents, had been sent for identification, were studied, described, and the descriptions had reached print, all of which is not likely to have happened between the end of May and July, when as stated by Meisner fascicles 2 and 3 of the second volume of the Plantae Preissianae had already been issued (at what previous date we do not know). There is certainly nothing to show that the paper of Schlechtendal preceded that of Nees. In default of such evidence, precedence may be determined by the second clause of Article 39 of the International Rules, which reads: "In the absence of proof to the contrary the date placed on the work containing the name or combination of names is regarded as correct." This, in the case of Nees's *Styloncerus multiflorus* is, as we have seen, "1846–47," while with Schlechtendal's *Pumilo argyrolepis* it is 1848.

ORIGIN AND IDENTITY OF PHARETRANTHUS. The genus *Pharetranthus* Klatt, published in Flora, lxviii. 203 (1885), was founded on specimens collected by Hugh Cuming (no. 2454). These were supposed to have come from the Philippine Islands both by Klatt, who described them, and by Schultz Bipontinus, who seems to have made a preliminary examination of them. The genus was tentatively placed in *Coreopsis* by O. Hoffmann in Engl. & Prantl, Nat. Pflanzenf. iv. Ab. 5, 243 (1890), an opinion which he later — l. c. iv. Ab. 5, 390 (1894), and Nachtr. zu iv. Ab. 5, 325 (1897) — revised by referring *Pharetranthus* Klatt to *Petrobium* R. Br. While the name *Petrobium* R. Br. must, according to the International Rules of Nomenclature, give way to the earlier and adequately published name of *Laxmannia* Forst. & Forst. f., the identity of *Pharetranthus*, supposedly of the Philippine Islands, with this peculiar monotypic genus, of the island of St. Helena, presents a taxonomic and geographic problem which seems never to have been discussed. Such an identity is certainly improbable on phytogeographic grounds, especially in the case of a species wholly unknown from intermediate localities. Dr. Klatt's type of his *Pharetranthus ferrugineus* is preserved in the Gray Herbarium, and in fact appears to be identical with *Laxmannia* Forst. & Forst. f., the "White-wood Cabbage-tree" of St. Helena. Examination of accessible works on the Philippine flora, including Mr. Elmer's recent enumeration of the *Compositae* of the Philippine Islands, fails to show any record of the species in question. Under these circumstances it seems highly probable that there was some confusion of labels or other slip or error in attributing the plant of Cuming to the Philippine Archipelago. In this connection it is to be noted with interest that on his return voyage Hugh Cuming stopped at St. Helena, where it is more than likely that he obtained the material upon which Dr. Klatt later founded his genus *Pharetranthus*. At all events such an origin would appear to be a permissible assumption or at least a justifiable working hypothesis until the plant can be re-discovered in the Philippine Islands if this ever happens. The synonymy of the species in question is as follows:

LAXMANNIA ARBOREA Forst. & Forst. f. Char. Gen. 94, t. 47 (1776). *Spilanthes arborea* (Forst. & Forst. f.) Forst. f. Com. Hort. Goett. ix. 67 (1787). *Spilanthes tetrandra* Roxb. in Beatson's Tracts, 301 (1816), which was the sterile plant, and *Bidens arborea* Roxb. l. c. (1816), which was the corresponding fertile plant. *Petrobium* R. Br. Trans. Linn. Soc. xii. 113 (1816). *P. arboreum* R. Br. ex DC. Prod. v. 502 (1836). *Drimyphyllum Helenianum* Burch. ex DC. l. c. (1836). *Pharetranthus ferrugineus* Klatt, Flora, lxviii. 204 (1885).

TRAGOCERAS SCHIEDEANUM Less. Linnaea, ix. 269 (1834). To the synonomy of this species should be added *Baltimora monocephala* Klatt, Ann. k. k. Naturh. Hofmus. Wien, ix. 360 (1894), a species founded upon a specimen collected by Knechtel at Chapultepec, Mexico, and now in the Gray Herbarium. The identity appears first to have been noted by Dr. J. M. Greenman, but seems not to have been hitherto recorded in print.

Monactis subdeltoidea, sp. nov., fruticosa ramosa; ramis flexuosis crassiusculis subteretibus vix striato-angulatis brunnescentibus tomentellis, indumento e pilis multicellularibus tenuissimis plus minusve inter se implexis composito; foliis alternis subdeltoideo-ovatis acutis nec acuminatis basi subtruncatis glandulari-denticulatis (glandulis inter se 3–5 mm. distantibus) supra tenuiter sed densiuscule pubescentibus subtus molliter tomentosis canescentibus, lamina 5–6 cm. longis 3–3.5 cm. latis paulo supra basin 3-nervata; petiolo cuneato-alato ca. 1.2 cm. longo ad insertionem laminae usque ad 7 mm. latitudine expanso; inflorescentia planiuscula multicapitulata, bracteis lanceolatis subsessilibus; capitulis radiatis 7 mm. altis, disco ca. 7 mm. diametro; involucri campanulati squamis sub-triseriatim imbricatis arcte appressis ovato-oblongis obtusis sordide lanoso-tomentosis; flosculis radialibus ca. 6 ♀, ligulis late oblongis vel ellipticis apice brevissime 3-dentatis 5–7 mm. longis 3–3.6 mm. latis laete flavis, tubo ca. 1.5 mm. longo plus minusve piloso; flosculis disci ca. 25 ☿, corollis flavidis, tubo 1.5 mm. longo faucibus subcylindricis 2 mm. longis, limbi dentibus 5 breviter triangularibus; achaeniis immaturis prismaticis 2.7 mm. longis omnino calvis glabriusculis. — On banks of the Machangara River, near Quito, Ecuador, 2750 m. altitude, 21 January, 1856; *W. Jameson*, no. 162 (type, in Gray Herb.). From the original *M. flaverioides* HBK. of Venezuela, as well as from the recent *M. Jelskii* Hieron. of Peru, the present species differs in its many-flowered heads, the disk-flowers being about 25, while in *M. flaverioides* they are said to be 5–10 and in *M. Jelskii* they are 6–7. Furthermore, the form of the leaf in the Ecuadorean plant is very different from either of the other species, the blade being more nearly deltoid with a truncate base somewhat sharply distinguishable from the cuneately winged petiole.

Montanoa tehuacana, sp. nov., fruticosa vel arborescens 3–5 m. alta ramosa; ramis plerisque oppositis divergentibus arcuato-adscendentibus foliosis leviter striatis tenuissime puberulis juventate brunneis deinde griseis; foliis oppositis, supra pallide viridibus scabris et cum pilis brevissimis basi incrassatis munitis, subtus canescenti-tomentellis reticulato-venosis, inferioribus 2 dm. longis 1.6 dm. latis patente trilobatis, lobis lateralibus latis crenato-angulatis, lobo terminali variabili vel obtuso vel acuto vel etiam acuminato in eodem specimine, petiolo usque ad 8 cm. longo in parte superiori cuneato-alato; foliis superioribus, i. e. ramulorum floriferum obovato-oblongis firmiusculis obtusis supra rugosis ca. 4 cm. longis ca. 1.5 cm. latis obsolete crenulato-serratis basi brevissime petiolatis et (supra petiolum) cordato-biauriculatis, auriculis rotundatis; capitulis laxe corymbosis graciliter pedicellatis ca. 3 cm. diametro (ligulis inclusis); involucri squamis ovato-lanceolatis anthesi ca. 6 mm. longis griseo-tomentellis; paleis a basi late ovata membranacea pallida in apicem longum spinosum patentem abrupte contractis.— Tufa bluffs near Tehuacan, Puebla, Mexico, 1680 m. altitude, 7 August, 1901, *C. G. Pringle*, no. 8585 (type, in Gray Herb.); in the vicinity of San Luis Tultitlanapa, Puebla, near Oaxaca, August, 1908, *C. A. Purpus*, no. 3105 (Gray Herb.) and no. 3104 (Gray Herb.). The last-mentioned specimen has the upper leaves closely sessile instead of being provided with the usual very short wingless petioles beneath the auricles, but the plant is otherwise so closely identical that it must be inferred that this variation is merely formal and trifling. The affinity of the species is clearly with *M. Pringlei* Robinson & Greenman, Proc. Am. Acad. xxxiv. 512 (1899), which, however, has leaves of quite a different type of serration and the involucral bracts of a peculiar obovate-spatulate form.

LEPIDESMIA SQUARROSA Klatt, Bull. Herb. Boiss. iv. 479, t. 7 (1896). This species, the type of a newly distinguished as yet monotypic genus, was founded upon a plant collected in dry places at Caimanera, Cuba, by von Eggers, May, 1889 (no. 5439). Dr. Klatt was inclined to regard his genus as being of the *Eupatorieae Ageratinae* and very nearly related to *Aschenbornia.* Hoffmann in Engl. & Prantl, Nat. Pflanzenf. Nachtr. 321, 322 places *Lepidesmia* next *Ageratum* and distinguishes it from that genus chiefly by the more imbricated involucral scales. However, even a cursory inspection of the type of *Lepidesmia*, as represented by fragments in the herbarium of the late Dr. Klatt, led the writer to believe that the plant could not belong among the *Eupatorieae*, and a careful dissection has shown that the style-branches, instead of having the clavate unappendaged form found in the *Eupatorieae*, are divided into a basal rather short thickish and somewhat compressed portion surmounted by a rather elongated attenuate and papillose appendage in the manner of many *Heliantheae.* In fact, it seems probable that the genus should be placed near *Isocarpha* R. Br. In habit, as well as in technical characters, it is not very unlike *I. oppositifolia* R. Br., which also possesses opposite leaves, which are lanceolate and subsessile, glomerate heads with subscarious involucre and chaffy receptacle. However, the distinct pappus, much smaller heads, and flattish receptacle furnish ample generic distinctions.

IOSTEPHANE TRILOBATA Hemsl. Biol. Cent.-Am. Bot. ii. 169 (1881). With this species the following appear to be identical: *Rudbeckia chrysantha* (Sch. Bip.) Klatt, Leopoldina, xxiii. 143 (1887), page 3 of reprint, and *Echinacea chrysantha* Sch. Bip. acc. to Klatt, l. c. (1887), page 4 of reprint. The species of Schultz Bipontinus seems never to have been described until taken up and transferred to *Rudbeckia* by Klatt. It rested upon Liebmann's no. 575, collected at Cubre de Estepa, Mexico. In the herbarium of the late Dr. Klatt, a collection now incorporated in the Gray Herbarium, there is a single head and an excellent sketch of Klatt's type, both of which clearly show the species to have been an *Iostephane*, identical so far as can be seen with the earlier *I. trilobata* of Hemsley. Here also should be placed, as it appears, the recently published *Gymnolomia scaposa* Brandegee, Univ. Calif. Publ. Bot. iv. 93 (1910).

Perymenium Peckii, sp. nov., fruticosum gracile 3–9 m. altum in plantis adjacentibus se suffulciens quasi scandens; caule tetragono scabro in speciminibus siccatis 4-sulcato brunneo, internodiis 4–5 cm. longis; foliis oppositis lanceolatis tenuibus graciliter petiolatis acuminatis obscure et remote serrulatis 3-nerviis basi rotundato-subacutis 5 cm. longis 1.5 cm. latis supra viridibus minute et adpresse pilosis subtus distincte pallidioribus molliter pubescentibus fere tomentosis non solum in nerviis sed etiam inter eas; petiolo 7–9 mm. longo; panicula oppositiramea ovoidea foliaceo-bracteata 1.3 dm. longa 1 dm. diametro, ramis curvato-adscendentibus, corymbulis ca. 2 cm. diametro 5–7-capitulatis, pedicellis gracilibus 2–8 mm. longis; capitulis ca. 5-radiatis 6 mm. altis; involucri ovoidei squamis inaequalibus late ovatis obtusis strigillosis; ligulis albidis apice profunde 2–3-dentatis vel etiam -lobatis ca. 4 mm. longis fertilibus; flosculis disci ca. 15; achaeniis valde immaturis compressis oblanceolatis; pappi aristis ca. 10 valde inaequalibus stramineis scabridis. — In openings in the forest, British Honduras, *Prof. Morton E. Peck*, no. 284 (type, in Gray Herb.). This species is most nearly related to *P. microcephalum* Sch. Bip., which, however, has longer bright yellow ligules nearly entire at the tip, and leaves of a very different pubescence, the lower surface being nearly smooth except along the strigillose nerves.

VERBESINA CARACASANA Robinson & Greenman, Proc. Am. Acad. xxxiv. 559 (1899). This species, hitherto known only from Venezuela, may be recorded from Colombia, where it was collected in Santa Marta, November, 1898–1901, altitude 460 m., by *H. H. Smith*, no. 510 (Gray Herb.). Mr. Smith's specimen examined is immature (still in bud), but shows clear identity with the Venezuelan plant. It was distributed as *V. diversifolia* DC., a species which has alternate leaves and many other differences.

Verbesina columbiana, sp. nov., ubique griseo-puberula verisimiliter herbacea alta robusta; caule teretiusculo exalato striato-angulato medulloso; foliis alternis pinnatifidis 2–3 dm. longis 1.2–1.7 dm. latis utrinque griseo-viridibus dense et scabriuscule puberulis, lobis ca. 7, oblongis vel oblongo-lanceolatis acuminatis serrulatis 1–7 cm. longis 0.7–2.5 cm. latis; petiolo 6–8 cm. longo bialato 1.5–1.7 cm. latitudine basi biauriculato; inflorescentia composite corymbosa plana

2.5 dm. diametro multicapitulata griseo-tomentella, pedicellis filiformibus 6–8 mm. longis; capitulis ovoideo-subglobosis ca. 38-floris anthesi ca. 5 mm. diametro; involucri squamis oblongis acutis vel acuminatis pallidis dorso molliter puberulis, extimis multo brevioribus apice obtusiusculis vel etiam rotundatis crassiusculis nigrescentibus; flosculis liguliferis ca. 5 pistilliferis, ligulis albis subquadratis 3-dentatis 2.5 mm. longis, tubo 2 mm. longo tomentello; corollis disci 3.5 mm. longis, tubo et faucibus tomentellis; acheniis obovatis late bialatis, faciebus plus minusve in media parte carinatis sursum scabridis vel tuberculatis, pappi aristis 2 subaequalibus. — Santa Marta, Colombia, December, 1898–1901, altitude 75 m., *H. H. Smith*, no. 671 (type, in Gray Herb.); also from the banks of the Magdalena River, Quematido, Colombia, 5 December, 1875, *André*, no. 222 (Gray Herb.). The latter specimen is said to have been herbaceous and 3–5 m. high. Mr. Smith's plant was distributed as *V. gigantea* Jacq., but it differs from that species of the Antilles in having heads about 38-flowered instead of about 20-flowered, in having broadly winged achenes, and in details of foliage and involucre. The related *V. myriocephala* Sch. Bip. of Mexico also has smaller subcylindric about 20-flowered heads and narrowly winged achenes.

Verbesina costaricencis, sp. nov., herbacea vel basi lignescenti alta; caule teretiusculo leviter striato-angulato glabro exalato purpurascenti glaucescenti medulloso; foliis alternis magnis longipetiolatis profunde pinnatifidis 1.5–2 dm. longis 1–1.4 dm. latis supra dense scabro-pubescentibus atroviridibus subtus pallidioribus molliter pubescenti-tomentellis, lobis ca. 11 lanceolato-oblongis acuminatis obsolete subremoteque serrulatis 7–10 cm. longis 2–3.5 cm. latis, rhachi alato 1–1.3 cm. lato, sinubus rotundatis; corymbis compositis terminalibus planiusculis multicapitulatis 1.5 dm. diametro basi foliaceo-bracteatis; capitulis obovoideis discoideis 8 mm. altis 5 mm. diametro; involucri squamis exterioribus valde inaequalibus anguste oblongis apice subherbaceis nigrescentibus rotundatis vel vix mucronulatis 1–4 mm. longis interioribus subaequalibus ca. 6 mm. longis tenuibus diaphanis acutiusculis glabriusculis margine erosis; flosculis liguliferis nullis, eis disci ca. 21; corollis 3.6 mm. longis, tubo proprio plus minusve constricto strigilloso brevi, faucibus cylindricis tubo duplo longioribus, limbi dentibus oblongo-lanceolatis; achaeniis compressis oblanceolatis sursum hispidulis basin versus attenuatis tenuiter costatis marginatis vix alatis; pappi aristis saepius 3 achaenium subaequantibus duabus inter se contiguis in angulo interiori, tertia eis opposita. — *V. nicaraguensis* J. D. Sm. Enum. Pl. Guat. v. 44 (1899), not Benth. — Rio Virilla, San José, Costa Rica, altitude 1100 m., December, 1895, *Ad. Tonduz*, no. 9833 herb. nat. Cost. (= no. 7068 distrib. J. D. Sm.). This plant is clearly distinct from *V. nicaraguensis* Benth., which has 8–10-rayed heads, widely winged achenes, and a different leaf-contour.

Verbesina gigantoides, sp. nov., robusta alta; caule crasso teretiusculo purpurascenti glaberrimo plus minusve pruinoso intus cum medulla alba constipato; foliis alternis pinnatifidis longe petiolatis firmiusculis supra glaberrimis lucidulis plus minusve ruguloso-bullatis subtus olivaceis molliter pubescentibus 2–3 dm. longis 1–2.5 dm. latis, rhachi alata ca. 2 cm. lata, lobis ca. 11 lanceolatis caudato-attenuatis saepe falcatis integerrimis vel obscure undulatis 8–15 cm. longis 2.5–4 cm. latis, infimis reflexis; sinubus rotundatis; petiolo teretiusculo purpurascenti glaberrimo omnino exalato; panicula ampla valde convexa pubescenti; bracteolis lineari-filiformibus; pedicellis 3–6 mm. longis; capitulis numerosissimis 5 mm. diametro 7 mm. altis ca. 20-floris; involucri squamis obovato- vel oblanceolato-oblongis abrupte acutiusculis margine ciliata excepta glabriusculis; flosculis liguliferis ca. 4–5 pistilliferis; ligulis albis oblongis 3.5 mm. longis apice leviter 3-dentatis; flosculis disci ca. 15, corolla albida subcylindrica, tubo pubescenti, limbi dentibus 5 oblongo-lanceolatis; antheris linearibus nigrescentibus vix connatis; achaeniis 3.5 mm. longis pyriformibus anguste alatis deorsum valde attenuatis, alis ciliato-laceris, pappi aristis 2 subaequalibus ca. 2 mm. longis. — *V. gigantea* Robinson & Greenman, Proc. Am. Acad. xxxiv. 561 (1899), in part, not Jacq. — From near Yajalon, Chiapas, Mexico, 21 November, 1895, *E. W. Nelson*, no. 3423 (type, in Gray Herb.). This is one of several habitally similar plants, which have been in a preliminary way referred to *V. gigantea* Jacq. Happily, through the careful definition and segregation of the West Indian species by Prof. Urban, Symb. Ant. v. 264–265 (1907), it has become possible to interpret more definitely the continental forms of this group.

Verbesina leucactinota, sp. nov., perennis verisimiliter herbacea robusta alta griseo-tomentella; caule subtereti leviter striato exalato; foliis alternis pinnatifidis supra viridibus scabriusculo-puberulis subtus molliter griseo-tomentellis 2 dm. vel ultra longitudine 1.3 dm. latis saepius 9-lobis; lobis lanceolatis 4–7 cm. longis attenuatis 1.3–2.3 cm. latis, sinubus rotundatis; petiolo late bialato basi cum auriculis magnis amplexicauli sed alis in caule non decurrentibus; inflorescentia paniculata magna valde convexa; bracteis foliaceis anguste lanceolato-oblongis acutis integris 4–8 cm. longis ca. 1 cm. latis basi biauriculatis; capitulis ca. 27-floris conspicue radiatis; flosculis liguliferis ca. 5; ligulis ellipticis albis breviter apice 3-dentatis 4 mm. longis; corollis disci albidis 3 mm. longis; antheris nigrescentibus conspicue exsertis;

achaeniis valde immaturis oblanceolatis; pappi aristis 2 subaequalibus achaenium subaequantibus. — *V. diversifolia* Britton, Bull. Torr. Bot. Club, xix. 150 (1892), not DC. — Coripati, Yungas, Bolivia, April, 1894, *Bang*, no. 2135 (type, in Gray Herb.). Though doubtfully referred to *V. diversifolia* DC. by Robinson & Greenman, Proc. Am. Acad. xxxiv. 562 (1899), this plant with wingless stem and about 9-lobed leaves now seems clearly distinct from that Brazilian species. It is nearer *V. gigantea* Jacq., from which, however, it differs in its more numerous rays, more strongly auriculate petioles, harsher pubescence, and in many other details. From *V. columbiana*, here described, it differs in its smaller less numerously flowered heads, more developed rays, etc. It is also near *V. myriocephala* Sch. Bip. of Mexico, but differs in its more convex inflorescence, scabrous-puberulent stem, narrow elongate and entire bracts, etc.

Verbesina (§ **Lipactinia**) **oligantha,** sp. nov., fruticosa 2–3 m. alta; caule teretiusculo exalato griseo scabrido-puberulo aetate lenticellis parvis late ellipticis brunneis aspero; foliis oppositis rhomboideo-ovatis 1.2–1.6 dm. longis 5–7 cm. latis acuminatis serratis basi cuneatis integris utrinque viridibus scaberrime puberulis, nerviis lateralibus principibus 3–4 plus minusve ex eodem loco (2–3 cm. supra basin) oriuntibus, ceteris remotioribus et pinnatim locatis; petiolo 1–1.5 cm. longo crispe et scabride puberulo; cymis compositis planis multicapitulatis densiusculis basi foliaceo-bracteatis, pedicellis filiformibus erectiusculis 1–7 mm. longis; capitulis 12 mm. altis 4 mm. diametro saepissime 7-floris; involucri squamis valde inaequalibus, exterioribus multo brevioribus ovatis 2–3 mm. longis interioribus oblongis abrupte acuminatis 6 mm. longis flosculos amplectentibus; corollis omnibus tubulosis flavis; achaeniis valde compressis oblanceolatis olivaceis in faciebus paulo pubescentibus apicem versus angulo interiori anguste alatis. — In granitic soil, Jimalcota, Mexico, altitude 300 m., 18 November, 1898, *E. Langlassé*, no. 644 (type, in Gray Herb.). It is clear that this species is closely related to *V. pauciflora* Hemsl. but it differs markedly in its less conspicuous but more scabrous pubescence, its broadly rhomboic-ovate leaves, and in its less herbaceous much smoother involucre.

Calyptocarpus blepharolepis, sp. nov., annuus prostratus multicaulis et fere a basi patente oppositirameus; caulibus ramisque gracilibus teretibus striatulis flexuosis cum pilis albis hirsutulo-pubescentibus plerumque bis bifurcatis; internodiis saepe longissimis; foliis oppositis petiolatis spatulato-obovatis integris apice rotundatis mucronulatis utrinque cum pilis albis basi incrassatis strigosis 2–2.5 cm. longis 1.1–1.4 cm. latis subtus distincte pallidioribus, petiolis 1 cm. longis hirsutis; capitibus in bifurcis arcte sessilibus 1.4 cm. diametro multifloris; involucri squamis oblongis biseriatim imbricatis subaequalibus abrupte acuminatis dorso glabriusculis leviter striatis margine conspicue albo-ciliatis; flosculis liguliferis ca. 8, ligulis brevissimis ovatis crassiusculis albidis viridi-striatulis vix 1.5 mm. longis pistilliferis, achaenio striatulo glabriusculo exalato apice longiuscule divaricatim 3-aculeato; pappi aculeis ca. 3 mm. longis; disci flosculis numerosis, achaeniis muricatis. — Tensaw, Alabama, 18 August, 1904, *S. M. Tracy*, no. 8946 (type, in Gray Herb.). This plant, distributed as *Calyptrocarpus tampicanus* Small, differs markedly from that species in its spatulate-obovate leaves, larger closely sessile heads, and especially in its involucral scales. These are dorsally nearly glabrous but on the edges conspicuously ciliate, while in *Calyptocarpus vialis* Less. (*Oligogyne tampicana* DC., *Calyptrocarpus tampicana* Small) the condition is reversed, that is to say the involucral scales are dorsally strigose-pubescent but the margin nearly or quite free from ciliation. The discovery of a second and clearly distinct species of the hitherto monotypic *Calyptocarpus* is of interest. From the weedlike nature and wide distribution of its Texano-Mexican congener, there must be some doubt whether the plant here described will prove really indigenous in its Alabama habitat, or whether it may not ultimately be found to be an introduction from some other region.

Balduina angustifolia (Pursh), comb. nov. *Buphthalmum angustifolium* Pursh, Fl. ii. 564 (1814). *Actinospermum angustifolium* (Pursh) Torr. & Gray, Fl. ii. 389 (1842). The distinctions by which some recent efforts have been made to separate the genera *Actinospermum* and *Balduina* do not appear to the writer to be of generic validity. The genera being united, priority of specific name requires the new combination here proposed.

Senecio fimbrillifer (Cass.), comb. nov. *Eupatorium auriculatum* Lam. Encyc. ii. 411 (1786), a specific name not available because of *Senecio auriculatus* Burm. f. Fl. Ind. 181 (1768). *Eupatorium scandens* Link, Enum. ii. 307 (1822) according to Lessing, Syn. Comp. 392 (1832), this name also not available because of the now valid homonym *Senecio scandens* Buch.-Ham. ex D. Don, Prod. Fl. Nepal. 178 (1825). *Cacalia fimbrillifera* Cass. Dict. xlviii. 460 (1827). *Senecio deltoideus* Less. Syn. Comp. 392 (1832). *Mikania auriculata* Willd. Sp. Pl. iii. 1745 (1804).

Senecio pyrifolius (Bojer), comb. nov. *Trixis pyrifolia* Bojer ex DC. Prod. v. 195 (1836). *Mikania pyrifolia* DC. l. c.; Klatt in Engl. Bot. Jahrb. xii. Beibl. 27, p. 22 (1890). *Senecio curvatus* Bak. Jour. Linn Soc. xx. 190 (1883). The identity of *Mikania pyrifolia* (Bojer) DC.

and the much later *Senecio curvatus* Bak. was recently noticed by the writer on successively examining the types preserved in the DeCandollean and Kew herbaria respectively. The identity appears to have been previously inferred by Dr. F. W. Klatt, for after determining Hildebrandt's no. 3626 as *Mikania pyrifolia* in Engl. Bot. Jahrb. xii. Beibl. 27, p. 22 (1890), he later cites the same number as *Senecio curvatus* Bak. in Ann. k. k. Naturh. Hofmus. Wien, vii. 299 (1892). Although the name *Senecio pyrifolius* was used in manuscript by von Martius for a Brazilian species, it was published only as a synonym of *Senecio ellipticus* DC. Prod. vi. 420 (1837) by Baker in Mart. Fl. Bras. vi. pt. 3, 318 (1884). This use of the name, especially as unaccompanied by independent description and therefore incapable of revival, seems in no way to preclude the new combination here made for the plant of Madagascar.

Saussurea baicalensis (Adams), comb. nov. *Liatris baicalensis* Adams, Mém. Soc. Nat. Mosc. v. 115 (1817). *Carphephorus baicalensis* DC. Prod. v. 132 (1836). *Saussurea pycnocephala* Ledeb. Ic. Fl. Ross. i. 15, t. 59 (1829), Fl. Alt. iv. 14 (1833), & Fl. Ross. ii. 661 (1845–46), which see for detailed synonymy. As Adams's original description of this species is excellent and detailed there seems no reason why according to present nomenclatorial rules the earliest though long-neglected specific name should not be restored as indicated above. The association of the species with *Liatris*, to which it has considerable habital resemblance, was not unnatural at a time when the relatively obscure tribal distinctions of the *Compositae* were unknown.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 7. — July, 1911.

CALANOID COPEPODA FROM THE BERMUDA ISLANDS.

By Calvin O. Esterly.

With Four Plates.

CALANOID COPEPODA FROM THE BERMUDA ISLANDS.[1]

By Calvin O. Esterly.

Presented by E. L. Mark, May 10, 1911. Received May 12, 1911.

The copepods mentioned in this paper were collected during June, July, and August, 1907. A small "open" plankton net was used, and both vertical and horizontal (surface) towings were made, but there is no special significance in vertical collecting with a non-closing net. Most of the collections were made close to Agar's Island. In addition, four hauls were made about two miles north of North Rock, three of these being vertical from about twelve fathoms.

The calanoid copepods are represented in Bermuda by five genera, one of which is new, and six species of which four are new. The list is as follows: *Acartia bermudensis* n. sp., *Acartia spinata* n. sp., *Calanopia americana* Dahl, *Clausocalanus furcatus* Brady, *Lampoidopus marki* n. gen., n. sp., *Pseudocyclops magnus* n. sp. I have given here very brief characterizations of the species previously described by others, as a basis for comparison with similar forms from other localities, and drawings of certain parts have been included for the same purpose. New forms are described and illustrated more fully.

Lampoidopus[2] marki[3] n. gen., n. sp.

Plate **1**, Figure 4; Plate **2**, Figures 13, 14, 20, 21; Plate **3**, Figures 25, 26, 28, 29, 30, 31, 34; Plate **4**, Figures 35, 38, 42.

The head and posterior margin of the last thoracic segment are smoothly rounded in both sexes (Plate , Figure 4; Plate **2**, Figures 14, 21). There are five segments in the cephalothorax of both male and female, the head being fused with the first segment of the thorax. The rostrum is present and consists of a fleshy rounded plate, which at its

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[1] Contributions from the Bermuda Biological Station for Research, No. 21.

[2] Λαμπάς, *torch*, εἶδος, *like*, πούς, *foot*, in allusion to the fancied resemblance of the last two joints of the outer ramus of the left fifth foot to the conventional representation of the flames of a torch (see Plate **3**, Figure 34).

[3] The species is named for my teacher, Dr. E. L. Mark.

base occupies nearly the entire distance between the bases of the anterior antennae (Plate **2**, Figures 20, 21).

The abdomen of the female is 3-segmented, the genital segment being as long as the other two; the second segment is a little longer than the third (Plate **1**, Figure 4; Plate **2**, Figure 13). The abdomen of the male (Plate **2**, Figure 14) is apparently 4-segmented. The four segments are of about equal lengths. The furcal rami in both sexes are about three and one half times as long as broad.

The anterior antennae reach to the end of the furca. Both antennae in the female are 25-jointed. The right one in the male is a grasping organ (Plate **4**, Figure 35) and is 23-jointed; the left is 25-jointed. The terminal portion of the grasping antenna is 4-jointed.

The other cephalic appendages are alike in the sexes. The posterior antennae have the inner ramus shorter than the outer; the former is 2-jointed and the latter 8-jointed. The blade of the mandible (Plate **3**, Figure 26) is well developed and has numerous rather fine teeth of irregular form on the cutting edge. The outer ramus is 4-jointed, the first three joints having each one bristle, the fourth joint having two; the inner ramus is 2-jointed, the first joint carrying three bristles and the second carrying eleven, as shown in Plate **3**, Figure 31. The maxilla (Plate **3**, Figure 25) has the rami and lobes well developed. The "outer border lobe" bears a group of three small bristles and a group of seven that are much larger. The outer ramus carries bristles of about equal sizes; the inner ramus has fourteen bristles altogether, disposed, as shown, in two groups of three bristles each and two of four bristles each. The masticatory lobe has ten of the very heavy spinose bristles and three delicate smooth bristles. The second lobe of the inner margin has five bristles, the third has four, and the second basal has five. The anterior maxilliped is rather short and broad (Plate **3**, Figure 28). There are seven lobes on the inner margin; the number of bristles on the lobes in order is 6, 3, 3, 3, 4, 2, 4. The posterior maxilliped (Plate **4**, Figure 38) is slender and weakly developed; it is 7-jointed, the endopodite containing five joints. The endopodite is as long as the second basal; the greatest breadth of the first basal is twice that of the second. The first basal has the bristles on the inner margin disposed in four groups, consisting of 1, 2, 4, and 3, respectively, beginning at the base. The joints of the inner ramus have the following number of bristles on the inner margin, beginning with the first joint: 4, 4, 3, 4, 4.

The four anterior pairs of swimming feet are alike in the sexes. Both rami in all the pairs are 3-jointed, and the first basal in all has one inner marginal bristle.

Table I, which follows, shows the number of bristles or thorns on the joints of the rami of the first four pairs of feet. The abbreviations are as follows: *Se.*, a bristle or thorn on the outer margin; *Si.*, a similar structure on the inner margin of any joint; *St.*, a bristle on the distal end of a terminal joint.

TABLE I.

Pair.	Joint.	Outer Ramus.			Inner Ramus.		
		Se.	*Si.*	*St.*	*Se.*	*Si.*	*St.*
I.	1	1	1	0	0	1	0
	2	3	1	0	0	2	0
	3	2	4	1	1	4	1
II.	1	1	1	0	0	1	0
	2	1	1	0	0	2	0
	3	2	5	1	2	5	1
III.	1	1	1	0	0	1	0
	2	1	1	0	0	2	0
	3	3	5	1	2	3	0
IV.	1	1	1	0	0	1	0
	2	1	1	0	0	1	0
	3	3	5	1	2	4	

The fifth pair of feet shows most marked peculiarities. These feet are symmetrical in the male. Each inner ramus is 1-jointed, that of the right foot being club-shaped (Plate **3**, Figure 30), that of the left foot (Plate **3**, Figure 34) shorter and broader. The outer ramus of the right foot is 2-jointed, that of the left foot 3-jointed with the terminal joint peculiarly modified (Plate **3**, Figure 34). It is split up into three or four parts, or slender processes, one of which branches and carries a very delicate lamellar structure that ends distally in fine hair-like divisions. The figure gives a better idea of the structure of this foot than is possible in a description. The end joint of the outer ramus of the left foot is of the same structure in all the specimens I have examined.

The right and left fifth feet of the female are symmetrical; the inner ramus is 2-jointed, the outer 3-jointed (Plate **3**, Figure 29). A peculiarity is the attachment of the terminal joint of the outer ramus at the middle of the inner margin of the second joint.

The average length of the males is 1.05 mm., of the females 1 mm.

The color of both sexes is brownish buff; the pigment is generally distributed through the body and appendages.

The only place where I found this copepod was in a cave in the small ledge-like island across from the bathing place at Agar's Island (see the map in Mark, : **09**, p. 2). The cave is a small one and is at the south-west end of the ledge. I have never seen a specimen of Lampoidopus that was taken anywhere else and it is my belief that the animals are not found outside the cave, at least, not any distance from it. Collections were not made in the water between Agar's Island and the ledge, but there were some from the ship channel, and this is rather close to the place where the cave is located in the ledge. The animals were very abundant in the cave; young in all stages of development as well as adults were taken. The only haul was made at high tide. A small net was fastened to the end of a pole and swept through the water inside the cave.

The most interesting thing connected with the finding of this copepod is that, so far as I know, the small cave is the only place near Agar's Island where the "hat" or "shade" coral (*Agaricia fragilis*) is found. Furthermore the coloration of the copepod is strikingly like that of the coral, the same brownish tint characterizing both. It is my belief that this is an example of protective coloration. If so it offers a new case among Copepoda especially, and plankton animals generally.

According to Steuer (: **10**, p. 282), complete lack of color, and hyalinity, is the best adaptation to a plankton life. Blue and violet are adaptive to the blue water of warm seas, and red, brown-red or dark violet belong to the abyssal zoöplankton. Steuer also states (p. 283) that creeping or swimming animals from the Sargasso Sea are characterized by brown or green shades. Taking these general observations into consideration with the circumscribed distribution of Lampoidopus, and the fact that the other copepods obtained are transparent and colorless or else bluish, it seems reasonable to regard the color of Lampoidopus as protective. It is certainly suggestive of this that these little copepods should have a coloration that is unusual in the group as a whole, that their distribution should be so limited, and that at the same time their colors should be so similar to that of the corals. I did not make collections in other caves, but it would be interesting to know if these copepods are found elsewhere and, if so, whether they are found generally with Agaricia.

Calanopia americana Dahl.

Plate **2**, Figures 12, 15; Plate **3**, Figures 27, 32; Plate **4**, Figure 39.

These copepods are very abundant around Agar's Island and very rare in the locality of North Rock. They may be easily recognized by their comparatively large size, the pointed posterior borders of the thorax

(Plate **2**, Figure 15), and the heavy, grasping antenna (the right) of the male (Plate **3**, Figure 32). The cephalothorax is twice as long in the mid-dorsal line as its greatest breadth (Plate **2**, Figure 12). The rostrum (Plate **2**, Figure 15) is very stout, and bifid, in both sexes. So far as the figures of Dahl ('**94**, Taf. 1, Fig. 23–26) are concerned, this seems to be the same species, though identification from his figures is not easy.

The length of the male is 1.2–1.3 mm., that of the female 1.4 mm.

The eye-spot is red; most specimens are otherwise colorless and transparent, but a few have red pigment in the mouth region, along the flanks and ventral surface of the body, and in the bases of the appendages.

Clausocalanus furcatus Brady.

Plate **1**, Figures 2, 7, 9; Plate **2**, Figure 11; Plate **3**, Figure 33; Plate **4**, Figures 36, 40, 44.

These copepods are small, but easily recognized by the heavy, bifid rostrum (Plate **1**, Figures 7, 9). The distal border of the second basal in the third and fourth pairs of feet is toothed in a way that is characteristic of the genus (Plate **3**, Figure 33). I think there is little doubt of the correctness of the identification of this species, though the proportions of the abdominal segments in the male (Plate **2**, Figure 11), or in the female, do not agree precisely with other accounts (Giesbrecht und Schmeil, '**98**, p. 27; Scott, :**02**, p. 403).

The animals are colorless and very transparent. The length of the males averages 0.8 mm., that of the females 1.14 mm. This species was much more abundant at North Rock than in any other place where collections were made.

Pseudocyclops magnus n. sp.

Plate **1**, Figures 6, 8; Plate **3**, Figure 23; Plate **4**, Figure 41.

The head and posterior borders of the last thoracic segment are smoothly rounded (Plate **1**, Figures 6, 8), and the rostrum is stout. The anterior antennae of the female (Plate **3**, Figure 23) are 17-jointed and about one-fifth as long as the entire body. The inner ramus of the fifth foot (Plate **4**, Figure 41) is 2-jointed, the first and second joints (of the original three) being fused; the end joint carries a stout, feathered bristle.

It is fairly safe to say that this form is new, though I found but one specimen, a female. The fifth foot differs from that of the species described before, and the size (length 1.1 mm.) is greater than that of *P. obtusatus*, the largest of the hitherto described species.

The animal was colorless and transparent, with a red eye-spot. It was taken in a haul at Agar's Island.

Acartia spinata n. sp.

Plate **1**, Figures 3, 5; Plate **2**, Figures 16, 19; Plate **3**, Figure 24; Plate **4**, Figures 37, 45.

The forehead is smoothly rounded in each sex, as are the posterior margins of the last thoracic segment; these margins are provided, in both the male and female, with heavy spines disposed in two sets (Plate **2**, Figures 16, 19). The posterior borders of the abdominal segments and likewise the furca are spinose on the dorsal side, and in the male (Figure 16) there are little spines on the sides of the second segment. The length of the cephalothorax along the mid-dorsal line is 3½ times its greatest width (Plate **1**, Figure 3). The genital segment of the female is about as long as the rest of the abdomen including the furca, and the second and third abdominal segments are of about equal lengths. In the male the genital segment is about one-third the length of the second segment, which is twice the length of the third. Rostral filaments are present (Plate **1**, Figure 5).

The anterior antennae reach back in the females to the end of the anal segment, and in the males about to the posterior border of the third thoracic segment. The second joint of the antenna in the female (Plate **4**, Figure 45) has a prominent spine on the ventral surface, and the third joint has a similar spine on the anterior margin at the base of the joint. That feature will distinguish this species from the other species (bermudensis) described here.

The fifth feet in each sex are of the usual form for the genus, but exhibit specific characters. Those of the male are shown in Plate **3**, Figure 24; those of the female in Plate **4**, Figure 37.

The males average 1.13 mm. in length, the females 1.18 mm.

The animals have a faint bluish tinge in the body when alive, while the eye is very dark blue, this being a noticeable feature of the species. These copepods are very abundant at North Rock and rather uncommon elsewhere, though taken about Agar's Island. The species belongs to the *bifilosa-tonsa-giesbrechti* group, but differs from all the other species in ways that are distinctive.

Acartia bermudensis n. sp.

Plate **1**, Figure 1; Plate **2**, Figures 10, 17, 18; Plate **3**, Figure 22; Plate **4**, Figure 43.

The females may be easily distinguished from those of the preceding species by the absence of spines on the anterior antennae. Another point is the character of the spines on the posterior border of the last thoracic segment; in *bermudensis* (Plate **2**, Figure 17) these are much smaller, shorter and more numerous than in *spinata* (Figure 16). In the males of *bermudensis* the ventral group of spines on the border of the last thoracic segment is replaced by hairs (Plate **2**, Figure 18). The distribution of spines and hairs on the abdominal segments is shown in Figures 17 and 18 of Plate **2**.

This species lacks the rostral filaments. In the females the anterior antennae reach back to the end of the genital segment, in the males to the posterior border of the third thoracic segment.

The genital segment in the females is almost as long as the rest of the abdomen (Plate **2**, Figures 10, 17), and the furca is about a third longer than wide. In the male the genital segment (Plate **2**, Figure 18) is three-fifths as long as the second segment; the second is a little longer than the third and three times as long as the fourth. The length of the cephalothorax along the mid-dorsal line is three times its greatest width (Plate **1**, Figure 1).

The fifth feet show specific characters. In the female (Plate **4**, Figure 43) the middle joint of the fifth foot carries a blunt flap-like process on the inner margin, which reminds one of an inner ramus. The fifth feet of the male are shown in Plate **3**, Figure 22.

This Acartia was common in hauls around Agar's Island, while *spinata* is quite rare in that locality; the reverse is the case in collections taken from the vicinity of North Rock. *A. bermudensis* belongs to the *clausi-discaudata* group.

The males average .93 mm. in length, the females .86 mm. The animals are transparent and practically colorless.

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PLATE 1.

Figure 1. Acartia bermudensis n. sp. Female, cephalothorax and part of abdomen, dorsal. × 113.

Figure 2. Clausocalanus furcatus Brady. Female, cephalothorax and part of abdomen, dorsal. × 113.

Figure 3. Acartia spinata n. sp. Female, cephalothorax and part of abdomen dorsal. × 113.

Figure 4. Lampoidopus marki n. gen., n. sp. Female, lateral. × 80.

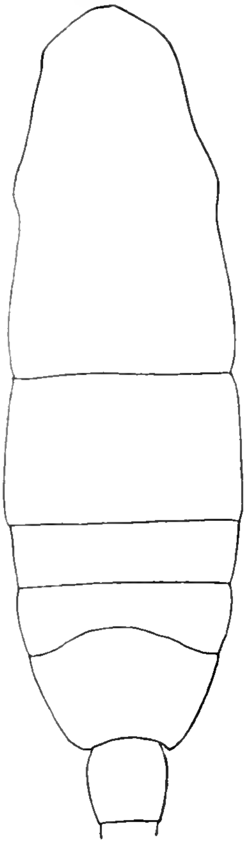
Figure 5. Acartia spinata n. sp. Female, forehead from below. × 245.

Figure 6. Pseudocyclops magnus n. sp. Female, last two thoracic segments and abdomen, lateral. × 266.

Figure 7. Clausocalanus furcatus Brady. Female, forehead to show rostrum, lateral. × 266.

Figure 8. Pseudocyclops magnus n. sp. Female, forehead showing rostrum, lateral. × 266.

Figure 9. Clausocalanus furcatus Brady. Female, lateral. × 93.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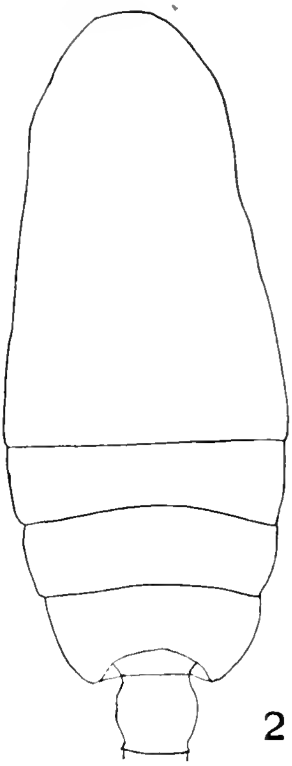
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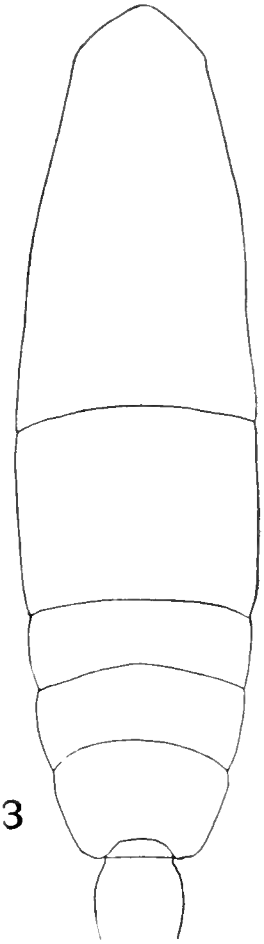
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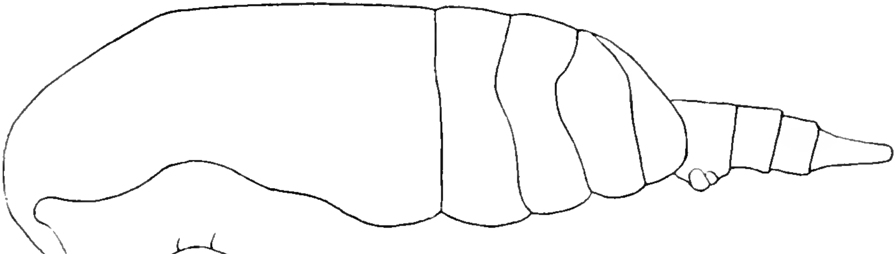
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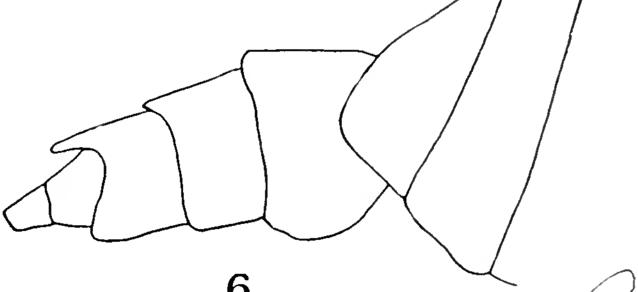
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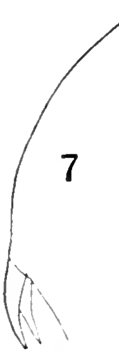
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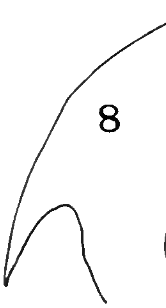
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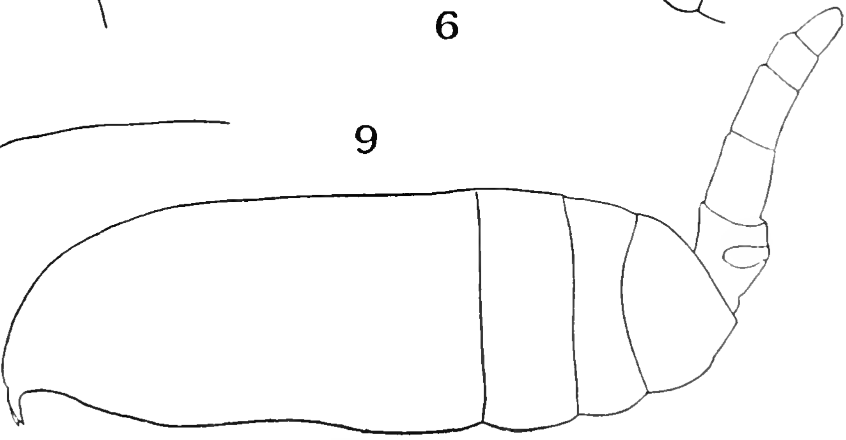
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PLATE 2.

Figure 10. Acartia bermudensis n. sp. Female, abdomen and part of last thoracic segment, dorsal. × 200.

Figure 11. Clausocalanus furcatur Brady. Male, abdomen and part of last thoracic segment (on left side), dorsal. × 183.

Figure 12. Calanopia americana Dahl. Female, cephalothorax and part of genital segment, dorsal. × 85.

Figure 13. Lampoidopus marki n. gen., n. sp. Female, abdomen and part of last thoracic segment, dorsal. × 200.

Figure 14. Lampoidopus marki n. gen., n. sp. Male, abdomen and last two thoracic segments, lateral. × 183.

Figure 15. Calanopia americana Dahl. Male, lateral. × 60.

Figure 16. Acartia spinata n. sp. Male, last thoracic segment and abdomen lateral. × 170.

Figure 17. Acartia bermudensis n. sp. Female, last thoracic segment and abdomen, lateral. × 390.

Figure 18. Acartia bermudensis n. sp. Male, last thoracic segment and abdomen, lateral. × 200.

Figure 19. Acartia spinata n. sp. Female, part of last thoracic segment, and the abdomen, lateral. × 200.

Figure 20. Lampoidopus marki n. gen., n. sp. Male, forehead showing rostrum, ventral. × 183.

Figure 21. Lampoidopus marki n. sp., n. gen. Female, anterior half of head, lateral. × 200.


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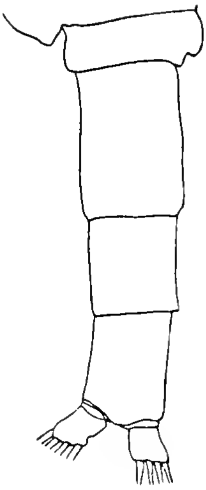
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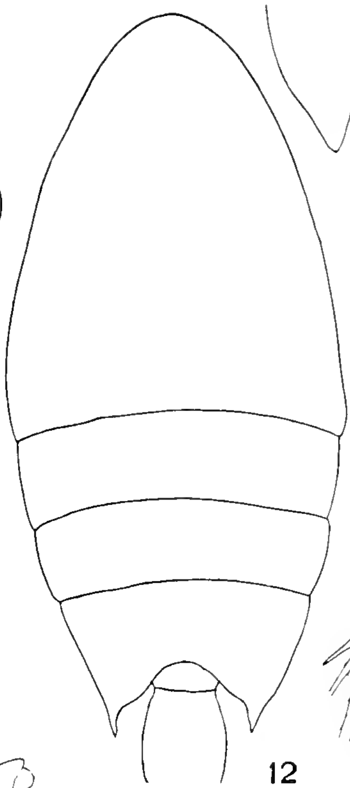
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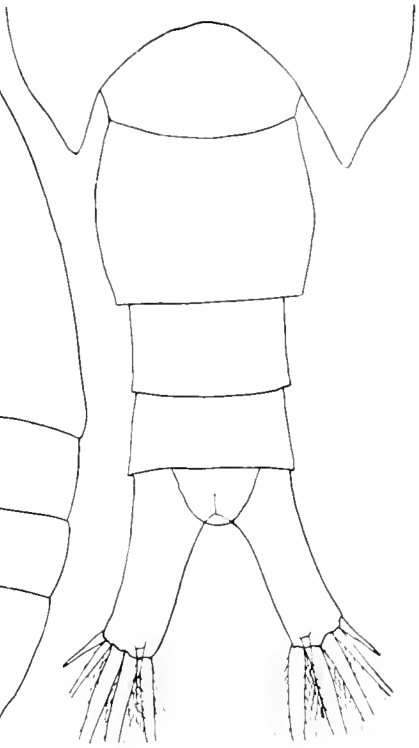
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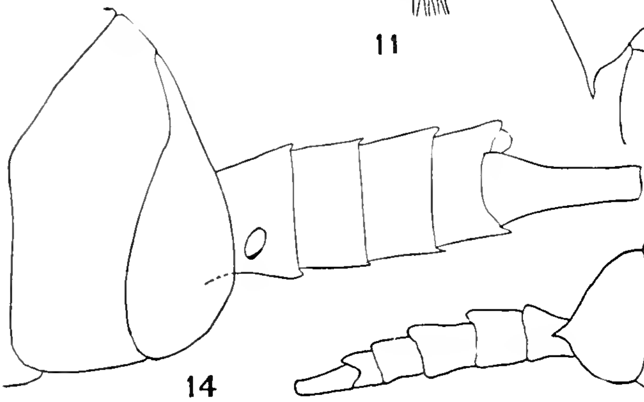
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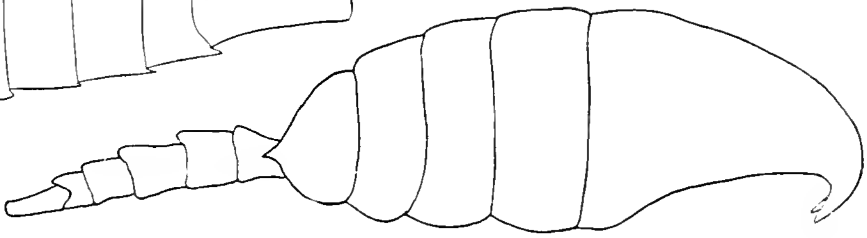
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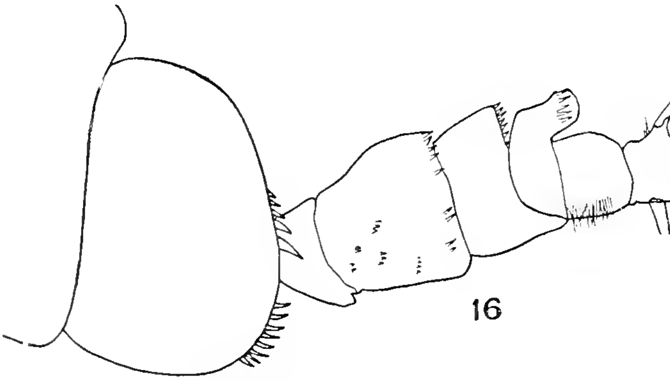
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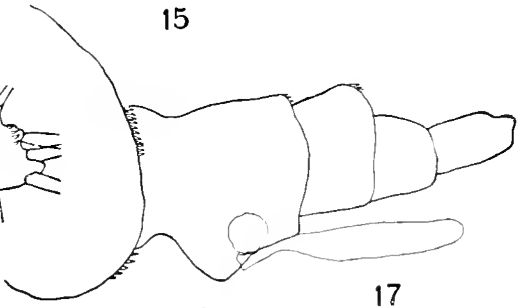
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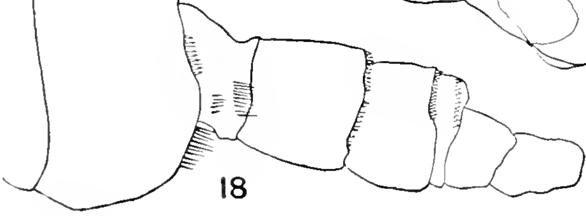
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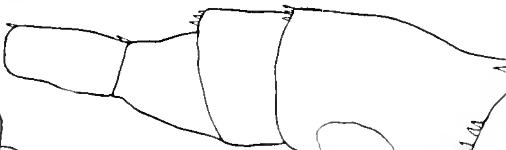
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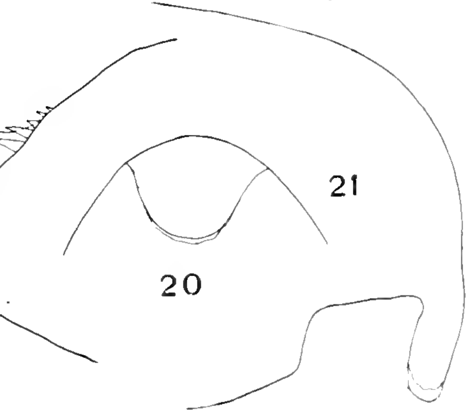
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PLATE **3.**

Figure 22.	Acartia bermudensis n. sp. Male, fifth pair of feet. × 352.
Figure 23.	Pseudocyclops magnus n. sp. Female, anterior antenna. × 375.
Figure 24.	Acartia spinata n. sp. Male, fifth pair of feet. × 375.
Figure 25.	Lampoidopus marki n. gen., n. sp. Female, maxilla. × 352.
Figure 26.	Lampoidopus marki n. gen., n. sp. Female, mandibular blade. × 352.
Figure 27.	Calanopia americana Dahl. Male, two terminal joints of right fifth foot. × 375.
Figure 28.	Lampoidopus marki n. gen., n. sp. Female, anterior maxilliped. × 352.
Figure 29.	Lampoidopus marki n. gen., n. sp. Female, fifth foot. × 352.
Figure 30.	Lampoidopus marki n. gen., n. sp. Male, right fifth foot; outer ramus at left of figure. × 352.
Figure 31.	Lampoidopus marki n. gen., n. sp. Female, rami of mandible. × 352.
Figure 32.	Calanopia americana Dahl. Male, the grasping portion of right anterior antenna. × 325.
Figure 33.	Clausocalanus furcatus Brady. Female, second basal, first and second joints of the outer ramus, and the inner ramus of the third foot. × 352.
Figure 34.	Lampoidopus marki n. gen., n. sp. Male, left fifth foot; outer ramus at left of figure. × 352.

ESTERLY.--CALANOID COPEPODS BERMUDA. PLATE 3.

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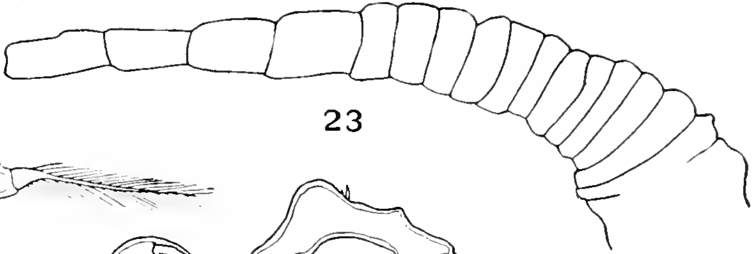

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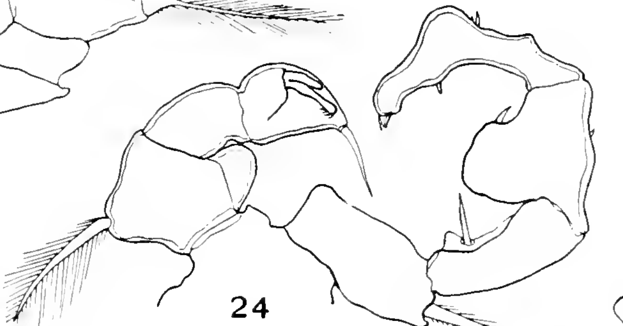

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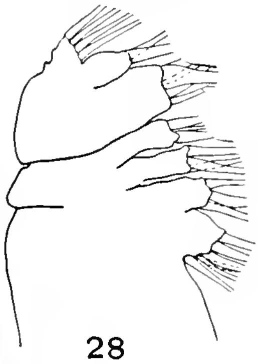

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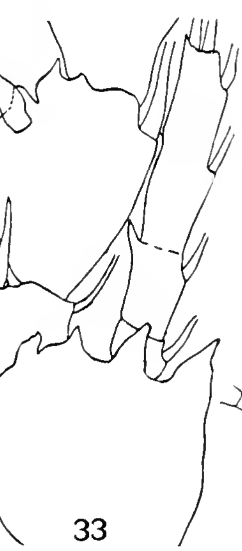

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PLATE 4.

Figure 35. Lampoidopus marki n. gen., n. sp. Male, geniculating part of right anterior antenna. × 470.

Figure 36. Clausocalanus furcatus Brady. Male, right foot of fifth pair. × 470.

Figure 37. Acartia spinata n. sp. Female, fifth foot. The bristle on the outer margin of the second joint is not shown entire. × 500.

Figure 38. Lampoidopus marki n. gen., n. sp. Female, posterior maxilliped. The bristles are not shown. × 113.

Figure 39. Calanopia americana Dahl. Female, fifth foot. × 500.

Figure 40. Clausocalanus furcatus Brady. Male, left foot of fifth pair. × 470.

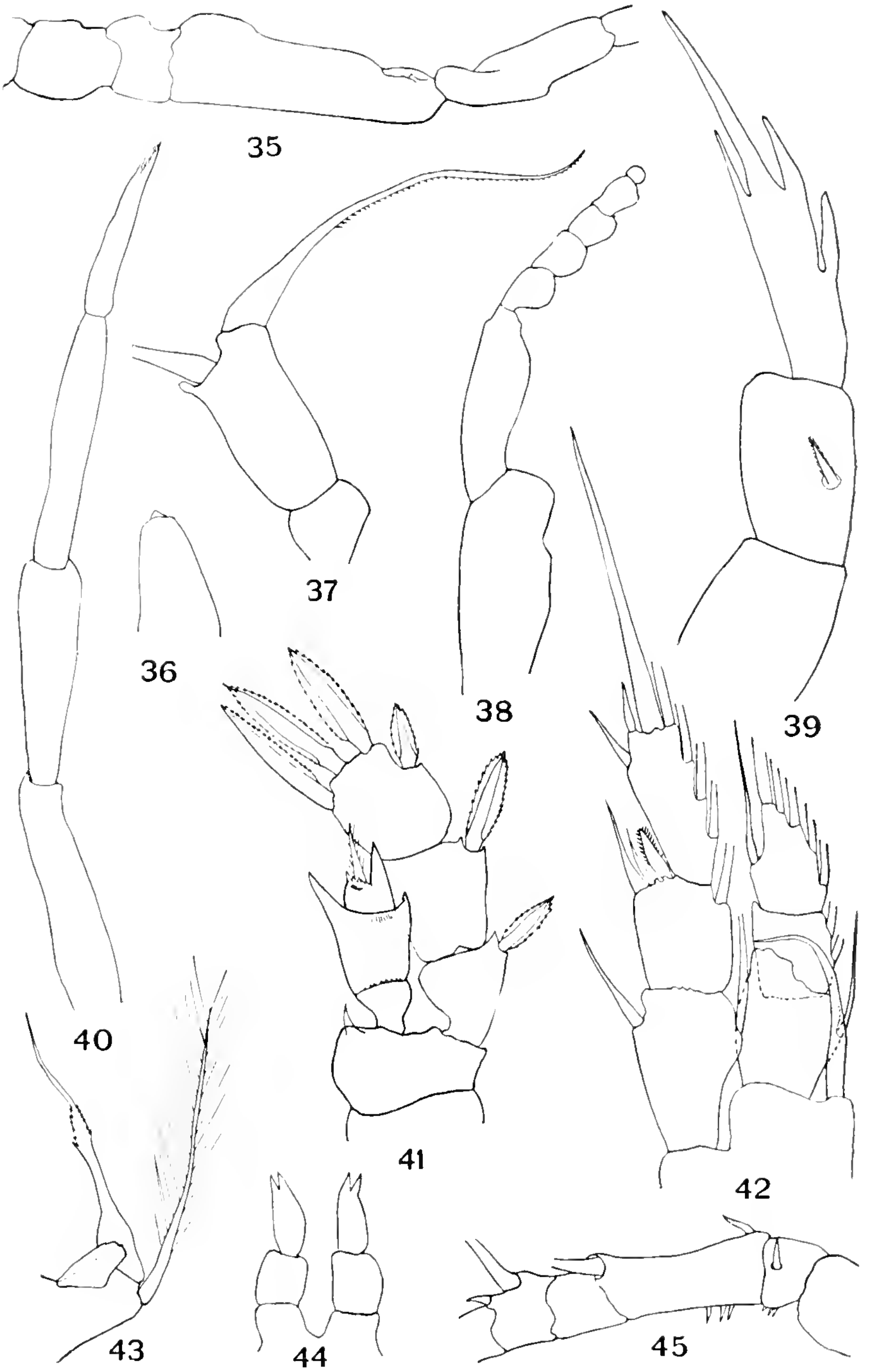
Figure 41. Pseudocyclops magnus n. sp. Female, fifth foot. × 500.

Figure 42. Lampoidopus marki n. gen., n. sp. Female, first foot. × 470.

Figure 43. Acartia bermudensis n. sp. Female, fifth foot. × 500.

Figure 44. Clausocalanus furcatus Brady. Female, fifth pair of feet. × 470.

Figure 45. Acartia spinata n. sp. Female, first five joints of anterior antenna from below. × 93.



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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 8. — November, 1911.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

THE VON WALTENHOFEN PHENOMENON IN SOFT IRON RINGS.

By Louis A. Babbitt.

With a Plate.

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Presented by B. O. Peirce, May 10. Received July 11, 1911.

BY LOUIS A. BABBITT.

THE purposes of the investigation described in this paper were two: first, to determine how the manner of growth of a magnetizing field of given final intensity about a mass of finely-divided iron affects the change which the field produces in the magnetic condition of this iron; second, to harmonize the results found by previous observers in the same field of inquiry.

About fifty years ago von Waltenhofen[1] observed that when the field in a solenoid used to magnetize a soft iron rod was suddenly reduced to zero by breaking the circuit, the remanent magnetism of the iron was, under certain circumstances, opposite in direction to that induced by the field just applied. This result, interpreted by means of Weber's theory of elementary magnets possessing inertia, led almost immediately to the conclusion that the magnetic condition of the mass of iron is affected by the manner in which the magnetizing field is built up. If, for example, the field were changed continuously in the same direction, in one instance by two steps and in the other by one, from one given value to another, the one-step method should produce, according to Weber's hypothesis, the greater magnetic change in the iron; for the greater velocity acquired by the elementary magnets under this method would cause them to rotate through a greater angle, and show a greater flux change in the metal. Similarly, a high electromotive force applied to the magnetizing circuit should, through the more rapid magnetization produced, give a larger magnetic change than a low voltage would, even though the final value of the current is the same in both cases.

From a commercial, as well as from a scientific point of view, this phenomenon is important. The calculations which precede electrical

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[1] Pogg. Ann., **120**, 650. Winkelmann, Hand. der Physik, **5**, 214.

construction are often based upon hysteresis diagrams or magnetization curves, which are supposed to show the magnetic characteristics of different specimens of iron and steel under given excitations, and, if the forms of these figures depend very much upon the manner of application of the excitations, it is essential that the observations be made under conditions approximately the same as those under which the iron will have to do its work. It is important, therefore, that the engineer should know how closely the test conditions and the working conditions must correspond, and a number of investigators have studied the subject.

At the outset the subject may be divided into two parts : first, the magnetization of large solid masses of iron ; second, the magnetization of finely laminated iron.

For the former it is almost unanimously agreed that, if the change in the magnetizing field is always the same in direction, in going from one value of the magnetic field to another, the manner in which that change is produced affects the total change of flux in the iron. Fromme,[2] Lehman,[3] Gumlich and Schmidt,[4] Heyse,[5] Rücker[6] and B. O. Peirce[7] have obtained results with various shapes of iron, such as toroids, ellipsoids and rods, which show this difference in the flux change to a greater or less extent. Rücker, for instance, found that in the case of soft iron it might amount to 30 per cent of the total flux change. For hard material the percentage was smaller.

In some early experiments I used a large, massive cast iron magnet weighing about 1500 kilogrammes. Its general shape is shown in Figure 1. The base is of rectangular cross-section, 40 cm. by 20 cm., 101 cm. long and 80 cm. high; the arms are cylinders of steel 25 cm. in diameter and are capped by rectangular pole pieces 4.5 cm. thick and 580 cm. in area. Four coils having a total of 2823 turns and a resistance of 12.4 ohms served for the magnetization.

The time required for the current to reach a constant value in such a system is very appreciable. Two to three minutes was not at all unusual. Such long, slow flux changes taking place in the iron could not be measured accurately by the long-period galvanometer[8] that had been constructed for this sort of work. However, it was found that

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[2] Wied. Ann., **43**, 181 (1891); **44**, 138 (1891).

[3] Ibid., **48**, 422 (1893).

[4] Elektrotecknische Zeitschrift, **21**, 1900.

[5] Inaug. Diss. Halle, p. 33, 1901.

[6] Inaug. Diss. Halle, 1905.

[7] These Proceedings, **43**, 155 (1907).

[8] These Proceedings, **44**, 1908.

a slight modification of the usual procedure in step-by-step ballistic measurements would give consistent results. Instead of keeping the secondary circuit closed during the whole flux change corresponding to a given step of the primary current, advantage was taken of the slow movement of the amperemeter and, when the current had attained a certain value in the primary, the secondary was broken. The flux change up to that point was recorded with more or less accuracy. The iron was then carried on around its hysteresis curve, and, when the primary current had reached the same value that it had at the instant when the secondary was broken, the secondary circuit was again closed, and it remained closed during the completion of the step of the primary current, thus giving a ballistic effect which measured the change of magnetic flux during the second part of the step in question. If two minutes are required for the complete flux change and a galvanometer with a period of five minutes be used, a division of the one step into four parts instead of two as just described will give a result having a probable error not greater than 0.4 of one per cent. The sum of the four throws will give the total flux change in that step. The application of this method to the various steps of an hysteresis curve will give results of any desired degree of accuracy up to the limit of the instrument. In fact, numerous tests showed that after the iron had been carried through a cycle a large number of times two successive cycles obtained in this way were equivalent both as a whole and in their corresponding steps to within one half of one per cent.

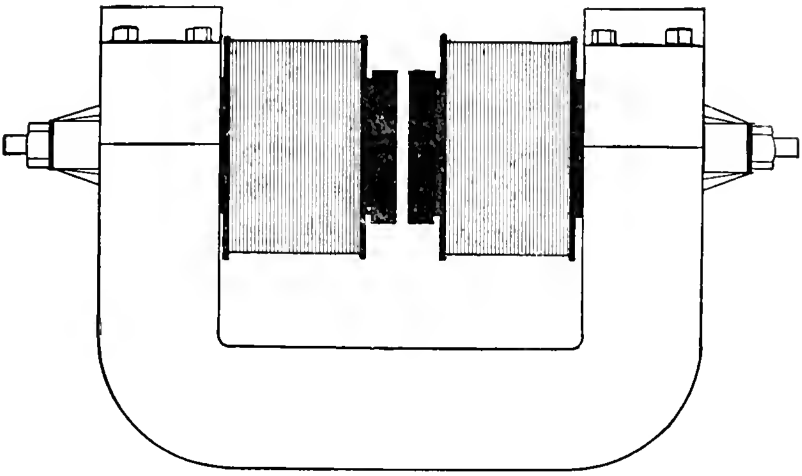

FIGURE 1.

The three curves A, C, and D of Figure 2, corresponding to 4, 28 and 56 steps respectively, were obtained in the manner just described. The maximum value of the magnetizing current and consequently the maximum H is the same for all three. In each case the iron was carried around its hysteresis cycle a large number of times. No demagnetization was attempted; the change from one curve to another consisted merely in the change of the number of steps.

The maximum value of B was approximately 6000. The vertical ordinate is in terms of throws of the galvanometer. If one half the throw for a complete reversal of the maximum H be taken as 833, the maximum values of B for the three curves would be represented by 824, 770, and 692; that is, for the introduction of four steps instead of one into the hysteresis curve, the maximum value of B has fallen 1 per cent, for 28 steps 7.6 per cent, and for 56 steps 17.4 per cent.

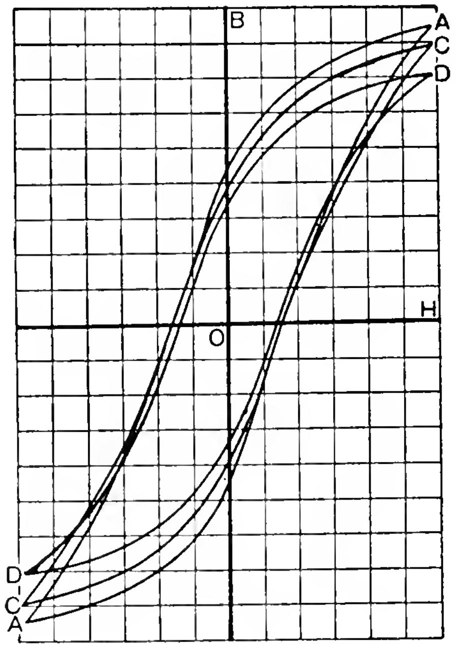

FIGURE 2.

For massive iron therefore it is undoubtedly true that a change in the number of steps of magnetization has a certain measurable effect on the final magnetic condition of the iron.

In such masses of iron the eddy currents can in no wise be neglected. There is nothing to show that the phenomena may not be accounted for by their action as well as by some inherent property of the iron itself; or indeed by both of these causes existing side by side. For more definite conclusions it is necessary to eliminate one of the factors. The former yields the more readily.

It has been shown that in the case of a long cylinder the reduction of the eddy currents[9] can be carried to any desired point by a sufficient lamination of the iron, and a toroid, if the radius of the ring be large enough in proportion to that of the solid mass, presents a form approximating that of a cylinder. While a mathematical demonstration will not be attempted, I think it safe to regard lamination as playing in my toroid the same rôle as in a cylinder, and by the elimination of eddy currents offering a means for deciding to what we are to attribute the effect of variation in the methods of magnetization.

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[9] These Proceedings, **43**, 161–182 (1907).

Along this line three investigators have worked Fromme[10] studied the difference in the magnetic condition of bundles of iron wires according as they were in the magnetizing solenoid when the current was applied or were put in afterward. To be sure, he found a difference; but since part of his process included handling the bundles while under the influence of the field it seems to me that we should not accept his results as conclusive. The jarring[11] and straining of the wires due to the handling might account for them. Rücker[12] took hysteresis curves consisting of various numbers of steps for a small toroid of soft iron wire and observed a decrease in the maximum flux through the iron as the number of steps was increased. For his specimen this decrease was the most pronounced when the induction per square centimeter, B, was about 4000 and amounted then to 6 per cent of the total induction. B. O. Peirce[13] compared step-by-step hysteresis curves of a toroid which had a finely divided core, with similar curves calculated from the manner of growth of the current in the magnetizing coil; an oscillograph supplied the necessary current-curves. Beyond the probable errors of this method he could detect no difference between the two sets of curves.

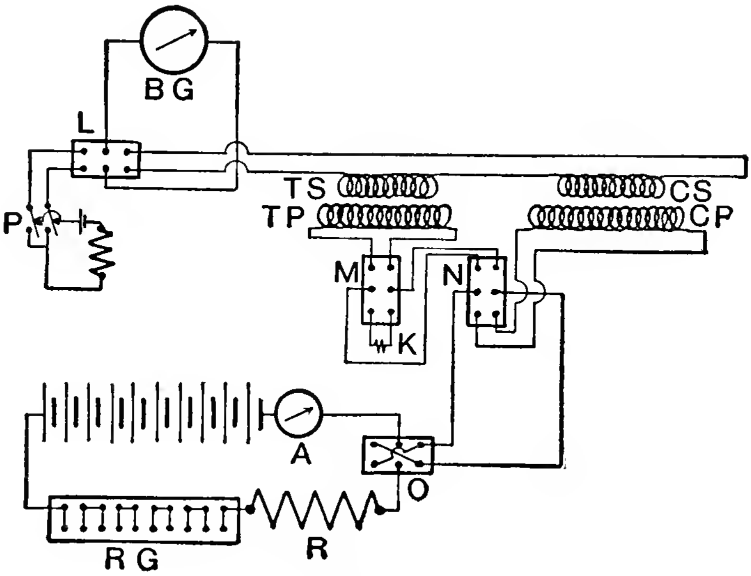

FIGURE 3.

At present, therefore, we have two diametrically opposed conclusions supported by experiment.

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[10] Wied. Ann., **4**, 76 (1878).
[11] Ibid., **5**, 345 (1878).
[12] Inaug. Diss. Halle, 1905.
[13] These Proceedings, **43** (1907).

The shape of the iron is an important consideration. That all unnecessary difficulties might be avoided, such as would be introduced by the poles of a broken magnetic circuit, the toroid was chosen, for my work, as the simplest and consequently the most suitable form.

The arrangement of the apparatus is briefly as follows. The primary of the toroid, TP, Figure 3, to be investigated, is connected in series with an amperemeter, A, a set of resistance gaps, RG, into which any desired resistance coil could be introduced, a rheostat, R, a reversing switch, O, and a set of ten storage cells. The double switch, N, allowed me to change from the primary of the toroid to the primary of the calibrating solenoid, CP. The switch, M, was for the purpose of introducing a resistance, K, approximately equal to that of the primary of the toroid, when it was desirable to reduce the field in it to zero without breaking for any length of time the flow of current from the battery. This device kept the current more nearly constant than would have been otherwise possible. The secondary circuit consisted of the ballistic galvanometer, BG, in series with the secondary of the toroid, TS, the secondary of the calibrating solenoid, CS, and the switch, L. This last permitted me to throw the galvanometer into the damping circuit. The flux changes produced in the iron core were measured by the throw of the ballistic galvanometer.

Description of the Apparatus.

The usual form of ballistic galvanometer with a period of about 15 seconds is not suited for this work. The total flux change in the toroid is not completed before the coil has swung considerably out of its zero position; and consequently the angular rotation of the coil is no longer proportional to that flux change. For my purposes I constructed an instrument similar to one used by Professor Peirce.[14]

The coil of the galvanometer, which was of the Ayrton-Mather type, was loaded by two brass balls to increase its moment of inertia. The whole was suspended by steel gimp; the current was conducted to and from the coil, of which the ends were soldered to the two vertical wires, by spirals of copper gimp similarly attached.

The increase in the inertia of the suspended system due to the two brass balls increased the period of the galvanometer in this instance to 65 seconds. As it was found by experiment that, if the secondary circuit were closed one half a second after the primary circuit, there was no perceptible deflection of the galvanometer, the period was re-

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[14] These Proceedings, **44**, 283 (1909).

garded as sufficiently great to register within the accuracy of the instrument the flux change that took place.

The throw was read by means of a telescope and scale; the distance of the latter from the mirror was 86 cm. Since the total possible deflection on either side of the zero amounted to 23 or 24 cm., it was necessary either to compare angles calculated from the deflection or to compute the angles for one set of deflections, add them, and determine the single deflection corresponding thereto. In other words, for throws of more than ten centimeters it was not admissible to regard the deflection as proportional to the flux change in the toroid.

The calibration by means of the standardizing solenoids showed that the throw could be obtained consistently, for any given quantity of electricity sent through the instrument, to within 0.1 mm. Thus for throws greater than 10 cm. 0.1 per cent and often 0.05 per cent was the accuracy attained. For such agreement three things were absolutely essential: the suspended system must be at rest before the throw commenced; the throw must be taken always in the same direction; the coil, in coming back, must never swing more than a few millimeters beyond its zero position. If it did go far beyond, the zero point was changed and the next deflection or two were not quite what they should be; usually too large. In this connection, too, it was observed that the first two and sometimes three throws taken in the day's work were in general larger than those that followed by a fraction of a millimeter; they were always thrown out of each set of results as doubtful. Although the care of complying with all the conditions made it necessary to spend from three to six hours in taking the data for any one of the curves presented later the accuracy of the results seemed to make it worth while.

One more peculiarity came out during the investigation. When the current in the primary of the calibrating solenoid was simply broken, instead of reversed as usual, and the deflection for the reversal calculated from the resulting throw, this was in general a few tenths of a millimeter greater than an observed deflection for a reversal. The difference appeared only when the total reversal gave a throw of more than 12 or 14 cm. It seemed as if somewhere in the secondary circuit there must be a slight leakage produced by the higher voltage of the complete reversal. In order to be sure of the amount of this difference a full reversal was taken in the calibrating test before each day's work as nearly as possible equal in throw to that produced by the reversal of the field to be used on the toroid during the day; then the throw was observed when the same current was broken, and the error calculated. It was hoped that the conditions in the secondary circuit when the current in the solenoid was reversed would be sufficiently like those existing when the field of the toroid was reversed to give the same leakage. As a matter of fact, the difference between the calculated and observed reversals for the solenoid were throughout so nearly equal to the corresponding difference when a reversal consisting of a number of steps was compared with a complete reversal of the field in the iron, that in all probability the conditions were approximately the same and the leakage likewise. Unfortunately this leakage was not taken into account at first because of the other greater inaccuracies then occurring in the work; it is applied, therefore, only to the work done on coils I and III, not to II.

The amperemeter was supplied with a number of shunts so that the constancy of the current could always be determined to within 0.1 per cent, and as a general rule more closely than that. It did not appear to be necessary to measure so exactly the true value of the current used; and no attempt was made to do so. However, it was given by the instrument within 0.5 per cent.

The resistances in the primary circuit were made of constantan wire set in enamel. For the moderate currents used, seldom over two amperes, their rise in temperature did not have any appreciable effect.

The primary and secondary solenoids used in calibrating the ballistic galvanometer were both carefully made. The primary consisted of 5526 turns of No. 18 B. & S. annunciator wire wound on a brass tube split longitudinally. The total length of the coil was 176.2 cm. The secondary consisted of 538 turns of well insulated wire wound on a wooden core. The primary was attached to the wall vertically at a distance of 15 feet from the galvanometer; inside it and equidistant from either end was hung the secondary. This arrangement being always constant allowed the testing of the galvanometer at the beginning and end of the day's work, and showed immediately whether any change had occurred.

Except for soldered joints the secondary was throughout a copper circuit. Thus all trouble from thermoelectric currents was eliminated.

Three toroids were used which for convenience we may designate as I, II and III. The second was the first to be experimented on, but the meaning of its data will be clearer if discussed after the more extensive investigation with toroid I.

The core of I was made out of carefully annealed soft wire. After the winding, the wires were insulated from each other by soaking the whole in shellac and drying it. A layer of paper covered the core; on it was wound a single layer of secondary divided into four parts. A second layer of paper, the first layer of the primary, a third layer of paper, and the second layer of the primary, followed in the order given. Care was taken to make the winding as uniform as possible. The data for the toroid are as follows:

Average diameter of the iron wire of the core	0.0254 cm.
Number of turns of iron wire in the core	600
Weight of iron in the core	98.23 gm.
Area of cross-section of the iron in the core	0.303 sq. cm.
Average radius of the iron ring	5.6 cm.
Secondary, 4 coils, No. 26, double silk insulation,	
Coil A	50 turns.
Coil B	75 turns.
Coil C	100 turns.
Coil D	340 turns.
Primary, 2 layers	
First layer	164 turns
Second layer	157 turns

The core II consisted of iron wire not so well annealed as that of I. Insulation was obtained by dipping the wound core into hot paraffine. The primary and secondary were put on with the same precautions as to paper insulation and the uniformity of winding as in the case of toroid I. The data for II are:

Average diameter of the iron wire of the core	0.0285 cm.
Number of turns of iron wire in the core	500
Weight of iron in the ring	88.1 gm.
Area of cross-section of the iron ring	0.318 sq. cm.
Average radius of the iron ring	5.55 cm.
Secondary, 4 coils, No. 26, double silk insulation,	
Coil A	157 turns.
Coil B	146 turns.
Coil C	154 turns.
Coil D	131 turns.
Primary, 2 layers,	
First layer	160 turns.
Second layer	160 turns.

The core of III[15] weighing 55 lbs. consisted of wire approximately one third of a millimeter in diameter. Insulation of the iron was effected by means of paraffine. The larger wire used for both primary and secondary afforded by its double insulation complete freedom from any appreciable leakage.

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[15] The same core was used by B. O. Peirce: These Proceedings, **43**, 5 (1907).

The demagnetization of toroids I and II was carried out in one of two ways. In one process the toroid was left with its primary in the primary circuit, Figure 3. By means of the reversing switch the field was reversed and after each reversal decreased by the addition of resistance from the rheostat and the gaps provided for that purpose. When the current had been reduced to about 0.1 of an ampere the toroid was disconnected and attached to the secondary of an alternating current transformer. This was movable and could be pulled along a track away from the primary which was connected to the 110-volt, 60-cycle lighting circuit. The further demagnetization was carried out in this manner.

The second method consisted of the introduction into the primary circuit, Figure 3, of a piece of apparatus designed to reverse the current automatically. The main features were a motor and four rods joined to the motor through gears and cranks. The cranks lowered the rods by pairs into mercury cups beneath. With one pair of rods in contact with the mercury, and with the proper electrical connections from the toroid to the rods, and from the mercury cups to the battery, the current flowed in one direction through the toroid; when the motor was turned until these two rods were raised and the other pair were in contact, the current flowed in the opposite direction. The running of the motor together with the introduction of resistance into the main circuit resulted in the demagnetization of the toroids. By keeping the amperemeter in the circuit it was possible to regulate the demagnetizing current so that it should never be above that already applied to the toroid. This is a distinct advantage over the first method, in that the history of the iron is better known and the effect of its previous magnetic history more easily determined. With the motor running so as to give three or four reversals of the field in the toroid per second, the resistance was introduced gradually from the rheostat and gaps until the current was not above 0.0003 ampere. The time given to one demagnetization by this device was between two and three hours.

The Investigation of Toroid I.

The primary and secondary of the toroid were connected with their respective circuits as shown in Figure 3. If M and the other switches be set so that the current flows through K, and if, after the core has been demagnetized, M be thrown over, the throw of the calibrated galvanometer will give means of calculating the B induced in the iron. Let the current be reversed by O while the secondary circuit is broken at L; make the secondary again at L and reverse O. The B calculated from this last throw will be in general different from the first B. If one repeats the process, amounting to carrying the iron around the hysteresis cycle, a sufficient number of times, it will be found that the value of B will become constant or at any rate very nearly so. Instead of computing B it will be just as satisfactory to compare directly the throws of the galvanometer. This will be done throughout the work.

Any one of the complete reversals just described will be referred to as a 1-step reversal. A 3-step reversal will consist of the following process. With a maximum of the flux in one direction at the start, the current is broken by throwing over M and thus putting K in the circuit. After the introduction of resistance and the reversal of O, M is thrown back to the primary of the toroid. Finally the resistance just introduced is cut out, by moving a rheostat arm, if it be in the rheostat, or by short-circuiting a coil, if it be in one of the gaps. For each of these three steps the flux change is recorded as a throw of the galvanometer. The angular displacement of the coil can be computed and from the sum of these angles the corresponding single throw in centimeters. By correcting for leakage one has the single throw that can be used as a basis for comparison. A 7-step reversal would consist of seven steps between the two flux maxima, and so on.

The result of carrying out such an operation is to go from one magnetic condition to another in a given number of steps. If the initial conditions be twice the same and the final inducing field twice the same, but the number of steps in one case different from that in the other, there are at hand the means for determining, by comparing the corresponding single throws of the galvanometer, what effect the number of steps has on a magnetic change. To satisfy the second of the two conditions is a comparatively easy matter. The first is more troublesome. However, if the iron be carried through a large number of hysteresis cycles, until the maximum B for the cycle is constant, a number of observations taken for 1-step reversals and then a number for 3-step reversals, it is certain that for the first 3-step reversal the initial conditions were the same as for the last 1-step reversal. Furthermore, if the following 3-step reversals give the same result as did the first 3-step reversal, it is fairly safe to assume that there has been no change in the iron after the first 3-step cycle. For two low values of H, 2.35 and 3.46, this process was carried out; the corresponding maxima for B were 820 and 1394.

In the first case, after the ballistic galvanometer was found to be working with its usual accuracy (0.1 per cent), the iron was carried through twenty-five 3-step reversals with a maximum field of 2.35.

The following observations were taken for the 26th and 28th reversals one 3-step reversal coming between the two. No measurements are here recorded for the odd-numbered reversals, which were, of course, in the opposite direction to the even-numbered ones.

Rev.	Amp. Read.	Ball. Galv.	Corresponding Single Throw.
26th	8.90 0.00	4.12	10.53
	0.00 5.94	4.07	
	5.94 8.90	2.31	

Rev.	Amp. Read.	Ball. Galv.	Corresponding Single Throw.
28th	8.90 0.00	4.12	10.55
	0.00 5.94	4.07	
	5.94 8.90	2.33	

The 29th to the 82d were 1-step reversals. Of these the 30th, 32d, 80th and 82d are recorded.

Rev.	Amp. Read.	Ball. Galv.	Average Throw.
30th	8.90	10.55	10.55
32d	8.90	10.54	
80th	8.90	10.51	10.51
82d	8.90	10.51	

The difference between the average of the twenty-seven even-numbered reversals, 30th–82d, and the average of the first two recorded 1-step reversals, 10.55, is 0.1 per cent. The flux change per reversal has decreased slightly, from 10.55 to 10.51, during the course of the 3-step reversals. That this is characteristic of the specimen during its early magnetic history will appear from the data following.

In this case the maximum value of H is 3.46, of B 1394. Thirty 3-step reversals were taken and then the 31st and 33d observed.

Rev.	Amp. Read.	Ball. Galv.	Corresponding Single Throw.
31st	13.27 0.00	6.45	
	0.00 8.26	8.40	23.06
	8.26 13.27	7.75	

Rev.	Amp. Read.	Ball. Galv.	Corresponding Single Throw.
33d	13.27 0.00	5.89	
	0.00 8.26	7.95	23.06
	8.26 13.27	8.75	

A set of 1-step reversals followed the 33d, out of which four are recorded.

Rev.	Amp. Read.	Ball. Galv.	Av. Throw for Galv. Read. 13.27.
35th	13.27	23.01	22.99
37th	13.26	22.94	
87th	13.26	22.56	22.58
89th	13.26	22.59	

Here the 1-step reversals give a smaller "throw," indicating a smaller flux change, than the 3-step reversals, but it is to be noted that the first 1-step reversal gave a throw very nearly as large as that given by the 3-step reversals, though the general tendency of the 1-step reversals was to reduce the throw.

A demagnetization and reversal of the order of steps, that is, putting the series of 1-step reversals first, yielded the following. Three of the first 55 reversals are recorded.

Rev.	Amp. Read.	Ball. Galv.	Average Throw.
51st	13.26	22.53	22.55
53d	13.26	22.57	
55th	13.25	22.56	

Of the 52 3-step reversals that followed the 1-step two are recorded.

Rev.	Amp. Read.	Ball. Galv.	Corresponding Single Throw.
105th	13.25 0.00	6.40	22.50
	0.00 8.26	8.32	
	8.26 13.26	7.34	
107th	13.26 0.00	5.91	22.50
	0.00 8.26	7.94	
	8.26 13.27	8.22	

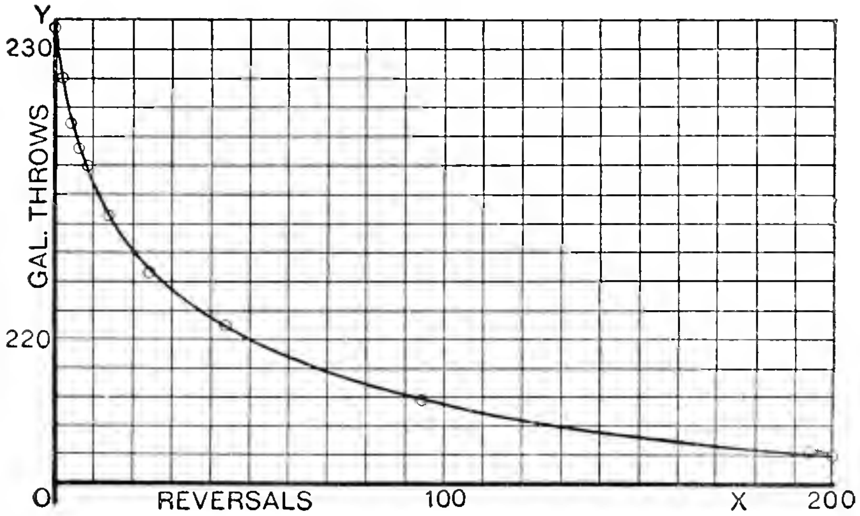

FIGURE 4. Set II: B 6000: first magnetization; all 1-step reversals except the 196th and the 198th, which are 3-step.

Again there is a very slight fall in the maximum B as the number of reversals increases. The 3-step and 1-step processes yield the same results to within 5 parts in 2250.

From these three sets of data it is evident that the effect of the method of magnetization is, in so far as the number of steps is concerned and these tests are carried, of no consequence. In the worst case the difference between the total flux change for 1-step and 3-step reversals is one third of one per cent, and in the best one tenth of one per cent.

It is important to note that such a statement applies only when the iron has reached such a state that it passes repeatedly through practically the same hysteresis cycle. For the first eight or ten reversals the cycle is changing rapidly and it may well be that, with the iron in that condition, the number of steps taken in going from one value of H to another does effect the final value of B. As it is of interest to settle this question too, the method of investigation must be changed somewhat.

Instead of reversing the field a large number of times before observing the throw of the galvanometer, let the throw be observed when the field is first applied and thereafter for every reversal. If the first throw be regarded as the zero reversal and be doubled in order to make it comparable with the others, a throw-reversal curve may be plotted as shown in Figure 4. Now, with due care that the demagnetizing current shall not rise above the magnetizing current just used, let the toroid be demagnetized by the motor attachment. Another throw-reversal curve taken exactly as before will show the manner in which the iron approaches a constant maximum of B on the second magnetization. A set of such curves giving the behavior of the iron on the first, fourth fifth, sixth, seventh, and eighth magnetizations are those of Figures 4, 5, 6, 7, 8, and 9 respectively.

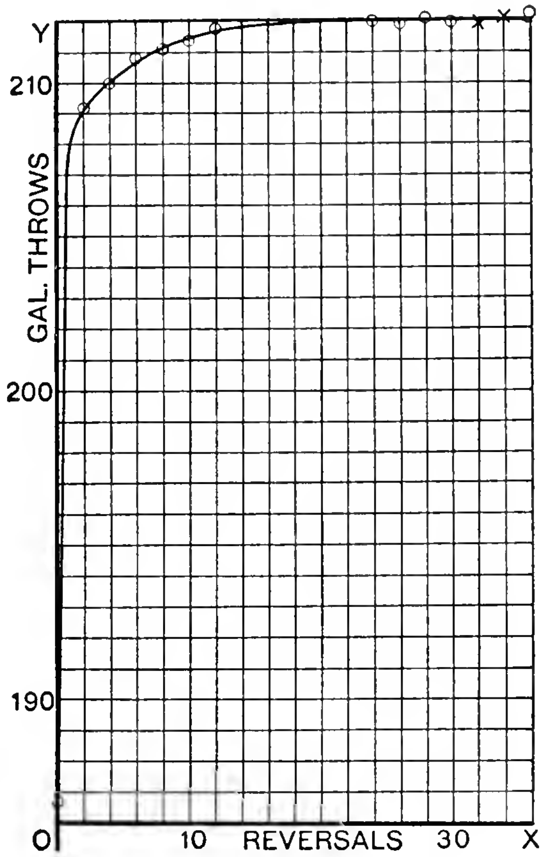

FIGURE 5. Set II: B 6000: fourth magnetization; all are 1-step reversals except the 32d and the 34th, which are 3-step.

It is evident that no two of the curves are exactly alike. The first shows a sharp fall of the maximum B as the field is reversed. On the other hand the second shows a rather rapid rise, as do the remainder. Even so, it is not possible to pick out the same reversal on any two consecutive curves and expect them to register the same flux change except by chance. This is true when the curves examined consist entirely of 1-step reversals up to and including the reversal in question.

It is, therefore, out of the question to expect any consistency in results obtained by comparing reversals if a process of demagnetization intervenes. If 1-step reversals on two successive curves are not comparable and, so far as can be seen, follow no exact law, it is not logical to obtain a hysteresis curve of a given number of steps, demagnetize the iron, obtain a second curve of a different number of steps, and, because the maximum B of one curve is greater than that of another, declare that the number of steps affects the magnetic condition of the iron.

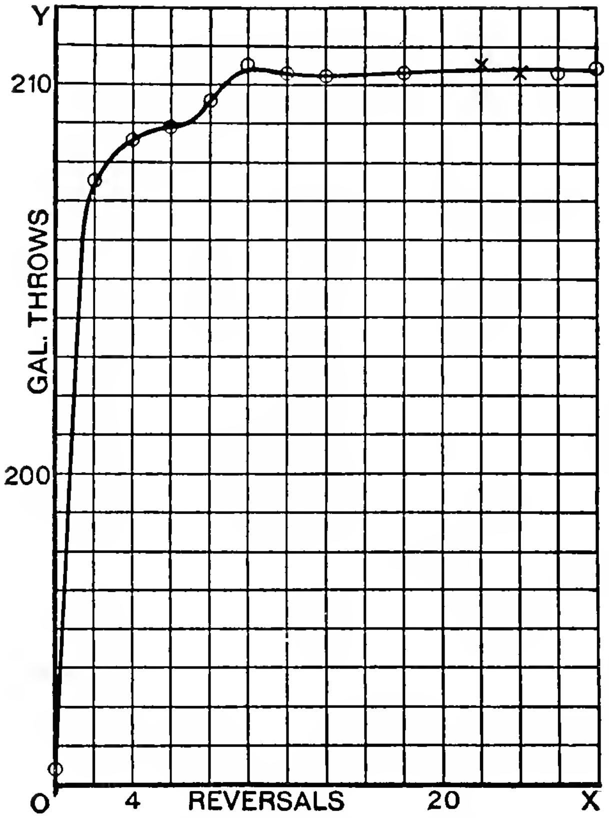

FIGURE 6. Set II: B 6000: fifth magnetization; ○ indicates 1-step reversals; × 3-step reversals.

This variation in magnetic condition is due, I suppose, to the past history which theoretically can never be twice exactly the same. It may depend on the previous magnetizations or demagnetizations or on both. No complete distinction between the effect of the two is possible, but some few things appear to be true. The remarkable drop in the first curve and rise in the second followed by the more rapid rise in the later curves seem to show the result of previous magnetic history, in particular, the previous magnetizations. For as the number of magnetizations increases, the curves assume more and more the same general form. The variations in the number of reversals required for any particular magnetization to reach a constant state, even after the form of the curve remains unchanged, leads one to suspect that the demagnetization plays an important part. If the iron be treated on each occasion with the same magnetic field, the process of demagnetization is practically the only variable. In it the number of reversals for any given magnetic field and sometimes the number of steps used varied considerably. There is no reason for supposing that a change in the demagnetizing process would not affect the non-magnetic condition. This is the initial condition for the next magnetization and, if not twice the same, might well be the cause of the variations observed in the early part of the magnetization-reversal curves. It seems to be the more probable cause, inasmuch as the previous magnetizations were pretty nearly alike and would be expected to give less haphazard variations than were actually observed. If the demagnetizing process for any given maximum of B, or at any rate that part of it which affected appreciably the non-magnetic condition of the iron, were carried out always in the same manner, I am inclined to believe that in most cases the sixth or seventh magnetization-reversal curves would be duplicated by those that followed. However, it seems to be impossible to obtain a second time the magnetic condition exhibited, for a given maximum of B, by any point of the first few curves. The same value of B might be obtained, but that does not mean the same magnetic condition; for the next reversal in the two cases would yield distinctly different values of B.

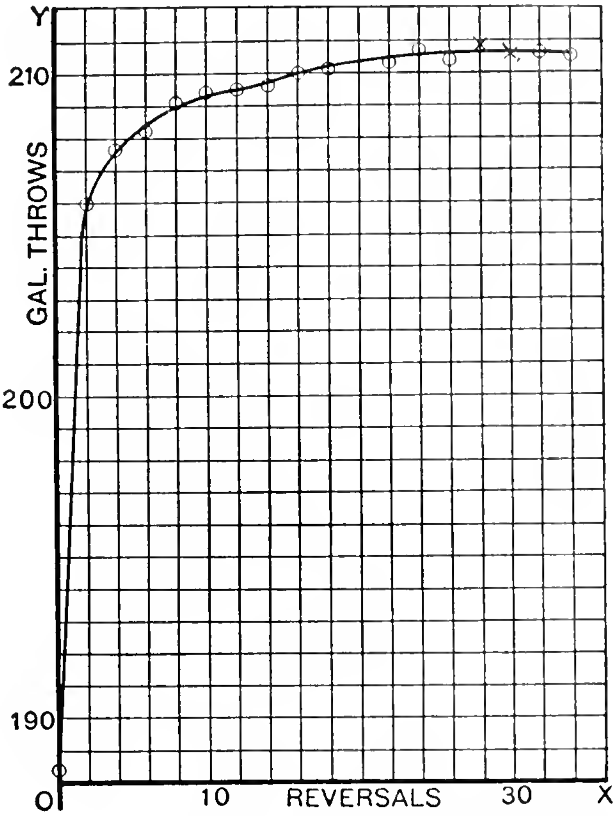

Figure 7. Set II: B 6000: sixth magnetization; ○ indicates 1-step reversals; × 3-step reversals.

The tedious process of making each demagnetization the same was not suited to the apparatus at hand and would require a large amount of time and trouble. Furthermore, the relative effect of the various parts of the demagnetizing process on the non-magnetic condition is practically unknown. These two facts eliminated for the present a continuation of the work by the comparison of any two curves separated by a process of demagnetization. Even such knowledge as I have indicated would be of no avail for the first few curves of a set, where it is probably impossible to duplicate any point of the magnetic condition.

The only method applicable was the following. In taking any one of the magnetization-reversal curves by 1-step reversals, for instance curve 7 (Figure 8), the observer introduced at one or two places, as at the fourth and fourteenth reversals, a reversal consisting of a larger number of steps. If the curve be plotted from 1-step reversals only and, after it has been drawn, the other reversals marked in their proper places, some conclusion as to the effect of the latter can be established. The case in which the iron has attained a constant cyclic change has been discussed; it is evident that for that condition this method will decide at once whether or not the number of steps has any effect. If the iron is still in the stage of variation, the early part of the curve, one cannot be so sure. However, if there is no abrupt change in the direction in going from the 1-step reversal just before the 3-step to that just following, and if the 3-step lies to within the expected error on the curve, it seems highly probable that the number of steps is immaterial. If the general shape of the curve in that region is about like that in the corresponding regions of the curves preceding and following, where the region consists wholly of 1-step reversals, the probability is correspondingly increased. Of course, no such similarity as this exists for the first three curves of a set with moderate flux density.

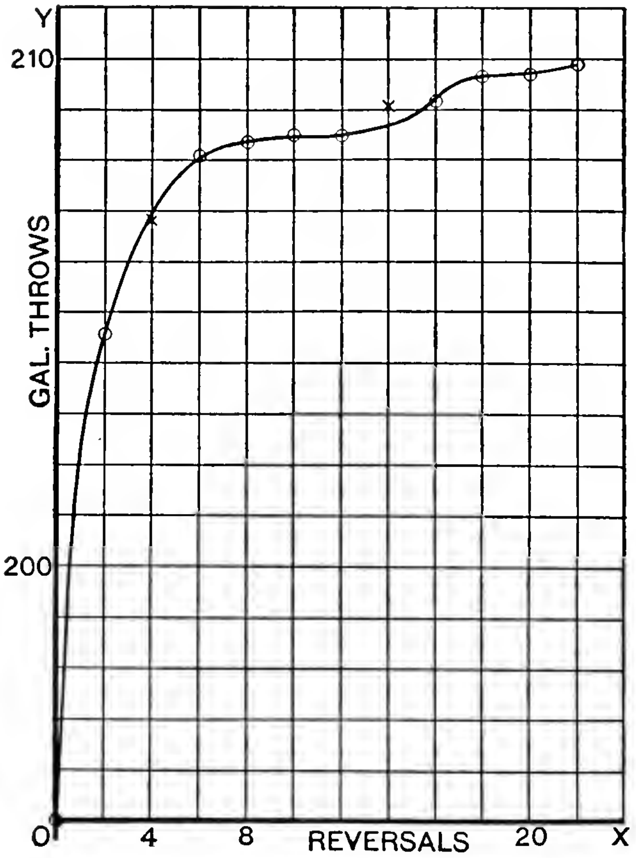

Figure 8. Set II: B 6000: seventh magnetization; ○ indicates 1-step reversals; × 3-step reversals.

The method of attack that has been outlined was carried out for approximately the following values of B per square centimeter, 3000, 6000, 7400, 10,100, 13,500, and 19,300, in the order named, and the data obtained have been plotted, in six sets, giving the curves shown.

There is no object in introducing all of the data; but as a typical example I select the fourth magnetization curve for B = 7400, Figure 13, and give both the data and method of treatment in full.

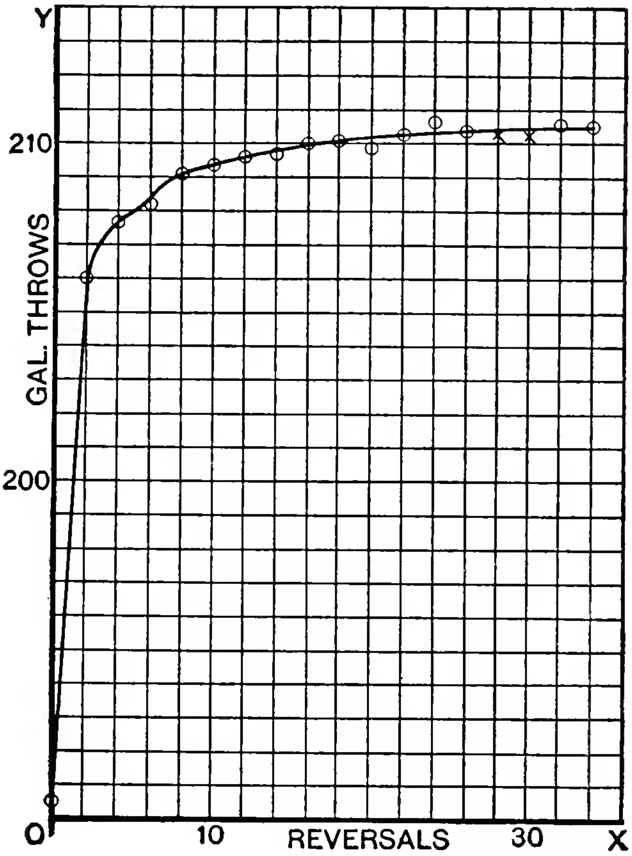

Figure 9. Set II: B 6000: eighth magnetization: ○ indicates 1-step reversals; × 3-step reversals.

Typical Set of Data.

The toroid has been demagnetized by the motor reverser. The process occupied about three hours and ended when the current had been reduced to 0.0003 amp.

The temperature of the room at the beginning was 18.5° C.

Test of Ballistic Galvanometer.

Reading of Amperemeter.	Throw on Reversing Current.	Reading of Amperemeter.	Throw on Opening Circuit.
7.16	16.77	7.15	8.29
7.16	16.78	7.16	8.31
7.16	16.76		

Average observed throw for reversal of current 7.16 is 16.78. The average calculated throw for the reversal of the current 7.16 is 16.77. These two values were so close that it was assumed that in this instance there was no leakage.

Data for Magnetization-Reversal Curve.

No. of Rev.	Reading of Amperemeter.	Throw of Ball. Galv. in cm.	No. of Steps in Reversal.
0	13.63	7.53	1
2d	13.63	16.61	1
4th	13.63	16.68	1
6th	13.63 to 0.00	1.70	5
	0.00 to 6.09	2.475	
	6.09 to 7.91	2.95	
	7.91 to 11.04	7.02	
	11.04 to 13.68	2.375	
8th	13.68	16.87	1
10th	13.67	16.90	1
12th	13.67	16.92	1
18th	13.67	16.94	1
20th	13.67 to 0.00	1.69	5
	0.00 to 6.09	2.465	
	6.09 to 7.91	2.95	
	9.91 to 11.03	7.265	
	11.03 to 13.67	2.385	
22d	13.67 to 0.00	1.67	5
	0.00 to 6.09	2.47	
	6.09 to 7.92	2.94	
	7.92 to 11.04	7.32	
	11.04 to 13.67	2.37	
24th	13.67	16.97	1

All odd numbered reversals were 1-step reversals.
The toroid was demagnetized and the galvanometer tested again.

Test of Ballistic Galvanometer.

Reading of Amperemeter.	Throw on Reversing Current.	Reading of Amperemeter.	Throw on Opening Circuit.
7.18	16.81	7.18	8.35

The temperature of the room at the end was 18.3° C.

The temperature of the room dropped gradually during the course of the work. However, as three hours were required for the completion of one such set of data, the change was very gradual, and owing to the care taken to keep windows, doors, and heating appliances unchanged during that period and for some time before it, the rate of the drop was practically constant. This would prevent anything more than a gradual change in the iron or the galvanometer and could not be regarded as the cause for any sudden variation in the curve.

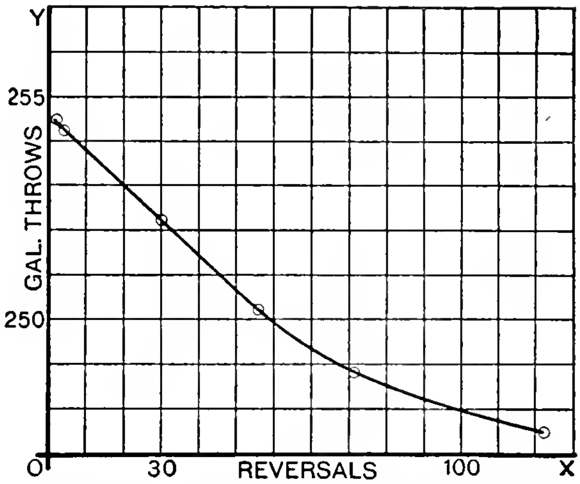

FIGURE 10. Set I: B 3000: first magnetization; ○ indicates 1-step reversal.

The galvanometer, as usual, showed that it could be relied on to give an accuracy of 0.1 of a per cent. The difference between a throw for a reversal, 16.77, calculated from breaking the primary circuit of the testing solenoid, and the observed throw for a reversal, 16.78, shows that there is in this case practically no correction for leakage. In fact the leakage seemed to occur only when most of the secondary of the toroid was in use. If one were not willing to make

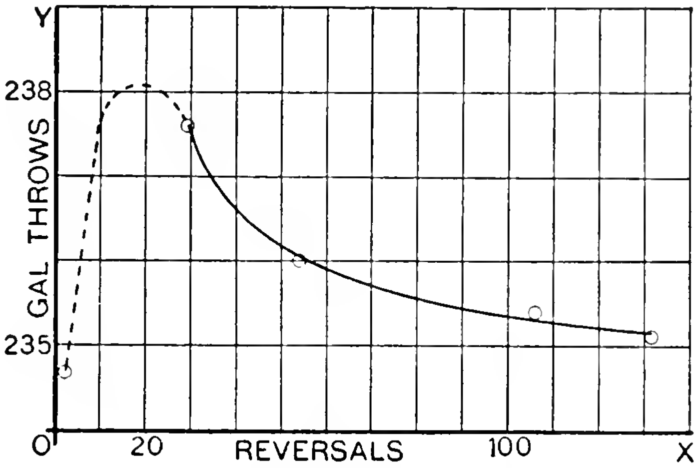

FIGURE 11. Set I: B 3000: third magnetization; all 3-step reversals.

this correction on the ground that it might not be the same for the reversal of the solenoid as for the reversal of toroid, one would find occasionally the reversals consisting of the larger number of steps giving a slightly greater flux change than the 1-step reversals. I have made the correction wherever it entered.

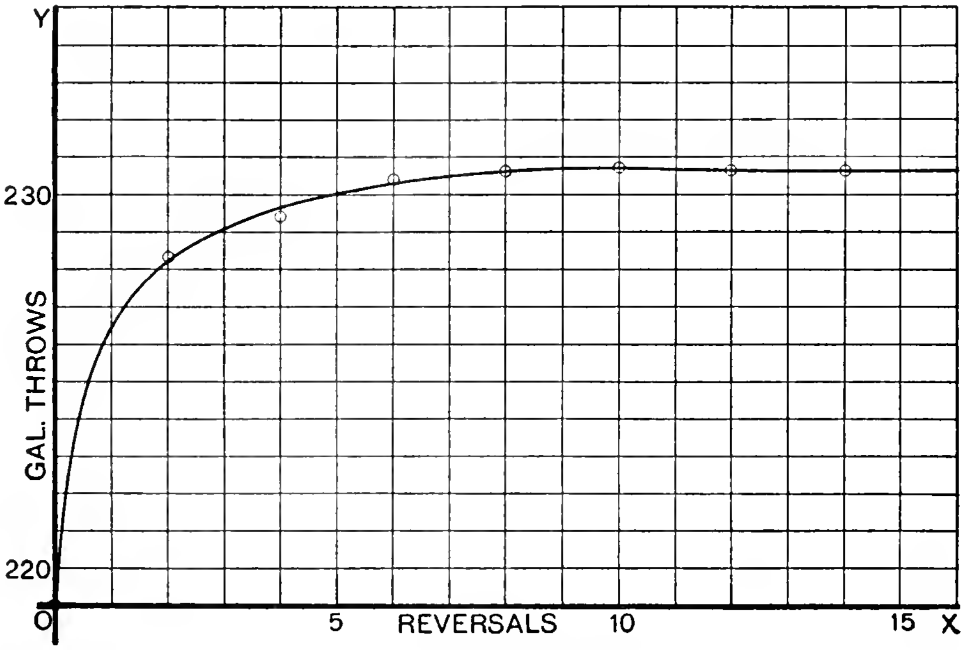

FIGURE 12. Set I: B 3000: tenth magnetization; ○ indicates 1-step reversals.

The throw, 7.53, due to the first application of the field was expressed in terms of degrees, doubled and changed again to a throw in centimeters in order that it might be on the same scale as the reversals. It is plotted as the zero reversal.

The 6th, 22d, and 24th are 5-step reversals. For each separate step of each of these the angular displacement of the coil was calculated. The five angles of any one reversal were added and turned again into centimeters throw of the galvanometer. A curve, Figure 13, was plotted from the 1-step reversals; millimeters were plotted throughout instead of centimeters. The 5-step reversals were added after the curve had been drawn in order that any variation might appear more plainly.

All the curves of the following six sets were obtained by the same method.

Discussion of the Curves.

Throughout, the reversals consisting of more than one step fall, with very few exceptions, to within 0.1 of a per cent on the 1-step curves. The exceptions occur where they are to be expected, namely, where there would be, with 1-step reversals only, fairly sharp changes in the direction of the curves.

A difference between the first magnetization-reversal curves and those that follow for the same maximum of B appears in each set. It is most noticeable for moderate values of B, from 4000 to 6000. In this region the first two or three curves of a set are of a decidedly different character; the fall in the induction as represented by the first seems to be characteristic, as does the rise and fall in the second and third magnetizations. The curves for the higher inductions show the rise and fall in the first curve and not a fall starting immediately. For any maximum of the induction the last curves of a set take on the same general shape — a sharp rise to a constant maximum value.

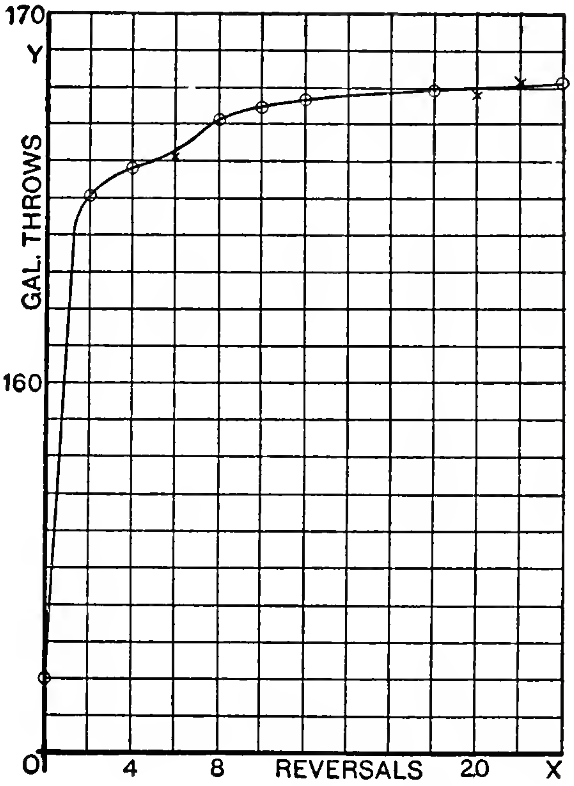

Figure 13. Set III: B 7400: fourth magnetization; ○ indicates 1-step reversals; × 5-step reversals.

The point brought out earlier becomes still more prominent and conclusive. It is that a comparison of the correspondingly numbered reversals on any two successive curves cannot be relied on for definite or decisive conclusions as to the effect of various processes of magnetization or production of the hysteresis cycle. It may be that if one chose those parts of the curves which indicated a constant value of B, the comparison would be of some value; but even here there is room for doubt.

THE INVESTIGATION OF TOROID II.

Coil II occupied the same position with respect to the circuit, (Figure 3,) as did coil I; the secondary was in series with the ballistic galvanometer and the secondary of the calibrating coil, the primary in series with the amperemeter, rheostats, and storage cells.

The method of demagnetization was that first used, the reversing switch (Figure 3), and the alternating current transformer. Certain features of the latter are important. The secondary could not be drawn continuously away from the primary without reducing the demagnetizing fields more rapidly than was deemed advisable. Hence it was moved a short distance and allowed to rest a few seconds. This reduced the field by steps and in such a manner that both the total number of steps and the number of reversals in each step were not regulated even roughly. Consequently no two magnetizations were exactly alike or approximately alike. In other words, the history of the iron just previous to what we have regarded as the initial condition, was subject to variation. It would be strange if the initial condition were not affected by this variation. In that case the result of the first application of the field to the iron after one demagnetization might well differ from that obtained by the first application after the next demagnetization.

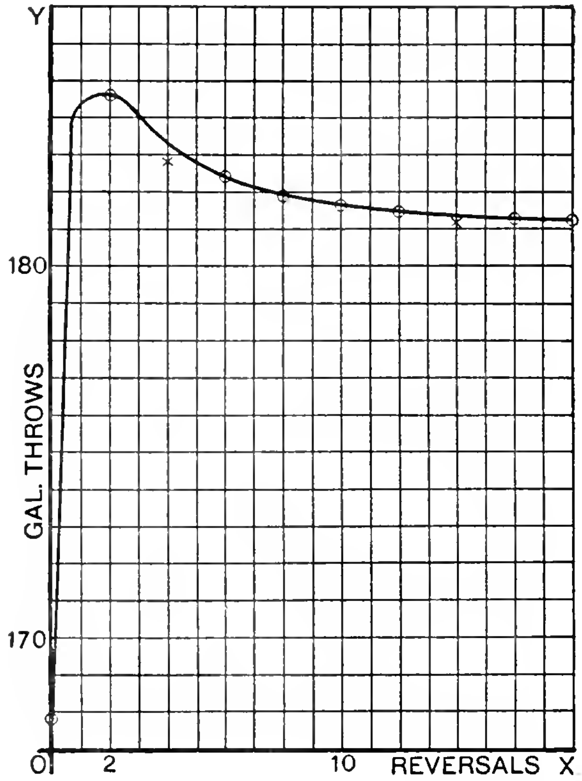

FIGURE 14. Set IV: B 10,100: first magnetization; ○ indicates 1-step reversals; × 5-step reversals.

The work on this coil was done before that on coil I, but as the results can be discussed more readily by reference to the more extensive data on the latter it was thought best to treat them in this order. The objection to any extended investigation with coil II lay in a weak consequent pole discovered at one point in the ring. The difficulties in the way of experimentation were sufficiently great without unnecessary additions, the effect of which was unknown; thus immediately after the discovery, core II was discarded and core I made.

The first two sets of data given below were taken in the following manner. The iron was demagnetized and the galvanometer tested. Then the magnetizing field was applied in one or more steps, as is indicated. A repetition of this process yielded the data under discussion. It is to be observed that the flux change recorded is that taking place when the iron is carried from zero magnetization to the first peak of the hysteresis curve.

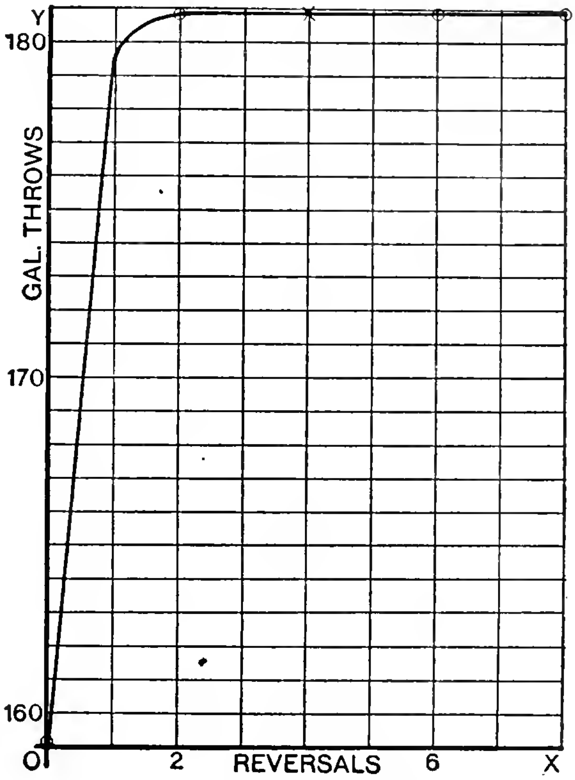

Figure 15. Set IV: B 10,100: second magnetization; ○ indicates 1-step reversals; × 5-step reversals.

First Set of Data.

The iron was demagnetized.

Test of Galvanometer.

Amperemeter Reading.	Ballistic Throw.
13.80	21.54
13.81	21.60
13.81	21.59

The iron was demagnetized by transformer and the field built up in one step:

Amperemeter Reading.	Ballistic Throw.
1.220	20.76

The iron was demagnetized and the field built up in one step:

Amperemeter Reading.	Ballistic Throw.
1.220	20.76

The iron was demagnetized and the field built up in two steps:

Amperemeter Reading.	Ballistic Throw.
0.641	23.92
1.221	6.67

The iron was demagnetized and the field built up in two steps:

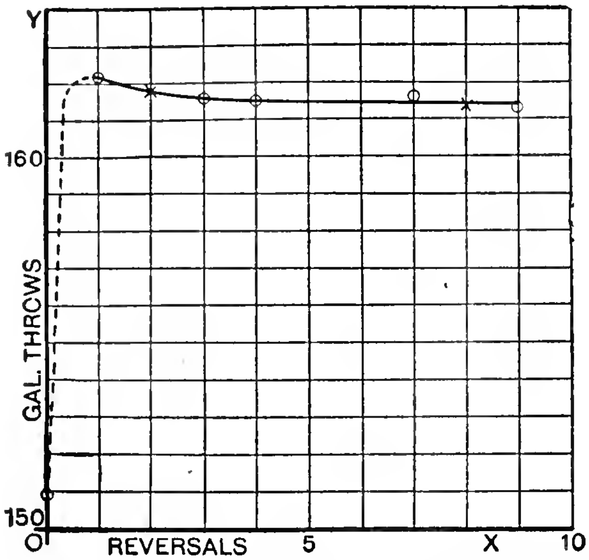

Figure 16. Set V: B 13,500: first magnetization; ○ indicates 1-step reversals; × 5-step reversals.

Amperemeter Reading.	Ballistic Throw.
0.641	13.94
1.221	6.65

Test of Galvanometer.

Amperemeter Reading.	Ballistic Throw.
13.77	21.46
13.77	21.44

The ballistic galvanometer showed a change of about seven parts in 2150 during the work. The average 1-step reversal calculated from the two 2-step reversals is 20.85. The current and so the field is slightly greater than for the 1-step reversals. However, it is doubtful if this would account for the difference between 20.76 and 20.85 with the flux B, at 13,000 as here. Probably the leakage due to the higher potential produced by the 1-step reversal and not taken into account for this core would make up the difference. At any rate one can be sure that for this particular core at this particular value of B the flux change due to two steps is not less than that due to one.

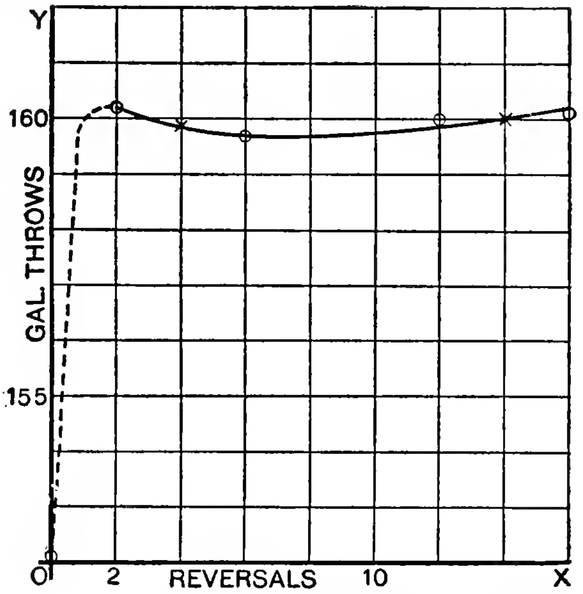

Figure 17. Set V: B 13,500: second magnetization; ○ indicates 1-step reversals; × 5-step reversals.

Second Set of Data.

The iron was demagnetized by the transformer.

Test of Ballistic Galvanometer.

Amperemeter Reading.	Ballistic Throw.
13.85	21.76
13.85	21.75

The iron was demagnetized by the transformer and the field built up in one step :

Amperemeter Reading.	Ballistic Throw.
1.218	20.81

A repetition of the process yielded the following :

Amperemeter Reading.	Ballistic Throw.
1.219	20.82

The iron was demagnetized by the transformer.

Test of Ballistic Galvanometer.

Amperemeter Reading.	Ballistic Throw.
13.78	21.54

The iron was demagnetized by the transformer and the field built up in two steps :

Amperemeter Reading.	Ballistic Throw.
0.640	13.94
1.220	6.64

The iron was demagnetized by the transformer and the field built up in two steps :

Amperemeter Reading.	Ballistic Throw.
0.640	13.96
1.219	6.58

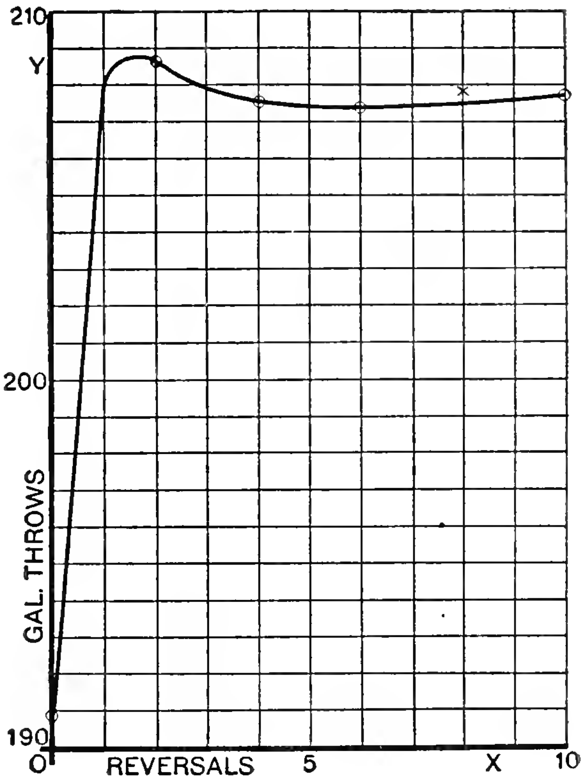

Figure 18. Set VI: B 19,300: first magnetization; ○ indicates 1-step reversals; × 5-step reversals.

The iron was demagnetized by the transformer.

Test of Ballistic Galvanometer.

Amperemeter Reading.	Ballistic Throw.
13.75	21.48

The iron was demagnetized by the transformer and the field built up in three steps :

Amperemeter Reading.	Ballistic Throw.
0.484	8.44
0.757	7.55
1.219	4.45

The iron was demagnetized by the transformer and the field built up in three steps:

Amperemeter Reading.	Ballistic Throw.
0.484	8.68
0.757	7.41
1.219	4.41

The galvanometer varied more than usual during the first two tests. If their average be taken to be used for the 1-step building-up intervening, the correction to be applied to 20.81 is about 0.05. That is, to make the 1-step building-up comparable to the 2-step and 3-step that follow there must be added 0.05 giving 20.86. The two 2-step processes give as the average calculated single deflection 20.81; the two 3-step processes 20.82. As before we have no data by which the leakage correction may be determined. However, the 2-step and 3-step processes to which it probably would not apply agree very closely. The 1-step process gives a flux change higher than the other two, but this may be due to the early variation of the galvanometer which would produce just that error in case the leakage correction were zero.

The maximum flux, B, was about 13,000.

Out of the many attempts made to obtain similar data for lower values of B, the two given above were the only ones of any value. As a sample of the results usually obtained I offer the following.

The iron was demagnetized by the transformer.

Test of Ballistic Galvanometer.

Amperemeter Reading.	Ballistic Throw.
14.26	22.22
14.26	22.21
14.25	22.17

The iron was demagnetized by the transformer and the field built up in one step:

Amperemeter Reading.	Ballistic Throw.
11.00	20.71

Four repetitions of the demagnetization and building-up of the current gave as four successive results those recorded.

Amperemeter Reading.	Ballistic Throw.
11.00	20.81
10.99	20.55
10.98	20.51
10.98	20.76

The galvanometer was not tested at the end of this set but on the next day it was found to be the same to within 0.1 of one per cent. The comparatively wide divergence between the flux changes in the iron as indicated by the instrument are far greater than any variation in it was ever found to be. When the 1-step process yields such heterogeneous results, it is not possible to draw any decided conclusions by comparing them with 2- or 3-step processes of magnetization. Taking an average in a case like this introduces an average error of 1½ per cent at the start. Consequently all such data were discarded.

One magnetization differs from the next only in the effects produced by the previous history of the iron. We may divide that into two parts : (1), the previous magnetizations, (2), the previous demagnetizations. If the variations were due to the former, we should expect at least that there would be a continuous change and not the jumps back and forth which were often more pronounced and numerous than those recorded above. In other words, a continuous rise or fall in the flux induced would not be unexpected ; but an alternation of the two, giving wavy curves no two of which can be superposed for the same maximum fields, leads one to suspect that some disturbing element enters which is more potent than the previous magnetization.

The demagnetization seems to be that element. Only by chance is it twice the same. In one instance it may consist of 500 reversals with a maximum field of 3, 260 with a maximum field of 2.8, 800 with a maximum field of 2.5, and so on ; in the next instance it may consist of 200 reversals with a maximum field of 3.1, 400 with a maximum field of 2.9, 350 with a maximum field of 2.6, and so on. The motion of the secondary, which could not be made continuous and of which the various small distances moved were by no means equal, would give just this sort of thing. To assume that such a variation in the process should not have its effect on the non-magnetic condition in which the iron is left is hardly safe. In fact, the results obtained when everything except this process is constant are so variable as to indicate in all probability that the cause of the variation lies here.

The trouble with this method led to one somewhat similar to that used on core I. The iron was demagnetized and then carried around a hysteresis cycle with a constant maximum field for any desired number of times. It was stopped at some point between the two maximum fields, brought to a zero inducing field by simply breaking the circuit, and carried on in the direction in which it was going originally to the peak of the hysteresis curve in one step. If the flux change is always the same when the one step is repeated, it is to be inferred that the one-step replacing a larger number does not have any appreciable effect on the fourth or fifth hysteresis cycle following, assuming that thāt is the number introduced between the two 1-step processes. If in continuing the work two steps be introduced in place of the one and they are in turn always the same, the same conclusion can be drawn in regard to their influence. If finally the flux changes produced by the 1-step and 2-step processes were identically equal, it is evident that, when the iron is retracing each time the same hysteresis curve, it makes no difference whether that part of the curve tested be passed over in two steps or one.

For a maximum flux of 13,000 the following data was obtained in the manner just described.

The iron was demagnetized.

TEST OF BALLISTIC GALVANOMETER.

Amperemeter Reading.	Ballistic Throw.
13.75	21.30
13.77	21.35

The iron was carried through 14.5 hysteresis cycles of forty-four steps each and back on the last half of the 15th until H was about 1.2. The field was then reduced to zero and the flux change observed on raising it to its full value in one step.

Amperemeter Reading.	Ballistic Throw.
1.220	21.89

The iron was carried through 4.5 cycles; the next half cycle was treated as above:

Amperemeter Reading.	Ballistic Throw.
1.222	21.98

The iron was carried through 4.5 cycles; the next half cycle was treated as above:

Amperemeter Reading.	Ballistic Throw.
1.223	21.92

The iron was carried through 4.5 cycles; the next half cycle was treated as above:

Amperemeter Reading.	Ballistic Throw.
1.224	21.96

The iron was carried through 4.5 cycles; the next half cycle was treated as above except that two steps replaced the one:

Amperemeter Reading.	Ballistic Throw.
0.760	17.92
1.223	3.92

After 4.5 more cycles the two steps were repeated in the next half cycle :

Amperemeter Reading.	Ballistic Throw.
0.642	15.82
1.223	5.98

After 4.5 cycles the two steps were repeated in the next half cycle :

Amperemeter Reading.	Ballistic Throw.
0.642	15.81
1.223	5.90

The iron was carried through 4.5 cycles ; the next half cycle was treated as at first — one step used :

Amperemeter Reading.	Ballistic Throw.
1.223	22.02

The iron was carried through 4.5 cycles ; the one step was used in the next half cycle :

Amperemeter Reading.	Ballistic Throw.
1.223	22.00

The iron was carried through 4.5 cycles ; the one step was used in the next half cycle :

Amperemeter Reading.	Ballistic Throw.
1.222	22.07

The iron was carried through 4.5 cycles ; the one step was used in the next half cycle :

Amperemeter Reading.	Ballistic Throw.
1.223	22.11

The average of all the 1-step processes except the first gives 22.01. The calculated 1-step reversal for the first 2-step process is 22.05, for the second 22.08, for the third 21.99. The average of these three is 22.04. This differs by three parts in 2200 from the average 1-step process. Since the average error for the latter is five parts in 2200 and for the former three parts in 2200, this difference is well within the error arising from other sources, and within ¼ per cent, it is safe to say that one step and two yield the same results. It will be observed that in the case of the two steps the dividing point was not the same for all three cases. What variation there was seems to have had no effect.

An 8-step reversal with a maximum B of 3100 was tried and compared with a 1-step reversal of the same field. The ratio of the former to the latter was as 914 to 922. By the use of a 10-step reversal and a maximum B of 8000, it was found that the 1-step reversal corresponding yielded a maximum B about 2 per cent smaller. Such an unexpected phenomenon led to the testing of the core, excited by a strong field, by means of iron filings spread on a sheet of paper directly above it. A slight consequent pole appeared at one spot. Lack of knowledge of the other factors entering into the work prevented any attempt to determine whether or not such a pole would affect the building up of the magnetic field. The core was immediately discarded.

In so far as they were consistent the results obtained from this core show that the number of steps taken in going from one magnetic condition to another is immaterial, provided the flux change be always in the same direction. The inconsistent results support my view that when a process of demagnetization intervenes between two processes of magnetization one is not at liberty to regard the first eight or ten hysteresis cycles that may be passed over in the first magnetization as necessarily equal to the corresponding hysteresis cycles of the succeeding magnetization. In fact, I should hesitate to compare any two sets of readings if I had demagnetized the specimen between the two.

If one were to take the trouble to go through exactly the same process in each demagnetization, that is, use exactly the same number of steps, reverse the field the same number of times, and see to it that the field maxima were always the same in both order and magnitude for the corresponding steps, it is presumable that in time one could get the iron into such a condition that consistent reversal-flux curves similar to those given for core I would be obtained. Then one would be justified in comparing the flux change produced by any given reversal with the corresponding flux change produced after the next demagnetization. Such a procedure would be extremely laborious. However, it is not inconceivable that certain parts of the demagnetization have a greater effect than others on the final non-magnetic condition and that attention to those alone would be sufficient to assure consistent results. There is an opportunity here for further research.

The Investigation of Toroid III.

The amount of iron in toroids I and II and as a consequence the time required for the building up of the current are, even for low voltages, comparatively small. Toroid III, on the other hand, supplies conditions more nearly comparable to the large, solid magnetic circuit used at first. With an applied voltage just sufficient to produce a medium flux density in the iron, approximately two seconds would elapse before the amperemeter in the primary circuit, Figure 3, would come to rest. To make sure that no small effects were masked by the size of I and II, III was tested in the same manner.

The circuit, Figure 3, remained unchanged in every respect save one, the ballistic galvanometer. The slow flux change in III required the use of an instrument having a much longer period. Recourse was had to one of the types used by Professor Peirce[16]; the new galvanometer constructed differed from the old in that the balls supported by the projecting rods were replaced by an aluminium disk weighted at the circumference by a brass ring, Figure 19 (Plate). The period of this heavy system was approximately five minutes; and the error introduced when the flux change was continuous and uniform for 20 seconds, 0.7 of one per cent; that is, the observed throw would be 0.993 times the true throw.

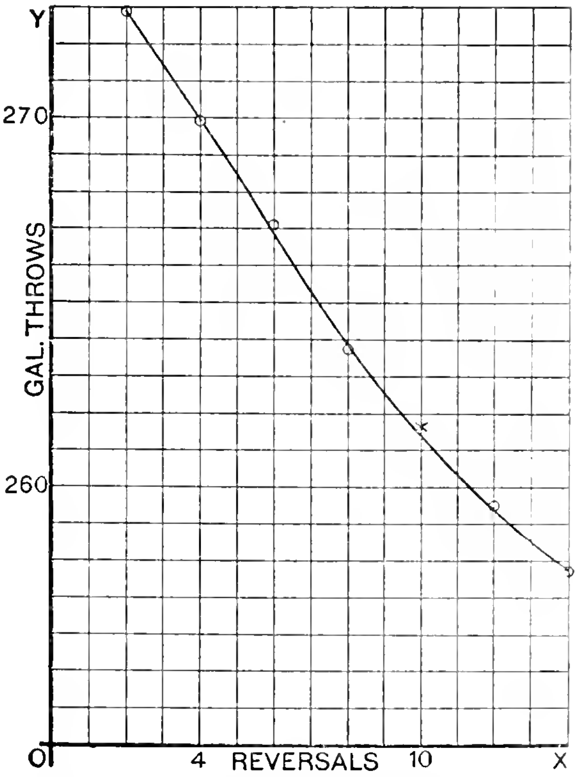

Figure 19. The value of B is 3000: the × indicates 24-step reversals, the ○ 1-step reversals.

The same care in manipulation that applied to the earlier instrument was necessary here. In fact the task of bringing the suspended

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[16] These Proceedings, **44** (1909).

system absolutely to rest was no small one and yet extremely important for accurate measurements.

The data for three curves was obtained with the maximum flux densities respectively of 800, 7650 and 14,000 per square centimeter. Since the method was almost exactly similar to that employed in the case of toriods I and II, it seems worth while to note only the difference. This lay in the demagnetization; for toroid III it was carried out wholly by the reversing switch, N (Figure 3), and the rheostat or resistance cells, R and RG.

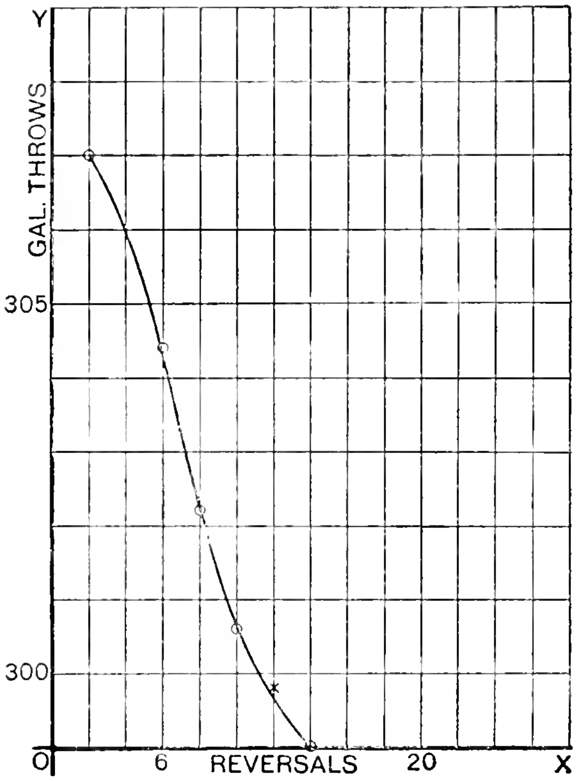

Figure 20. The value of B is 7650: the × indicates 22-step reversals, the ○ 1-step reversals.

The accuracy with which the long-period galvanometer could be handled was fully as great as that of the shorter. The only error introduced lay in the 0.7 of one per cent; and this was eliminated to a considerable extent. For while about 0.7 of one per cent of the throw would be lost when 1-step reversal was taken, a corresponding loss occurred in the reversals consisting of a larger number of steps, for the same field reversed. It was found that a large proportion of these small steps required about 20 seconds for their completion; as a consequence their sum would be less than the true sum. From observations as to the time in the two instances and the size of the throws I should regard it as very probable that at least half the error was cancelled by this introduction of the same inaccuracy in the two cases compared.

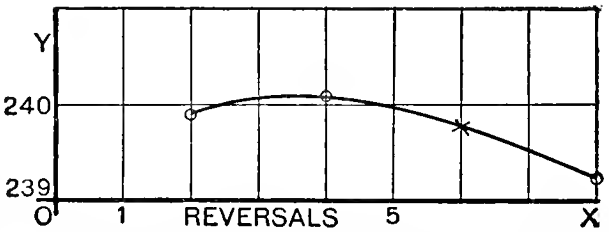

Figure 21. The value of B is 14,000: the × indicates 28-step reversals, the ○ 1-step reversals.

The three curves, Figures 19, 20 and 21, show the results of the investigation.

Evidently the 24-, 22- and 28-step reversals fall very nearly on the corresponding 1-step curves and are for all practical purposes equal in their flux change to the 1-step reversals.

Some of the peculiarities that appeared in the early curves of toroids I and II do not appear in these curves so prominently. However, III has been magnetized a large number of times in previous investigations and could not be expected to yield other than the results actually obtained.

SUMMARY.

The uniformity of the results for all three toroids leads to the conclusion that, in the early stages of its magnetic history, the condition of the iron is constantly changing. During this stage of transition no given condition can be repeated by any of the ordinary methods of demagnetization and remagnetization; but as the mass is subjected again and again to the magnetizing process it attains more and more nearly to a condition such that, for all practical purposes, any magnetic state may be repeated as often as desired.

The process of demagnetization affects, by the manner in which it is carried out, the first few hysteresis curves that follow. This effect, in so far as the present investigation determined its extent, consists in a change in the maximum induction attained when the maximum field for the particular curve in question is applied.

The various stages through which the iron passes during its early magnetic history are the more numerous for the low flux densities and disappear almost completely as the point of saturation is approached. It is possible that, if one started with a high flux density and came down to the lower, another set of phenomena might appear.

The work on the large solid magnet showed conclusively that the form of the hysteresis curve depended upon the number of steps employed. The corresponding experimentation on finely divided masses, both large and small, indicated that the hysteresis cycle was not affected by the number of steps. Such was found to be the case in three distinct specimens of iron; for wherever the curves could be exactly determined, the points derived from the two methods of procedure, one by a small number, and the other by a large number of steps, fell, within 0.1 of one per cent, on a smooth curve. An obvious reconciliation of the two results lies in regarding the eddy currents, and not any inherent property of the iron, as responsible for the observed variations in the hysteresis curve. In other words, whatever variation exists due to a special property of the iron seems to amount to less than 0.001 of the total flux change.

In general, therefore, any method of obtaining an hysteresis curve of finely laminated iron will permit one to forecast its future action. It is assumed, of course, that we have carried it past the transitional stage. On the other hand, for solid masses of iron that method should be employed which corresponds as nearly as possible to the future working conditions.

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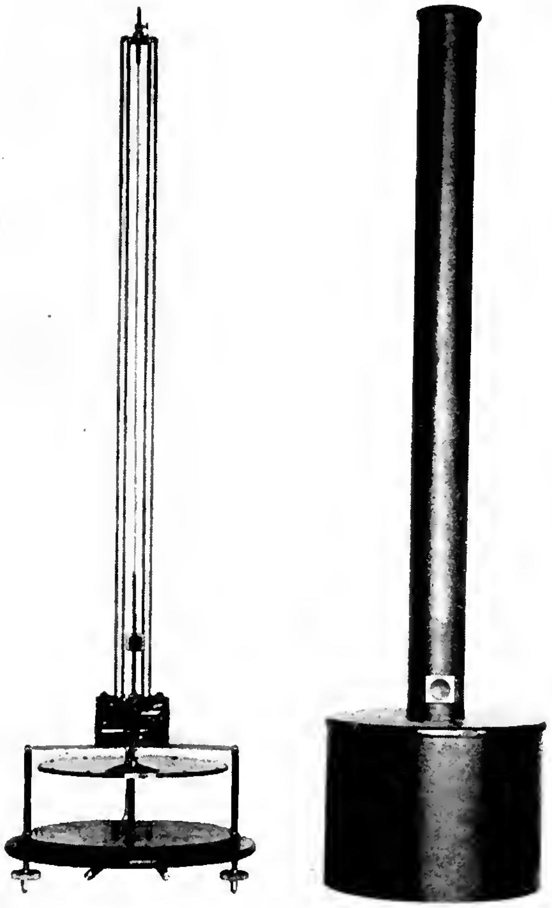

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 9. — November, 1911.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

A NEW METHOD OF IMPACT EXCITATION OF UNDAMPED OSCILLATIONS AND THEIR ANALYSIS BY MEANS OF BRAUN TUBE OSCILLOGRAPHS.

By E. Leon Chaffee.

With Seven Plates.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

A NEW METHOD OF IMPACT EXCITATION OF UNDAMPED ELECTRIC OSCILLATIONS AND THEIR ANALYSIS BY MEANS OF BRAUN TUBE OSCILLOGRAPHS.

By E. Leon Chaffee.

Presented by G. W. Pierce. Received July 11, 1911.

Introduction.

Electrical oscillations are at present of interest chiefly on account of their practical applications to radio-telegraphy and radio-telephony. The production and study of very rapid oscillations is also of intense theoretical interest, and the applications of oscillations in high frequency measurements and in research are of no small importance.

Previous to the last few years practically the only method of producing oscillations was by means of the disruptive discharge of a condenser across a comparatively long spark gap between metallic terminals in air. Under such conditions a train of damped oscillations is produced at each spark. The duration of these trains is very short in comparison with the interval of time between them. It is evident that such an intermittent and impulsive system is ill adapted to accurate electrical measurements; and for use in wireless telegraphy the system is noisy, inefficient, besides which the necessity of using high potentials increases the danger and the difficulty of insulation. For wireless telephony, where a regular and continuous radiation of power is necessary, the long spark method is absolutely useless.

In the last few years there have come into extensive use the short gap or quenched spark method, and the arc methods of producing electrical oscillations. These methods make use of the characteristics of very short spark gaps between large parallel metal surfaces, or the peculiar characteristics of certain forms of arcs. The advantages of these methods of generating oscillations lie in their greater efficiency, the absence of noise, the much greater regularity and continuity of the resulting oscillations, and the use of low potentials. The trains of oscillations either follow each other very closely or, as with the arc method, the oscillations are continuous with no intervals of inactivity.

For the purpose of this article it will be sufficient simply to mention and to classify the short gap and arc methods according to the characteristics of the resulting oscillations, and to designate the types by the names of their observers or discoverers. There are three such types, namely: the Duddell or singing arc oscillations; the Poulsen oscillations; and the Wien oscillations, or the so-called "Stosserregung."

The Duddell[1] oscillations are produced when a direct-current carbon arc in air is shunted by an oscillatory circuit. This method of producing oscillations is characterized by the fact that the arc always remains lighted, that is, the condenser current is at every instant less than the supply or main current. These oscillations are of small energy and limited in frequency to about 10,000 per second which fact renders them impracticable for radio-telegraphy.

The Poulsen[2] oscillations are produced by the Poulsen arc, which is essentially a Duddell arc between a water-cooled copper anode and a carbon cathode; this arc takes place in a magnetic field and in an atmosphere of some hydro-carbon gas. In this case the arc is extinguished at each oscillation, the condenser current at some instants being greater than the supply current. The Poulsen oscillations are much more intense than the Duddell type, and much higher frequencies can be attained; the energy, however, grows rapidly less as the frequency is increased. Frequencies of a million or more can be obtained but with small energy. Although the Poulsen oscillations are used in wireless signaling they have some disadvantages, such as low efficiency, and the characteristic change of wave length with changing arc length and arc current.

Under the head of Wien[3] oscillations fall those produced by the Lepel[4] arc, the Peukert[5] arc, etc. The generators for oscillations of this class consist of two or more very short gaps between large metallic surfaces separated by paper, or by a thin film of oil, and so mounted as to exclude the air. The gaps are connected in series and shunted by an oscillatory circuit similar to the arrangement for the other forms of

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[1] W. Duddell, Journ. Inst. Elect. Eng., **30**, 232 (1900).

[2] V. Poulsen, British Patent Specifications, 15,599 of 1903.

[3] Max Wien, Physik. Zeitsch., **11**, 76, Feb. 1, 1910.

[4] Lepel, Electrician (London), **63**, pp. 142, 157, 174, 345, 376 (1909); **64**, pp. 153, 386 (1909–10); G. W. Nasmyth, Phys. Rev., **32**, No. 1, 103 (1911).

[5] Peukert arc, Electrician (London), **64**, 361, 550.

generators. Loosely coupled to this primary circuit is a secondary circuit in which are induced the Wien oscillations. At each breaking-down of the gap a highly damped train of oscillations ensues, which produces in the secondary circuit the two ordinary coupling waves. During the interval between the ending of one primary train and the beginning of the next the secondary circuit oscillates in its own free period. Thus there are produced oscillations of three periods, the latter being of the most importance.

All of the above mentioned methods for producing oscillations were tried without success by the author in an attempt to obtain oscillations of a frequency of more than 10^7 vibrations per second, and of sufficient regularity, continuity, and intensity for use in another investigation. After the failure of the then known methods, further experimentation produced the new oscillation gap and method which are to be studied in the following contribution. The method in some particulars closely resembles the Poulsen method, but in electrical action the system is quite different from any included in the three classes mentioned above.

The oscillations of this new system do not fall in any of the three classes of oscillations mentioned, but are, as will appear later, intermediate between the Poulsen and Wien types. The oscillations produced are unlike the Poulsen oscillations in that their period is but very slightly affected by changes of supply current and not at all by changes of arc length, and they are sinusoidal in wave form. The oscillations are different from the Wien type in being continuous, and having but one period, which is practically the free period of the circuit in which the oscillations are induced.

It is shown in the following article that this new system produces oscillations superior to the other systems in regularity, which, with its simplicity, commends its use in the laboratory and in practice. It is the only method known by the author for producing intense continuous oscillations at extremely high frequencies. The author has obtained continuous and practically undamped oscillations of several amperes at 20 meters wave length, which corresponds to a frequency of 1.5×10^7 oscillations per second.

The following article is presented in three parts. In Part I it is proposed to give the general characteristics of the oscillation gap. In Part II the oscillations are studied more in detail by means of Braun tube oscillographs, and Part III contains a few practical considerations and applications of the oscillations.

Part I.

The General Characteristics of the Oscillation Gap.

(1) *Description of Apparatus.*

The gap consists essentially of an aluminum cathode and an anode of some other metal such as copper or silver, both water or air cooled and surrounded by an atmosphere of moist hydrogen. The active surfaces of the terminals are accurately parallel planes of one or two square centimeters area, and adjustable as to distance separating them, which, for the best results, is about .07 mm. Large terminals are undesirable on account of the increased electrostatic capacity of the gap, which must be small in comparison with the main capacity of the circuit.

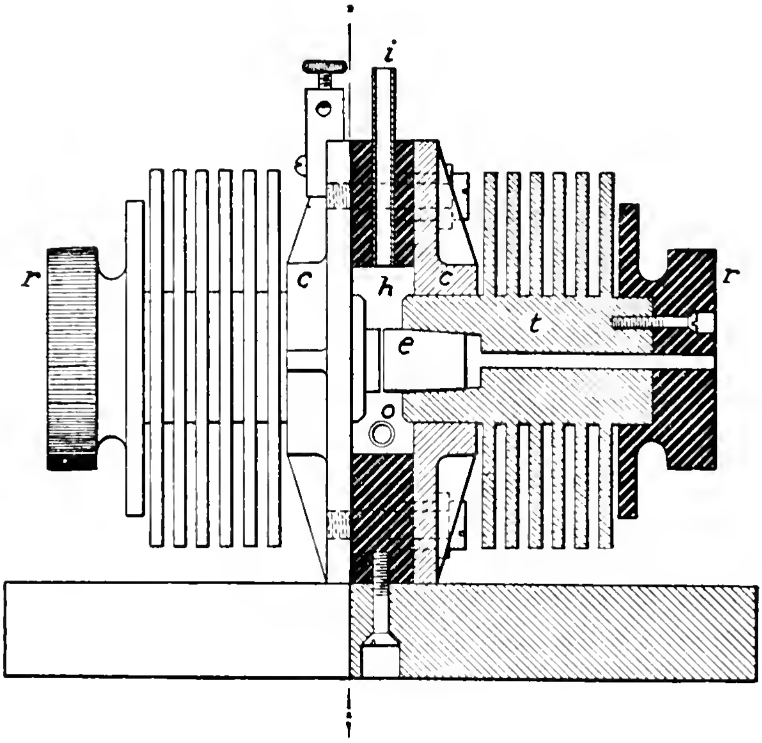

Figure 1. Air-cooled *Cu-Al* Discharge Gap. ½ natural size.

For the cathode, aluminum is the only metal which gives at all satisfactory results, and the gap should be constructed so that the terminals can be occasionally renewed. After the gap has been in operation for some time the aluminum becomes pitted and covered with a very hard oxide which is difficult to remove. One electrode was operated, however, for over one hundred hours with fairly satisfactory results at the expiration of that time.

Several metals work well as anode, the latter apparently playing very little part in the action of the gap. It appears, however, that the denser metals of high cathode drop, such as copper and silver, are desirable. The anode, with occasional cleaning, will serve indefinitely.

Although the amount of heat produced in the gap is small, some method of cooling the terminals is necessary. Air cooling by means of radiating vanes is to be preferred on account of convenience and simplicity. Figure 1 gives the details of an air-cooled gap, the right-hand half in section. At *e* there is shown the *Al* electrode which is held by a taper-fit in the massive terminal *t*. Opposed to this *Al* electrode is a similarly shaped copper electrode held by taper-fit in a similar massive terminal. These terminals are threaded and engage in the side castings *c c*, and are provided with blackened metallic radiating vanes as shown. The side castings are separated by a thin slab of hard rubber or asbestos board, which has a central circular hole to serve for the gap chamber *h*. Rubber handles *r r* are for use in adjustment. The inlet and outlet for the hydrogen are shown at *i* and *o*. The drawing is one half size.

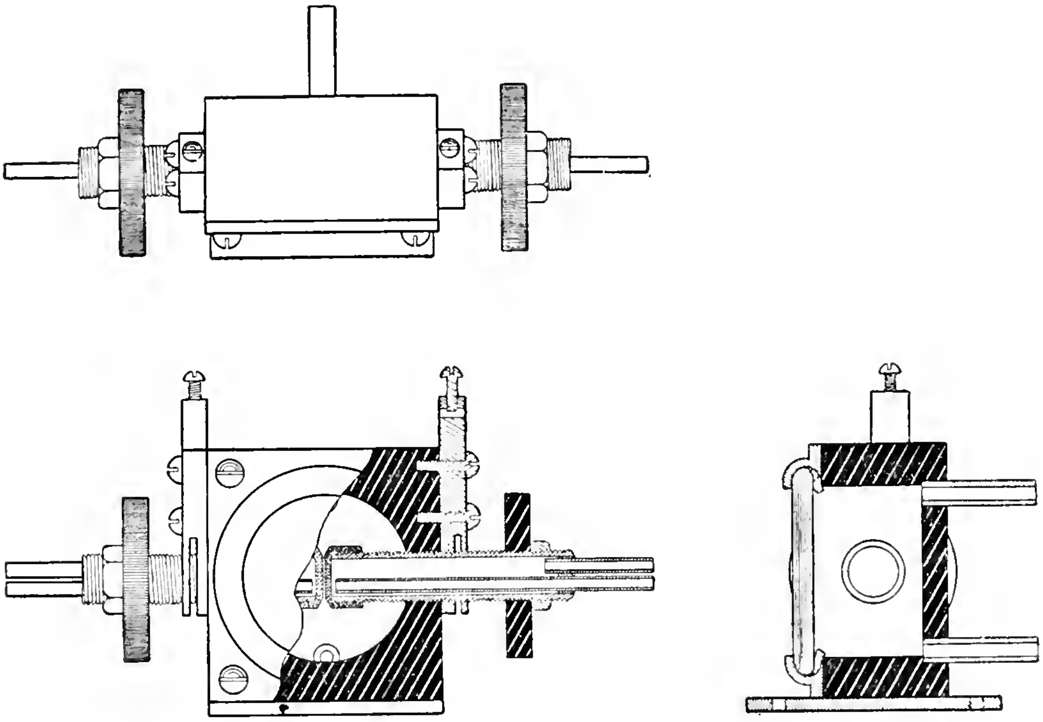

Figure 2. Details of Water-cooled *Cu-Al* Gap. $\frac{2}{5}$ natural size.

A water-cooled gap as shown in Figure 2 was, however, used throughout this investigation. By reference to the drawing this gap is seen to consist of two hollow threaded electrodes capped with aluminum and copper, respectively, and each provided at the outside end with an inlet and outlet tube for the passage of the cooling water. The terminals are enclosed in a hard rubber casing provided with a circular glass front. Hard rubber disks attached to the electrodes serve for adjusting handles. The figure is a reduction in the ratio of 5 to 2.

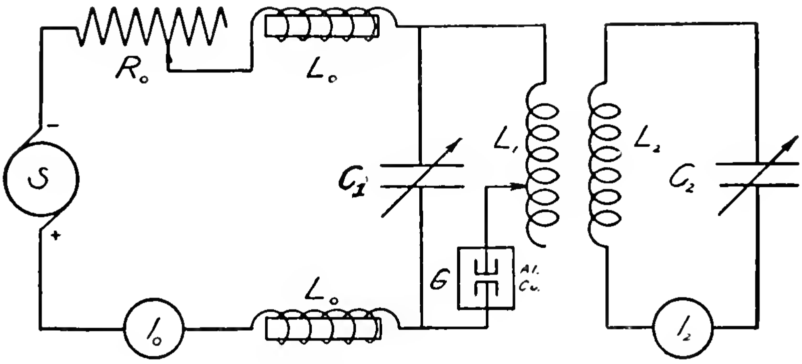

FIGURE 3. Diagram of Connections.

The general diagram of connections is shown in Figure 3. S is a source of direct current of a few hundred volts, and, in what follows, 530 is to be assumed unless otherwise stated. I_0 is a D. C. ammeter which measures the current in the supply circuit. This circuit also contains the two inductances or choke coils L_0 L_0, and a variable resistance R_0, capable of reducing the current to about 0.2 ampere. In the following experiments L_0 L_0 are ordinary A. C. arc-light inductances, and R_0 is a resistance, adjustable in one half ampere steps, in series with a variable copper-sulphate electrolytic resistance. C_1 and C_2 are variable air condensers, G the gap, L_1 and L_2 the variable primary and secondary of the closely-coupled oscillation transformer, and I_2 a hot-wire ammeter.

(2) *Operation of Gap.*

The system will start automatically if the distance between the terminals is not much greater than 0.1 mm. In appearance the discharge resembles a very minute arc, of an intense reddish-purple color, absolutely quiet and stationary. The discharge remains at one point on the electrodes for several minutes until the aluminum is slightly pitted, when it suddenly shifts to another point. When the discharge is examined by means of a spectroscope only the primary hydrogen spectrum appears with an occasional weak flashing-up of a few of the aluminum lines. Plate **1** *b* gives the discharge spectrum with an aluminum comparison spectrum. The nature of the discharge will be considered more in detail in Part II, but it is evident from the figure that the metals are not vaporized, and the indications are that the conduction is entirely by gaseous ionization.

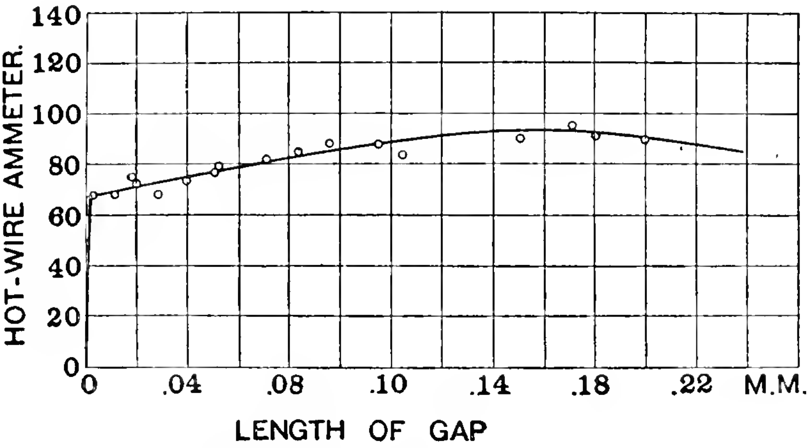

FIGURE 4. Effect of Changing Length of Gap.

I_0 = .335 ampere.
λ_2 = 106 meters.
$C_1 = 112 \times 10^{-5}$ μ.f.
$C_2 = 60 \times 10^{-5}$ μ.f.

When the secondary oscillations are examined by means of a wave meter, but one wave with exceedingly sharp tuning is observed. On account of the steadiness of the oscilliations it is often difficult to set the wave meter — which makes use of a telephone receiver as the detecting device — without the use of a chopper or interrupter in the wave meter circuit.

The change in wave length of the secondary oscillations with changing supply current is very much less than is observed with the Poulsen and Lepel generators. This point is, however, more profitably considered later, after a better understanding of the action of the gap has been gained.

In order to show the effect on the intensity of the secondary oscillations of varying the length of the gap, the curve shown in Figure 4 was taken. It is seen that the intensity of the secondary current, as measured by the hot-wire ammeter, does, to some extent, depend upon the length of the gap, but not to the extent that might be expected. At 0.19 mm. the secondary current is a maximum, but at about this length of the gap the discharge begins to hiss and become unsteady. For other values of the main current, I_o, the curve would be slightly different, but, in general, the best results are obtained with a gap length of from .04 to .09 mm.

The effect of changing the pressure of the hydrogen was investigated. Apparently atmospheric pressure gives the most satisfactory results, although, for decreased pressure, the oscillations are possibly slightly more intense until the pressure of about 10 or 20 cm. is reached, when they rapidly become weaker. Increased pressure is decidedly detrimental.

Before entering upon an explanation of the curves and results it is essential that a comprehensive idea of the operation of the system be had. To this end the following brief review of the events during one cycle is introduced, the details of which will be considered more at length later. It is clearest, in tracing the sequence of phenomena, to begin at the instant after the system has been started, when the potential of the primary condenser C_1 (Figure 3) has attained a value sufficient to break down the high resistance of the gap. The gap resistance rapidly falls to a very low value as the discharge of condenser C_1 and the main current I_o, which was previously flowing into C_1 and which remains practically constant on account of the inductances L_o L_o, rush across the gap and through the primary coil L_1. This current rush takes place according to a definite positive loop of current with respect to time, the shape, amplitude, and duration of which depend upon the constants of the circuit, the rapidity of absorption of energy by the secondary circuit, and, to a slight extent, upon the conditions of the gap and strength of the main current I_o. The condenser C_1 is discharged and charged somewhat in the opposite direction by this positive current rush. If conditions are right the discharge stops as soon as I_1 becomes zero, there being no inverse current. The secondary receives a certain increment of energy from this discharge, and continues to oscillate after the primary discharge stops.

This absence of inverse current above referred to is due to the combination of three conditions. First, and most important, is the practically instantaneous re-establishment of the high initial gap resistance when the current becomes zero, due probably to the formation of an insulating oxide film on the aluminum; second, the higher cathode drop of the anode metal; third, the absorption of energy by the secondary, although rectification usually takes place without this aid.

At the end of the above mentioned current-rush the current through the gap is zero and the condenser C_1 has an inverse charge. Since the main current must remain constant it is now flowing into C_1, it having been gradually shifted over to C_1 as I_1 decreased toward zero. The main current I_0 flows into C_1 at a practically constant rate, neutralizing the inverse charge and charging it in the initial direction. The potential difference of C_1 increases uniformly, attaining a much higher value than exists outside the choke coils.

Impressed across the gap is the potential difference of the condenser C_1 plus the ripples induced in the primary circuit by the secondary current, these potential ripples serving as a trigger to start the primary discharge on a second cycle in the proper phase relation with the secondary oscillation.

It is evident from the above consideration that, on account of the inductances L_0 L_0, the condenser C_1 can attain a much higher difference of potential than that of the source, the magnitude of this condenser potential being determined by the breaking-down potential of the gap. It is also clear that, if this breaking-down potential be assumed approximately constant, the number of discharges of C_1 per second depends upon the main current I_0.

The duration of each primary discharge does not, as has been stated, depend upon the supply current, so that it is only the duration of the interval between primary discharges which changes with varying main current. The secondary continues to oscillate during these intervals with decreasing amplitude according to the damping of the secondary circuit. In what follows the number of secondary oscillations to one primary discharge and charge is spoken of as the "inverse charge frequency referred to the secondary oscillation" or simply I. C. F.

From what has been said it is clear that the secondary receives periodic impulses from the primary, the frequency of these impulses depending upon the main current and the capacity of the primary condenser. During the intervals of non-activity of the primary circuit the secondary circuit oscillates in its own free period and with damping determined solely by the conditions of the secondary circuit, such as resistance and radiation. The secondary oscillation cannot, then, strictly be called undamped. The amplitude of the oscillation can, however, be maintained practically constant by making the primary impulses occur every two or three secondary oscillations, and, if the damping in the secondary circuit be small, the resulting oscillations are then almost perfectly undamped and continuous.

In order that the maximum energy be transferred to the secondary circuit there are two conditions of syntony, as they may be termed, to be fulfilled. In the first place the primary discharges must always occur in the proper phase relation with the secondary oscillation, or, in other words, the I. C. F. must be a whole number. This is, as has been pointed out, more or less automatically regulated by the reaction of the secondary oscillation on the primary circuit, but not entirely so for low values of I. C. F. The second condition of syntony is that the *shape* of the primary wave or current-rush must be such that the resulting electromotive force impulses in the secondary circuit, due to the different parts of the primary wave, bear the proper phase relation to the secondary wave. With a fixed secondary circuit the first condition can be obtained by varying the main current I_o, or the primary capacity C_1. The second condition of syntony can be established by changing the primary inductance L_1.

(3) *Observations and Discussion of Results.*

The two conditions of syntony are illustrated by the curves of Figures 5 and 6. In Figure 5 the full line curve gives the variations of the secondary current, I_2, plotted to an arbitrary scale, as the main current, I_o, is varied, and shows maxima and minima of I_2 as the first condition of syntony is more or less perfectly fulfilled. The dotted disconnected lines give the maximum wave length readings of the wave meter, excited by the primary discharge, as ordinates plotted to the variable I_o. The third dot-and-dash curve is the wave meter reading when the secondary circuit is open. This figure is a fair representation of several curves taken under different but similar conditions.

In explanation of Figure 5 attention is called to the following facts. It is evident that if the potential to which the condenser is charged is practically the same under all conditions, — and experiment shows that this is approximately the case,— then with a given C_1, the number of discharges per second in the primary circuit is roughly proportional to the current I_o. This actual spark frequency produces in the wave meter an effect corresponding to a wave of that frequency. This primary fundamental wave length, as it will be called, plotted to I_o would give a curve of the general shape given by the dot-and-dash line in the figure. When, however, the secondary circuit is closed the secondary current exerts an equilibrating influence on the primary discharge, helping it to occur, as has been stated, at a definite time in relation to the secondary current, thereby forcing the primary circuit to operate according to the short horizontal lines. For instance, by reference to the figure it is seen that, for a supply current of 0.7 ampere, the unforced primary fundamental wave length is 350 meters. The frequency corresponding to this is about 860,000 per second, which means that there are that number of primary discharges occurring per second. When, however, the secondary circuit, having a natural wave length

$\lambda_2 = 95$ metres, is closed, conditions are different on account of the absorption of energy by the secondary circuit, and the primary discharges at a rate corresponding to a wave length of about 280 meters. This is about three times λ_2, showing that the I. C. F. is 3. As the supply current is decreased the primary is forced by the secondary to discharge at this rate until the current has become so small that the slower rates corresponding to I. C. F.'s of 4 or 5 are more stable. When conditions are least forced for these values of I. C. F. a maximum of secondary current is observed as shown at $I_0 = 0.46$ in the figure. It is seen that for the steep part of the dot-and-dash curve the I. C. F. jumps between several successive values. It is also now easy to understand that the maxima of secondary current naturally occur at values of I_0 where the I. C. F. is less forced.

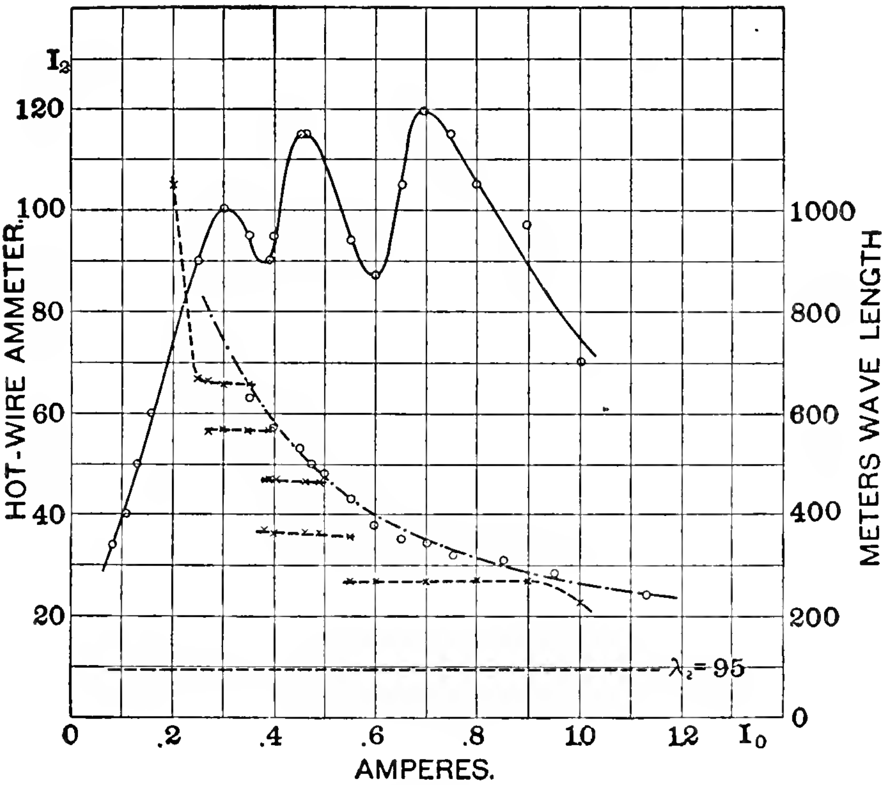

FIGURE 5. Illustration of Syntony to Charge Frequency.

$\lambda_2 = 95$ meters.
$C_1 = 80 \times 10^{-5}$ $\mu.f.$
$C_2 = 60 \times 10^{-5}$ $\mu.f.$

The second condition of syntony, namely, the syntony of wave form, is represented in Figure 6. In this case the hot-wire ammeter reading was taken in the secondary circuit as an inductance, in series with the primary of the oscillation transformer, was varied, the abscissa scale being in turns of the coil. The disconnected curve, marked λ_1, represents the primary fundamental wave length plotted to turns of inductance. The curve of secondary current shows the marked maximum when, the I. C. F. remaining constant, the primary discharge loop has the best duration compared to the period of the secondary oscillation. The forcing by the secondary oscillation of the primary to discharge at the frequency corresponding to a wave length of 138 meters is well shown by the λ_1 curve.

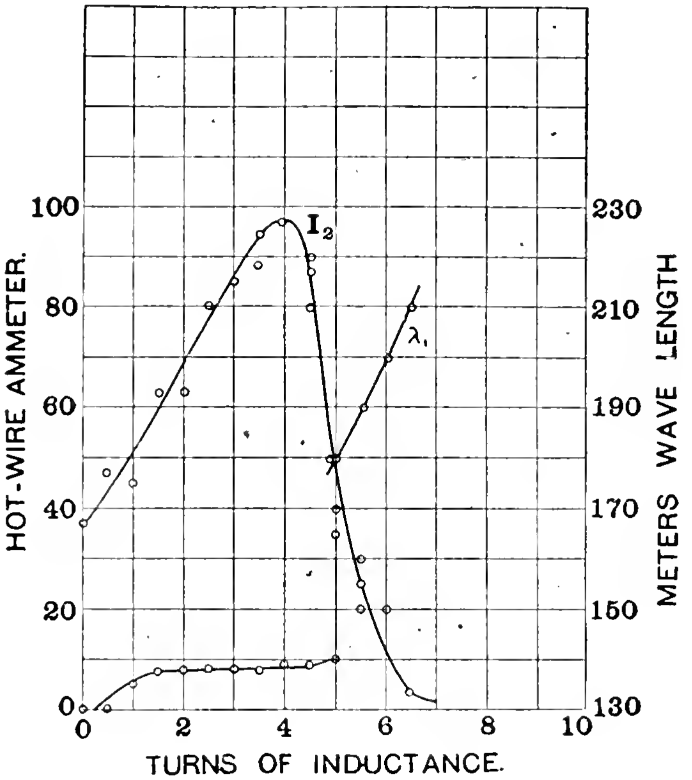

FIGURE 6. Curve showing Syntony to Wave Form.

λ_2 = 86 meters.
Io = .75 ampere.
$C_1 = 60 \times 10^{-5}$ $\mu.f.$
$C_2 = 40 \times 10^{-5}$ $\mu.f.$

A very interesting and useful chart, in showing the way in which the variables change, is shown in Figure 7. This diagram was taken for

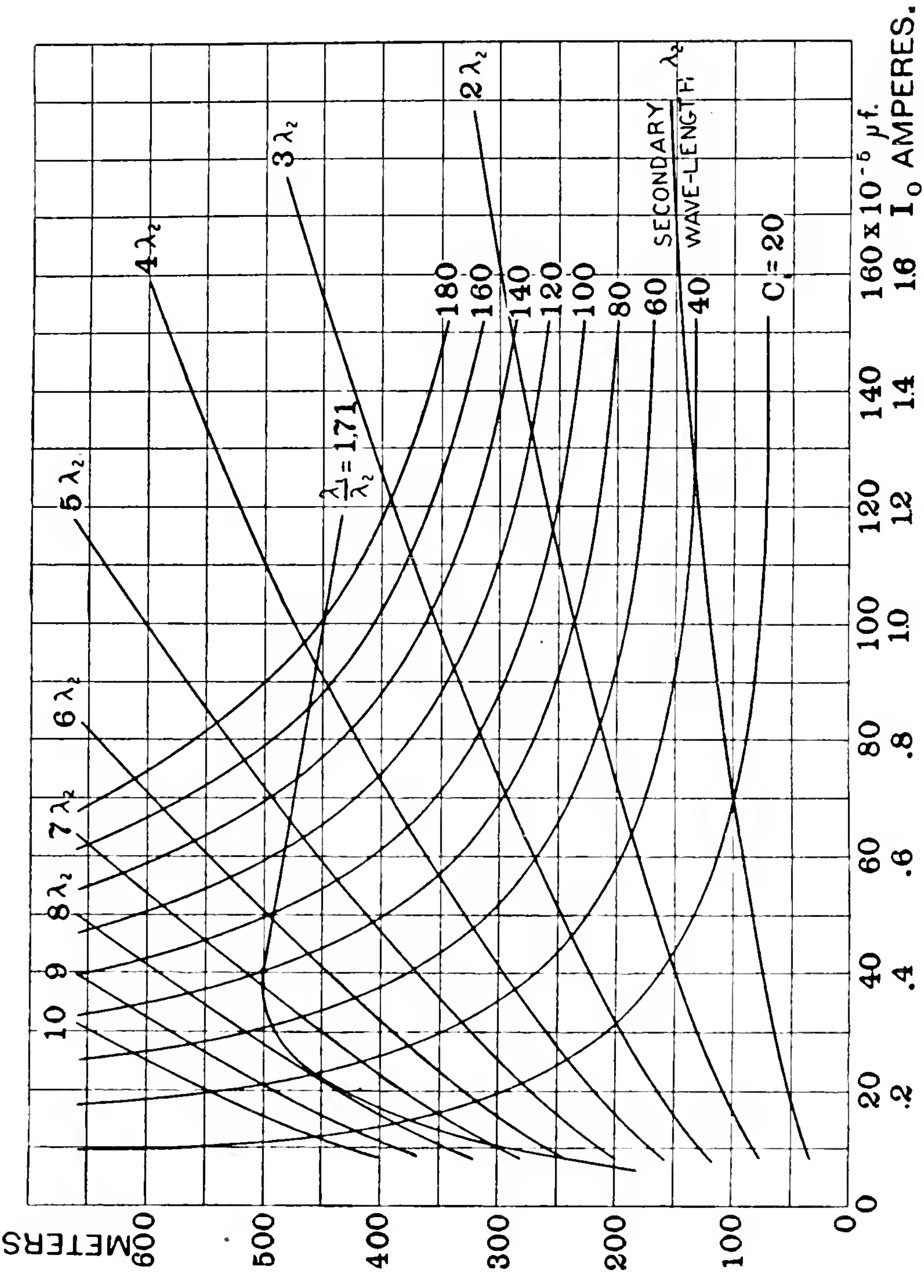

Figure 7. Experimental Chart.

particular values of L_1, L_2 and the coefficient of coupling of the two circuits, and is not general so far as the scales are concerned. The shape of the curves is general, however, and, it is hoped, may prove explanatory of the relations of the many variables.

The curves resembling hyperbolas are each for a constant primary capacity plotted with main current, I_o, as abscissae, and fundamental wave length of the primary discharge frequency as ordinates. The lower curve, marked "secondary wave length," gives the capacity of the secondary circuit as abscissae and the resulting syntonic secondary wave length as ordinates. The other similar curves are got by multiplying the ordinates of the last-mentioned curve by 2, 3, 4, etc. The remaining curve marked $\frac{\lambda_1}{\lambda_2} = 1.71$, needs a word of explanation. Several measurements were taken of the natural period of the primary circuit when adjusted to give maximum secondary current, for different secondary wave lengths, and it was found that this natural primary period divided by the corresponding secondary period was, in every case, within one or two per cent of the quantity 1.71. This would be slightly different for different coefficients of coupling. The curve in question is the locus of the intersections of the vertical C_2 lines and the C_1 curves which fulfill this condition.

The use of the diagram of Figure 7 may be made clearer by the following. Suppose that the secondary wave length desired is 75 meters. The secondary wave length curve gives $40 \times 10^{-5}\,\mu.f.$ as the secondary capacity, and passing vertically up to the $\frac{\lambda_1}{\lambda_2}$ curve, it is seen that the primary capacity must be $80 \times 10^{-5}\,\mu.f.$ If, now, the vertical $C_2 = 40$ line be followed to the intersection of the $3\lambda_2$ curve, and then horizontally to the same $C_1 = 80$ curve, and down to the current axis, one gets the current $I_o = 1.1$. This current gives the discharge frequency, with $C_2 = 80$, corresponding to a wave length of 225 meters, which is three times the secondary wave length, and therefore shows that, with that I_o, the primary condenser is discharging every third secondary oscillation. In other words, the I. C. F. is 3. Similarly it is seen that for an I. C. F. of 4 the main current must be 0.69 amperes; for I. C. F. equal to 5, I_o must be 0.54 amperes, etc.

Among other things the diagram shows that in general the supply currents which give the large values of I. C. F. differ but slightly, which is an advantage for some purposes. It is readily seen that small values of I. C. F. are impossible to obtain unless the wave length is short and the supply current very large.

The coupling between the primary and secondary circuits should be very close. In order to attain this the primary and secondary coils were wound parallel on the same frame so that they interlocked. The diameter of the coils is about 5 inches, and from one to seven or eight turns were used. Direct coupling is almost as satisfactory as magnetic coupling, but for regularity and freedom from harmonics the latter is to be preferred, and was used throughout this experiment. The closeness of the coupling, or, what is of more importance, the mutual inductance between the primary and secondary circuits, should, for the best results, be adjusted according to the amount of power delivered by the secondary circuit. The connection between the mutual inductance and the conditions in the secondary circuit is shown by the curves of Figures 8, 9 and 10.

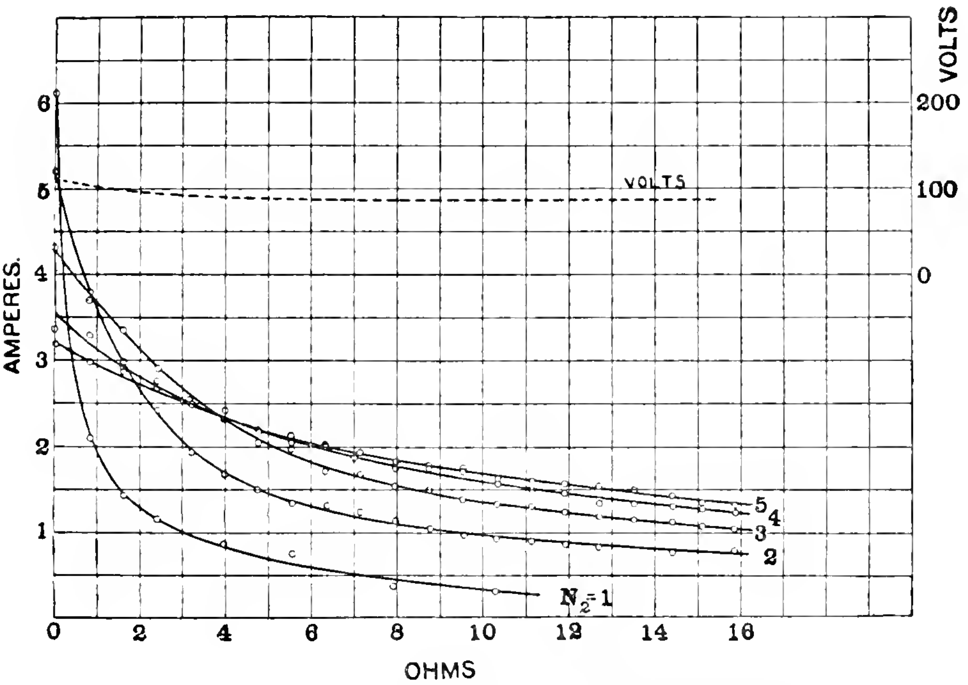

FIGURE 8. Current Curves, with Changing Resistance.

λ = 100 meters.
I_0 = .55 ampere.
$C_1 = 175 \times 10^{-5}$ μ.f.
$C_2 = 86 \times 10^{-5}$ μ.f.

In taking the curves of Figure 8, the primary supply current, the primary capacity, and the secondary wave length were kept the same in order to maintain constant the two syntony conditions, while a resistance in the secondary circuit was varied for different numbers of turns on the secondary helix. The primary capacity was 175×10^{-5} μ.f.;

the supply current was 0.55 ampere, and there were four turns on the primary helix. The secondary wave length was 100 meters and the curves 1–5 give the values of I_2 in amperes for the designated number of turns on the secondary coil, as the resistance in the secondary circuit was varied from 0 to 16 ohms. On the same diagram appears the voltage across the gap for the several conditions.

These, and some of the curves shortly to be considered, are plotted for, or in terms of, turns of secondary helix, the primary helix remaining unchanged. With the apparatus used the mutual inductance between the two circuits is not exactly proportional to the number of secondary turns on account of a slight variation in the position of the coils, but nearly enough so, so that the number of secondary turns can be considered as proportional to the mutual inductance between the primary and secondary circuits.

The resistance used in the secondary circuit was an oil-cooled manganin wire resistance, wound non-inductively, and with a wire of such a diameter that the high frequency resistance is considered to be practically the same as the ordinary resistance.

It is clear, on examination of the current curves of Figure 8, that if a large current in a circuit of small resistance is desired, the mutual inductance should be small. If, on the other hand, there is a considerable radiation of power from the secondary circuit, or if the circuit contains a large resistance, it is necessary that the mutual inductance be large.

The reason for this necessary change in mutual inductance to suit the various conditions is to be sought in the reaction of the secondary current on the primary circuit. It is probable that the coupling should be as close as possible consistent with a certain reaction, above which the primary conditions, such as phase, etc., would be affected to the extent of causing the power to decrease. Suppose then it be assumed that the *permissible* reaction on the primary is constant, and that the current in the secondary is proportional to M, the coefficient of mutual inductance. Then it follows that the reaction voltage, E_1, in the primary is

$$E_1 = \text{const.} \propto M I_2.$$

But $I_2 \propto \frac{M}{R_2}$ if the wave length and primary current are constant.

Therefore

$$E_1 \propto \frac{M}{R_2} = \text{const., or } M^2 \propto R_2.$$

If, now, M be assumed proportional to N_2 the above expression may be written,

$$N_2^2 = KR_2, \text{ where } K \text{ is a constant.}$$

This is the relation which must probably approximately hold in order that the reaction of the secondary current on the primary circuit may not exceed a certain amount, and is, therefore, for a given R_2 or radiation coefficient of the secondary circuit, the condition for maximum power. This will later be shown experimentally to be nearly true.

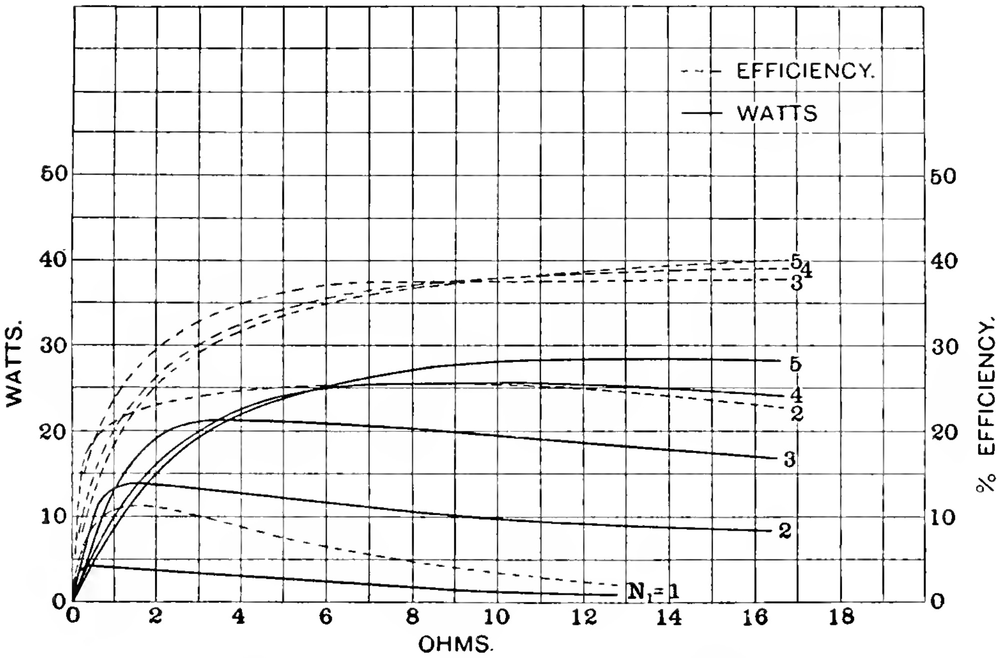

FIGURE 9. Power and Efficiency Curves with Changing Resistance.

λ_2 = 100 meters.
I_o = .55 ampere.
$C_1 = 175 \times 10^{-5}$ $\mu.f.$
$C_2 = 86 \times 10^{-5}$ $\mu.f.$

In Figure 9 is plotted the power, $I_2^2 R_2$, in watts dissipated in the secondary resistance for the conditions represented in Figure 8, from which the curves of Figure 9 were obtained, and, also, the corresponding efficiencies (dotted lines) exclusive of the power lost in the outside resistance, R_o, are shown. The heat lost in R_o is omitted in calculating the efficiencies because, as will be stated later, by a proper choice of generator this resistance can be left out.

The full line curves of Figure 10 were derived from those of Figure 8, and are constant secondary current curves plotted to the ratio of secondary to primary turns of helix as ordinates, and secondary resistance as abscissae. The ordinate scale is, as has been pointed out, practically proportional to the mutual inductance between the two circuits, but, for the sake of definite units, is expressed in terms of turns of helix. The curves were derived by taking the intersections of the horizontal, 1, 1.5, 2, 3, 4, and 5 ampere coördinate lines with the

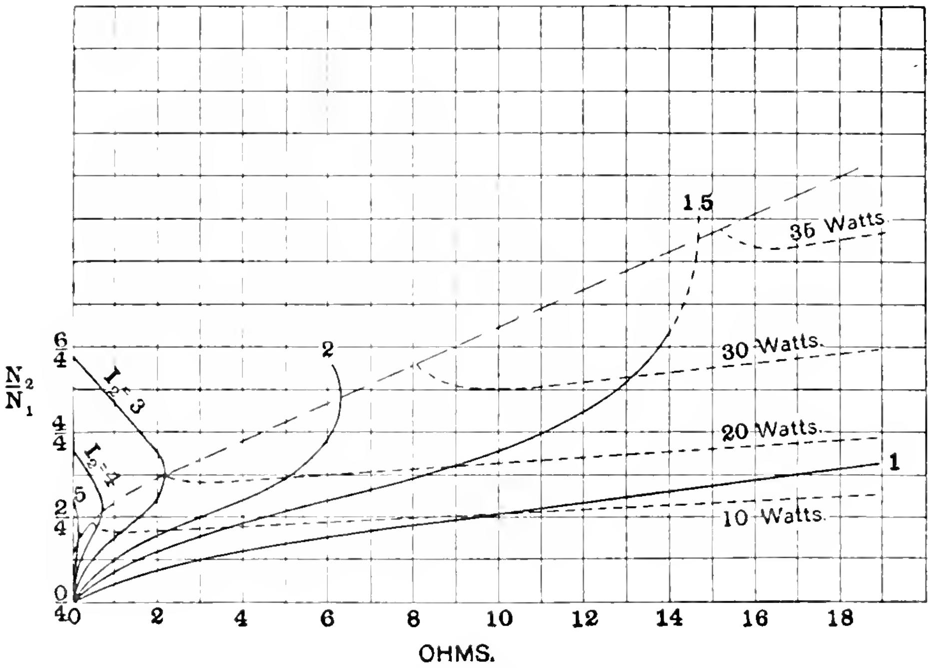

FIGURE 10. Power Curves Derived from Figure 8.

λ_2 = 100 meters.
I_0 = .55 ampere.
$C_1 = 175 \times 10^{-5}$ $\mu.f.$
$C_2 = 86 \times 10^{-5}$ $\mu.f.$

secondary current curves of Figure 8, and plotting to the corresponding secondary resistances. The dot-and-dash curve is drawn through the points of maximum slope of the constant current curves, and is the locus of the points representing maximum power output. It is approximately a parabola, expressible in the form

$$\left(\frac{N_2}{N_1}\right)^2 \propto R_2, \text{ or, since } N_1 = 4 = \text{const.},$$

$$N_2{}^2 = K_1 \, R_2 \text{ where } K_1 \text{ is a constant.}$$

This is the same expression which was previously derived by assuming the existence of a maximum permissible reaction of the secondary current on the primary circuit, and shows that, within the errors of experiment, the assumption is fairly well borne out.

The remaining dotted curves of Figure 10 are calculated constant-watt curves, and enable one to tell at once the power being delivered under any condition represented by the full line curves of the diagram. Apparently the larger the secondary resistance and the greater the number of turns on the secondary of the helix, the greater would be the power output, but it will be seen that the distance between the constant-watt curves rapidly increases, making it necessary to very much increase R_2 and N_2 to give a slightly larger output. Therefore the curves do show the existence of a limit to the power derivable from one gap. These curves also show that with a small number of turns on the secondary helix it is impossible to deliver to the secondary a large amount of power no matter what the resistance is in the secondary circuit. It is clear, as has been said before, that the mutual inductance must be large, and the radiation or resistance large in order to obtain a large amount of power from the secondary circuit.

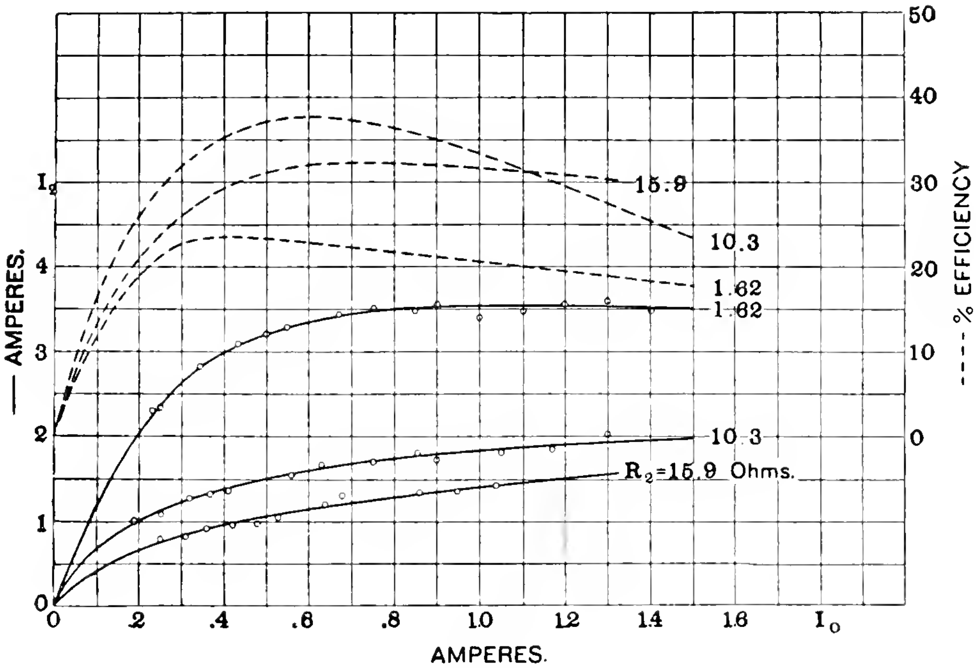

FIGURE 11. Power and Efficiency Curves with Changing Current, $[I_0]$.
$\lambda_2 = 100$ meters.
$C_1 = 175 \times 10^{-5}\ \mu.f.$
$C_2 = 86 \times 10^{-5}\ \mu.f.$

The curves of Figure 8 and those of Figures 9 and 10, which were derived from Figure 8, were taken when the supply current, I_0, was maintained constant at .55 amperes, the current which, with a wave length of 100 meters, gives about the best average efficiency for all conditions. The curves of Figure 11 show the effect on the efficiency of changing the supply current, I_o. The secondary wave length was maintained constant at 100 meters, and there were 4 turns on both the secondary and primary of the helix. The full line curves show the variations in current in amperes in the secondary circuit for three values of secondary resistance, as the main supply current, I_o, is varied from 0 to 1.5 amperes. The dotted curves give the efficiencies for the three curves plotted to the right hand scale. The relative magnitudes of the efficiencies would be slightly different for other values of $\frac{N_2}{N_1}$, but the curves show that for 100 meters wave length in the secondary, the maximum efficiency is obtained when the gap is operated on a supply current of from 0.3 to 0.8 ampere, the exact magnitude of the supply current for maximum efficiency depending on the resistance in the secondary circuit.

All of the data given above are for a wave length of 100 meters in the secondary circuit. The shape of the curves would be similar for other wave lengths but the scales different. If the secondary wave length were longer the primary condenser would be larger, and the supply current for maximum efficiency would be greater, but the gap does not work steadily under any conditions with a supply current greater than about 1.5 amperes.

In conclusion of Part I, a few words should be said concerning the variation in frequency of the secondary oscillations as the supply current is changed. Although this point has not as yet been investigated at all thoroughly, the conclusions drawn from some experiments and observations show that the frequency of the oscillations increases slightly, and practically linearly, as the supply current is increased. This increase is from 1 per cent to 10 or 12 per cent for a change of supply current from .2 to 2 amperes, and depends upon the adjustments, the percentage increase being greater the closer the coupling, and the greater the number of primary discharges per second.

It is improbable that this change in frequency with changing supply current can be attributed, as is done in the case of the Poulsen and Lepel arcs, to the change in slope of the voltage-current characteristic, for a change in gap length, which changes the slope of the $E-I$ curve more than a change in supply current, does not cause a detectable change in frequency. If there is a change in frequency due to change of gap length, it is less than 1 per cent for a change of gap length from .005 to 0.15 mm.

It is thought that the variation of frequency with changing supply current is due to a wavering or shifting of the period of the secondary oscillation between a forced condition, when the primary is in action, and the free period of the secondary circuit, when unaffected by the primary discharge, this wavering being more often and of a greater effect on the resultant or average wave length the greater the number of primary discharges per second. The number of primary discharges is proportional to the supply current, so that according to the above assumption, the change in frequency would be directly proportional to the supply current.

The large changes in frequency with changing arc current and arc length is a serious disadvantage in the use of the Poulsen arc, but with the system being studied, the change of frequency is so small and the supply current and arc length remain so very constant that there is, under all ordinary circumstances, practically *no* change in frequency.

PART II.

ANALYSIS OF OSCILLATIONS BY MEANS OF BRAUN TUBE OSCILLOGRAPHS.

In Part I the general characteristics of the aluminum-cathode oscillation gap were studied, but little idea could be obtained as to the instantaneous relations of the variables. It is the purpose in Part II to analyse, by means of the Braun cathode-ray tube, the entire sequence of events during a complete cycle of changes, and to develop a clearer idea of the nature of the oscillations and the action of the gap. Before attacking the problem, however, it is necessary to describe the additional apparatus made use of in the following experiments:

(1) *The Braun Tubes and Accessory Apparatus.*

The Braun cathode-ray tube is a most valuable piece of apparatus for delineating transient electrical phenomena. Its use has been described by Braun,[6] Zenneck,[7] and others,[8] but a few words from the author's experience with the use of the Braun tube in connection with high frequency currents may be of interest.

The Braun tubes used in the following work were imported from Germany, but it was found necessary to alter them. The aluminum

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[6] F. Braun, Wied. Ann., **60**, 552 (1897); Elektrot. Ztschr., **19**, 204 (1898).

[7] Zenneck, Ann. d. Physik., **9**, 497 (1902).

[8] J. M. Varley, Phil. Mag., **3**, 500 (1902); Varley and Murdock, Electrician (London), **55**, 335 (1905).

or mica diaphragms, which serve to limit the cathode stream to a small pencil, were replaced by glass diaphragms, sealed into the tubes and having the shape of a truncated cone. The apertures of the diaphragms are from .5 to .7 mm. in diameter, and give a very sharply defined luminous spot of about 1 to 1.5 mm. diameter on the fluorescent screen. Figure 12 shows the general form of the tubes and the glass diaphragms.

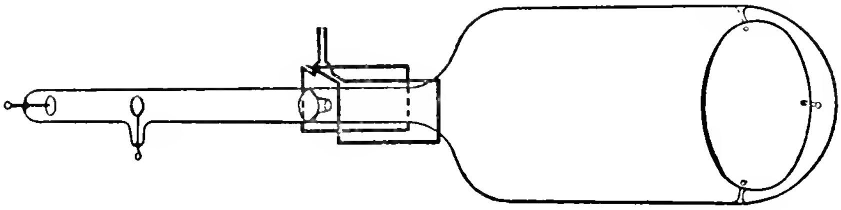

FIGURE 12. Braun Tube and Deflecting Coil.

Braun tubes making use of electrostatic deflection of the cathode beam were also used in parts of the experiment. They are essentially the same as those just described with the addition of the two electrostatic deflecting plates. These plates are about 8 by 2.5 cm. in dimensions, and are sealed inside the tubes about 2.5 cm. apart.

Several Braun tubes have been made at the laboratory, and it was found important that the distance between the cathode and the anode should not be less than about 15 cm. A very sensitive fluorescent screen for visual observation is made by dusting very finely powdered willemite over a piece of mica or glass freshly painted with a thin coat of water glass, although according to Zenneck a zinc sulphide screen is to be preferred for photography and was used in this research.

In order that the cathode beam may be homogeneous, that is, have at all times the same velocity and consequently the same deflection under a certain force, it is necessary that the potential of the source causing the discharge be very constant. This restriction, of course, excludes induction coils and transformers, and practically limits the desirable sources to either the large static machine or the high potential battery.

If a static machine is used, one of many plates is necessary in order to give sufficient intensity to the cathode beam, and if possible the plates should have no sectors or carriers.

The ideal source of current for a Braun tube is the high-voltage secondary battery, capable of giving a potential of from 10,000 to 20,000 volts. In order to control the current, should the vacuum drop, the current from such a plant should pass through two or three feet of running water in glass tubes. In this investigation the Braun tubes were operated on Professor Trowbridge's large 20,000 cell battery, which has proved of the greatest value in this and other work. Usually not over 20,000 volts were used, that being sufficient, under proper adjustment of vacuum, to give a very intense and homogeneous cathode beam.

The proper adjustment of the vacuum is of the utmost importance, and depends entirely upon conditions. For the greatest intensity of the spot and, at the same time, the greatest sensitiveness, the pressure inside the tube should be as high as possible consistent with a clearly defined spot. After some experience, the appearance of the discharge about the cathode serves as the best indicator as to the exhaustion. The best results are usually obtained when the luminous stream from the center of the cathode is about 1 mm. in diameter, although in special cases a higher or perhaps a lower exhaustion is desirable. The vacuum, however, changes when using large currents, making it necessary that the tubes be in connection with a mercury pump. The Gaede rotary pump was used in this investigation.

If a pump in connection with the tube is not convenient, a vacuum regulator, containing potassium chlorate or some other substance such as is used on X-ray bulbs, is suggested for lowering the vacuum when necessary.

In order to eliminate the deflection of the beam by the earth's magnetic field, the tubes are mounted with their axes parallel to the earth's magnetic force, which mounting gives the tubes an inclination of about 70° with the horizontal. The camera, for photographing the oscillographs, was directed downward, viewing the upper or front surface of the fluorescent screen. Plate **1** *a*, shows the general arrangement of apparatus.

The deflecting coils, when used with high frequency current, can, of course, contain no iron. The coils, which were used in this investigation for the magnetic deflection of the cathode beam, are composed of from two to sixteen rectangular turns of copper wire, .325 cm. in diameter, half of the turns being on either side of the tube. The turns are about 7 or 8 cm. in width, and from 10 to 12 cm. in length. A nearly uniform field within the coil is secured by making the width of the rectangular turns $\sqrt{2}$ times the distance between the planes of the two parts of the coil.

When using high frequencies, the difference in potential between two parts of the same coil, due to inductance, is sufficient to cause very large electrostatic deflections of the cathode beam. This disturbance is most effectually eliminated by surrounding the tube inside the coil by a split solenoid of fine insulated copper wire wound on a paper tube. This device completely shields the cathode beam from electrostatic disturbances, but allows the magnetic forces to pass undiminished.

When the Braun tube is used for alternating currents of commercial frequencies, or for phenomena taking place in a few hundredths of a second, the velocity of the luminous spot over the screen is small enough to give a visible streak of light even if the phenomenon lasts for only one cycle.

When high frequency currents are used, however, the velocity of deflection of the cathode beam is so great that it is necessary that the luminous spot travel over the same path thousands of times a second in order that even a visible effect may be observed, and many more times if a photographic record is to be taken with a reasonable exposure.

It is then apparent that, if a sequence of instantaneous phenomena is to be delineated by causing the cathode beam to trace out a pattern on the fluorescent screen of the Braun tube, the cycle of events must repeat many hundreds of thousands of times a second, and with such regularity that the spot of light will, each cycle, travel over exactly the same path.

When using the Braun tube for studying electrical oscillation, this is usually more or less of a difficult condition to attain on account of the uncertain and variable action of most forms of discharge gaps. The gap and system under consideration is, however, so regular and constant that it is not at all difficult to obtain photographs of patterns representing cyclic changes, many of which recur three million times a second with practically no variation.

Plates 1–7 are a few of over fifteen dozen photographs taken representing various conditions, and give unmistakable evidence of the remarkable regularity and continuity of the oscillations of the *Cu-Al* gap. The photographs were taken on Seed's Gilt Edge No. 27 plates, and exposures of from 3 to 30 seconds were made. The figures are practically natural size.

(2) *The Primary Wave.*

The observations for determining the shape and phase, with respect to the secondary oscillation, of the primary current rush were obtained by leading the primary and secondary currents each through a 4-turn deflecting coil about the Braun tube, the two coils making an angle of 90° with each other. The arrangement is diagrammatically shown in Figure 13, where the letters have the before mentioned significance.

There is obtained on the fluorescent screen by this arrangement a perfectly definite and well defined pattern, which gives the corresponding instantaneous values of the primary and secondary currents. Plate 1 *c*, is one of many photographs of such a pattern, taken with an exposure of about 15 to 30 seconds, and represents the conditions when adjustments are made for maximum energy in the secondary circuit.

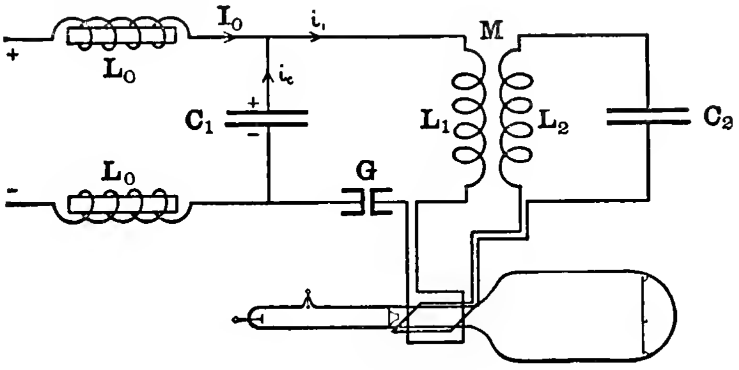

FIGURE 13.

Knowing, as will be adequately proved later, that the secondary oscillation is sinusoidal, the primary current, plotted to time, and its phase relation to the secondary current, can readily be derived from the patterns mentioned above. In *c* of Plate 1 the vertical distance d_1 to the primary loop above, from any point on the horizontal line distant d_2 from the center or undeflected spot, gives the instantaneous primary current, i_1, and the simultaneously secondary current, i_2. A sine curve of amplitude represented by the secondary deflection is drawn, and the time coördinate for any corresponding values of i_1 and i_2 is the time, obtained from the sine curve, at which the current coördinate is i_2. The direction of the spot of light is indicated by the arrows. The curve marked I_1, in Figure 14, shows the development of two figures, both reduced to the same scale for better comparison. I_2 in the figure is the secondary current. Seven such developments were made representing entirely different conditions, but in each case the phase of I_1 with respect to I_2 was practically the same as is shown in Figure 14, and the shapes of the I_1 curves differed so slightly that, to save confusion, they are not reproduced.

Examination of the photograph and of the developments show, as was stated in Part I, that there is no inverse current. Although the primary wave appears to have twice the period of the secondary oscillation, if the slope of the curve, or $-\frac{di_2}{dt}$ which is proportional to the resulting induced electromotive force in the secondary circuit, be plotted, a curve of the same period as I_2 is obtained. This e. m. f. curve is shown at E in Figure 14.

If, now, the ordinates of the e. m. f. curve be multiplied by the corresponding values of the secondary current, a quantity proportional to the instantaneous rate at which energy is being transferred to the secondary is obtained, and if plotted, gives the curve marked W in Figure 14. The portions of the curve below the axis of time are negative, and represent a return of energy to the primary circuit. The algebraic sum of the areas under the four loops is proportional to the total energy permanently delivered to the secondary circuit in one cycle. It is apparent that very little energy is returned to the primary circuit, and that the second half of the primary loop gives the greater amount of energy to the secondary circuit, the first part of the primary discharge being more or less irregular on account of the sudden breaking down of the high initial gap resistance and the superposed higher harmonics resulting from the sudden shock to the system.

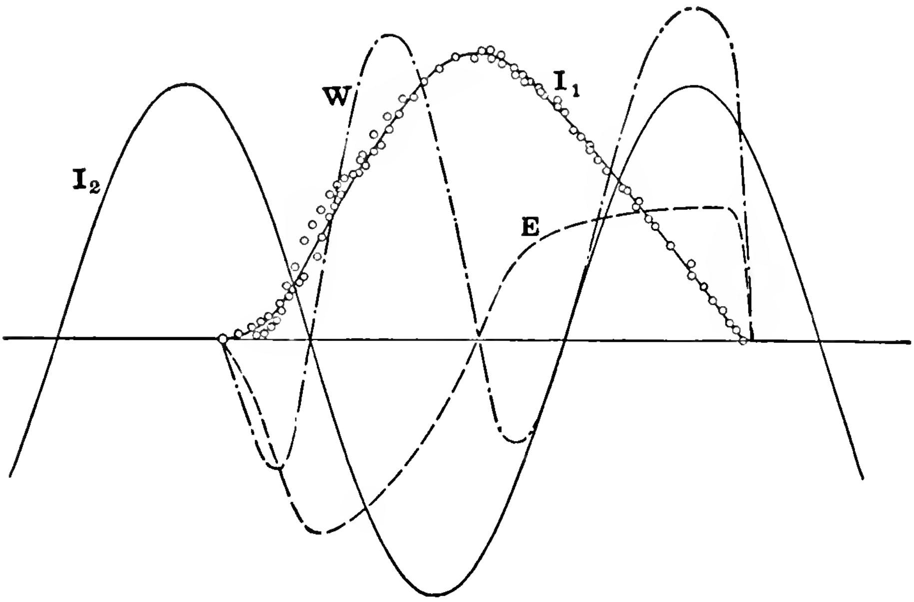

FIGURE 14.

I_1 . . . . . Primary Discharge Wave.
I_2 . . . . . Secondary Wave.
E . . . . . Electromotive Force due to I_1.
W . . . . . Power Delivered to Secondary Circuit.

In Part I it was stated that the primary current loops occur every two or more secondary oscillations. In this case the primary wave, considered as an intermittent function, could be analyzed into harmonics. Instead, however, of analyzing the current wave, the equivalent problem of expanding the resulting e. m. f. wave into harmonics can easily be done if, as is seen by reference to Figure 14 to be roughly true, the e. m. f. curve be assumed to be an intermittently repeated sine cycle.

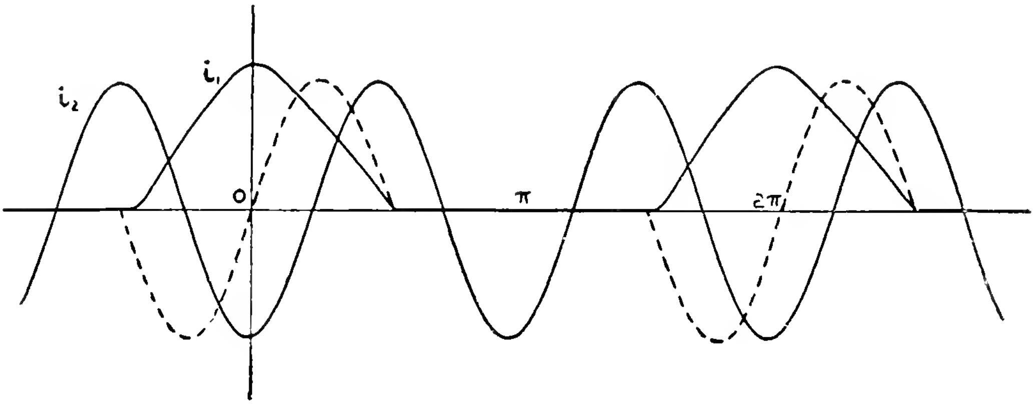

FIGURE 15.

Suppose the particular case of a discharge every two secondary oscillations (I. C. F. = 2) be considered in detail. Figure 15 indicates the conditions of the problem. The full line sine curve, marked i_2 represents the secondary oscillation which has thus far been considered, or in other words, the primary harmonic of maximum intensity. The other full line, marked i_1, is the primary discharge, and the dotted line the approximate e. m. f. wave which was referred to above.

The function

$$e = E \sin 2x \Big|_{0}^{\pi/2} \qquad e = o \Big|_{\pi/2}^{\pi}$$

is to be developed into a Fourier series of the form

$$e = a_1 \sin x + a_2 \sin 2x + a_3 \sin 3x + \ldots\ldots$$

where any coëfficient a_m is given by the expression

$$a_m = \frac{2}{\pi} \int_0^{\pi} f(x) \sin mx \, dx = \frac{2}{\pi} \int_0^{\pi/2} E \sin 2x \sin mx \, dx$$

The result is expressed below.

$$e_2 = E\ (.43 \sin x + .50 \sin 2x + .26 \sin 3x - \\ .061 \sin 5x + .028 \sin 7x - .017 \sin 9x + \ldots.)$$

If the harmonies are to be expressed in terms of time and the period of the e. m. f. wave, which is the same as the period of the secondary oscillation, the substitution

$$2x = 2\pi nt \qquad \text{or}$$

$$x = \frac{2\pi nt}{2} \qquad \text{is to be made.}$$

Then $e_2 = E\left(.43 \sin 2\pi\left[\frac{n}{2}\right]t + .50 \sin 2\pi nt + .26 \sin 2\pi\left[\frac{3n}{2}\right]t - .061 \sin 2\pi\left[\frac{5n}{2}\right]t + .028 \sin 2\pi\left[\frac{7n}{2}\right]t - .017 \sin 2\pi\left[\frac{9n}{2}\right]t + .\ .\right)$

The results for I. C. F. equal to 3 and 4 are given below.

I. C. F. = 3

$$e_3 = E\left(.21 \sin 2\pi\left[\frac{n}{3}\right]t + .33 \sin 2\pi\left[\frac{2n}{3}\right]t + .33 \sin 2\pi\left[\frac{3n}{3}\right]t + .24 \sin 2\pi\left[\frac{4n}{3}\right]t + .10 \sin 2\pi\left[\frac{5n}{3}\right]t - .04 \sin 2\pi\left[\frac{7n}{3}\right]t - .\ .\ .\right)$$

I. C. F. = 4

$$e_4 = E\left(.12 \sin 2\pi\left[\frac{n}{4}\right]t + .21 \sin 2\pi\left[\frac{2n}{4}\right]t + .26 \sin 2\pi\left[\frac{3n}{4}\right]t + .25 \sin 2\pi nt + .20 \sin 2\pi\left[\frac{5n}{4}\right]t + .13 \sin 2\pi\left[\frac{6n}{4}\right]t + .\ .\ .\ .\right)$$

A classification of the harmonies is given in the adjoining table, where the columns are headed according to the I. C. F.

The coefficients of the various terms in the developments mean very little, but the existence of most of the harmonies, given in the table, has been verified by wave meter readings.

A much more beautiful proof of the existence of the harmonies is presented by Braun tube oscillographs. If, in addition to the arrangement of circuits shown in Figure 13 for obtaining the primary wave form, another adjustable secondary circuit be used, excited by the primary current, and having a deflecting coil also about the Braun tube and parallel to the primary deflecting coil, the pattern observed on the fluorescent screen is the resultant of the deflections of the first sec-

I. C. F.	1	2	3	4	5	6	7
Primary Harmonics	n	$\frac{n}{2}$	$\frac{n}{3}$	$\frac{n}{4}$	$\frac{n}{5}$	$\frac{n}{6}$	$\frac{n}{7}$
		n	$\frac{2n}{3}$	$\frac{2n}{4}$	$\frac{2n}{5}$	$\frac{2n}{6}$	$\frac{2n}{7}$
		$\frac{3n}{2}$	n	$\frac{3n}{4}$	$\frac{3n}{5}$	$\frac{3n}{6}$	$\frac{3n}{7}$
			$\frac{4n}{3}$	n	$\frac{4n}{5}$	$\frac{4n}{6}$	$\frac{4n}{7}$
		$\frac{5n}{2}$	$\frac{5n}{2}$	$\frac{5n}{4}$	n	$\frac{5n}{6}$	$\frac{5n}{7}$
				$\frac{6n}{4}$	$\frac{6n}{5}$	n	$\frac{6n}{7}$
		$\frac{7n}{2}$	$\frac{7n}{3}$	$\frac{7n}{4}$	$\frac{7n}{5}$	$\frac{7n}{6}$	n
			$\frac{8n}{3}$		$\frac{8n}{5}$	$\frac{8n}{6}$	$\frac{8n}{7}$
		$\frac{9n}{2}$		$\frac{9n}{4}$	$\frac{9n}{5}$	$\frac{9n}{6}$	$\frac{9n}{7}$
			$\frac{10n}{3}$	$\frac{10n}{4}$		$\frac{10n}{6}$	$\frac{10n}{7}$
		etc.	$\frac{11n}{3}$	$\frac{11n}{4}$	$\frac{11n}{5}$	$\frac{11n}{6}$	$\frac{11n}{7}$
			etc.		$\frac{12n}{5}$		
				etc.	etc.	etc.	

ondary current, and, at right angles to it, the sum of the deflections due to the primary and the second secondary currents. If, now, the second secondary capacity be varied, there suddenly appears on the fluorescent screen, as resonance for one of the harmonics of the primary is obtained, a Lissajou's figure corresponding to the ratio of frequencies of the two secondary oscillations. In addition to the simple Lissajou's figure, which is due to the free vibration of the two secondaries, there appears a less intense irregular loop due to the intermittent primary discharges.

Plate **1**, cuts *d* and *e*, and *a* and *b* of Plate **2** are photographs of a few of the patterns obtained by the above described method. The second secondary circuit was a wave meter with its coil parallel to the primary deflecting coil, from which it received its impulses. An examination of the primary loop is often instructive in giving the relation of the primary discharge to the secondary oscillation. It is seen that the regular Lissajou's figure may or may not be complete according to the value of the I. C. F. In *b* of Plate **2** the ratio of frequencies is 3 : 1, and the I. C. F. is 3, so that the primary discharges occur once for every journey of the spot over the pattern, thereby distorting a part of the Lissajou's figure.

Cuts *b–f* of Plate **2** are due simply to the deflections of the two secondary oscillations, the second secondary circuit receiving its impulses from the same primary coil which excited the first secondary circuit. Some of the photographs shown were purposely taken with a slight difference in phase to show the double line. Cut *e* of Plate **1** represents the same ratio of frequencies as that of cut *a* of Plate **2** but with a considerable shift in phase.

A consideration of cuts *d–f* of Plate **2** shows that, although the coupling was close, the secondary currents do not depart from the sinusoidal form even while the primary impulse occurs. A possible rough explanation of this non-departure from the sinusoidal form can be had from a consideration of the shape of the primary wave form shown in Figure 14. The primary impulse I_1 of Figure 14 is seen to be approximately a cosine curve, of the same period as the free secondary oscillation, plus a constant, until the maximum current is attained, when the current decreases in a straight line. But by substitution in the differential equation for an oscillatory circuit, one finds that a cosine wave plus a constant or linear function of the time satisfies the conditions of a sine secondary oscillation. The proof of this proposition is not given here.

The shape of the primary wave form, which has just been considered, is determined principally by the changes in resistance which take place in the gap. If there were no change in resistance, and the influence of the secondary current were negligible, the form of the primary current rush would be given by the familiar equation

$$i_1 = \frac{Q_0}{\sqrt{R_1^2 C_1^2 - 4 L_1 C_1}} (e^{-\alpha t} - e^{-\beta t}),$$

where $$\alpha = \frac{R_1C_1 + \sqrt{R_1{}^2C_1{}^2 - 4L_1C_1}}{2L_1C_1}$$

and $$\beta = \frac{R_1C_1 - \sqrt{R_1{}^2C_1{}^2 - 4L_1C_1}}{2L_1C_1}.$$

Q_o is the initial charge in the primary condenser C_1, and L_1 and R_1 are the inductance and resistance in the primary circuit. The curve, which represents this equation, is, as is well known, a rise and fall of current with respect to time, and is aperiodic or oscillatory according as $R_1{}^2$ is greater or less than $4L_1/C_1$. The critical resistance above which the discharge is non-oscillatory is, for the circuits which were used in this investigation, of the magnitude of 100 ohms. As will be seen later, the average resistance of the gap is so low compared to this quantity that the existence of no inverse current cannot be attributed solely to the aperiodic nature of a discharge through a high resistance. Moreover, if the average resistance were high enough to cause the discharge to be aperiodic, the end of the discharge would be asymtotic to the time axis.

The resistance of the gap very rapidly drops from a very high value at the start to a low value. Since the resistance is a function of the current, and very probably a function of the time of which we have no knowledge, it is impossible to derive any exact mathematical expression for the current curve. A consideration of the physical aspects will, however, reveal to some extent the reasons for the shape shown. If, in the differential equation for the primary circuit,

$$L_1\frac{di_1}{dt} + M\frac{di_2}{dt} + R_1i_1 + \frac{\int_o^t i_1dt}{C_1} = \frac{Q_o}{C_1},$$

the term R_1 is suddenly decreased, it is evident that the term $L_1\dfrac{di_1}{dt}$ will prevent at first a rapid change in current. This, in part, explains the slow rise of current as shown by the first part of the primary wave form. As the discharge progresses the resistance becomes lower, and the current increases, following more closely one of the exponential discharge curves of low resistance. For reasons previously given, the discharge stops as soon as the current becomes zero.

(3) *The Resistance of the Gap.*

It is interesting, by assuming an approximate expression for the primary wave form, to calculate the change in resistance of the gap necessary to give the observed primary current curve. An examination of the experimental curves of Figure 14 shows that the first part of the primary wave can be approximately represented by the expression

$$i_1 = I_1\ (1 - \cos\omega\ t).$$

where now i_1 represents the instantaneous value, and I_1 the maximum value of the primary current, and ω is $2\ \pi$ times the secondary frequency. Time is reckoned from the beginning of the primary discharge.

The corresponding expression for the secondary wave is found by measurements of Figure 14 to be

$$i_2 = I_2 \sin\left(\omega t + 115^\circ\right).$$

These expressions can now be substituted in the differential equation for the primary circuit,

$$L_1\frac{di_1}{dt} + M\frac{di_2}{dt} + R_1 i_1 + R_b i_1 + \frac{\int_o^t i\,dt}{C_1} = \frac{Q_o}{C_1},$$

in which R_b is the resistance of the gap, R_1 is the resistance of the rest of the primary circuit.

Also

$$i_c = i_1 - I_o. \quad \text{(See Figure 13)}$$

whence

$$L_1 I_1\,\omega \sin\omega t - M I_2\,\omega\cos\left(\omega t + 115^\circ\right) + (R_1 + R_b) I_1 \left(1 - \cos\omega t\right)$$
$$+ \frac{(I_1 - I_o)t}{C_1} - I_1\frac{\sin\omega t}{\omega C_1} = \frac{Q_o}{C_1}$$

Solving for R_b there results

$$R_b = \frac{\dfrac{Q_o}{C_1} - \dfrac{(I_1 - I_o)t}{C_1} - I_1\left(L_1\omega - \dfrac{1}{C_1\omega}\right)\sin\omega t + M I_2\omega\cos\left(\omega t + 115^\circ\right)}{I_1(1 - \cos\omega t)}$$
$$- R_1$$

$$= \frac{\dfrac{Q_o}{C_1} - \dfrac{I_1 - I_o}{C_1}t - I_1\left(L_1\omega - \dfrac{1}{C_1\omega} + .91\,M\omega\,\dfrac{I_2}{I_1}\right)\sin\omega t - .42\,M I_2\cos\omega t}{i_1}$$

if R_1 be neglected.

If appropriate values for the constants of this expression be taken, and R_b plotted to the current i_1, the curve shown by the dotted line of Figure 16 is obtained.

The change of resistance of the gap can be obtained experimentally by use of a Braun tube provided with electrostatic deflecting plates. These electrostatic plates are connected directly across the gap as shown by Figure 17, causing a deflection perpendicular to that caused by the total current through the gap. In this way a trace of the voltage-current characteristic curve is obtained from which can be derived the resistance corresponding to any current.

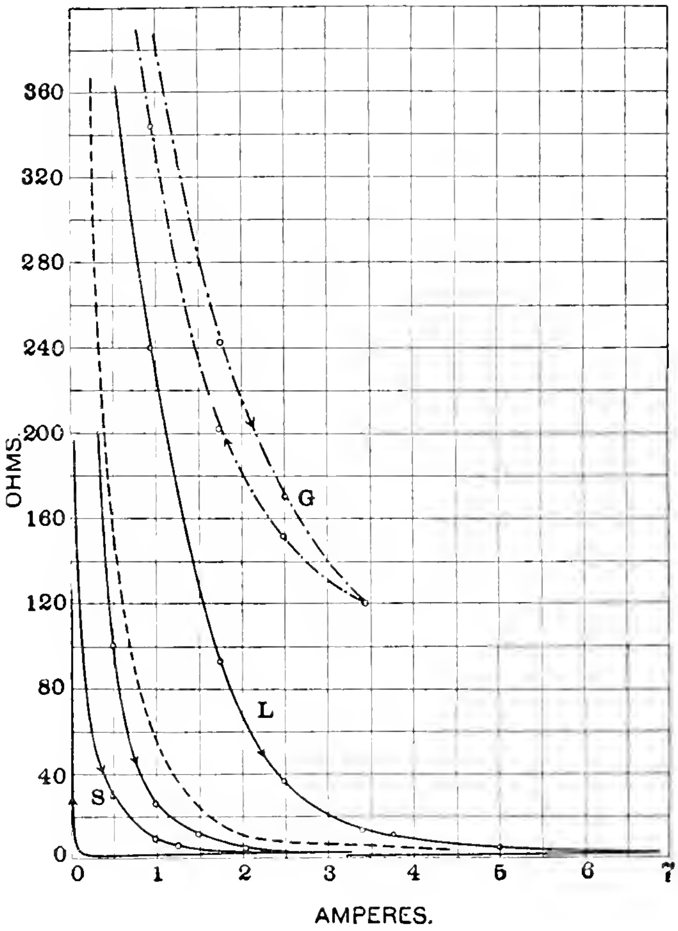

FIGURE 16. Resistance Curves of *Cu-Al* Gap.
G . . . . Glow Discharge.
L . . . . Discharge with Very Long Gap.
S . . . . Discharge with Very Short Gap.
Dotted curve . . . . Calculated.

Cuts *a–e* of Plate **3** are photographs of *E–I* characteristic curves as above described. Cut *a* represents the conditions for a very long gap. The path of the spot of light, in tracing this figure, may be understood from the following. As the condenser charges there is no current through the gap, and hence no current deflection, but the potential of the condenser increases to a certain value determined by the breaking-down potential of the gap. This charging is represented in the photograph by a movement of the luminous spot from *A*, its undeflected position, to *B*, the potential at which the gap breaks down, which in magnitude, in this case, is equal to about 450 volts. The instant that the gap breaks down the potential drops, and the current through the gap increases giving the curve, from *B* to *C*, roughly resembling a hyperbola. As the current decreases, represented by the line *CA* in the photograph, the potential remains practically zero, showing that after the gap has been once ionized the resistance remains low until the current becomes zero. The current does not increase in the negative direction for reasons previously given. During the passage of the primary current the capacity, C_1, has been completely discharged and charged in the reverse direction so that, as soon as the current stops, the full potential of the reversed condenser is brought to bear across the gap. This is represented by the point *D*. Current is now, however, flowing into C_1 at a constant rate, causing the fluorescent spot to move along the voltage axis from *D* to *B* to begin a new cycle.

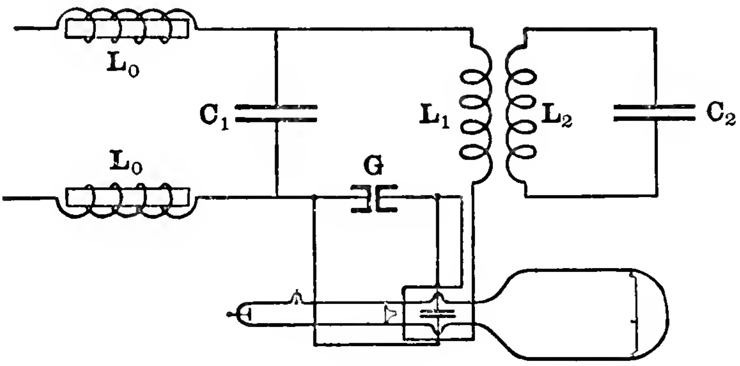

FIGURE 17.

The same kind of diagram is shown in cuts *b* and *c* of Plate 3 for shorter gaps. It is evident, as would be expected, that as the gap is shortened, the *E–I* curve closes in toward the two axes.

It is also seen that with a very short gap the current increase is oscillatory. These oscillations are very rapid, having a wave length of the magnitude of four or five meters, and on account of the extremely high frequency cause the large potential oscillations shown by the blurred space in cut *d* of Plate 3.

The reason for these superposed higher frequency oscillations is easy to understand if we consider again the rapid drop in resistance represented by the very steep resistance curve for a short gap. A decrease in resistance means an increased current, but the increase in current further causes a decrease in resistance. This action promotes an unstable condition, and would cause a tremendously sudden rush of current if the inductance of the whole circuit did not exert a controlling action. The effect is, however, that the terminals of the gap and the wires in the immediate vicinity of the gap are suddenly robbed of electricity, and because of the inductance of these terminal lead wires, the terminals are charged in the opposite direction. When the potential of the reversed terminals attains a sufficient value this momentary current rush stops and reverses. It is evident, without further consideration, that the conditions are right for the observed superposed oscillations, these oscillations being more intense at the gap and extending back with diminishing amplitude into the primary circuit. This effect will be very apparent in some of the pictures yet to be considered.

Cut *e* of Plate **3** is a photograph taken when, on account of the dryness of the hydrogen, practically nothing but a glow discharge could be obtained. The gap in this particular case was traversed by a high frequency current. The photograph is introduced only for the small curved point at the right hand end of the potential deflection, which is the characteristic of the glow discharge.

Cut *f* of Plate **3** was taken in the same manner as the pictures just described except for the addition of a secondary deflection coil parallel to the primary coil about the tube. In this way there is obtained a spreading out of the diagram, and a clearer view of the actual path of the luminescent spot. The helical path from right to left results from the secondary current oscillation, and superposed primary potential oscillations due to the influence of the secondary vibrations on the primary circuit, both occurring during the charging of the primary condenser. The abrupt end represents the point at which the gap breaks down and the spot moves very rapidly, at first, over the primary discharge loop.

The change in resistance with changing current, derived from these E–I characteristics, gives curves of the general shape shown by the full line curves of Figure 16. The curve marked L was derived from cut *a* of Plate **3**, and represents the change in resistance of a very long gap. The other two full-line curves are for shorter gaps, and, in the extreme corner, is suggested the condition for decreasing current which completes the cyclic resistance changes.

It is seen, on examination of Figure 16, that the dotted curve, derived from an assumed expression for the primary wave form, agrees well in shape with the experimental curves (heavy lines). The scales of the curves serve only to give an approximate idea of the magnitudes of the resistances at different currents, for the position of the curves depends upon the arc length and undoubtedly upon the period of discharge. It is worthy of note that the resistance at zero current is very high, thus admitting of a high initial charge in the primary condenser before the gap breaks down. The resistance curves are very steep, being much steeper than the corresponding curves for the Poulsen arc. It is, in part, this steepness which adapts the gap to the production of very high frequency oscillations. The very rapid reëstablishment of the high resistance is also of primary importance in the action of the gap with high frequencies.

The upper dot-and-dash curve is for the curved point at the end of the potential deflection in cut *e* of Plate **3** just mentioned, and represents the conditions for glow discharge.

(4) *The Inverse Charge Frequency* (*I. C. F.*).

Reference has often been made to the I. C. F., the value of which, as was stated, depends upon the wave length of the secondary oscillation, the size of the primary condenser C_1, and the value of the supply current I_0. In order to show that the I. C. F. has, under most conditions, a perfectly definite value, and at the same time, to illustrate some other points concerning the system, the photographs of Plate **4** were taken.

The arrangement of circuits, for the figures under discussion, was as follows: Two parallel deflecting coils were placed about the Braun tube, and so situated as to deviate the cathode beam in a direction perpendicular to the electrostatic deflection. One of these coils was connected in the primary circuit and the other in the secondary circuit. The electrostatic deflecting plates were connected to the terminals of the primary condenser C_1.

The oscillograms of Plate **4** represent, therefore, the sum of the primary and secondary currents by deflections in the vertical direction, and the potential of C_1, by deflections in the horizontal direction. In all of the cuts the straight lower portion results from the secondary oscillation during the charging of C_1, when the gap current is zero.

The explanation of cut *b* will serve for all of the pictures of Plate **4**. At point *A* the condenser C_1 is charged to a potential sufficient to jump across the gap. When the primary discharge begins, the spot of light moves very rapidly at first over the loop *ABC*. This discharge starts or maintains the secondary oscillation, so that the vertical deflection is due to the primary current plus the simultaneous secondary current. During the discharge the potential of the primary condenser falls and increases in the opposite direction, so that, at the end of the discharge, represented at *C*, the condenser potential is reversed. At point *C* the primary discharge is completed. The rest of the diagram from *C* to *A* is due to the secondary oscillation, which causes the vertical deflection, and the uniformly changing potential of the primary condenser while charging, which causes the horizontal deflection from *C* to *A*.

The number of secondary oscillations taking place during one primary cycle, and which has been called the I. C. F., is clearly shown by the photographs. In the case of cut *b*, the secondary completes one period during the primary discharge, and three complete secondary periods during charging from *C* to *A*, so that the I. C. F. is 4.

The instant at which the primary discharge begins and ends with reference to the secondary wave, is shown to be the same as was derived in the section on the primary wave. The high harmonic oscillations in the primary which occur, as has been mentioned, after the high resistance of the gap is broken down, are apparent in the beaded appearance of the upper loops of the oscillograms.

In cuts *a–e* of Plate **4** the spot travelled over the patterns in an anti-clockwise direction. The I. C. F.'s are respectively 3, 4, and 6. In cuts *a* and *b* the undeflected position of the spot is shown, and the relative magnitudes of the direct and inverse potentials of the primary condenser can be noted.

The beats, shown in cuts *c–f* of Plate **4**, are due to the interference of two oscillations in a doubly-periodic secondary system employed in this case. The second-secondary oscillation is due to the vibration of an helix, a few turns of which were included in the secondary circuit. The luminous spot in cut *d* travelled in a clockwise direction.

(5) *Resistance Damping.*

In order to obtain an oscillogram of a variable which is a function of time, it is necessary to use some device which will give a uniform time axis to the figure. For instance, if it is desired to obtain an oscillograph of the commercial alternating current, one passes the current through the deflecting coil about the Braun tube. There appears on the screen a straight line, which results from the to-and-fro movements of the luminous spot over the same straight path. In order to see the current wave developed with respect to time, it is necessary to observe the line deflection in a revolving mirror, its axis being parallel to the line deflection. If a photograph is to be taken, it is further necessary to drive the mirror by some synchronous device so that the image of the developed figure may be stationary on the photographic plate for a time sufficient to make the exposure. This synchronizing device is not difficult to arrange when using commercial alternating currents, but when it is desired to take an oscillogram of a high frequency current or condenser discharge, it is usually impossible to make the necessary synchronization. When using high frequency currents, the velocity of the spot of light on the fluorescent screen is so great that, in order to obtain a photograph, it is necessary that the cycle of changes, as shown by the pattern on the screen, be repeated many hundred thousand times with such regularity and certainty that the image is always in exactly the same position. The requirements of both the acting system and the synchronizing device are very exacting.

The development of the time axis can be most effectually accomplished with the system under discussion by the very simple connection which was used in the last section. The electrostatic plates, which cause a deflection perpendicular to the current coils, are connected to the terminals of the primary condenser C_1. During the interval between primary discharges, when the primary condenser is charging, the primary current is zero, and the main or charging current is almost perfectly constant on account of the large inductances in the mains. This uniform charging causes a uniform increase in potential of the condenser C_1, and hence a uniformly developed time axis on the fluorescent screen. The oscillations of the secondary, or any effect started by the primary discharge, is thereby developed, as is shown by the lower portions of the cuts of Plate 4.

This arrangement for the development of current or potential deflection with respect to time is of the greatest use in many ways. Its application will be illustrated here by showing the damping curves with oscillations of a frequency of two million or more per second.

Cuts *a* and *b* of Plate 5 represent the damping of the secondary oscillations due to the addition of resistance in the secondary circuit. The primary capacity and supply current were so adjusted as to give large values of the I. C. F. in order that as many secondary oscillations as possible might appear in the damped oscillation trains shown. The adjustments for the pictures of Plate 5 were so made that each oscillation train is just completed before the beginning of the next. The trains, therefore, succeed each other with no intervals of rest. By adjustments of the supply current or primary capacity it is possible to lengthen or shorten the interval between the primary discharges, and by varying the resistance in the secondary circuit the number of oscillations in one train or the damping can be varied at will. The damping is evidently exponential in fulfilment of the familiar theory.

Cuts *c–f* of Plate 5 and cut *a* of Plate 6 are the results of adding to the arrangement of circuits just considered, a second secondary circuit, excited by the primary discharge and with its deflecting coil placed parallel to that of the first secondary. There results, therefore, a doubly-periodic secondary system having two secondary circuits inductively coupled together. The doubly-periodic secondary oscillation gives the beats and curious figures shown. Cuts *c* and *d* are due to the addition of two oscillations differing widely in frequency. As will be seen from the description of the figures, the second oscillation is in one case over twice and in the other case almost three times the frequency of the main secondary oscillation.

Cut *a* of Plate 6 shows beats taken with almost undamped oscillations. The wave lengths are not recorded but they were probably of the magnitude of 100 meters.

(6) *Damping in a Circuit Containing a Spark Gap.*

When the dissipation of energy in an oscillatory circuit is proportional to the square of the current, as is the case in a constant resistance, the damping is exponential. If, however, the resistance is a function of the current the energy dissipation is no longer proportional to the square of the current, and the damping no longer exponential. For instance, the resistance of a spark gap or arc is a function of the current, the resistance being greater the smaller the current through the gap.

Richarz and Ziegler[9] in 1900 observed, in a revolving mirror, the straight line deflection which is produced in a Braun tube when a condenser is rapidly discharged across a spark gap and through the deflecting coil. The frequency of the oscillations was very low. On account of the impossibility of taking a photograph, we have only their description of the phenomenon as seen in the revolving mirror. In appearance the figure resembled the backbone of a fish, or, in other words, a long straight line, due to the undeflected spot, and at intervals along the line pairs of equally inclined short straight lines, as one would indicate an arrow point. The short lines were due to the more intense maximum deflections during a train of oscillations, the separate oscillations being entirely undiscernible. The results showed that the damping due to a spark gap is not exponential but approximately linear.

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[9] F. Richarz u. W. Ziegler, Ann. d. Phys., **1**, 468, 1900.

Zenneck,[10] in 1904, obtained further experimental proof of the approximately linear damping due to a spark gap. He photographed the line deflection, and by a process of projection from the several brighter spots, due to the decreasing amplitudes of the oscillations, derived the damping curves. Frequencies up to 1800 per second were used by him.

Heydweiller,[11] in 1906, showed that the results obtained by the above mentioned experimenters can be deducted theoretically. Heydweiller assumes, in deducing the linear damping, that the gap has a characteristic expressible in the form.

$$e = a + \frac{b}{i}$$

where e and i are the voltage across and current through the gap, respectively, and a and b are constants. He further assumes that b is negligible, which reduces the conditions to the assumption of a constant voltage across the gap. Solving the differential equation for the discharge of a condenser across a constant potential gap, he obtained rectilinear damping.

If a discharge gap be substituted for the secondary resistance in the arrangement of circuits which was used in the last section for obtaining plain resistance damping, very clear oscillograms can be obtained of the oscillation trains when the damping is caused by a gap. Although the inherent irregularity of some metallic gaps, when used in the secondary circuit, causes some irregularity of the oscillographs, yet good photographic records can be obtained, as is shown by the cuts of Plates 6 and 7. In order to obtain a potential sufficient to maintain the discharge across the secondary gap, it was necessary to use a large primary condenser and supply current, and to make the ratio, $\frac{N_2}{N_1}$, of the secondary to primary turns on the helix large.

Cuts *b* and *c* of Plate 6 show two of the pictures first taken, and illustrate well the linear damping. The gap length was very short; the terminals were of aluminum.

Further investigation showed that the oscillation train took on entirely different aspects according as the discharge could be classed as a *pure arc*, or a *spark discharge*. When the discharge is a pure arc, the separate oscillations are regular and practically sinusoidal, and the damping is still linear. If the discharge is classed as a spark discharge,

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[10] J. Zenneck, Ann. d. Phys., **13**, 822, 1904.

[11] R. Heydweiller, Ann. d. Physik., **19**, 646, 1906.

although the damping is linear, the separate oscillation loops are distorted as will appear presently.

Cut *d* of Plate 6 represents the condition when the discharge terminals of the secondary gap are carbon. The discharge was quiet and very brilliant, resembling, as indeed it was, the pure carbon arc operating, however, at a frequency of 5.7×10^5 oscillations per second.

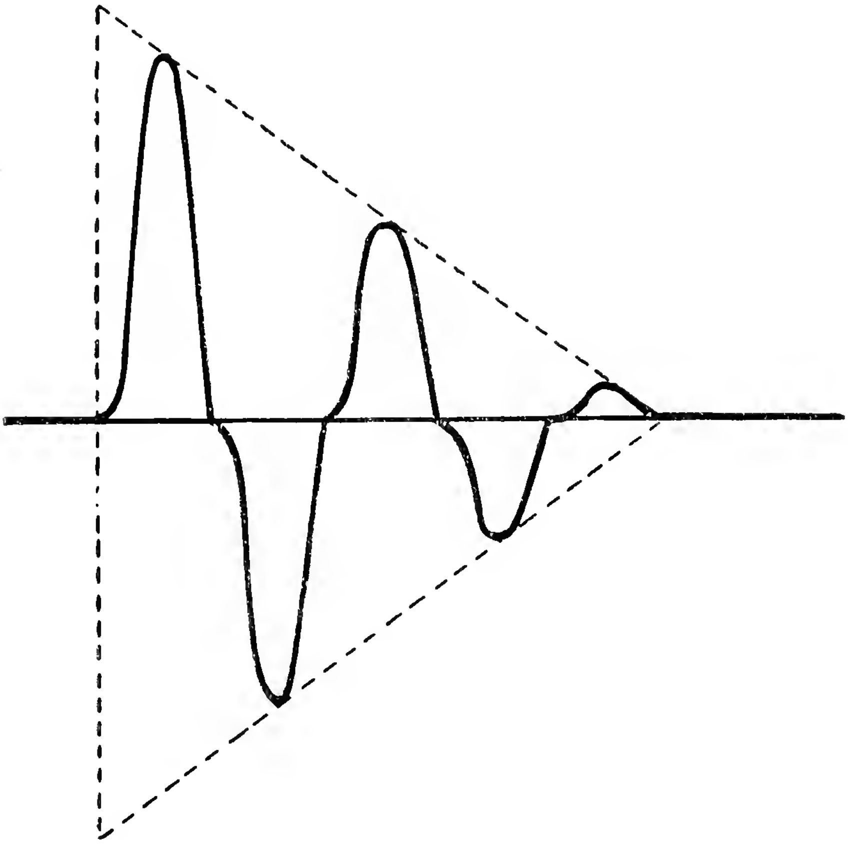

FIGURE 18. Form of Spark Gap Damping Curve.

Cut *e* of Plate 6 gives the appearance of the oscillogram when the terminals are of aluminum in air. The discharge in this case, as well as for cuts *b* and *c*, was probably a pure arc due to the carbon and other impurities in the aluminum. In appearance, the discharge was brilliant and similar to the carbon arc.

Magnesium terminals usually give the pure-arc discharge-form of damping curve, due probably to the large amount of magnesium vapor present in the discharge, or possibly to the burning of the magnesium into the oxide.

Cut *f* of Plate 6 and the pictures of Plate 7 represent the appearance of the *spark discharge* oscillograms. When the temperature of the discharge is kept low the conductivity of the gap is not maintained over the interval of zero current by the presence of incandescent metallic or carbon vapor, and the high resistance of the gap is partially established at each crossing of the axis by the current curve. This necessitates a reionization of the gas at the beginning of each current loop, or the breaking down of a possible oxide film, thereby distorting the wave in the neighborhood of the axis, as is shown by the figures.

The general form of the curve for spark damping, which is indicated in the photographs, was at times momentarily clearly outlined on the fluorescent screen and is shown by the drawing of Figure 18. Apparently, in some of the photographs, the loops begin, in point of time, before the ending of the previous loop. This apparent paradox is due to the slight shift in the time axis resulting from the reaction of the strong secondary discharges upon the potential of the primary condenser.

The oscillogram photographs of spark damping here shown were taken for aluminum terminals because of the greater regularity of the discharge between terminals of that metal. Many other metals were tried, such as copper, cadmium, zinc, etc., and in practically every case in which the discharge was a spark-discharge, the oscillations took the same form as is shown in Figure 18.

When one of the terminals is carbon or magnesium, the current loops on one side of the time axis are of the pure arc form, while those on the other side are of the spark-discharge form.

If the terminals are dissimilar there is usually evidence of a rectifying effect. Particularly is this so if one terminal is of aluminum and the other of copper or iron. Cut *d* of Plate 7 shows this rectification.

The effect of hydrogen on the discharge is indicated by cuts *e* and *f* of Plate 7, which were taken under the same conditions except for the H surrounding the gap terminals in the case of cut *f*. The hydrogen serves, in this case, principally to ensure a spark rather than an arc discharge, and probably increases the damping.

The outward appearance of the discharge is in no way an indication as to whether the oscillogram takes the arc or spark form. The form of the oscillogram serves conveniently to differentiate between the pure arc and the spark discharges, when the terms arc and spark are applied to discharges operating on alternating currents. The discharge of the *Cu-Al* oscillation gap, which has been studied in this investigation, cannot, according to this definition, be called an arc, but is a spark discharge.

The photographs here shown of gap damping furnish in no way a complete discussion of the subject, but are presented to give additional proof of the existence of linear damping in a circuit containing a spark gap, and to show that there are two distinct forms of the oscillation trains according to the nature of the gap.

(7) *Notes Concerning the Mechanism of Conduction in the Cu-Al Gap.*

Very little can at present be given concerning the exact nature of the conduction which takes place in the gap under discussion and the office of the necessary hydrogen. No oscillations can be obtained unless the gap is immersed in some gas rich in hydrogen, but the latter alone gives by far the best results. In any case the gas must be moist. As was shown early in Part I, the absence of metallic vapor indicates that the conduction is probably affected entirely by the ionization of the surrounding gas. Since, as was also observed, the metal used for the anode makes little difference in the operation of the gap, and since aluminum is the only metal which works at all well as cathode, it is safe to say that it is the aluminum cathode, working in conjunction with the hydrogen, which gives the characteristic properties of the oscillation gap which has been partially studied in the foregoing pages. It might be mentioned here that magnesium acts to some extent as cathode, but, on account of its low vaporizing point, works very irregularly and unsatisfactorily. The discharge, in this case, is intensely green showing vaporization.

The fact that moisture in the hydrogen is necessary indicates that an oxidation of the aluminum plays some part in the operation. The necessity of an hydrogen atmosphere leads one to believe that perhaps a reduction of the ever present aluminum oxide film at some time during the cycle may take place, there possibly being a cyclic change of oxidation and reduction of the aluminum determined by the temperature at various instants during one primary discharge. For instance, it may be that some action such as follows takes place. At the beginning of the discharge, the thin oxide film makes necessary a high breaking-down potential in order to start a discharge. As soon, however, as the discharge is started, H ions are conveyed to the aluminum cathode, and, since the atmosphere about the terminal is H, reduce the oxide film. The free surface of the aluminum is thereby exposed, and the resistance drops to a low value. This reduction would be the greater the larger the current, and there would result the very rapid drop in resistance which is shown in the curves of Figure 16. As soon as the discharge stops the aluminum partially reoxidizes, thereby reëstablishing the initial high resistance.

It is probable that the regularity of the gap is partly due to the fact that the discharge takes place for some time at one definite point on the aluminum, this confinement of the discharge to one place resulting possibly from the protecting oxide film over the rest of the surface.

Part III.

Practical Considerations and Applications.

(1) *Practical Considerations.*

From a practical point of view interest centers on the question of the amount of power obtainable from the system. The gap is not a high-power generator of electrical oscillations; its advantages lie in simplicity and regularity. The conditions for maximum power were considered in Part I, and it was seen that the maximum power efficiently obtained from one gap at 100 meters wave length is about 40 to 45 watts. It is probable, although no extensive tests have yet been made, that the power obtainable is greater at longer wave lengths.

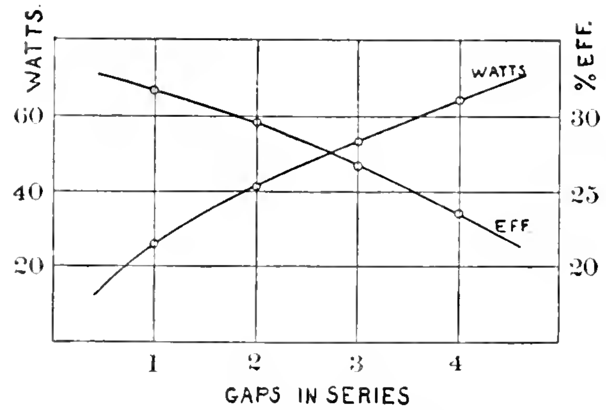

Figure 19. Gaps in Series.

If greater power is required, gaps can profitably be operated in series. Two gaps work perfectly and three gaps well on 500 volts, with much increased power output. Four gaps were satisfactorily run on 1000 volts, but in general there is a slight sacrifice of regularity of operation as the number of gaps in series is increased.

The amount of power obtained, when gaps are operated in series with a definite supply current, is not directly proportional to the number of gaps. When two gaps are operated in series, the power output is almost twice that from one gap. When more gaps are connected in series, the gain in power is much less, the greater the number of gaps the less the gain in power output.

The average voltage across one gap ranges from 90 to 150, but is, under most conditions, about 100. As the number of gaps in series is increased, the current being constant, the voltage across the series is practically proportional to the number of gaps.

The efficiency of the system, when gaps are operated in series, decreases as the number of gaps is increased.

The following table and the curves of Figure 19 give an idea of the result of increasing the number of gaps in series. The values of the efficiency and power may be somewhat misleading as the adjustments were not for conditions of maximum power and efficiency. The general shape of the curves, however, may prove of interest:

No. of Gaps.	I_0.	E.	R.	I. R.	Eff.
1	.55	145	15.9	25.5	32.5 %
2	.55	260	15.9	39.3	27.5
3	.55	360	15.9	55.0	27.0
4	.55	500	15.9	64.8	23.6

As was stated in Part I, a proper choice of dynamo permits the omission of the external resistance. The dynamo, for use in this manner must be characterized by a rapidly falling voltage-current curve in order that the voltage will increase if the discharge tends to stop. The high voltage on open circuit of a generator of this kind also serves automatically to start the gap or gaps.

(2) *Applications.*

Various applications of the continuous oscillations might well be spoken of, but reference will be made to only three, i. e.: the use of the oscillation system in conjunction with a Braun tube for demonstration; the calibration of a wave meter by means of harmonics; and wireless telegraphy and telephony.

The simplicity and convenience of the system as a generator of continuous high frequency oscillations render the apparatus particularly suitable for demonstration and laboratory use. Especially is the system of value when used in connection with a Braun tube, for, with such an equipment, many of the phenomena of electrical oscillations can be visualized, such as the damping due to resistance, the damping due to radiation in an antenna, etc.

As was pointed out in Part II, two secondary circuits of different periods can be caused to oscillate, the exact ratio of frequencies being given directly by the resulting Lissajou's figure. If, then, the period of one of the secondary circuits is fixed and accurately determined in some manner, the period of the second variable secondary circuit is given in terms of the first or standard. In this way, with proper adjustments, a large number of determined periods can be obtained, and an accurate calibration of a wave meter made.[12]

---

[12] Suggested by Professor G. W. Pierce.

The system can, of course, be readily used for wireless telegraphy provided some method such as a chopper be used for making audible the continuous transmission of power. One gap operating on from .5 to .8 ampere will undoubtedly transmit up to 70 miles with some advantages over the other systems. In addition to the advantages of high efficiency, one wave length, etc., is the great gain in simplicity and regularity, and the advantage of working directly on the commercial voltages for hours with no attention.

One of the most interesting applications of the aluminum-copper gap is its successful use in wireless telephony. Professor G. W. Pierce and the author have given the apparatus a thorough test in connection with wireless telephony, and have carried on conversations for several hours at a time between two distant stations with practically perfect articulation. The remarkable constancy and regularity of the system as a generator of continuous oscillations has been proved to be of great value for the wireless transmission of articulate speech. This will probably be the subject of a later communication.

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PLATE 1.

MOUNTING OF BRAUN TUBE.

a.

b.

Spectrum of Gap
with
Aluminum Comparison.
Spectrum.

c.

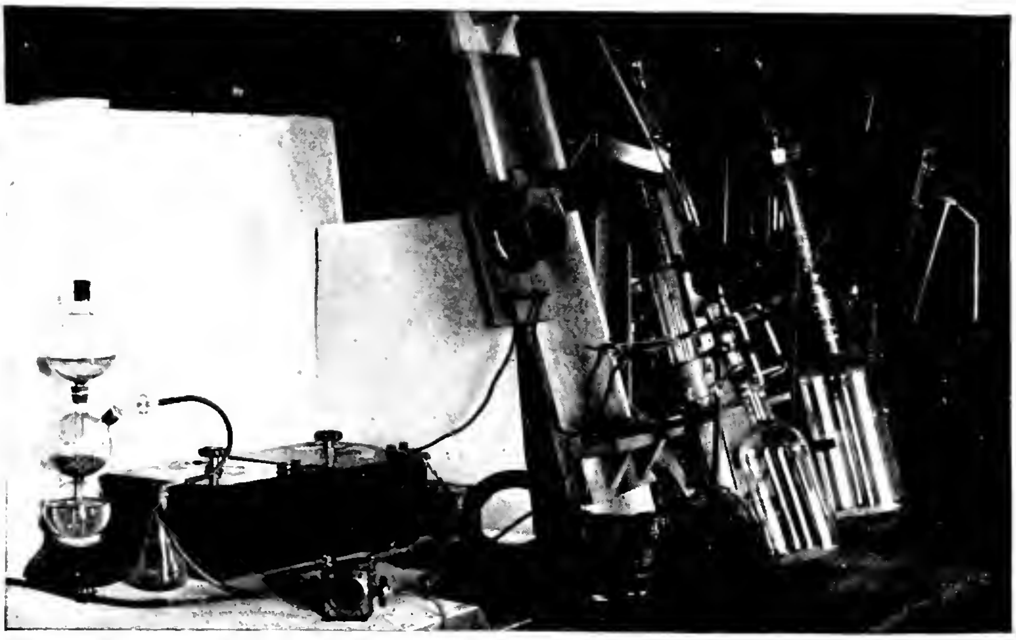
I_0 = .73 ampere.
λ_2 = 110 meters.
I. C. F. = 5.

d.

λ_2 = 118 meters.
λ_3 = 236 meters.
Ratio = 1:2.
I. C. F. = 4.

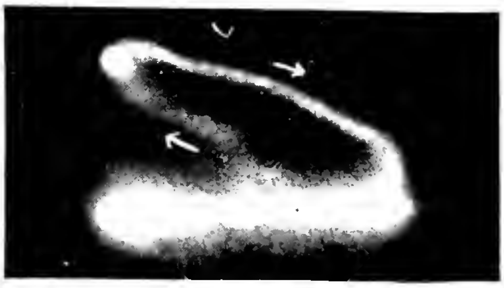
e.

λ_2 = 76 meters.
λ_3 = 114 meters.
Ratio = 2:3.
I. C. F. = 4.



a

b



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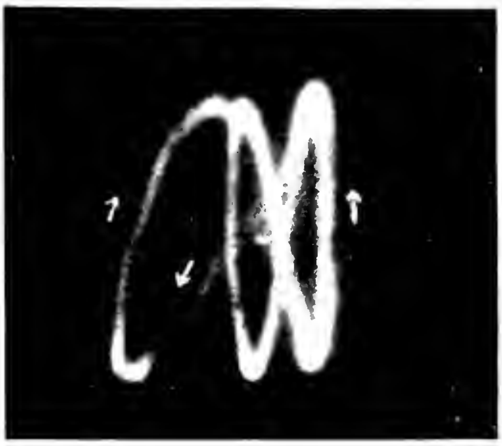


d

e

PLATE **2**.

Lissajou's Figures.

a.

$\lambda_2 = 80$ meters.
$\lambda_3 = 120$ meters.
Ratio 2:3.
$I.\ C.\ F. = 6$.
$I_0 = .65$ ampere.

b.

$\lambda_2 = 158$ meters.
$\lambda_3 = 474$ meters.
Ratio 1:3.
$I.\ C.\ F. = 3$.
$I_0 = 1$ ampere.

c.

$\lambda_2 = 173$ meters.
$\lambda_3 = 231$ meters.
Ratio = 3:4.

d.

$\lambda_2 = 180$ meters.
$\lambda_3 = 300$ meters.
Ratio = 3:5.

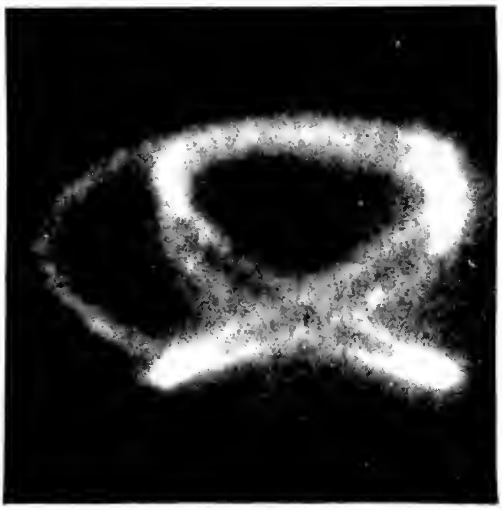
e.

$\lambda_2 = 200$ meters.
$\lambda_3 = 250$ meters.
Ratio = 4:5.

f.

$\lambda_2 = 180$ meters.
$\lambda_3 = 315$ meters.
Ratio = 4:7.

CHAFFEE.—IMPACT EXCITATION OF ELECTRIC OSCILLATIONS. PLATE 2.



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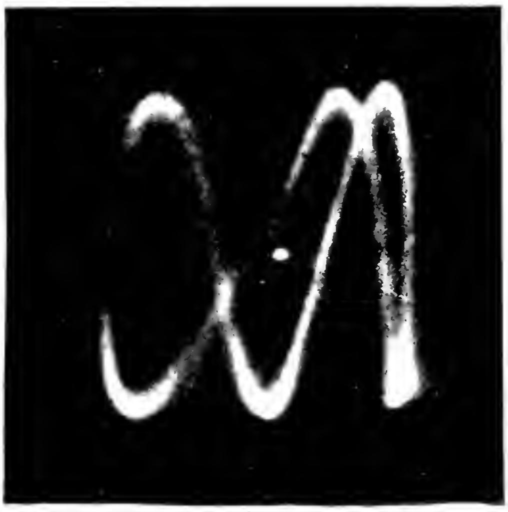

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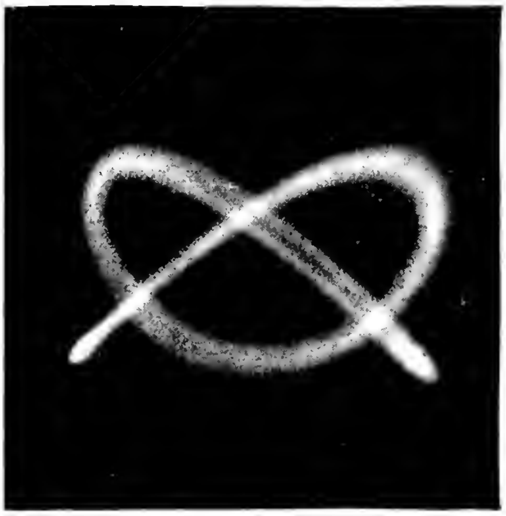

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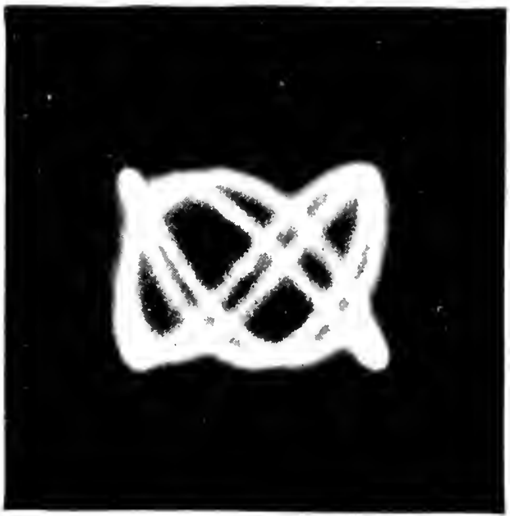

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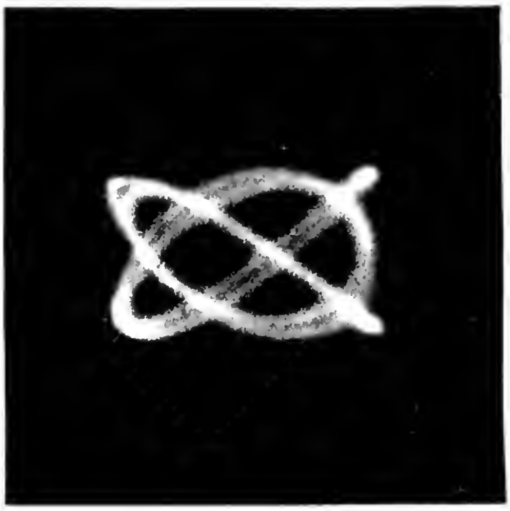

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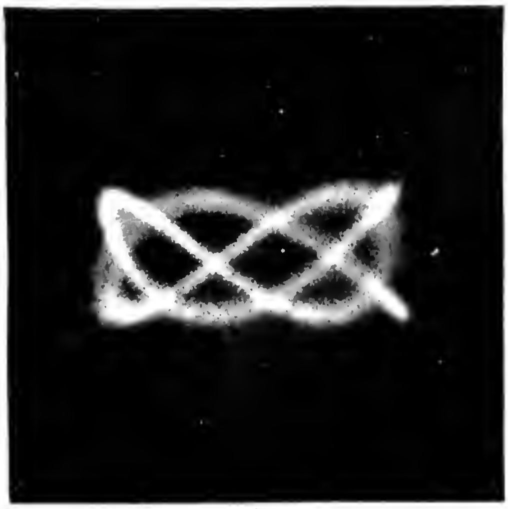

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PLATE **3**.

$E-I$ CHARACTERISTICS.

a. — *Very Long Gap.*

I_0 = .55 ampere.
1 cm. = 4.5 amperes (vertical).
2 cm. = 250 volts (horizontal).

b. — *Long Gap.*

I_0 = 1.0 ampere.
1 cm. = 4.25 amperes (vertical).
1 cm. = 250 volts (horizontal).

c. — *Short Gap.*

I_0 = .54 ampere.
1 cm. = 1.3 amperes (vertical).
1 cm. 230 volts (horizontal).

d. — *Very Short Gap.*

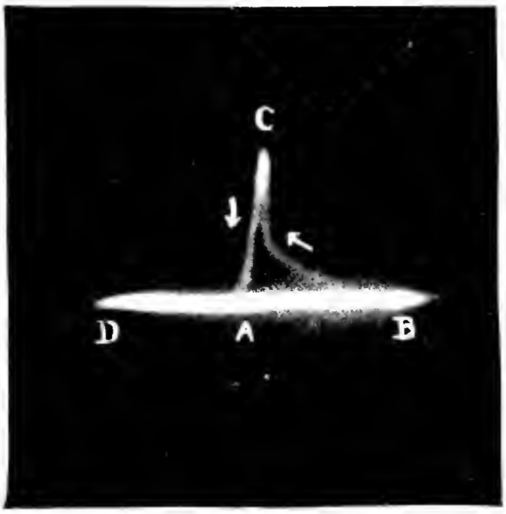
I_0 = 1.5 amperes.
1 cm. = 4.25 amperes (vertical).
1 cm. = 250 volts (horizontal).

e.

Cu-Al gap operating on oscillatory current. Characteristic of Glow Discharge shown at the end of the potential deflection.

f.

λ_2 = 268 meters.
I_0 = .5 ampere.



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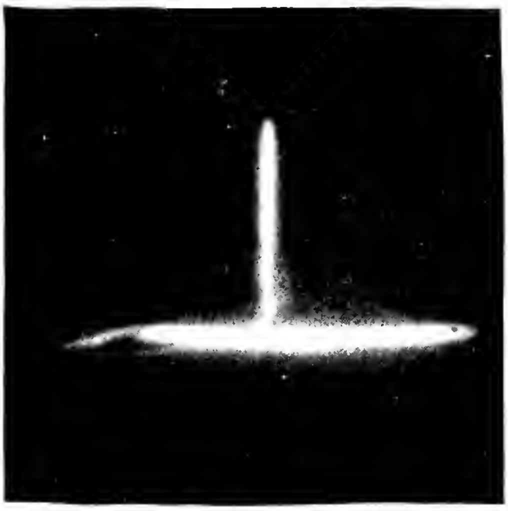
b



c

d

e

f

PLATE 4.

a.

λ_2 = 185 meters.
I_o = .85 ampere.
C_1 = 178 × 10^{-5} $\mu.f.$
$I. C. F.$ = 3.

b.

I_o = .68 ampere.
C_1 = 110 × 10^{-5} $\mu.f.$
$I. C. F.$ = 4.

c.

λ_2 = 180 meters.
I_o = .32 ampere.
$I. C. F.$ = 6.

d.

λ_2 = 78 meters.
I_o = .63 ampere.
$I. C. F.$ = 9.

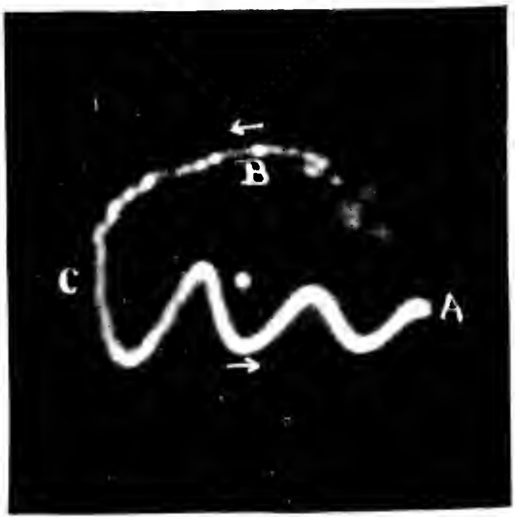
e.

λ_2 = 88 meters.
I_o = .4 ampere.
C_1 = 170 × 10^{-5} $\mu.f.$
$I. C. F.$ = 11.

f.

λ_2 = 65 meters.
I_o = .5 ampere.
$I. C. F.$ = 7.


a



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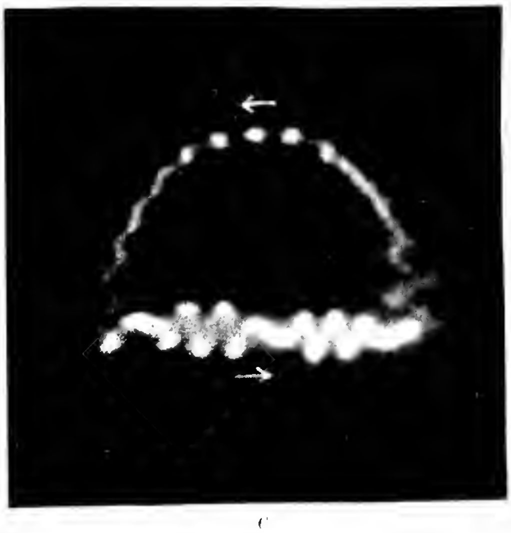
c


d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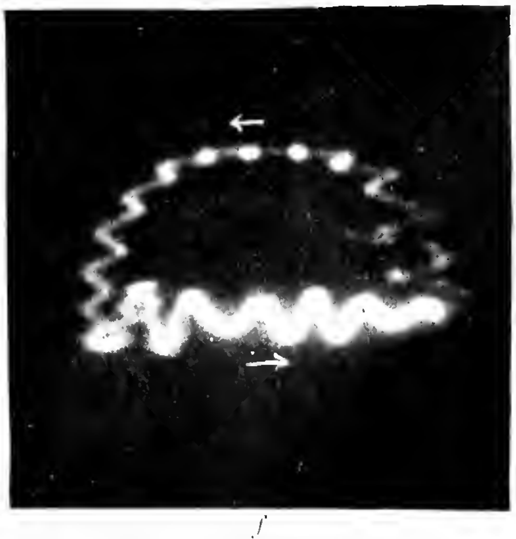
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PLATE 5.

RESISTANCE DAMPING AND BEATS

a.

$R_2 = 5.9$ ohms.
$\lambda_2 = 112$ meters.
$I_o = .35$ ampere.
$C_1 = 150 \times 10^{-5}\ \mu.f.$
$I.\ C.\ F. = 12.$

b.

$\lambda_2 = 400$ meters.

c.

$\lambda' = 154$ meters.
$\lambda = 325$ meters.

d.

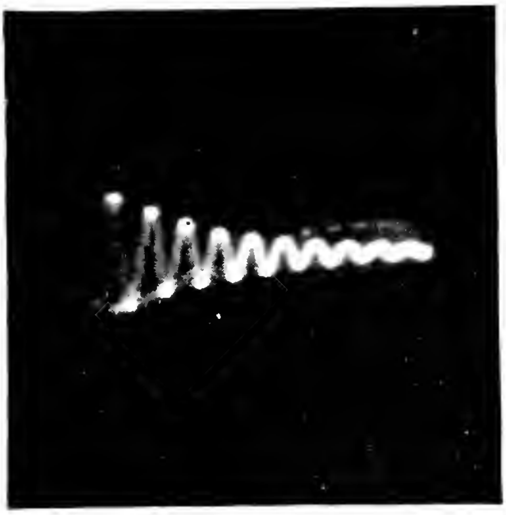
$I_o = .4$ ampere.
$\lambda' = 140$ meters.
$\lambda = 390.$
$R_2 = 6$ ohms.

e.

$\lambda = 370$ meters.
$\lambda' = 290$ meters.

f.

$\lambda = 215$ meters.
$\lambda' = 255$ meters.



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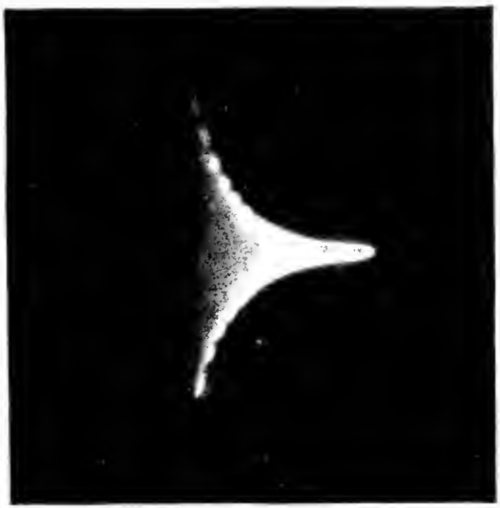

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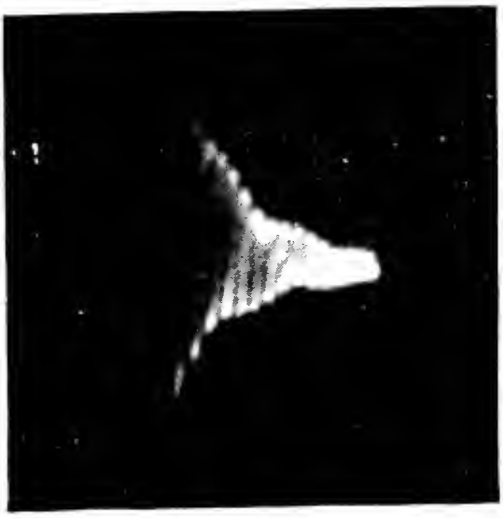

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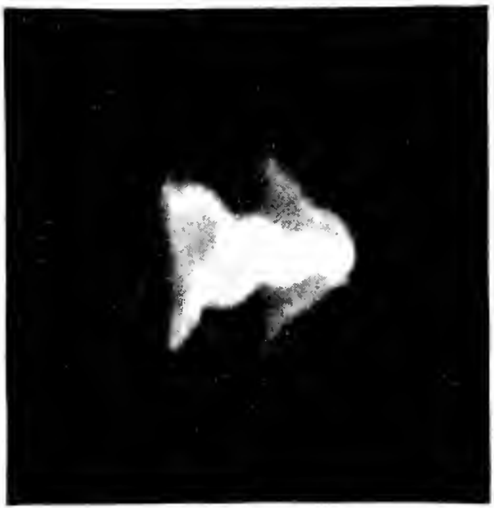

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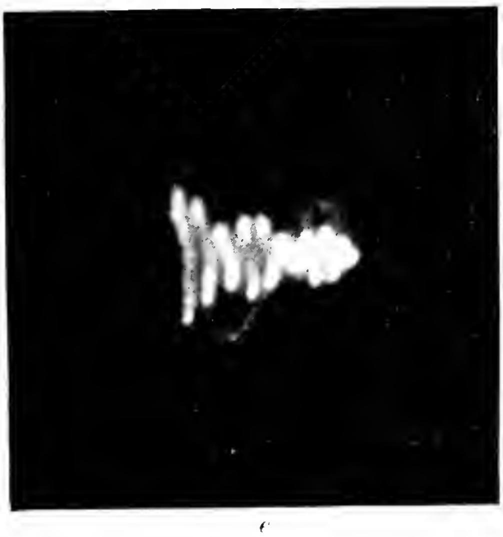

e

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PLATE 6.

GAP DAMPING OSCILLOGRAPHS.

a.
Beats.

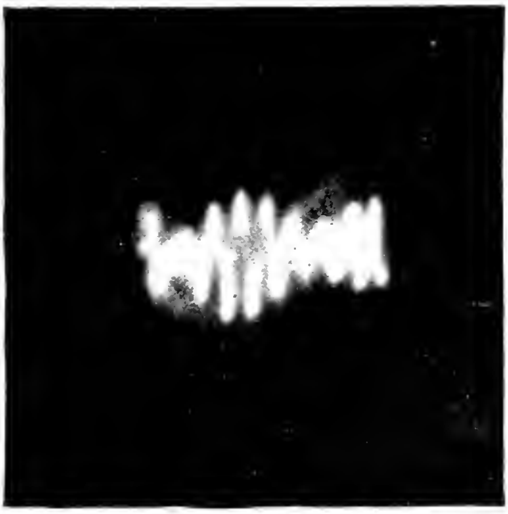
b. — *Al-Al in H.*
$\lambda = 520$ meters.
$I_0 = 1.2$ amperes.

c. — *Al-Al in Air.*
$\lambda = 525$ meters.
$I_0 = 1.2$ amperes.

d. — *Carbon-Carbon in Air.*
$\lambda = 525$ meters.
$I_0 = 1.4$ amperes.

e. — *Al-Al in Air.*
$\lambda = 575$ meters.
$I_0 = 1.5$ amperes.
Water cooled

f. — *Al-Al in H.*
$\lambda = 575$ meters.
$I_0 = 1.9$ amperes.
Water cooled.


a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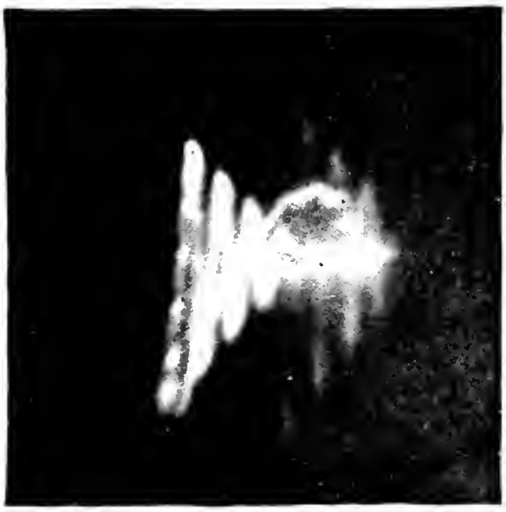
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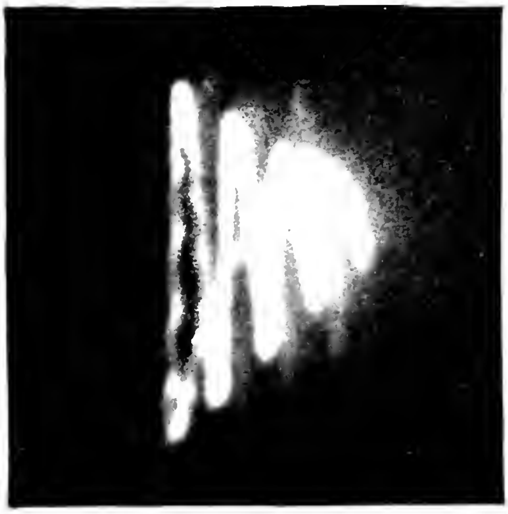
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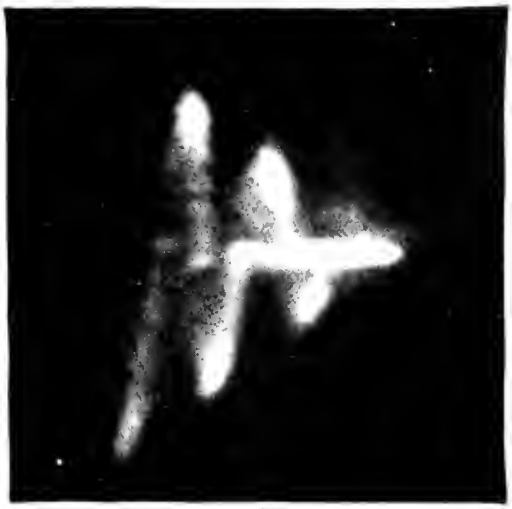
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PLATE 7.

GAP DAMPING.

a. — *Al-Al in Air.*
$\lambda = 525$.
Water cooled.

b. — *Al-Al in Air.*
$\lambda = 525$ meters.
Water cooled.

c. — *Al-Al in H.*
$\lambda = 525$ meters.
Water cooled.

d. — *Cu-Al in H.*
Shows rectification.

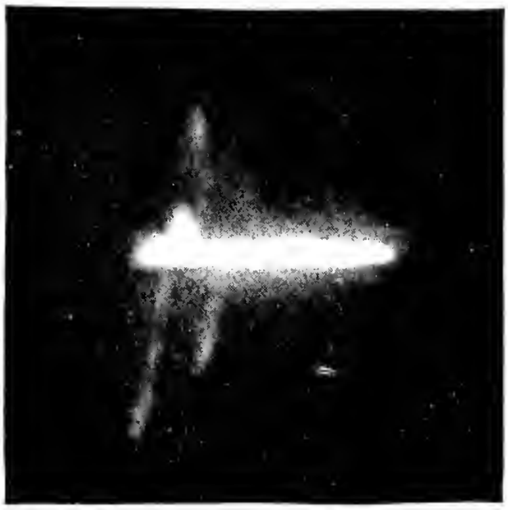
e. — *Al-Al Arc in Air.*
$\lambda = 525$ meters.
$I_a = 1.3$ amperes.

f.
Same as Figure 5, except hydrogen instead of air surrounded gap.

a

b

c



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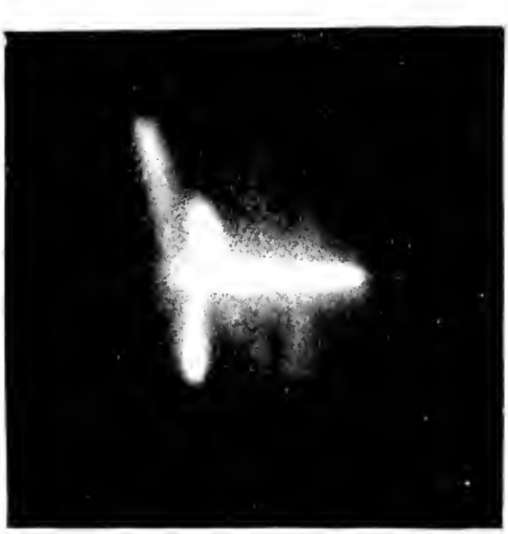

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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 10. — December, 1911.

THE WAVE POTENTIAL OF A CIRCULAR LINE OF SOURCES.

By A. G. Webster.

THE WAVE POTENTIAL OF A CIRCULAR LINE OF SOURCES.

By A. G. Webster.

Presented December 14, 1910. Received October 11, 1911.

The fundamental solution of the wave equation

$$\frac{\partial^2 \phi}{\partial t^2} = c^2 \Delta \phi, \tag{1}$$

obtained by putting $\phi = u e^{int}$, so that u satisfies

$$\Delta u + \kappa^2 u = 0, \tag{2}$$

and representing a source, is $u = e^{ikr}/r$ ($r =$ distance from source). Now we have Hankel's formula for an arbitrary function,

$$F(r) = \int_0^\infty \lambda d\lambda \int_0^\infty \rho d\rho\, F(\rho)\, J(\lambda\rho)\, J(\lambda r), \quad (J = J_0, \text{ Bessel's func.}) \tag{3}$$

and putting $\qquad F(r) \equiv e^{ikr}/r,$

$$\frac{e^{ikr}}{r} = \int_0^\infty \lambda d\lambda \int_0^\infty d\rho\, e^{ik\rho}\, J(\lambda\rho)\, J(\lambda r), \tag{4}$$

and since

$$\int_0^\infty d\rho\, e^{ik\rho}\, J(\lambda\rho) = \frac{1}{\sqrt{\lambda^2 - \kappa^2}}, \tag{5}$$

this gives

$$\frac{e^{ikr}}{r} = \int_0^\infty \frac{\lambda d\lambda\, J(\lambda r)}{\sqrt{\lambda^2 - \kappa^2}}. \tag{6}$$

If we now use r in a different sense as

$$r^2 = x^2 + y^2, \quad \text{while} \quad R^2 = x^2 + y^2 + z^2,$$

we easily obtain the solution

$$\frac{e^{ikR}}{R}=\int_0^\infty\frac{e^{-z\sqrt{\lambda^2-k^2}}\,\lambda J(\lambda r)\,d\lambda}{\sqrt{\lambda^2-\kappa^2}}\,. \tag{7}$$

This result was given by Sommerfeld, Ann. der Phys. 1909, Bd. 28, p. 683.

From this I obtain for a *ring* of sources of radius a,

$$u=\int_0^\infty\frac{e^{-z\sqrt{\lambda^2-k^2}}}{\sqrt{\lambda^2-\kappa^2}}\,\lambda\,J(\lambda r)\,J(\lambda\,a)\,d\lambda, \tag{8}$$

which reduces to (7) when $a=0$, and when $\kappa=0$, to

$$u=\int_0^\infty e^{-z\lambda}\,J(\lambda r)\,J(\lambda a)\,d\lambda, \tag{9}$$

the well-known expression for the Newtonian potential of a ring ; and when $r=0$, to

$$u(z)=\int_0^\infty\frac{e^{-z\sqrt{\lambda^2-\kappa^2}}}{\sqrt{\lambda^2-\kappa^2}}\lambda\,J(\lambda a)\,d\lambda, \tag{10}$$

which can be shown to be equal to

$$e^{i\kappa\sqrt{z^2+a^2}}/\sqrt{z^2+a^2},$$

the correct expression for points on the axis of symmetry.

Now since

$$J(\lambda r)=\frac{1}{\pi}\int_0^\pi e^{i\lambda r\cos\omega}\,d\omega, \tag{11}$$

we have

$$\begin{aligned}u&=\int_0^\infty\frac{e^{-z\sqrt{\lambda^2-\kappa^2}}}{\sqrt{\lambda^2-\kappa^2}}\,\lambda J(\lambda r)\,J(\lambda a)\,d\lambda\\&=\frac{1}{\pi}\int_0^\infty\int_0^\pi\int_0^\pi d\vartheta d\omega e^{i\lambda(r\cos\omega+a\cos b)-z\sqrt{\lambda^2-\kappa^2}}\,.\,\frac{\lambda d\lambda}{\sqrt{\lambda^2-\kappa^2}}.\end{aligned} \tag{12}$$

We will divide this into two parts, the integrals from 0 to κ, and κ to ∞. Putting now

$$\lambda=\kappa\sin\phi,\quad\sqrt{\lambda^2-\kappa^2}=i\kappa\cos\phi,\quad d\lambda=\kappa\cos\phi\,d\phi,$$

$$A = \int_0^\kappa e^{-z\sqrt{\lambda^2-\kappa^2}} \frac{\lambda J(\lambda r)}{\sqrt{\lambda^2-\kappa^2}} J(\lambda a)\, d\lambda$$

$$= \frac{-i\kappa}{\pi^2}\int_0^\pi\int_0^\pi d\theta\, d\omega \int_0^{\pi/2} e^{i\kappa[(r\cos\omega + a\cos\theta)\sin\phi - z\cos\phi]}\cdot \sin\phi\, d\phi, \qquad (13)$$

and developing the exponential,

$$= \frac{-i\kappa}{\pi^2}\int_0^\pi\int_0^\pi d\theta\, d\omega \int_0^{\pi/2} \sum_0^\infty \frac{1}{s!}\{i\kappa[(r\cos\omega + a\cos\theta)\sin\phi - z\cos\phi]\}^s \cdot \sin\phi\, d\phi.$$

Developing by the polynomial theorem,

$$= \frac{-i\kappa}{\pi^2}\int_0^{\pi/2}\sin\phi\, d\phi \int_0^\pi\int_0^\pi d\theta\, d\omega \sum_{s=0}^{s=\infty}\sum_{l,m,n}^{l+m+n=s} \frac{(i\kappa)^s (r\cos\omega\sin\phi)^l (a\cos\theta\sin\phi)^m (-z\cos\phi)^n}{l!\; m!\; n!}.$$

Integrating according to θ and ω, the odd powers vanish, and

$$A = -i\kappa\sum_0^\infty\sum_0^\infty\sum_0^\infty \frac{(i\kappa)^{2(l+m)+n}\, r^{2l}}{(2l)!\,(2m)!\,n!}\, \frac{1\cdot3\cdot5\ldots(2l-1)a^{2m}1\cdot3\cdot5(2m-1)(-z)^n}{2\cdot4\cdot6\ldots 2l\cdot2\cdot4\cdot6\ldots 2m} \times \int_0^{\pi/2} \sin\phi^{2(l+m)+1}\cos^n\phi\, d\phi, \qquad (14)$$

$$= -i\kappa\sum_0^\infty\sum_0^\infty\sum_0^\infty (i\kappa)^{2(l+m)+n} \frac{r^{2l}a^{2m}}{(2\cdot4\cdot6\ldots 2l)^2(2\cdot4\cdot6\ldots 2m)^2} \times \frac{(-z)^n(l+m)!\,\Gamma\left(\frac{n+1}{2}\right)}{n!\,2\Gamma\left(\frac{2(l+m)+n+1}{2}+1\right)}, \qquad (15)$$

$$A = -i\kappa\sum_0^\infty\sum_0^\infty\sum_0^\infty \frac{(i\kappa)^{2(l+m)+n}(l+m)!\, r^{2l}a^{2m}(-z)^n}{2^{l+m}(l!)^2(m!)^2 n!(n+1)(n+3)\ldots[n+2(l+m)+1]}. \qquad (16)$$

In order to obtain the real part we will proceed differently.

$$B = \int_\kappa^\infty e^{-z\sqrt{\lambda^2-\kappa^2}} \frac{\lambda}{\sqrt{\lambda^2-\kappa^2}} J(\lambda r)\, J(\lambda a)\, d\lambda, \qquad (17)$$

and putting

$$\lambda^2 - \kappa^2 = \kappa^2 t^2, \qquad \frac{\lambda d\lambda}{\sqrt{\lambda^2 - \kappa^2}} = \kappa dt,$$

$$B = \kappa \int_0^\infty e^{-\kappa z t} J(\kappa r \sqrt{1 + t^2})\, J(\kappa a \sqrt{1 + t^2})\, dt, \tag{18}$$

which by means of the formula

$$J(\alpha x)\, J(\beta x) = \sum_0^\infty \sum_0^\infty \frac{(-1)^s \alpha^{2(s-p)} \beta^{2p} \left(\frac{x}{2}\right)^{2s}}{(p\,!)^2\, [(s-p)\,!]^2} \tag{19}$$

becomes

$$B = \kappa \int_0^\infty \sum_{s=0}^{\infty} \sum_{p=0}^{p=s} e^{-\kappa z t} \frac{(-1)^s (\kappa r)^{2(s-p)} (\kappa a)^{2p} (1 + t^2)^s dt}{2^{2s} [p\,!\,(s-p)\,!]^2}$$

$$= \kappa \sum_{s=0}^{s=\infty} \sum_{p=0}^{p=s} \sum_{q=0}^{q=s} \frac{(-1)^s (\kappa r)^{2(s-p)} (\kappa a)^{2p}}{2^{2s} [p\,!\,(s-p)\,!]^2} \frac{s\,!}{q\,!\,(s-q)\,!} \int_0^\infty t^{2q} e^{-\kappa z t} dt$$

$$= \kappa \sum_{l=0}^{l=\infty} \sum_{m=0}^{m=\infty} \sum_{n=0}^{n=\infty} \frac{(-1)^{l+m} \kappa^{2(l+m-n)-1} r^{2l} a^{2m} (l+m)\,!\,(2n)\,!}{2^{2(l+m)} (l\,!\,m\,!)^2\, n\,!\,(l+m-n)\,!\, z^{2n+1}}. \tag{20}$$

$$u = \sum_{l=0}^{l=\infty} \sum_{m=0}^{m=\infty} \frac{(-1)^{l+m} \kappa^{2(l+m)} (l+m)\,!\, r^{2l} a^{2m}}{2^{l+m} (l\,!\,m\,!)^2} \sum_{n=0}^{n=\infty}$$

$$\left(\frac{-(i\kappa)^{n+1} (-z)^n}{n\,!\,(n+1)(n+3) \ldots [n + 2(l+m) + 1]} + \frac{(2n)\,!}{2^{l+m}\, n\,!\,(l+m-n)\,!\, z^{2n+1}} \right).$$

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 11. — December, 1911.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

THE MEASUREMENT OF HYDROSTATIC PRESSURES UP TO 20,000 KILOGRAMS PER SQUARE CENTIMETER.

By P. W. Bridgman.

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Presented by G. W. Pierce, October 11, 1911. Received October 6, 1911.

In these Proceedings, Vol. XLV, Numbers 8 and 9, 1909, two methods of measuring hydrostatic pressures were described and applied up to 6800 kgm./cm.^{2}. The first method was by means of an absolute gauge of the freely moving piston type; the second method depended ultimately on the first, and utilized the change in the electrical resistance of mercury under pressure. The pressure reached with these two forms of gauge was higher than the highest previous accurately measured pressures, which extended to only 3000 or 4000 kgm./cm.^{2}; but since the earlier paper, the region of attainable and measurable pressures has been still further extended to over 20,000 kgm., so that a re-examination of the gauges there proposed became necessary. Both of the previous methods were found to become inapplicable at pressures much higher than 6800 kgm., the first because of the yielding of the steel of the gauge and the second because of the freezing of the mercury. In this paper the modifications of these two methods are described with which it has been found possible to reach these higher pressures. The freely moving piston gauge has been changed in design so that it has been possible to reach 13,000 kgm., and has been provided with a different reading device. The second method, involving the change in resistance of mercury, has been replaced by another method using the change in resistance of manganin wire. With this an indicated pressure of 20,670 kgm. has been reached. This paper is occupied with a discussion of the calibration, the corrections, and the details of manipulation of these gauges.

The Absolute Gauge.

The novel features of the gauge described in the previous paper which made it possible to more than double the pressure range of

Amagat were the smallness of the piston exposed to pressure (1/16 inch), and the fact that the pressure cylinder in which this piston moved was exposed to pressure on the external as well as on the internal surface, so that the effect of the increasing pressure was to decrease the internal bore of the cylinder and so decrease the leak. The application of pressure to the outside of the cylinder was made through the medium of the packing.[1] The figure referred to shows that the disposition of the packing was such that the cylinder was exposed externally to pressure over the lower end, and to none at all over the upper. At high pressures the effect of such an arrangement is invariably to pinch off the cylinder, the packing forcing its way into the cylinder and separating the upper from the lower end. Two things are necessary to produce this effect: external pressure and non-support of one of the ends. The action is similar to that of a roll of putty which, when squeezed in the hand, will ooze out sidewise if the ends of the roll are left free, but may be prevented by compressing the ends of the roll between the fingers of the other hand.

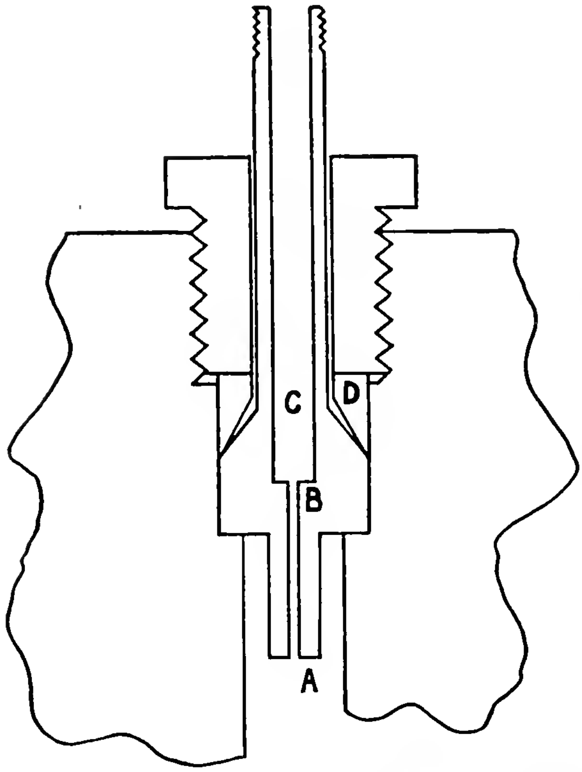

FIGURE 1. The absolute gauge; shows the cylinder of the gauge and the method of mounting it in the containing vessel.

In the new form of gauge the two novel features, smallness of piston and a cylinder exposed to pressure on the outside, have been retained, but the manner of applying the packing has been so changed as to avoid the pinching-off effect. The new gauge is shown in Figure 1. The cylinder AB is placed lower down than in the former gauge, so that now it is in the part of the metal subjected to hydrostatic pressure only. The packing, which now takes the form of a cone of soft steel, D, is placed above the upper end of the cylinder. This new form

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[1] See Figure 2, p. 205, loc. cit.

gains at three points. The soft steel packing, which takes the place of the rubber, does not transmit pressure hydrostatically and so exerts a smaller pinching-off effect; the cylinder is made of hardened nickel steel instead of tool steel, so that it has a higher yield point and more effectively resists what pinching-off effect there is; and the cylinder itself, which is the only vital part, is placed entirely beyond the reach of this effect. Even in this form, however, the soft steel packing does flow sufficiently to produce the beginning of the effect. After the application of the maximum pressure the bore at C showed a very marked decrease. But since nothing depends on the size of the bore at C, no inaccuracy is introduced.

This form gives up one advantage claimed for the former gauge, namely, that by changing the area over which the packing is distributed it becomes possible to some extent to control the distortion of the cylinder and so the leak. But this question of leak proved of much less importance than was anticipated, it being possible to range from 0 to 13,500 kgm. without inconvenient leak at any point. The leak does, however, as anticipated, become less at higher pressures, partly because of closing up of the crack, so that some sort of control of the leak would become necessary if the crack should ever close up completely. But it has been found possible with the present form of gauge to provide an effective control of leak by providing for the highest pressures a piston slightly smaller than normal. This is evidently easier than to attempt so to design the gauge that the adaptability for different pressures should be secured by changing the packing. The need for even this procedure of changing the piston would probably be slight in practise, for as already stated, one piston sufficed up to 13,500 kgm., and the gauge itself would probably not stand much more.

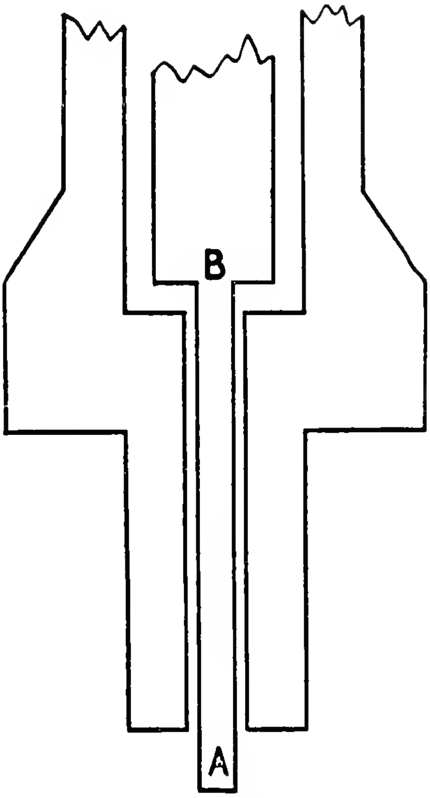

FIGURE 2. The absolute gauge; shows enlarged detail of the cylinder and the piston.

It is evident that the new form given the gauge makes necessary a recomputation of the correction for distortion. The effect of this distortion is to change the effective area of the piston and so to change the total thrust exerted on the piston by a given hydrostatic pressure. As previously explained, this correction is calculated mathematically and is merely a rough approximation. Its justification is that the correction is in any event exceedingly small, and that no easy experimental method of determining it directly presents itself. The correction is to be made by finding the change in the mean area of the cylinder and the piston at the lower and the upper ends, and taking the mean of these two changes. This gives the change in the effective area of the cross-section as was proved in the former paper.

The stress system on the piston and cylinder is as follows. On the piston there is the longitudinal thrust produced by the action of hydrostatic pressure on the end at A, and the equal and opposite thrust of the equilibrating forces at B. This thrust is uniform throughout the length of the piston. In addition there is the normal pressure on the curved surface exerted by the liquid which is slowly flowing out through the crack between piston and cylinder. At A this pressure is equal to the total hydrostatic pressure, and regularly decreases from here outward to zero at B. On the cylinder there is externally a uniform hydrostatic pressure over nearly the entire length; internally the same distribution of pressure as acts on the piston. At the inner end A the resultant of these two systems of stress is effectively a uniform hydrostatic pressure on both piston and cylinder, under which both shrink uniformly. If r and R are the radii of piston and cylinder initially, and r' and R' the corresponding values under pressure, we have evidently:

At the lower end $$r' = r\left(1 - \frac{pk}{3}\right)$$

$$R' = R\left(1 - \frac{pk}{3}\right).$$

New effective radius $$= \frac{r' + R'}{2} = \frac{r + R}{2}\left(1 - \frac{pk}{3}\right).$$

Effective area changed by $$-\frac{2pk}{3}$$

$$= -4 \times 10^{-7} \times p$$

$$\left[\begin{array}{l} p \text{ is pressure in kgm./cm.}^2 \\ k = \text{compressibility} = 6 \times 10^{-7} \end{array}\right]$$

At the end B, the piston is exposed merely to the thrust p. It will be assumed that the strain is the same as that under a thrust p uniform throughout the entire length.

Then at B
$$r' = r\left(1 + \frac{p\sigma}{E}\right)$$
$$= r\,(1 + 1.4 \times 10^{-7} \times p),$$
where σ is Poisson's ratio, assumed $= 0.28$, and $E =$ Young's modulus, taken as 2×10^6 kgm./cm.^{2}.

This correction for the distortion of the piston is not open to serious question, because of the smallness of the diameter compared with the length. But the calculation of the distortion of the cylinder at the upper end is open to much more serious question, because the irregular shape and unknown action of the packing produce an unknown stress system in the mass of metal about the upper end. In place, then, of a calculation, the experimental fact was used that in all probability the crack between piston and cylinder would not completely disappear at less than 15,000 kgm., since the piston still possessed some freedom of motion at 13,000. Discussion of this experimental fact is given later. It will be assumed, then, simply that the distortion is proportional to the pressure, and that the combined distortion of cylinder and piston will produce complete closing at 15,000. The initial size of the crack was determined experimentally, by measuring the piston and the effective area, to be 0.00035 inch.

This gives at the upper end $R' = R\,(1 - ap)$.

When the crack closes $r' = R'$

or $$r\,(1 + 1.4 \times 10^{-7} \times p) = (r + 0.00035)\;(1 - ap).$$

Substituting $$r = 1/16,$$

we find $$a = 2.3 \times 10^{-7}.$$

At B $$R' = R\,(1 - 2.3 \times 10^{-7} \times p).$$

Whence $$r' + R' = r + R + \frac{r+R}{2}\,[(1.4 - 2.3) \times 10^{-7} \times p].$$

Effective radius, $$\frac{r' + R'}{2} = \frac{r+R}{2}\,(1 - 0.45 \times 10^{-7} \times p).$$

Effective area decreased by $0.90 \times 10^{-7} \times p$.

The average change of effective area, top and bottom, which is the correction desired, is therefore $- 2.4 \times 10^{-7} \times p$.

The correction found in this way is to be regarded as an upper limit, the assumption being made that the crack will close up at 15,000 kgm. The correction found by this assumption is somewhat doubtful. A lower limit to the correction can be found by making the assumption as far removed as possible from that made above, namely, that at the upper end the cylinder suffers no change of internal radius. The change of effective area at the upper end is due to enlarging of the piston alone, therefore, and is evidently $1.4 \times 10^{-7} \times p$. In this case the change in the effective area is $1.3 \times 10^{-7} \times p$. The upper and the lower limits differ only 1/10 per cent at 10,000 kgm. The correction applied in the following work was taken as the mean of these two limits, $1.8 \times 10^{-7} \times p$, and the observed gauge readings have been increased in this ratio. This happens to be the same as the correction used for the former gauge.

The experimental evidence used in part of the above approximations requires brief mention. The calculations given above show a more rapid closing of the crack at the end B, so that the tendency of the piston would be to bind at the upper end. This was verified experimentally by the fact that the upper end of the piston was always more brightly polished after a little use than the lower end, and that sticking could be avoided at the higher pressures by making the piston slightly conical. To accomplish this it was sufficient to make the upper end 0.0002 inch less in diameter than the lower. The figure above for the initial width of the crack at the upper end (0.00035 inch) was obtained by combining with the conicality the measured value for the effective area to be described later.

In actual use care was necessary to be sure that the sticking was really due to closing of the crack, and not to viscosity in the fluid transmitting pressure. In the early experiments, in which the transmitting fluid was molasses and glycerine, almost complete sticking was found at pressures as low as 7500. That this was not due to closing of the crack was shown simply by warming the whole apparatus, thus decreasing the viscosity without materially decreasing the size of the crack. It was thus possible to reach 13,000 with very much less sticking than at 7800 at the lower temperature, and also with much less leak, showing an actual decrease in the size of the crack at high pressures. The liquid finally adopted for use in this work was a mixture of glucose with glycerine and water. Glycerine and water were first mixed in equal parts, and then the glucose thinned with this mixture to a best consistency found by experiment. The advantage is that the pressure effect on viscosity is much less than for the molasses and glycerine mixture, so that a mixture of given consistency will work over twice the pressure range of the molasses mixture.

The functioning of the gauge at high pressures is therefore prevented by two effects, — increased viscosity of the liquid, and closing of the crack. In view of the fact that the gauge still worked at 13,500 when both these effects were operative, the estimate made above that the functioning would cease at 15,000 by the closing of the crack only would seem to be amply low. The maximum value set on the correction above is probably, therefore, too high.

The calibration of the piston and cylinder at low pressures to determine the effective cross-section was carried out by the method used in the previous paper. Some such indirect method of calibration was made necessary by the fact that the dimensions of the small piston are so small as to make accurate direct measurements of its effective diameter impossible. The method consisted in hanging weights on the piston to be calibrated and on a larger piston of known area, in such a proportion that the pressure produced by the two pistons should be the same. This is done most simply by connecting the two freely moving pistons to the same pressure chamber, keeping the weights on one piston invariable, and changing those on the other until neither rises or falls. The details of the method were the same as that described before, the same comparison piece of apparatus being used.

The results of the comparison showed an effective diameter for the piston of 0.06250 inches. The measured diameter was only 0.0623 inches at the larger end and 0.0622 inches at the center, showing a crack between piston and cylinder 0.0003 inches wide at the center, 0.00025 inches at the lower end, and 0.00035 inches at the upper end, as used in the calculation above.

In the earlier measurement of high pressures, the thrust was found by hanging weights directly on the piston, and determining by trial that weight which produced neither rise nor fall of the piston. This has the advantage of ideal accuracy, but has several serious disadvantages of manipulation. Flexibility of design in the apparatus is sacrificed because the gauge must be kept vertical. The scale pan and weights become increasingly cumbersome at high pressures, so that an assistant is needed. And worst of all, it requires considerable time to make a reading. This is a fatal objection where the pressure must be read instantaneously, as in experiments to be described in a following paper on the freezing of mercury by the method of electrical resistance.

The present gauge was made direct reading and instantaneous by causing the thrust to produce a measurable deflection in a stiff spring. The new process is related to the old exactly as weighing with a spring balance is to weighing with separate weights. The spring balance is less accurate, but very much more convenient. The accuracy obtainable with the new device was, however, sufficient for all requirements. There is an added advantage in that the stroke of the piston over the entire pressure range may be very much decreased. The stroke of 12 mm. in the previous work was reduced to 1.5 mm. in this form. This ensures greater strength at the upper end where the piston projects unsupported from the cylinder, and also ensures greater accuracy, the piston always playing in approximately the same part of the cylinder.

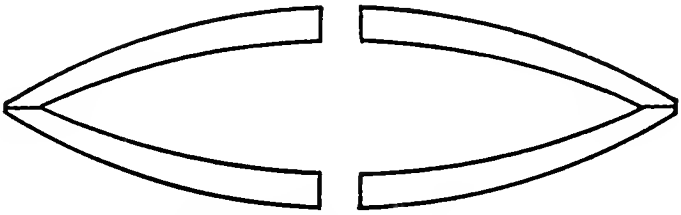

FIGURE 3. The springs with which the thrust on the piston is measured.

Several forms of spring were tried. The form finally adopted as giving the great stiffness desired without inconvenient bulk was that of a saucer. Two of these saucer-shaped springs were used, placed rim to rim, and the thrust applied at the center (see Figure 3). This arrangement has the advantage of avoiding all friction when the circumference of the saucer increases under pressure, since here the two saucers support each other and move together without slipping.

The choice of steel is of great importance. The most suitable of the many kinds tried was one manufactured by the Halcomb Steel Co. in the form of sheets.

Much experimentation was necessary before the best dimensions and the best heat treatment of the springs was found. The sheet from which the springs were cut was 0.105 inches thick. This was cut into discs 2 1/2 inches in diameter, with a 1/4-inch hole through the center. The disc was then turned on one flat face so as to decrease regularly from 0.105 inches at the center to 0.035 inches at the edge. It was given the saucer shape in a die while hot, the depression at the center being about 1/4 inch. The greatest care was necessary in hardening to prevent warping. This was conveniently done by heating to a bright red heat in a bath of molten lead so as to secure a uniform heat, and then quenching by plunging edgewise into water. The temper was drawn by heating to 370° C. in oil. The temperature was important: 360° C. was too low. Finally, after tempering, the springs were ground flat on the edge to provide a bearing surface against each other. Warping due to hardening was most distinctly shown by variations in the width of the ground strip. A pair of springs so made will support indefinitely at the center a weight of 1350 pounds without permanent set. The deflection under this load is 2 or 3 mm. The actual working pressure did not exceed 650 lbs.

The small motion of the springs was magnified by a simple mirror device, and observed with a telescope and scale rigidly attached to the frame holding the springs. The scale distance was only 30 cm., but it was nevertheless possible to obtain a magnification of over 1500 times with perfect consistency and freedom from back lash or tremor. The magnification was doubled by reflecting twice from the moving mirror. The size of the piston, sensitiveness of the springs, and optical magnification were altogether such that 8 kgm./cm.^{2} on the gauge produced a deflection of 0.1 mm. at the observing telescope. This gives 1/10 per cent as the accuracy of the pressure readings at 8000 kgm./cm.^{2}; proportionally more at the higher pressures.

All of the parts connecting together the springs and the mirrors were made of steel. This has the advantage of avoiding any motion of the mirrors which might be produced by changes of temperature of the surrounding atmosphere. The only temperature effect is that due to the change in the elastic constants of the steel spring with variations of temperature. This was so small that no appreciable error is introduced under the ordinary conditions of use.

Any device for measuring the magnitude of a stress by the deflection of a spring must be subjected to pretty careful scrutiny before the measurements can be accepted as accurate, because there are disturbing effects, such as elastic after-working and hysteresis, which complicate matters. It was hoped to reduce these effects to a negligible value by using as the working stress less than half the stress at the elastic limit as mentioned above. But even with this precaution it seemed desirable to calibrate carefully the springs under working conditions.

In order to facilitate the comparison, the springs, multiplying mechanism, and telescope and scale were rigidly connected in one piece. This could be screwed either to the end of the absolute gauge for the purpose of measuring the thrust on the piston, or to the calibrating device. The calibration was effected at first by hanging weights on a stirrup, but this process, always discontinuous and sometimes as complicated as applying two, removing one, applying two, etc., was so unlike the process of loading during actual use that another method was seen to be necessary. Two freely moving pistons were used, as when finding the area of the 1/16-inch piston, both communicating with a Cailletet pressure pump of the Société Genevoise. One piston, 1/4 inch in diameter, was the same as that used in the previous work. Weights were suspended directly from the upper end of this piston. This piston was kept in constant rotation by a small motor so as to avoid friction. The other freely moving piston, 5/16 inch in diameter, was in direct hydrostatic communication with the 1/4-inch piston, and at its upper end pressed directly against the springs to be calibrated. (This 5/16-inch piston could be rotated by hand as occasion required to destroy friction.) From the weight on the 1/4-inch piston, and the areas of the 1/4-inch and the 5/16-inch pistons, the thrust on the springs could be calculated. The area of the 5/16-inch piston was found in the same way as that of the 1/16-inch piston. The method has all the advantages of the discarded method of the direct application of weights, namely, complete freedom from all elastic effects and hysteresis, and in addition permits very much more convenient and flexible application of pressure.

The procedure of the calibration was to place a weight on the 1/4-inch piston, completely depressing it. The piston was then floated again by raising the pressure to the equilibrium value with the Cailletet pump. The 5/16-inch piston was then rotated to destroy friction, and the deflection of the spring read. Eleven such steps were made with increasing and decreasing pressure, making twenty-two steps in all. The same weights were used in all the calibrations, so that the results were strictly comparable. The pressure exerted by the fluid, as given by the gauge of the Geneva pump, was also recorded as a check. The accuracy of the other readings was so great, however, that these check readings could never be used.

Calibration with this device was first made to find whether the gauge had any error of position, since it was generally calibrated vertically, but used horizontally. This could evidently be done very simply by changing the position of the cylinder with the 5/16-inch piston, a change in the calibrating procedure which could not be made so simply when weights were directly applied. The result of the calibration in the horizontal position showed no detectable error due to this change of position. Of course no such error was to be expected, since all the parts were very stiff in comparison with their weights.

A second result of the calibration was that the springs show no elastic after-effects. By this is meant the gradual creep after application of a load, and gradual recovery after removal. The effect is generally most pronounced at the two ends of the pressure range. These springs, however, showed no tendency to yield viscously under the maximum stress, and never showed any wandering of the zero after release of pressure.

A third result of the calibration was that the springs do not follow the linear law, but are increasingly deflected at the higher pressures. The change was not large, but perfectly distinct, about 6 per cent less weight being required to produce a given deflection at 650 lbs. than initially. This is rather surprising in a substance like this spring steel, which ordinarily follows the linear law to the elastic limit. The effect is evidently due here to the change of geometrical shape, the springs becoming so much flatter under the higher stresses that the geometrical configuration as such has a lower elastic constant, although the elastic constant of the material itself is unaltered. It is customary in the mathematical treatment of the bending of thin rods or plates to assume that the deflection remains proportional to the stress up to the elastic limit. This experiment shows that this approximation may become invalid at considerably less than the elastic limit.

TABLE I.

Relation between Load and Deflection of Springs without Device for Avoiding Hysteresis.

Load Kgm.	Mirror Deflection.		Load Kgm.	Mirror Deflection.	
	Increasing Load.	Decreasing Load.		Increasing Load.	Decreasing Load.
00.00	0.00	0.00	95.62	8.52	8.64
16.26	1.42	1.49	112.27	10.06	10.18
33.37	2.94	3.02	128.27	11.55	11.66
49.35	4.35	4.45	143.32	12.97	13.07
65.54	5.81	5.91	160.18	14.57	14.64
81.59	7.24	7.36	173.85	15.90	

A fourth result was that the gauge does show some hysteresis, a result which was not expected in view of the second result. For as a general rule, hysteresis and elastic after-effects, while not directly related, occur together, both being evidence of some molecular instability. Table I., giving the difference between the reading under increasing and decreasing pressure, shows the usual magnitude of the effect. The first column in the table gives the total load at each step. The effect is much less than that due to departure from linearity mentioned above, so that here we have a hysteresis loop of the unusual shape shown in Figure 4. The lag in similar cases is usually so great that the curvature with decreasing stress is the reverse of that with increasing stress, so that the loop has the general shape of a double convex lens. Furthermore the loop is usually very nearly symmetrical with respect to the line joining the extremities. This is the only example of a loop of the above shape known to the writer. This single example is sufficient to show that there is no necessary connection between hysteresis and departure from the linear relation between stress and strain, as might be supposed if all loops were of the ordinary type.

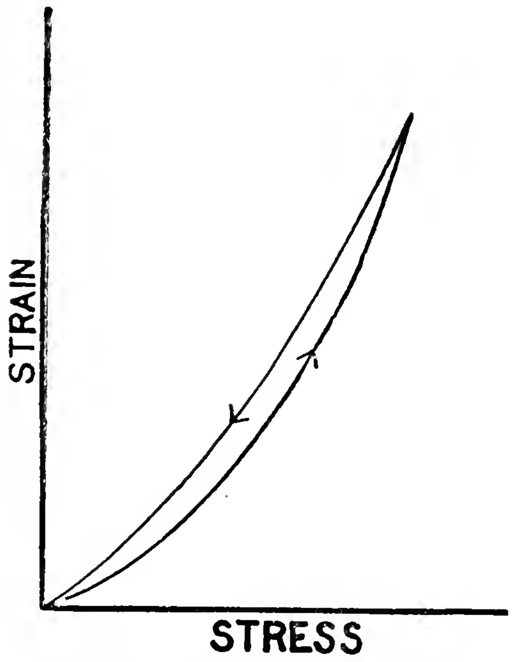

FIGURE 4. Shows the unusual nature of the hysteresis cycles described by the springs.

This hysteresis, while comparatively small, was nevertheless sufficient to reduce the accuracy of measurements made with the gauge far below that desired. A method of avoiding hysteresis was therefore adopted. It depends on the fact, well known for magnetism, that if the stress is varied cyclically by small amounts about any fixed point, a small hysteresis loop is described about this point. The result is that if stress is relieved from the point A (see Figure 5) after increasing pressure, the path AB will be described, while if it is increased from the point C after decreasing pressure, the path CB is described. Suppose that during increasing pressure the point D has been reached, or that during decreasing pressure the same stress, shown at E, has been reached. The difference between the points E and D represents the error due to hysteresis. To make the readings at these two points the same, we may evidently apply a small extra load at D, raising the stress to A, and then remove the extra load, or at E we may remove a slight portion of the load to C and then reapply it. The same point B is finally reached, and the pressure readings have become single valued. The extra load necessary to apply or remove must be determined by experiment, and would be expected to vary at different parts of the hysteresis loop.

This extra load was applied in practise by a very simple lever arrangement, by which the springs could be deflected one way or the other before making readings. The following set of readings, picked at random from a great number, shows how nearly it was possible to avoid hysteresis by the method. The difference of readings is seldom more than the possible error of reading. The small extra load applied or removed before making these readings was constant over the entire range, being sufficient to produce a deflection of about 2.0 divisions. It is evidently not quite enough at the higher pressures and a little too much at the lower pressures. The mean of the two readings nowhere differs from either reading by more than the errors of observation, however, and this simpler procedure was therefore adopted.

The most inconvenient fact disclosed by the calibration was that the constant of the springs varies slowly from time to time. Over two or three days no change whatever is to be noticed, but in a week or a month there are likely to be changes beyond the limits of error. The change is irregular and has no apparent connection with temperature changes. No temperature effect within the limits of working room temperatures was ever found. The change is doubtless due to some slow process of molecular accommodation going on within the metal itself. At one time the springs were permanently deformed by a violent explosion, so that the deflection under the same load was increased in the ratio 16:14. After this deformation for a month or more the change with time was more rapid than usual. The table shows the magnitude of the variation with time. The first set of three, January–April, 1910, was made at intervals during constant use of the gauge. During this time the gauge constant decreased and then increased again. The explosion referred to above took place on December 24, 1909. The last two readings, September 6 and 24, 1910, were made after the springs had been resting for about four months. The constant is in general higher, but the greatest increase has come at the middle of the range, so that the relation between stress and strain is more nearly linear than before. After this prolonged period of rest, the gauge has remained much more nearly constant than before.

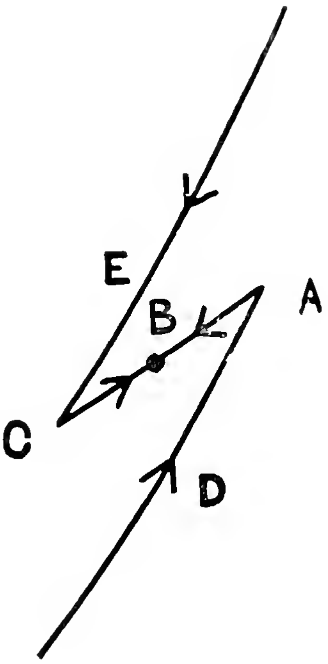

FIGURE 5. Detail of a hysteresis loop, showing the method of avoiding the effects of hysteresis in making the readings with the springs.

TABLE II.

RELATION BETWEEN LOAD AND DEFLECTION OF SPRINGS WITH DEVICE FOR AVOIDING HYSTERESIS.

Load Kgm.	Mirror Deflection.		Load Kgm.	Mirror Deflection.	
	Increasing Load.	Decreasing Load.		Increasing Load.	Decreasing Load.
00.00	0.00	0.00	95.62	8.50	8.50
16.26	1.43	1.42	112.27	10.02	10.04
33.37	2.94	2.92	128.27	11.51	11.54
49.35	4.35	4.34	143.32	12.98	12.94
65.54	5.80	5.79	160.18	14.54	14.54
81.59	7.23	7.23	173.85	15.85	

TABLE III.

SHOWING VARIATION OF SPRINGS WITH TIME.

Load Kgm.	Mirror Deflection.				
	Jan. 1.	March 30.	April 27.	Sept. 6.	Sept. 21.
16.26	1.65	1.63	1.65	1.66	1.66
33.37	3.37	3.32	3.36	3.38	3.38
49.35	5.00	4.95	4.98	5.02	5.03
65.54	6.68	6.58	6.65	6.70	6.70
81.59	8.37	8.25	8.35	8.39	8.40
95.62	9.86	9.74	9.83	9.88	9.89
112.27	11.66	11.63	11.64	11.69	11.70
128.27	13.42	13.28	13.40	13.44	13.47
143.32	15.09	14.96	15.09	15.14	15.15
160.18	17.00	16.88	17.02	17.05	17.08
173.85	18.60	18.52	18.63	18.63	18.65

This change of gauge constant with time demands that frequent calibration be made. In all the work of the following papers in which considerable accuracy was desired, such calibrations were made every few days. It is not much trouble to make this calibration. The twenty-two readings with increasing and decreasing pressures can be made in the course of half an hour. When the gauge is so calibrated, and the procedure for avoiding hysteresis is adopted, the readings are consistent to the limit of sensitiveness. This has already been stated to be about 8 kgm./cm.^{2}.

The gauge in actual use has shown itself very convenient. The readings may be made rapidly and immediately after the application of pressure, since there are no thermal effects such as dissipation of heat of compression. The temperature effect is so small that it may be used directly in the room without a thermostat, and the leak is so slight that it may be used in entire comfort in measuring many high-pressure effects. Where applicable, the gauge is more convenient than the electrical resistance gauge and it has been used whenever possible.

The Manganin Resistance Gauge.

In the earlier paper a method was described for measuring high pressures by measuring the electrical resistance of pure mercury under pressure. The method had the advantage of being perfectly reproducible, so that any one could at any time measure pressure without recourse to the then inconvenient fundamental standard of pressure. The advantage has been in large part offset by the devising of the convenient form of absolute gauge described in the first part of this paper. Moreover, the method becomes inapplicable at somewhat higher pressures than those reached formerly because of the freezing of the mercury. Thus at 0°, the freezing pressure is about 7500 kgm./cm.^{2}. Aside from this difficulty, which might be avoided by placing the mercury in a separate vessel, maintained at higher temperature, there are numerous inconveniences of manipulation, as, for instance, that the mercury must always be kept in an upright position. But the greatest inconvenience of all is that the glass capillary containing the mercury is always shattered by an explosion, and explosions become more and more frequent at high pressures.

There are frequently situations, however, where the absolute gauge becomes unavailable, and where a gauge with some of the properties of the mercury gauge becomes desirable. For instance, it is often necessary to secure absolute freedom from leak, and this is obviously impossible with a freely moving piston as in the absolute gauge.

Measurements of compressibility or of change of volume during freezing, as in two following papers, demand this property of freedom from leak.

The method of pressure measurement adopted here, and which secures freedom from leak, has already been described by Lisell.[2] He measured the effect of pressure on the resistance of manganin wire, and proposed that the change of resistance be used as a measure of pressure. Lisell found the effect of pressure between 0 and 4200 atmos to be linear, and showed that there was no appreciable temperature effect between 0° and room temperature. But Lisell also showed that different specimens of manganin show slightly different pressure coefficients, so that the advantage of reproducibility must be given up. Lately, Lafay[3] has also measured the pressure effect on manganin up to 3500 kgm. and has found nearly the same pressure coefficient as did Lisell.

The data of this paper show by direct comparison with the absolute gauge that the manganin is suitable as a pressure gauge over much wider ranges of pressure. Up to 13,000 kgm. the relation is linear within the errors of the absolute gauge. It would not have been surprising if this had not been true, in view of the fact that manganin has a pressure coefficient which is positive instead of negative like that of all the pure metals. Furthermore, over this pressure range the readings are entirely free from hysteresis or creep. This is opposed to the work of Lussana,[4] who found various temporary effects after the application of pressure. His results have not been verified by subsequent observers, however, and the entire absence of the effect here under a very much wider pressure range would seem to make pretty certain that there was some obscure source of error in Lussana's work.

The manganin used in this work was of German manufacture, No. 38, double silk covered, of about 30 ohms to the meter. With change of temperature it shows a maximum resistance at about 27°. The coils were of about 100 ohms resistance, the wire being wound non-inductively on itself in the form of a toroid, about 1 cm. in diameter and 5 mm. thick. To protect the wire, the toroid was covered with a winding of fine silk ribbon, only the ends of the wire being exposed in order to make connections with the insulating plug. This plug was of the same design as that shown in the previous paper, except that it was made of hardened nickel steel instead of tool steel.

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[2] Lisell, Om Tryckets Inflytande på det Elektriska Ledningsmotståndet hos Metaller samt en ny Metod att Mäta Höga Tryck (Diss. Upsala, 1903)

[3] Lafay, C. R., **149**, 566–569 (1909).

[4] Lussana, Nuov. Cim., **10**, 73–84 (1899); **5**, 305–314 (1903).

The apparatus for producing and measuring pressure consisted of two cylinders connected by a tube of nickel steel. In the lower cylinder the pressure was produced and measured. The absolute gauge of the first part of this paper was screwed directly into the side of this cylinder. The cylinder itself was of Krupp chrome nickel steel, 8 inches outside diameter, 1 1/8 inches inside diameter. It was placed in a hydraulic press of 200 tons capacity, and the pressure produced by a 1 1/8-inch piston forced into the cylinder by the ram of the press. The upper cylinder, also of Krupp chrome nickel steel, 4 1/2 inches outside and 9/16 inch inside diameter, contained the manganin wire to be tested. The connecting tube to the lower cylinder passed through the bottom of the tank of a thermostat, which surrounded the upper cylinder, and with which the temperature could be kept constant to 0.01°. No such temperature precaution was necessary for the absolute gauge. The lower cylinder was filled with the mixture of glucose and glycerine needed to secure tightness of the piston of the absolute gauge, and the upper cylinder was filled initially with either kerosene or gasolene, in which the manganin coil was directly immersed. The action of pressure was to compress the kerosene, glucose passing from the lower cylinder to the lower part of the upper cylinder. The compression was never sufficient, however, to bring the glucose into contact with the manganin. Although kerosene or gasolene are somewhat inconvenient because of their high compressibility, still their use was made necessary by the fact that a heavier oil freezes under pressure, so that it does not transmit pressure hydrostatically to all parts of the wire. The kerosene is also known to become stiff like vaseline at say 10° and 8000 kgm., but the viscosity is not so great as to introduce irregularities. When either kerosene or gasolene is used, the insulating qualities of the plug are practically perfect without requiring any special precautions. The insulation resistance was always over 10 megohms, which was the limit of the measuring device conveniently at hand. Formerly, in working with mercury, pressure was transmitted by a mixture of water and glycerine. It was necessary to specially protect the separate parts, and even then the insulation resistance was never greater than several hundred thousand ohms.

The electrical measurements were made by the same null method and on the same Carey Foster bridge as those described in the former paper.

In making the calibration and in using the gauge, there is one fact to be borne in mind which has its analogy in the mercury resistance. This is the seasoning effect of pressure; the gauge does not respond to the first application of pressure in the same way that it does to the second or subsequent applications; there is a gradual settling down to a steady state. In the case of mercury, this was due to the equalization of strains in the containing capillary of glass. In the case of the manganin, some such process of accommodation must be going on within the mass of the metal. This is shown principally by drift of the zero, but the pressure coefficient may change slightly. The seasoning process occupies more time for the manganin than for the glass; it may extend over as much as a month after the first application. It is hastened by frequent applications of pressure, but may apparently run to completion in sufficient time after only one application. To effect the seasoning, it does not seem to be necessary to subject the coil to the maximum pressure under which it is contemplated using it. The coil used to the highest pressure reached in this work, 20,500 kgm., had been seasoned by the application of not more than 12,000 kgm., yet it showed no further change after the application of a pressure 8500 kgm. in excess of the seasoning pressure.

TABLE IV.

Pressure Coefficient of Resistance of Manganin.

Pressure Kgm./cm.^{2}.	$\frac{\Delta R}{pR_0} \times 10^9$.	Pressure Kgm./cm.^{2}.	$\frac{\Delta R}{pR_0} \times 10^9$.
1260	2272	9290	2302
2610	2282	8000	2304
3810	2299	6450	2302
5000	2301	4790	2304
6180	2299	3250	2291
7210	2300	1740	2308
8230	2302	1000	2272

The results obtained with one such well-seasoned coil at 0° are shown in the table. In making the comparison with the absolute gauge all the precautions described in the first part of the paper were observed. It is seen that within the limits of error of the pressure readings, the change of resistance is proportional to pressure.

To show within what limits different pieces from the same spool of wire give the same results, three coils were made from the ends and the middle of a length of wire of 70 m. The constants for the separate coils at 0 were $.0_52301$, $.0_52307$, and $.0_52325$, in the order of the coils, a variation of one per cent. The temperature effect was found by measuring these same coils again at 50°. These same three coils gave 2295, 2319, and 2320 respectively. One of the coils measured at —12° showed no measurable difference between —12° and 0°.

The maximum pressure to which these calibrations were made varied somewhat with the temperature, because at the lower temperatures the mixture of glucose and glycerine used with the absolute gauge became viscous so rapidly with increasing pressure as to transmit pressure very slowly. At the low temperatures the pressure was increased until this limit was reached. The slow flow of glucose from the lower to the upper cylinder might occupy an hour or more before the equilibrium was complete. The fact that there was such a process of flow was definitely shown by the slow fall of pressure in the lower cylinder as indicated by the absolute gauge, with a simultaneous slow rise of pressure in the upper cylinder, as indicated by the manganin resistance. At 0° the maximum reached was in one case 11,000 kgm. This was probably too high for complete equalization of pressure, for the change of resistance was 1/2 per cent too low at this maximum. The measurements at 0° were not usually carried as far as this, 9500 being the more usual limit. Slight differences in the composition of the glucose mixture made very pronounced differences in the viscosity at high pressure. At 50° the highest reached was 12,000. Even here the viscosity was very considerable. On one occasion pressure was pushed to 13,000 at 50°. There was the same slow equalization of pressure, extending over about half an hour, as was found at 0°. At the end of this time the resistance had nearly acquired the value given by a linear relation, when the experiment was terminated by an explosion. The final reading below this at 11,500, at which there was also some viscous yield, completely satisfied the linear relation.

We may conclude, therefore, that over the temperature range 0°–50° the pressure resistance relation is linear within 1/10 per cent of the change of resistance, up to 13,000 kgm. This was proved by actual experiment at 50° to 12,000, and to 9500 at 0°. The extrapolation to 13,000 at 0° is comparatively slight, and is made all the more probable by the fact that our usual experience would lead us to expect greater departure from linearity at higher temperatures, and no such departure was found.

Although different specimens of manganin do not have the same constant, still it may be worth while comparing the results found here with those of other observers so as to give an idea of the magnitude of the variation of the effect. Lafay[5] found 2.16×10^{-6} per kgm./cm.^{2} as the effect on one specimen. Lisell[6] found for two specimens of annealed wire 2.13×10^{-6} and 2.08×10^{-6}; for three specimens of hard drawn wire results from 2.279×10^{-6} to 2.338×10^{-6}. The data of this paper, which are for hard drawn wire, vary from 2.295×10^{-6} to 2.325×10^{-6}.

Four of these manganin resistance gauges have been in almost constant use for over a year. As compared with the mercury gauge they have had the advantage of greater convenience and ease of manipulation, even over the pressure range within which the mercury remains fluid. During the work explosions have been of frequent occurrence, the shock of any one of which would have broken the glass capillary containing the mercury. It is not necessary to apply elaborate temperature precautions as for the mercury. The only temperature correction necessary to apply is a small one for the shift of the zero. This may be determined accurately enough by hanging a thermometer in the air of the room near the cylinder containing the manganin. At room temperatures of 20° a change of temperature of 1° demands a pressure correction of only 5 kgm.

As compared with the absolute gauge of the first part of the paper, each form has distinct advantages. Where available, the absolute gauge is more convenient, because it is direct reading and immediate. But the absolute gauge has the disadvantage of leak, so that often the manganin gauge becomes absolutely necessary. Futhermore, it has the disadvantage of being more cumbersome. This means that all parts of the apparatus in connection with the gauge must be correspondingly enlarged. This is often a fatal disadvantage, entirely apart from any considerations of expense or convenience, because in order to reach the highest pressures, the steel parts must be hardened, and it is not possible to harden large steel cylinders. The upper limit of pressure attainable will have to be reached with comparatively small apparatus. The reason for not pushing the absolute gauge to its limit was not so much fear of destroying the gauge as the fact that the large 8-inch steel cylinder containing the gauge was of soft nickel steel, and that the yield point would have been reached at 15,000 kgm. This cylinder had been previously seasoned by applying pressures up to 28,000 kgm., which had the effect of increasing the internal diameter

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[5] Lafay, loc. cit.

[6] Lisell, loc. cit.

from 5/8 inch to 1 1/8 inches, but even this was not sufficient to raise the limit permanently to over 15,000 kgm.

The compactness of the manganin gauge makes it particularly adapted for working with the highest pressures where everything must be in one piece because of the impossibility of making connecting tubes. The gauge has been so used in a number of experiments on the freezing of water under pressure. The gauge was screwed into one end of a large steel cylinder, the plunger was pushed in from the other end, and the water was in the space between. The dimensions were kept down so that the entire block, together with a part of the hydraulic press, could be placed in a thermostat.

The manganin gauge may be used by extrapolation to measure pressures beyond the reach of the absolute gauge. It has been so used in investigating the freezing of water up to an indicated pressure of 20,500 kgm., and this limit could without doubt be exceeded. The limit is not in the manganin itself, but in the hardened steel parts, which have a tendency to stretch too much at pressures as high or higher than 20,000 kgm. Of course the use of any standard by extrapolation is undesirable, but at present any means of measuring these very high pressures with probable accuracy is welcome. In any event, the extrapolation from 12,000 to 20,000 is very much less than the extrapolation from the previous maximum of 4000 to 12,000, which is here shown by actual experiment to be justified. What is more, it will be an easy matter to translate high-pressure readings in terms of a manganin gauge into absolute pressures, if at any time the direct calibration is extended from 13,000 to 20,000, and proves that a linear extrapolation is not sufficiently accurate.

The only serious disadvantage in the manganin gauge as thus far described, when compared with either the mercury gauge or the absolute gauge, is the fact that it is not readily reproducible, so that each new coil of wire must be calibrated against an absolute gauge. This disadvantage may be obviated by the use of fixed pressures of reference analogous to the melting points of the metals used as points of reference in thermometry. The linearity of the relation between resistance and pressure having been established by the work of this paper, it is necessary to know for each coil only the change of resistance corresponding to a single known pressure in order to fix completely the behaviour of the coil.

Such pressures of reference are given very conveniently by the points of transition between the various kinds of ice and water. For low pressures such a pressure of reference is given by the pressure of transition from ice I to ice III, using Tammann's[7] notation. This pressure is very nearly independent of temperature between —22° and —30°. This particular transformation has the advantage that the reaction runs with very great velocity and is accompanied by a comparatively enormous change of volume, 20 per cent, so that in any piece of apparatus, once given the two phases, the equilibrium pressure is automatically set up almost immediately. This pressure has been found to be 2120 kgm. at —23°. For higher pressures, the transition point at 0° from water to a hitherto unknown variety of ice, ice VI may be used. This point has been found by experiment to be 6370 kgm. Equilibrium is reached more slowly than for the transition I–III, but for work at higher pressures the use of this transition point will give a more accurate calibration. This method of calibration has actually been used, with satisfactory results, for two other coils than the four mentioned above.

The calibration of the manganin resistance without the use of an absolute gauge may of course be effected by comparison with any other accurately measured pressure phenomenon. For instance, the calibration may be made by comparing the manganin resistance with the mercury resistance, the data for which have been already published.

Summary of Results.

Two gauges for high pressures are described in this paper. The first is an absolute gauge which has been used up to 13,000 kgm. The construction of the gauge is described, the correction for distortion is determined, and the reading mechanism is discussed. A procedure is given for freeing the deflections of the springs with which the thrust is measured from hysteresis. All of the factors may be determined with sufficient accuracy so that the gauge is accurate to the limit of accuracy of reading, 1/10 per cent at 8000 kgm./cm.^{2}. The second gauge is a manganin resistance. This is shown to be suitable for the purpose, since there is complete freedom from hysteresis and elastic after-effects. The relation between pressure and resistance is shown to be linear up to 12,000 kgm., but the gauge has been used by extrapolation up to 20,500. The accuracy of the readings with this is at least as great as with the absolute gauge. The relative advantages for various kinds of experiment of these two forms of gauge are discussed. Finally, by the use of standard pressures of reference it is

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[7] Tammann, Kristallisieren und Schmelzen, pp. 315–344 (Barth, Leipzig, 1903).

shown that a manganin resistance gauge may be calibrated without direct reference to an absolute gauge.

This investigation was a necessary preliminary to the measurement of various thermal properties of mercury and water under pressure, the expenses of which have been partially defrayed by several liberal appropriations from the Rumford Fund of the American Academy of Arts and Sciences.

Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.,
October, 1911.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 12. — December, 1911.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

MERCURY, LIQUID AND SOLID, UNDER PRESSURE.

By P. W. Bridgman.

With a Plate.

Investigations on Light and Heat made and published with Aid from the
Rumford Fund.

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MERCURY, LIQUID AND SOLID, UNDER PRESSURE.

By P. W. Bridgman.

Presented by G. W. Pierce, Oct. 11, 1911. Received Oct. 6, 1911.

Introduction.

This paper is an attempt to present for the liquid and solid phases of a single simple substance, mercury, data corresponding to the data which have been collected for the gaseous and liquid phases of many substances. These latter data are the relations connecting temperature, pressure, and volume of the gas together with the changes involved when the gas passes to the liquid state. Out of these data have come the theories of the molecular structure of gases and vapors, and the various relations connecting the gaseous with the liquid phase, of which the theory expressed by the equation of van der Waals is the best known. The corresponding work for the liquid and solid phases, that is, the mapping out of the pressure-volume-temperature surface of the liquid and the determination of the quantities involved in the change from the liquid to the solid state, has never been done. As a result, the theory of liquids is entirely undeveloped, and the theory of the relation between liquid and solid hardly begun. For instance, the fundamental question as to the existence of a critical point for the liquid-solid states analogous to that for the vapor-liquid is as yet unsettled.

The apparent reason for this neglect of the thermodynamic data for the liquid and solid is merely experimental difficulty. Whereas for a vapor the critical pressure never exceeds a few hundred atmospheres, the pressures involved in a corresponding study of the liquid-solid phases are of the order of tens of thousands of atmospheres. These pressures are so high as to tax to the utmost the tightness of every joint and the strength of the steel vessels. In this present work it has been found possible by a special packing device, which secures absolute freedom from leak, and by the use of the highest grades of steel manufactured, to reach 30,000 and even 40,000 atmos on the first application of pressure. On subsequent applications rupture may come at half the first maximum. This subsequent early rupture is due to the fact that these pressures are greatly in excess of the theoretical limit of the steel, so that there is a distortion of the inner parts far beyond the elastic limit and consequent rapid fatigue. The pressures reached in this paper are not the greatest attainable because of the questionable scientific economy of pushing pressures to a value where rupture may occur at any moment and destroy valuable apparatus and time.

The previous work in this field is wholly below 5000 kgm. The two principal investigators are Amagat,[1] who studied the compressibility and the thermal dilatation of a number of liquids up to 3000 atmos, without, however, touching on the change of state liquid-solid; and Tammann,[2] who studied the change of state liquid-solid, without determining the behavior of the liquid, over a range of pressure of usually about 3000 kgm., but reaching a few times to 4000 and once to 4800. There are no liquids common to the work of both Amagat and Tammann, so that the complete data are not known for even a single liquid.

The previous work done on mercury is almost negligible for the present purpose. Accurate compressibility determinations run only to 500 kgm. (the highest are by Richards [3]), and the effect of pressure on freezing point has been observed only by Tammann, [4] who found results up to 2000 kgm. that are inconsistent among themselves by 30 per cent.

The data of this paper cover a range of 12,000 kgm., and give both the changes of volume of the liquid with temperature and pressure, and the thermodynamic data required on the freezing curve. The temperature range corresponding to this wide pressure range is comparatively small, since at 12,000 kgm. the freezing temperature has been raised to only 20°, that is, through a range of 60°.

In addition to the data connected more intimately with pressure, several quantities relating to solid mercury at atmospheric pressure have incidentally been determined. It has been a surprise to find how untrustworthy the commonly accepted data for solid mercury are. Thus the only determination of the latent heat of melting dates back to 1838, before the value of the melting temperature itself was known more accurately than within 3°.

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[1] Amagat, Ann. de Chim. et Phys. (6), **29**, 68–136, 505–574 (1893).

[2] Tammann, Kristallisieren und Schmelzen (Barth, Leipzig, 1903).

[3] Richards, Pub. Carnegie Inst. Wash., No. 7 (1903), and No. 76 (1907).

[4] Tammann, loc. cit., p. 248.

The experimental material of the paper, with respect to both subject matter and experimental method, falls naturally into two parts. The first is concerned with the p-v-t surface of the liquid. To map this the isothermal compressibility of the liquid was found at two temperatures, 0° and 22°, and combined with the known dilatation at atmospheric pressure. This is sufficient to cover the region in question, because the change of dilatation with temperature is slight. The second part is concerned with the changes taking place on the freezing curve. Thermodynamically, the data required are the change of volume on passing from liquid to solid and the variation of freezing temperature with pressure. From these the latent heat may be calculated by Clapeyron's equation. Two independent methods were used; one which gave both the change of volume and the relation between temperature and pressure on the freezing curve, and another which gave only the freezing curve. In addition still another method was used in determining the change of volume on freezing at atmospheric pressure.

In the conclusion, the data collected are discussed from the point of view of their bearing on present theories of the liquid state, and the change solid-liquid. These data for a single substance cannot justify by any means an attempt at a new theory. This is simply a first step, indicating in a general way the nature of the effects to be expected at high pressures. From this point of view there are considerations both for and against the use of mercury. On the one hand, the compressibility and thermal dilatation of mercury are comparatively small, so that the change in these quantities under the pressure range employed is not nearly as great as it would be for many organic liquids; but on the other hand, the internal structure of mercury is probably at least as simple as that of any other known substance, so that in the liquid state the results are not complicated by entrance of polymerization, and on the freezing curve the results are not complicated by the entrance of allotropic forms, as they are in the case of water, for example.

The discussion of the methods and the possibilities of error has necessarily been somewhat minute and painstaking. It is hoped that this will be pardoned when it is realized that the field in which these measurements are made has been hitherto practically unworked, and is one where there are several unusual sources of error to be guarded against. At the same time it is a field in which, by the exercise of proper precautions, an accuracy equal to that of the greater number of physical measurements can be reached. The accuracy of nearly all of the following measurements is of the order of 1/10 per cent.

Contents.

THE P–V–T SURFACE OF MERCURY.

The Compressibility of Liquid Mercury.

This first section of the paper is devoted to a determination of the compressibility of mercury at 0° and at 22°. The question of experimental method is important, since the compressibility of mercury is small, and there are various effects which make determinations at high pressures much more difficult than over a smaller pressure range. The section comprises a discussion of the method and the various errors to be avoided, an experimental determination of the compressibility of the steel, which was needed in the computations, the actual data for the compressibility of mercury, with a somewhat detailed discussion of the way of adjusting them so as to give the best results, and finally, a calculation from the data of the change of the various physical properties of mercury under pressure.

One of the chief difficulties in the experimental investigation of the properties of bodies under pressure is the determination of the correction for the distortion of the containing vessel. This is particularly true in the case of compressibility, where the change of shape and volume of the containing vessel is an effect of the same kind as that being measured, and may often constitute a large part of the total change.

To correct for the distortion of the containing vessel only indirect methods are open, as direct observation of the vessel under high pressure is out of the question. All of those indirect methods which are primary, that is, which do not assume the correctness of the work of some other observer, endeavor to determine in one way or another the compressibility of the material of the containing vessel. This may be done by measuring Young's modulus and the bending or the torsion coefficient, and from these calculating the cubic compressibility by the identical relations of the theory of elasticity; or it may be done with the introduction of less questionable assumptions by measuring the linear compressibility and then multiplying by three for the cubic compressibility. This latter method in somewhat different forms has been adopted by Richards [5] and the author. [6] Once the compressibility is known, the change of volume of the vessel is found immediately by multiplying the compressibility by the pressure. This assumes that the containing vessel changes volume without changing shape. This assumption, which is made universally, seems necessary and unavoidable. There can be little question, however, that the assumption is not entirely justified. There are outstanding discrepancies between the determination of the same compressibility by different observers, or by the same observer with different apparatus, or indeed by the same observer with the same apparatus on different occasions, that are beyond the limits of error of the measurements. For instance, four very careful determinations of the compressibility of mercury by de Metz [7] differed among themselves by 5 per cent. The containing vessels were all of the same kind of glass, and the elastic constants had been determined by direct experiment. The only explanation of these discrepancies seems to be that the distortion of the containing vessel is irregular, so that there is change of shape as well as change of volume. The irregularities in the results introduced by irregularities in the piezometer will, of course, be proportional to the total correction introduced by the envelope, and will be greatest in the case of the most incompressible liquids. Thus for mercury in a glass envelope, the correction for the envelope is 60 per cent of the whole effect, while for water it is only 5 per cent.

There can be no doubt that these irregularities are due to lack of homogeneity in the containing vessel, either imperfect annealing or actual variation in the constitution of the material from point to point. It is inconceivable that a perfectly homogeneous body of any shape,

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[5] Richards, loc. cit., 1907.

[6] Bridgman, These Proceedings, **44**, 255–270 (1909).

[7] De Metz, Wied. Ann., **47**, 706–742 (1892).

when exposed to purely hydrostatic pressure, should suffer anything except mere change of volume without change of shape. If, however, the substance be heterogeneous, so that the elastic constants vary from point to point, then the application of hydrostatic pressure will be followed by change of shape, yielding of one part at the expense of another. If the pressure is high enough, it is conceivable that the elastic limit may be exceeded in some places and not in others, resultingin greatly exaggerated change of shape. Even if the elastic limit is not exceeded, there are other effects which will produce irregular action, such as elastic after-effects and hysteresis, and these effects become rapidly more prominent at high pressures. It follows, therefore, that the irregularities of compressibility determinations over a wide pressure range are going to be more than proportionally greater than the irregularities over a narrow range.

All previous determinations of compressibility have been made under fairly favorable conditions. The work to the highest pressures has been done by Amagat, to 3000 atmos, in which he determined the compressibility of the compressible liquids in a glass envelope. His determinations of the compressibility of the most incompressible liquid, mercury, were only to 50 atmos. The highest accurate work on mercury seems to have been done by Richards to 500 atmos, a comparatively low pressure. Richards also used glass piezometers. The highest previous work of any sort on mercury seems to have been done by Carnazzi,[8] to 3000 atmos, also with a glass piezometer. His accuracy was not such as to justify more than two figures in the final result.

In determining the compressibility of mercury to pressures as high as 12,000 kgm., as it was desired to do in this paper, we have conjunction of the causes most unfavorable to accuracy; low compressibility of the liquid, and greatly exaggerated irregularity in the distortion of the containing vessel. The employment of a glass containing vessel would seem to be out of the question. In a previous paper,[9] the linear compressibility of glass has been determined directly to 6800 kgm. Over this lower range, irregularities were found amounting to 4 per cent. In using a glass piezometer, this irregularity would be magnified by the fact that the compressibility of glass is high compared with that of the mercury. The ideal substance is one which can be obtained in a state of great homogeneity, and which at the same time has as low a compressibility as possible. Steel has these properties in a

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[8] Carnazzi, Nuov. Cim. (5), **5**, 180–189 (1903).

[9] Bridgman, loc. cit.

higher degree than any other substance, the compressibility being as low as any except the platinum metals, and the homogeneity in annealed pieces of soft steel being nearly perfect. The use of a piezometer of steel in determining the compressibility of mercury up to 6800 kgm. has been described in the paper cited above. The advantages of the steel piezometer have been discussed there, and independent experimental evidence has been presented showing that the compressibility of a piece of mild steel is the same in every direction, and that therefore the piezometer does not change its shape. The results obtained with this method were regular, and in so far justify the use of this material; but further work has led to the conviction that there was present in the method a source of error for which it is hopeless to attempt to calculate the correction. This error is concerned with the leak past the freely moving piston; this leak is less on increasing than on decreasing pressure, so that the previous results are all too small. It seems impossible to determine in what way the error so introduced will vary with the pressure. The total magnitude of the error is probably between 2 and 3 per cent.

The method adopted here attempts to keep the advantage of the steel piezometer, while doing away with the uncertainty of the freely moving piston. It was not possible to secure so regular results with the new method as with the old, but on the other hand, any constant source of error seems to be excluded. The method is a modification of one used by Aimé [10] in 1842, and since used in many modified forms by other experimenters. In the original form, the liquid to be investigated was placed in a glass bulb provided with a fine capillary communicating with a vessel containing mercury. The whole affair was then lowered into the sea. Here the increase of pressure forced mercury into the bulb, where it fell to the bottom and remained. On withdrawing from the sea, the maximum volume compression was measured simply by weighing the mercury forced in. Aimé's results were very irregular and incorrect. The most obvious trouble with this method is the tendency of the mercury to collect in drops at the mouth of the capillary. On release of pressure, this drop flows back through the capillary, and the resultant compressibility appears too low. The difficulty may be minimized by making the capillary very small. This is an easy matter when the capillary is made of glass, but when steel is used as here, some special construction must be devised. The form of piezometer adopted is shown in Figure 1. The upper piece B, screws into the shell A. A tight joint between the two is made simply

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[10] Aimé, Ann. de Chim. et Phys., **8**, 257–280 (1843).

by tightly forcing the narrow edge C on the upper part B into the flat seat at D. It is not desirable to attempt to use any packing material. At the lower part of B there is a very fine channel, E, opening into A. This channel is made by carefully drilling in B a 1/16 inch hole and then plugging the hole with a pin along which a fine scratch has been made. This fine scratch takes the place of the glass capillary when the piezometer is made of glass. It is thus possible to regulate the size of the channel at pleasure. It is a matter of the greatest ease to make such a channel that a pressure of only a few pounds to the square inch will force mercury through it in drops just barely perceptible to the eye, and much too small to be measured by any ordinary balance. In all the work with these piezometers no effect was ever found suggesting in any way the possibility of error introduced by clinging of mercury to the mouth of the channel.

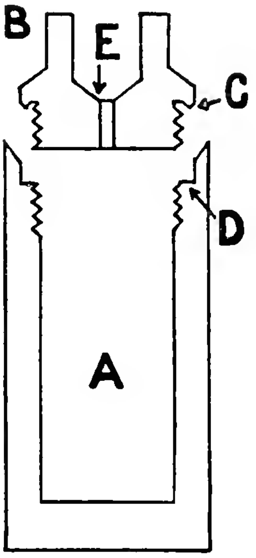

FIGURE 1. The steel piezometer. This is filled with the liquid under investigation and exposed to hydrostatic pressure all over. The pressure forces a measurable quantity of mercury into the chamber A through the fine channel at E, and from this quantity of mercury the change of volume of the liquid originally filling A may be found.

The piezometer may be used in either of two positions, upright or inverted. When used upright, the body A is filled with the liquid to be investigated, water for example, and the cup at B with mercury. The entire piezometer is then placed in a pressure chamber surrounded on all sides by a liquid, to which pressure is applied. This takes the place of lowering into the sea in Aimé's experiment. Mercury flows in through the narrow channel to equalize the pressure within and without, and drops to the bottom. On release of pressure, the water bubbles out through the mercury in B. The piezometer is then unscrewed, the mercury in A weighed, and the total change of volume at the maximum pressure calculated. Into this calculation enter the compressibility of the steel of the piezometer and the compressibility of the mercury. The latter can then be found in terms of the compressibility of water by nearly filling the piezometer with mercury on which floats a little water to fill the piezometer completely. On application of pressure mercury drops through the layer of water, and on release water comes out.

In the inverted position, a sufficient quantity of mercury is placed in the piezometer to cover the bottom, and the fluid with which the piezometer is surrounded in the pressure chamber is chosen the same as that within the piezometer. On the application of pressure, this fluid is forced in, rising through the mercury, and on release the mercury comes out. The quantity of mercury left is weighed, from which the desired change of volume of the fluid is calculated. Here again it is necessary to know the compressibility of the steel of the piezometer and the mercury. The determination of the compressibility of the mercury in the inverted position is as simple as that for finding the compressibility of water in the erect position. The entire piezometer is filled with mercury, and placed inverted in the water by means of which pressure is transmitted. On application of pressure, water bubbles up through the mercury, and on release of pressure, mercury comes out. The compressibility of the water is involved here only as a correction for the volume of the water forced in. In practice, however, it was found desirable to include a little water initially with the mercury, so as to fill completely all the corners. The object of using the piezometer in the inverted position, aside from the check on accuracy afforded by two different arrangements of the apparatus, was to find if possible any effect of the drop clinging to the mouth of the channel. In view of the fact that the surface tension of mercury is greater than that of water, it seemed plausible that the minimum size of a bubble of water that would detach itself from the mouth of the channel and rise through the mercury would be less than the drop of mercury that would fall through water. No such difference could be found, however, in any of the work.

It has been noticed that the method demands the knowledge of two compressibilities besides that of the fluid to be investigated. In the case of mercury these two compressibilities are those of steel and water. The correction for the steel was determined independently by measuring the change of length of a rod under pressure and will be discussed more in detail later in this paper. The effect of the water is small at the low pressures, being simply the change of volume of the slight amount of water forced in, but at higher pressures, where the water may lose as much as 20 per cent in volume, the correction for the change of volume of the water will be 20 per cent for the inverted position and 30 or 40 per cent for the upright position. Given, then, the correction for the steel, it is still necessary to run two sets of determinations to get the compressibility of either water or mercury, and naturally these two determinations give the compressibility of both water and mercury. The data for the water are to be given in a following paper. In calculating the compressibility from these two sets of data, one for the water and the other for mercury, the method of successive approximations was applied. The compressibility of water was first calculated, assuming the compressibility of the mercury to be constant at its initial value at atmospheric pressure. A curve was then plotted giving the volume of water against pressure. From this curve for water, an improved curve for mercury was calculated, from which again a better curve for water was found. In practice it was not necessary to carry the steps further than this.

The relations connecting the compressibility of the water and the mercury with the observed weights of mercury, etc., are given below.

Notation.

V = initial volume of Piezometer,
V_{H_2O} = ” ” ” water,
V_{Hg} = ” ” ” mercury.

Then $V = V_{H_2O} + V_{Hg}$.

Δv_{H_2O} = shrinkage per initial unit vol. of water at pressure under consideration.

Δv_{Hg} = ” ” ” ” ” ” mercury ” ” ” consideration.

Δv_{Fe} = ” ” ” ” ” ” steel ” ” ” consideration;

and in addition :

in the upright position

ΔV_{Hg} = vol. at atmos. pressure of mercury forced in by the pressure in question.

in the inverted position

ΔV_{Hg} = vol. of mercury forced out, etc.

ΔV_{Hg} is the same thing as the volume of the water forced in. The corrected volume of the piezometer at any pressure is evidently V–V.Δv_{Fe}. It is a simple matter to verify the following equations:

Upright position

$$\Delta v_{H_2O} = \frac{\Delta V_{Hg} + V\Delta v_{Fe} - \Delta v_{Hg}\,(\Delta V_{Hg} + V_{Hg})}{V_{H_2O}},$$

$$\Delta v_{Hg} = \frac{\Delta V_{Hg} + V\Delta v_{Fe} - V_{H_2O}\,\Delta v_{H_2O}}{V_{Hg} + \Delta V_{Hg}}.$$

Inverted position

$$\Delta v_{H_2O} = \frac{\Delta V_{Hg} + V \Delta v_{Fe} - V_{Hg} \Delta v_{Hg}}{V_{H_2O} + \Delta V_{Hg}},$$

$$\Delta v_{Hg} = \frac{\Delta V_{Hg} + V \Delta v_{Fe} - \Delta v_{H_2O} (V_{H_2O} + \Delta V_{Hg})}{V_{Hg}}.$$

The following gives a discussion of the minor experimental details that it was necessary to observe.

Considerable care is necessary in filling the piezometer to ensure complete exclusion of air. The procedure in filling was as follows. The piezometer A with the cover B held loosely over it in a suitable frame was placed in a test tube containing distilled water. The test tube was then connected to the air pump and the water boiled under reduced pressure at room temperature, removing the occluded air. The piezometer was then removed from the test tube, the weighed quantity of mercury introduced, and then replaced in the test tube which was again exhausted as before. The mercury had been cleaned with acid and was freshly distilled. Finally, before raising the piezometer above the surface of the water, the cap B was screwed into place with a simple key. Removing from the test tube, the cap B was tightened home by applying a spanner.

This tightening of the cap must be done with especial care, and to irregularities in this most of the irregularities in the data could be traced. Since the piezometer is made of a very mild steel, it is a comparatively easy matter to screw the cap in too far, stripping the thread or shearing off the shoulder. This was avoided by graduating around the top of A, and always screwing B in to the same mark. But even at best, to secure a tight joint, it is necessary to force the cap in pretty tightly, exceeding the elastic limit locally, and thereby introducing probable irregularities as explained before. When the method was first used, a great deal of trouble was found from such irregularities. This was shown most convincingly by the fact that the volume of the piezometer did not remain constant, but changed very slightly after each application of pressure, usually becoming less. This change of volume is not entirely due to the effect of the joint, because it could be mostly removed by annealing. Nevertheless, since the effect of annealing is to remove internal strains, and since internal strains are doubtless introduced at the joint, there is probably some irregular action introduced at the joint. This source of error remains the chief objection to the method, although it can be greatly reduced by proper manipulation. This consists in careful previous annealing, and seasoning by subjecting to pressure several times before the series of measurements is begun. One at least of the previous applications should be to a pressure as high if not higher than that to be reached during the measurements. After treatment like this the piezometers show no further change of volume, and the results with any one are fairly regular. It is a question, however, how good a criterion uniformity of results and permanency of volume are for the uniform compression of the piezometer without change of shape. It must be confessed there seems no valid reason why the piezometer after proper seasoning should not settle down into a steady state in which it gives consistent results with change of shape, and probably it does. The difference of the results with different piezometers is probably to be explained by this effect. The best that can apparently be done is to take the mean of the determinations with several piezometers, all of which individually give consistent results. All of these considerations apply chiefly to determining the compressibility of the incompressible mercury; they have much less weight, and indeed are almost negligible when applied to water.

There is one particular way in which it is very easy to produce irregular results by strains in the piezometer, and one which caused much trouble before the correct explanation was found. If the pressure is pushed too high, the water freezes with sudden decrease of volume. This was not expected when entering on this work, since the freezing curve of water as found by Tammann[11] gives no evidence of the existence of ice above zero. The fact is that there are other forms of ice besides those found by Tammann, one of which is stable at room temperatures. This will be treated in a following paper. The sudden decrease of volume during freezing is accompanied by a rush of liquid through the narrow channel, and, while this rush is taking place, by a momentary excess of pressure outside over that inside. This excess pressure may produce volume set, or if not sufficiently great for that, at least set up internal strains which produce irregularities on subsequent determinations. The irregularities so introduced may be comparatively very high; as much as 10 to 15 per cent in the case of mercury on the next determination. The next value is nearly always too low. The irregularities become smaller with subsequent determinations, but the only satisfactory way is to anneal the piezometer again. Many of the early data had to be discarded because of this freezing effect.

As a consequence of the unforeseen freezing of water at temperatures

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[11] Tammann, loc. cit., p. 315-344.

above zero under high pressure, it is impossible by this method to push the compressibility determinations of mercury to the freezing curve of mercury, as was desired. The difference between the freezing pressure of water and mercury is not very great, comparatively speaking, being about 1500 kgm./cm.^{2} at 15°. By pushing the pressure into the unstable region for water, it is possible to come closer than this to the freezing curve for mercury. At 0° the approach was made to within 700 kgm., and at 22° to within 1000 kgm. Attempts to come closer than this failed. On several occasions the two piezometers, one filled with water and the other with mercury and water, were subjected to pressure simultaneously beyond the freezing pressure of water. The water alone successfully withstood this subcooling, but the water with the mercury always froze. Even when freezing took place, a rough value for the compressibility could be found by using in the calculations the change of volume of the water on freezing. A compressibility for the mercury was thus found lying on a smooth curve with the values at lower pressures, but of course any such procedure as this is questionable. In view of the strong probability that the compressibility of mercury shows no unusual features in the unreached region, it seemed unnecessary to take the measures that would be needed to explore this region, such as the employment of some auxiliary fluid other than water whose freezing point is higher than that of mercury.

It may be mentioned as confirming these views as to the part played by internal strain in making the results irregular, that the irregularity was always much greater after the freezing had taken place after high super-pressures; that is, after the freezing presumably had been most rapid, and the excess pressure on the outside with its resulting deformation greatest.

It will be noticed that the method is essentially an integrating arrangement for measuring the total increase of pressure during the process; that is, at every increase of pressure mercury is forced into the piezometer whether the previous maximum is thereby exceeded or not. In using the method it is essential, therefore, that pressure should be increased continuously to the maximum with no retrogressions. The form of pressure apparatus used made this particularly easy to accomplish. Pressure was produced by a hydraulic ram, the larger piston of which was 6 inches in diameter and the smaller 1 1/8 inches. The 6-inch piston was actuated by the pressure pump of the Société Genevoise, the pressure being run as high as 600 kgm./cm.^{2}.

The motion of the piston was very slow because of the large volumes involved. About 50 strokes of the pump were necessary for an increase of pressure on the high pressure side of 1000 kgm./cm.^{2}. Furthermore, the friction of the packing material, while not very great, retarded greatly the quickness with which the piston moved in response to an increase of pressure. The piston might continue to move for some minutes in response to an increase of pressure on the low-pressure side. The result was that the step-like advance of pressure with each stroke on the low-pressure side was entirely wiped out and converted into a continuous advance on the high-pressure side. The only way in which a retrogression of pressure was likely to occur was by dissipation of the heat of compression. If pressure is rapidly pushed to a maximum, there is produced an increase of temperature. The final equilibrium pressure is lower than the maximum, which corresponds to an unknown temperature. The difficulty was avoided by compressing so slowly that as the pressure approached the maximum the compression was sensibly isothermal. With the apparatus so designed as to reduce the volume of the transmitting fluid to a minimum, it was easy to attain this condition. By comparing results with slower and more rapid compressions a safe rate was found. The maximum pressure of 12,000, for example, could be reached with entire safety in seven or eight minutes. On releasing pressure there was the reverse effect due to cooling, but it is readily seen that there is no error introduced here unless there is actual retrogression of pressure, which is just as easy to avoid as with increasing pressure.

The temperature was kept constant during the compressibility determinations by surrounding the pressure cylinder with a suitable bath, at 0° with ice and water, and at 22° with an electrically regulated thermostat. The piezometers were always submerged for some minutes in this bath before the final adjustments were made. Thus if the compressibility of water were being determined with the piezometer in the upright position, the piezometer was submerged in a test tube of water placed in the bath without the mercury in the upper cup. After temperature equilibrium had been reached, the upper cup was carefully dried with filter paper and the mercury introduced, the lower part still being in the bath. If the piezometer was to be used in the inverted position the procedure was more simple, merely waiting for temperature equilibrium while submerged in the upright position under water or mercury as the case might be. The variations of temperature in the bath at 22° were never more than a few hundredths of a degree. The actual temperature was read with a standardized thermometer.

The volume of the piezometers was found by weighing when full of water at a known temperature and when empty. The filling was performed in the manner above and was more satisfactory than filling with mercury and weighing, since by the use of water it was possible to entirely fill the cracks. The total volume of the piezometers was 1 or 2 cm.^{3} for water and 3 or 4 cm.^{3} for mercury. These small dimensions were necessary to keep the size of the apparatus down within reason, as it was necessary to have the walls of the retaining vessel very heavy in order to withstand the pressures. The cylinder in which the piezometers were placed had a hole 9/16 inches in diameter and was 4 inches on the outside. The small volume of the piezometers places no restriction on the accuracy of the results, however. The weight of the mercury involved in the compression might rise to 3 or 4 gm. for the higher pressures. Weighings were made to 0.0001 gm., so that any error in the weighings is entirely negligible.

Pressure measurements were made with an absolute gauge. This gauge and the various precautions to be observed in its use are described in a previous paper.

Compressibility of the Steel Piezometers.

The experimental determination of the correction for the compressibility of the steel piezometer demands special consideration. The fact must be emphasized that there is no method of determining compressibility in which the compressibility of all the substances concerned can be determined directly, that is, by the application of hydrostatic pressure. There is always a residuum, whatever the method. Thus in the present work, the compressibility of both the water and the mercury involve the compressibility of the steel containing vessels. If an attempt were made to determine by independent experiment the cubic compressibility of the steel, the compressibility of the vessel in which the steel was contained would turn up as a new unknown. The difference of the compressibility of two substances is all that it is possible to get by direct experiment. To get the absolute compressibility of either, the compressibility of the other, the unknown residuum, must be determined by some indirect method. To ensure the greatest accuracy, this residuum should be so chosen as to be as small as possible in comparison with the compressibility in question. Steel, as has been mentioned, is an admirable substance from this point of view.

There are a variety of methods open for the indirect determination of compressibility, all of which depend in some way on the theory of elasticity. A method frequently adopted is to measure two independent elastic constants of a material, such as Young's modulus, or the torsion coefficient, or the bending modulus, and from these to calculate the compressibility by the identical relations of the theory of elasticity. In applying the identical relations, the assumption must be made that the material obeys Hooke's law within the stress range employed, and that it is perfectly homogeneous and isotropic. With these assumptions the identical relations are rigorously exact. The first of these assumptions seems open to but little question. It is the second which is likely to give the most trouble, particularly when the substance experimented on is in the form of hollow tubes, as when the elastic constants have been determined for glass. This method was employed by Amagat [12] and by de Metz,[13] among others.

Another method is to measure the linear compressibilty of the substance in question when subjected to hydrostatic pressure all over and to calculate the cubic compressibility simply by multiplying the linear compressibility by three. This seems preferable to the method of the last paragraph, because the assumptions are reduced to a minimum. The stress, a hydrostatic pressure, is in this method the same during the indirect determination of the cubic compressibility as it is during the actual use of the material in the piezometer. There seems much less chance for complications to be introduced by nonhomogeneity of the material than there is when the compressibility is calculated from two elastic constants, such as Young's modulus and the torsion coefficient. The only assumption made here is that the material is equally compressible in every direction, an assumption which is open to verification by direct experiment. This verification has been made by previous experiments in the paper cited. This method has also been used by several previous experimenters, for example Buchanan,[14] Amagat,[15] and Richards.[16]

In the paper already cited, the linear compressibility of steel was determined at room temperatures up to 6500 kgm./ cm.^{2}. These data were inadequate for the present purpose, however, because they did not run to high enough pressures, and the effect of temperature on compressibility was not determined. But the method there used is entirely satisfactory, and new results have since been obtained by it for the purposes of this paper. Briefly, the method consists in enclosing the metal to be experimented on, which is in the form of a rod, in a long steel cylinder, within which it is exposed to the action of hydrostatic pressure all over. The change produced by the pressure in the length of the rod with respect to that of the cylinder is measured by a ring

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[12] Amagat, C. R., **107**, 618–620 (1888). Ann. de Chim. et Phys. (6), **22**, 95–141 (1891).

[13] De Metz, loc. cit.

[14] Buchanan, Proc. Roy. Soc. Lon., **73**, 296 (1904).

[15] Amagat, C. R., **108**, 727–730, 1889.

[16] Richards, loc. cit.

slipping on the rod. The change of length of the cylinder itself is measured directly from the outside.

In the previous work the rod was enclosed in a cylinder of soft tool steel. The maximum pressure, 6500 kgm., was beyond the elastic limit of this steel, so that the material did not remain isotropic. That the elastic limit was exceeded is shown by the considerable hysteresis in the observed elongation of the cylinder. The fact that there is hysteresis suggests that possibly there may be also some slight degree of warping. It was stated in the former paper that the only assumption made in the whole work was in regard to this matter of warping, that is, whether the change of length of the cylinder is the same internally as externally. The effect is probably slight, and in the absence of any plausible way of calculating it was neglected altogether.

Apart from the question of the method used in the present work, and not affecting its validity in the least, there was an error made in the previous paper in the calculations from the data. Correction for this error increases the former value for the compressibility of this steel from 5.30×10^{-7} to 5.59×10^{-7} at 20°. This also will change the value for the compressibility of mercury, as will be explained later.

The tool steel cylinder was not available for the present work, because it would not reach the pressure reached here, 10,000 kgm./cm.^{2}. Another cylinder of nickel steel of the same dimensions as the former one of tool steel was made, therefore, and hardened in oil. With this heat treatment, the elastic limit should be somewhere near 15,000 kgm. The pressure was purposely kept at a low value, never exceeding 10,000 kgm., so as to run no risk of producing set in the inner layers of the cylinder. That no such heterogeneity was introduced is made probable by the fact that the cylinder showed no hysteresis, the relation between extension and pressure being linear both for increasing and decreasing pressure. The former measurements of this extension were made directly with a microscope, reading to 0.001 mm. For this work here, a much more sensitive scheme was used, an adaptation of the Maarten's mirror device so fast coming into general use among engineers. The magnification employed here gave a motion of the scale of 5 cm. for an actual elongation of 0.025 mm. The sensitiveness is, therefore, at least twice that of an interference system, there is also the advantage of great simplicity and steadiness, and best of all, the reading is given directly on a scale, there being no necessity for keeping track of fringes. The Maarten's mirror device disclosed no hysteresis in the elongation of the nickel steel cylinder. The freedom from heterogeneity as shown by the absence of hysteresis makes plausible also the absence of warping, although no direct measurements of this warping were possible.

An attempt was made to show directly the presence of warping by measurements of the change of length of the exterior of the cylinder. Measurements of the extension were made over the middle third and the middle two thirds of the cylinder. Any very large warping might be expected to destroy the proportionality of extension to length, since presumably the warping is confined to the neighborhood of the ends. No such effect could be found, however, within the limits of error which were about 1 per cent.

The argument for the probable absence of warping may be stated as follows. The change of internal length of the cylinder with which we are concerned was measured between two points at each of which the internal diameter of the cylinder undergoes an abrupt change. If the elastic limit of the steel were exceeded, the resulting set and heterogeneity would naturally appear first at these places of sudden change in the dimensions. The effect of heterogeneity at these places would be to produce warping, that is, sections originally plane would no longer remain plane. On the other hand, if the material were never strained beyond the elastic limit, the warping would be negligible. Now the cylinder has been shown by direct experiment to show no hysteresis, and therefore probably not to have been strained beyond the elastic limit. The cylinder, therefore, probably also shows no warping. In any event, one would seem justified in accepting the readings of a cylinder showing no hysteresis in preference to one where the hysteresis might amount to 16 per cent. The effect of warping, whatever it is, can be only slight, since it is itself only a correction on a 5 per cent correction term.

The new determinations made for this work with the nickel steel cylinder were made on the same specimens as those formerly used, which were from the same piece of steel as the piezometers. Determinations were made at two temperatures, 10° and 50°, and up to 10,000 kgm./cm.^{2}. There were only a few changes from the experimental procedure of the previous work. Pressure was measured by measuring the change in the electrical resistance of a coil of manganin wire, instead of a capillary of mercury. This is the pressure gauge that was used in the later work of this paper, and it has been described in detail in a previous paper. The fluid transmitting pressure was usually kerosene instead of the former mixture of water and glycerine. At 10° and at pressure above 8000, the kerosene becomes so viscous that the ring on the test rod no longer slides freely. The great irregularity of the points first obtained was traced to this effect. It may be avoided by using gasolene instead of kerosene at the higher pressures. At 50° the kerosene may be used without trouble over the entire pressure range. The results obtained were not quite so regular as the former results, doubtless because it was impossible to place the cylinder in a position so favorable to the entire removal of all particles of grit after every application of pressure. In this work the cylinder was placed vertically in a thermostat, whereas in the former work it was placed horizontally.

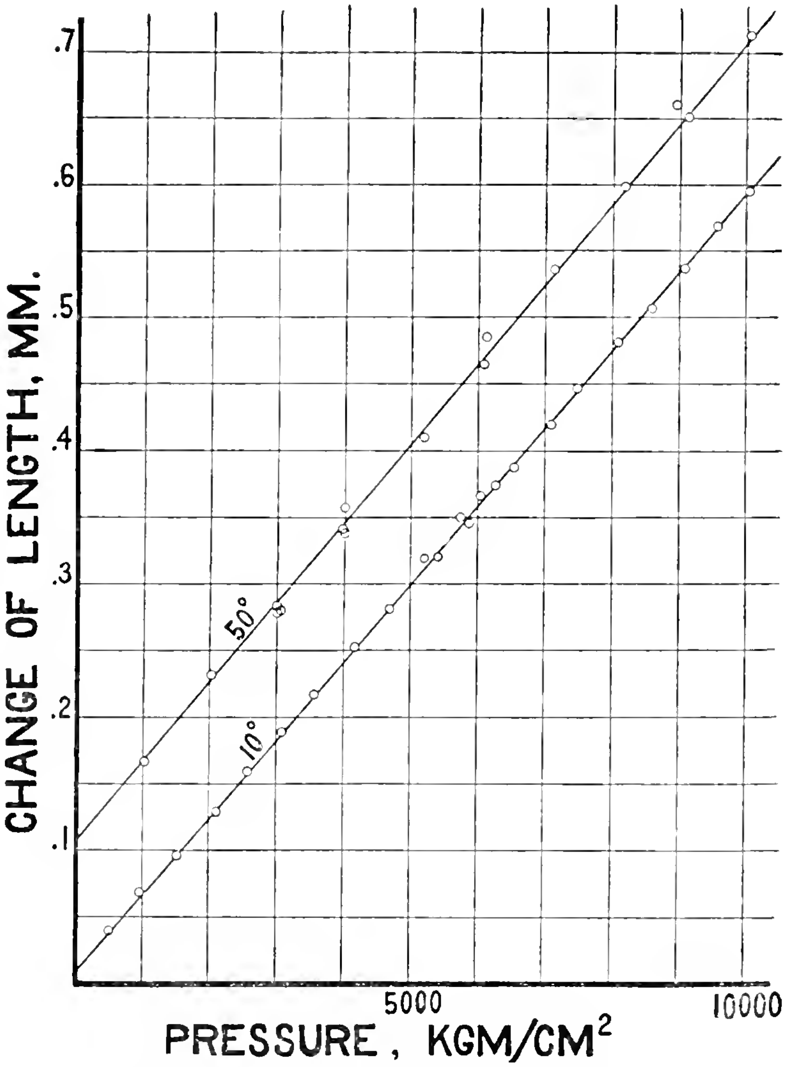

FIGURE 2. Shows the change of length at two temperatures of a bar of bessemer steel 29.95 cm. long under uniform hydrostatic pressure. The zero reading for each of these temperatures is arbitrary.

The results are shown in Figure 2. The values found for the compressibility were 0.0_6583 at 10° and 0.0_6601 at 50°. The result of the previous determination in the tool steel cylinder at 20° was

0.0_6559. A repetition of the former experiment with the tool steel cylinder gave 0.0_6568 at 20°. It is to be noticed that this value is higher than that previously found, and in the direction toward that shown by the nickel steel cylinder. During the repetition of the experiment the tool steel cylinder also showed less hysteresis than in the early determinations, probably due to the gradual disappearance of the heterogeneity introduced by the previous high pressure during the two and one half years for which the cylinder had been resting. During this last set of determinations the pressure was never raised above 4000 kgm., which is below the elastic limit of the steel.

Whether the true explanation of the discrepancies is to be found in the warping of the cross-section of the cylinder or not, the fact seems to be that when the elastic limit of the material is exceeded there is resulting hysteresis in the elongation, and that this hysteresis is accompanied by low values for the compressibility, the greater the hysteresis, the lower the values. It seems to be justifiable therefore, to accept as most probably correct the values given by this new determination with the nickel steel cylinder. The values given above and the temperature coefficient deduced from them were used in the following computations.

It is to be noticed that the elongation of the nickel steel cylinder under internal pressure, which has appeared in the above as a correction factor, is sufficient to give the cubical compressibility of the nickel steel. This is because, as was pointed out by Mallock[17] in 1904, the elongation of a hollow closed cylinder under internal pressure involves only one elastic constant, the cubic compressibility. This gives for the cubic compressibility 6.2×10^{-7} at 20°. The results are not accurate enough to give the temperature coefficient by this method. The high value of this result compared with that by the direct observation of linear compressibility (62 against 58), is probably due to the difference in the materials, the latter value being for an almost pure iron, while the former is for a nickel-chrome alloy with little or no carbon. (Krupp's trade number for this steel is E. F. 60.0.) It was shown in the previous paper that carbon alone makes very little difference in the result.

This same method, the elongation of a hollow cylinder under internal pressure, has been recently used by Grüneisen[18] in determining the cubic compressibility of various metals at different temperatures. His results for two different specimens of iron at 18° varied from $58. \times 10^{-8}$ to $63. \times 10^{-8}$. The temperature effect on this last speci-

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[17] Mallock, Proc. Roy. Soc. Lon., **74**, 50 (1904).

[18] Grüneisen, Ann. Phys., **33**, 1239-1274 (1910).

men was found to be 3.1×10^{-8} for 100°, against 1.8×10^{-8} for 40° as found above. Grüneisen does not give the temperature coefficient for the iron with the lower compressibility.

In view of the agreement of the results found here with those of Grüneisen, there can seem to be little doubt but that the results found by Richards [19] are affected by some constant error as has been claimed by Grüneisen.[20] The fact that the results here were found by as near an approach to a direct method as possible, that is, by the measurement of the linear compressibility, which also was the method used by Richards, and the fact that these results agree with those of Grüneisen, which were obtained by more indirect methods from the theory of elasticity, would seem to nullify Richards' contention that the results of other observers have been in error because the theory of elasticity gives results 30 per cent out of the way. Richards found for iron 38.5×10^{-8} against 58.3×10^{-8} above. Since his value for the compressibility of mercury depends directly on his value for the compressibility of iron, the effect of the correction will be to change very appreciably the value for the mercury, as will be mentioned later. The source of error in Richards' work is not entirely clear. He used an electrical method, in which contact was made with a drop of mercury resting on the top of the rod of iron to be measured. Change of shape of this drop of mercury under pressure seems the most likely source of error.

The Data for the Compressibility of Mercury and Calculation of Results.

Determinations were carried out at two temperatures, 0° and 22°. The range is sufficient to give the variation of compressibility with temperature. To get the second temperature derivative of compressibility, observations at several other temperatures would have been necessary, as well as a higher degree of accuracy than was possible to attain in this work. The final values given are the mean of a large number of determinations. At 0°, five different piezometers were used, and over 90 determinations made over the pressure range from 0 to 7000 kgm. At 22°, two piezometers were used, and 38 points determined between 0 and 11,000. The points at 0° were obtained first and show considerable irregularities. As familiarity was gained with the method, and the several sources of error mentioned above became recognized, it was found possible to obtain more

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[19] Richards, loc. cit.

[20] Grüneisen, Ann. Phys., **25**, 849 (1908).

regular results. The values at 22° were found after this experience had been gained, and with the two piezometers giving the best results at 0°.

The points obtained with all five piezometers at 0° are shown in Figure 3, and the points with the best two of these piezometers in Figure 4. The points found with the two piezometers at 22° are shown in Figure 5. The greater regularity of these points is manifest. In both of these figures not all the points actually obtained have been represented, for four or five points, obtained directly after the freezing of the water at too high a pressure, have been discarded.

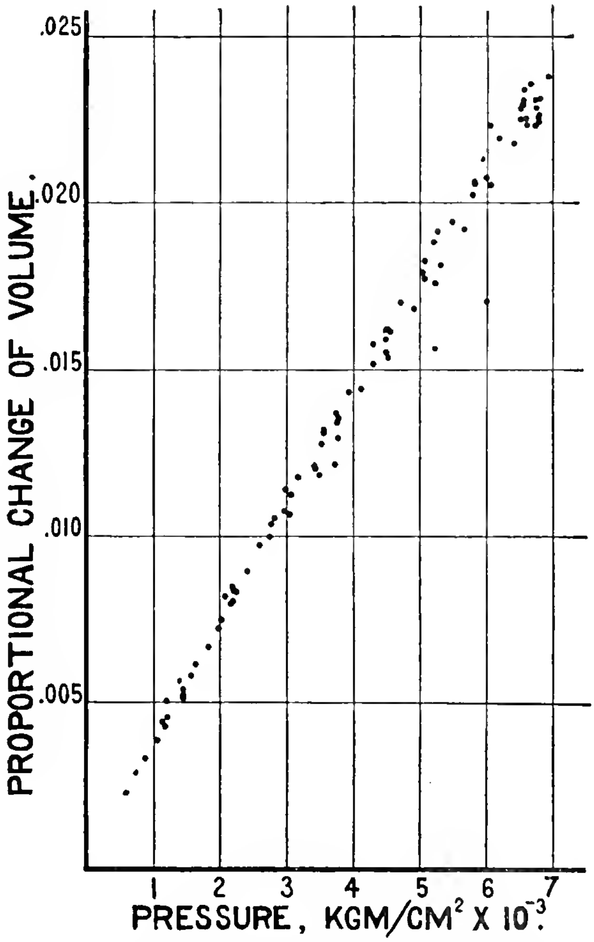

Figure 3. Collection of all the results with five piezometers for the compressibility of mercury at 0°.

The data were adjusted and the final values computed in the following way. The work was done independently at each temperature. A straight line was first drawn passing through the assemblage of points. It was not necessary that this line pass through the origin. The deviation of the observed points from the points calculated by the linear formula was then determined. The deviations from this line for each piezometer separately were then plotted on a very much enlarged scale against pressure, and a smooth curve drawn through these deviation points. This deviation curve, together with the fundamental linear equation, gave the best smooth curve connecting change of volume with pressure as determined by each piezometer separately. From these best smooth curves (five at 0°), points were determined at even pressure intervals, 500 or 1000 kgm. apart. At each of these evenly distributed pressures, the weighted mean of these five points was taken as the best point at this pressure. Weights were assigned to the smooth curves obtained with each piezometer inversely as the arithmetic difference between the observed deviation points and the smooth deviation curve. The weights at 0°

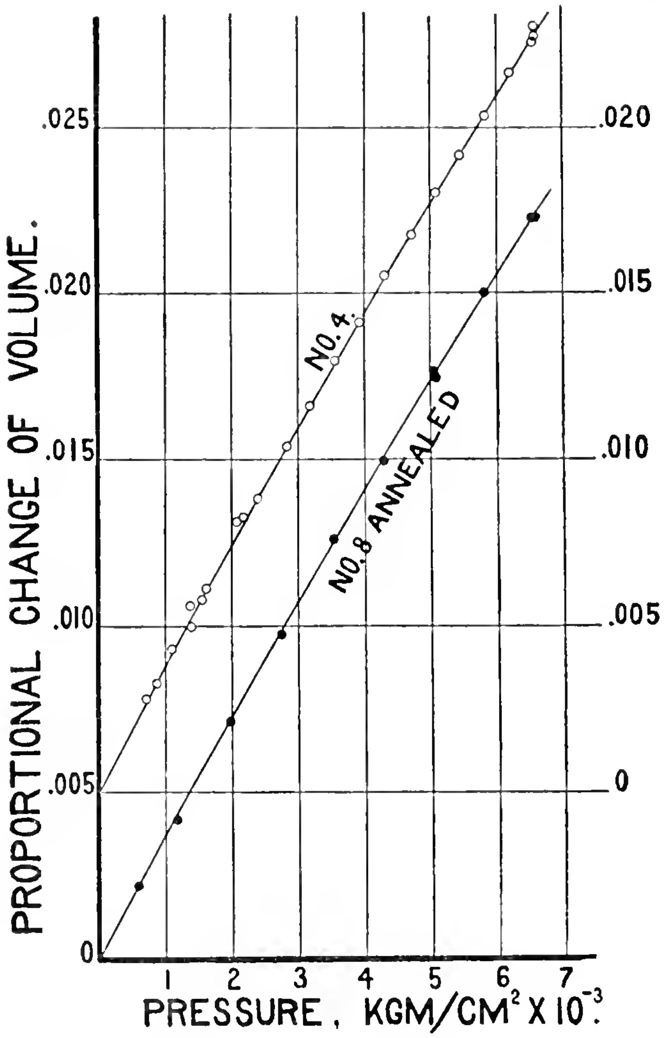

FIGURE 4. The results with the two best piezometers for the compressibility of mercury at 0°. The right-hand vertical scale refers to No. 4, the left-hand scale to No. 8, annealed.

varied from 1 to 7. Finally, a parabola was passed through these best points, the deviations of these weighted best points from the parabola were plotted against pressure, and the smooth curve through these deviations, together with the parabolic formula, was taken as giving the best possible relation between change of volume and pressure.

This was the process used in the final determinations. It has been already explained that the calculation was by means of a method of successive approximations, and that it was necessary to calculate the compressibility of the water as well as that of the mercury. The details of this approximation process have been discussed already in the general discussion of the method. Reference is made to a following paper for the values for the compressibility for water. The procedure in the first steps of the approximation process did not need to be so elaborate as in the above final calculation.

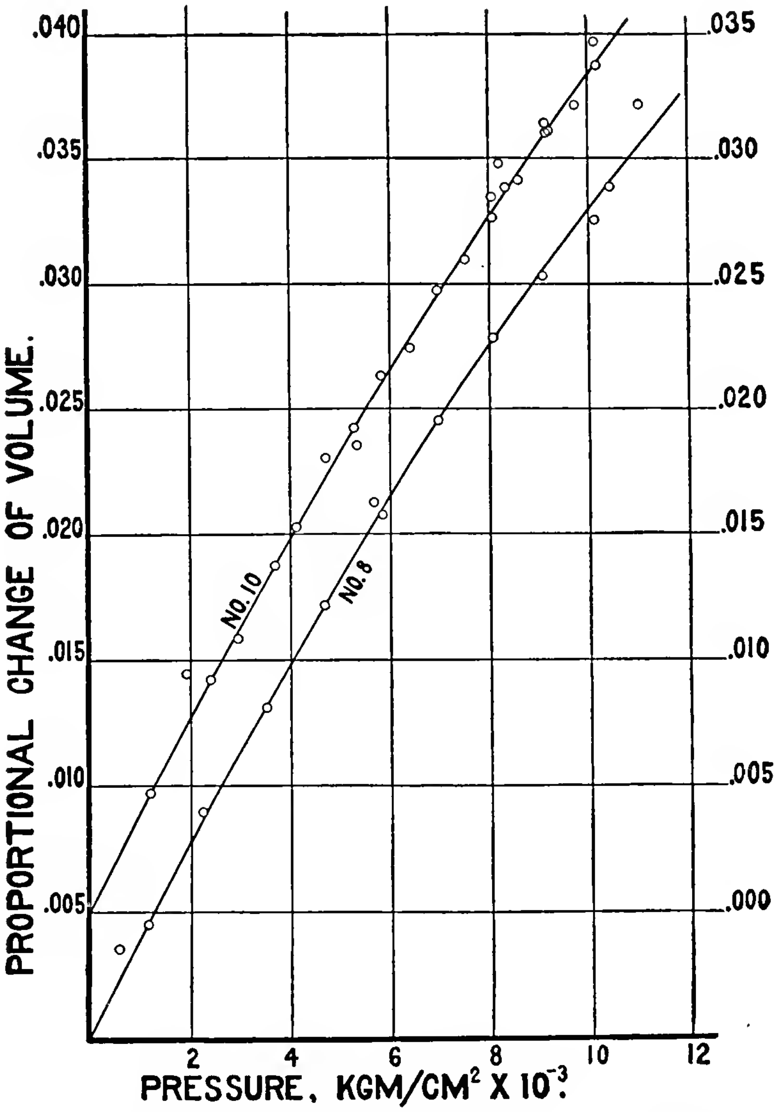

FIGURE 5. The change of volume of liquid mercury at 22° as obtained with two piezometers. The right-hand scale is for No. 10, the left-hand one for No. 8.

The data for 0° and the steps in the final process of adjustment are shown in the tables. Table I. shows the points in the order in which they were determined. The actual computation from the data it is not necessary to show. The formula has already been given by which these computations were made. In Table I., the values for the change

TABLE I.

DATA FOR COMPRESSIBILITY OF HG AT 0°.

Pressure, kgm./cm.²	Δv_{H_2O} (used in computation).	Δv_{Hg}.
PIEZ. NO. 4.		
5270	0.1415	0.01913
4520	1290	1621
3750	1147	1370
3000	0991	1142
2220	0796	0847
1450	0578	0538
6050	1527	1709
6770	1617	2283
1000	0414	0337
500	0224	0170
2210	0794	0802
1410	0564	0512
2180	0786	0797
3090	1009	1128
3740	1145	1215
4500	1286	1543
4500	1286	1566
5290	1418	1568
5270	1415	1760
6030	1525	2078
6760	1616	2310
PIEZ. NO. 10.		
1190	0.0485	0.00453
2010	0740	0745
2780	0939	1035
5950	1513	2135
6670	1605	2362
694	0298	0297
3570	1110	1310
4490	1284	1620
5220	1407	1881
PIEZ. NO. 8.		
6810	0.1622	0.02245
6800	1620	2259
6070	1530	2227
5330	1427	1816
4540	1294	1533
3770	1151	1295
3020	0994	1068
2230	0798	0831
1440	0574	0519
1050	0432	0385
1830	0690	0667
2610	0897	0977
3400	1074	1211
4140	1222	1443
4910	1358	1685
5680	1476	1926
6420	1575	2182
6070	1530	2068
4560	1297	1614
3790	1154	1357
2990	0987	1074
6820	1622	2316
6630	1601	2234
PIEZ. NO. 8, annealed		
6940	0.1636	0.02383
6540	1591	2255
5810	1495	2027
5050	1380	1790
4300	1251	1521
3540	1104	1279
2750	0931	0998
1980	0730	0722
PIEZ. NO. 8 (*cont.*).		
1170	0.0477	0.00425
595	0259	0224
5090	1387	1771
6600	1598	2259
PIEZ. NO. 11.		
6570	0.1594	0.02298
6200	1547	2197
5450	1442	1941
4720	1325	1704
3940	1184	1434
3180	1028	1179
2400	0844	0896
1620	0631	0617
870	0366	0335
6570	1594	2310
5830	1497	2064
6570	1594	2340
5840	1499	2064
5090	1387	1829
4300	1252	1578
3550	1106	1320
2820	0948	1054
2090	0766	0819
1380	0553	0562
710	0305	0288
1390	0557	0502
2180	0786	0835
1550	0610	0582
1110	0455	0441
2190	0788	0836
6540	1590	2289

of volume of the water, which entered into the computation, are also given, as this effect is rather large. Roughly, the correction introduced by the water was about one third of the total effect due to the change of volume of the mercury. These values for water were taken from the values to be given in greater detail in the following paper.

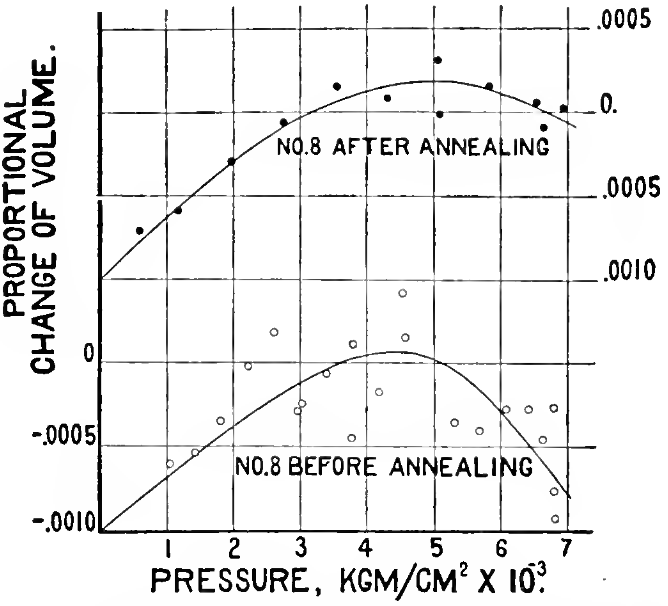

FIGURE 6. The deviations from linearity of the points obtained with one piezometer. This shows the irregularities in the results introduced by internal strains.

Figure 6 gives the deviations of the observed points of two of the sets of readings of Table I. from a straight line. This line, of the form $\Delta V = a + bp$, does not happen to pass through the origin, but gives $\Delta V = 0.001$ at $p = 0$. All the deviation curves, therefore, start from the point $\Delta V = -0.00100$. In Table II. are given the values calculated with the help of the deviation curves for the five piezometers at pressure intervals of 500 kgm., together with the weighted mean of these values. Finally in Table III. are shown the values calculated by the parabolic formula, the weighted experimental values, the deviations, and the finally accepted values, obtained with the smooth deviation curve shown in Figure 7.

The change of volume at any pressure and 0° may be found, either by constructing a curve through the points of Table III., or more accurately by computing at any pressure the change of volume by the formula

$$\Delta v = ap + bp^2,$$

TABLE II.

Adjustment of Data — Final Values of Compressibility of Hg at 0°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	Δv_{Hg} at 0°.						Calculated $\Delta v = ap + bp^2$.	Deviation.	Final value.
	No. 4.	No. 8.	No. 10.	No. 11.	No. 8 annealed.	Weighted mean.			
500	0.00180	0.00180	0.00196	0.00192	0.00187	0.00187	0.00190	−0.00003	0.00189
1000	0362	0361	0389	0385	0369	0372	0376	−4	0374
1500	0549	0543	0569	0577	0553	0560	0561	−1	0559
2000	0737	0721	0753	0763	0731	0739	0741	−2	0739
2500	0921	0899	0931	0945	0909	0917	0919	−2	0918
3000	1100	1070	1110	1120	1086	1096	1094	+2	1095
3500	1272	1246	1285	1292	1259	1269	1267	+2	1269
4000	1442	1414	1458	1458	1428	1437	1436	+1	1439
4500	1606	1576	1630	1628	1596	1605	1602	+3	1605
5000	1777	1735	1795	1793	1761	1770	1767	+3	1769
5500	1923	1889	1955	1954	1934	1929	1927	+2	1929
6000	2073	2039	2111	2111	2084	2085	2085	0	2085
6500	2220	2192	2244	2268	2244	2239	2241	−2	2240
7000	2366	2344	2390	2422	2404	2394	2393	+1	2393
....	4	2.5	1.5	5	10	Weights	....	....	....

Calculated values are by the formula

$$\Delta v = ap + bp^2$$

$$a = 0.0_5 3818$$

$$b = -\log^{-1} 19.7569 - 10$$

TABLE III.

Data for Compressibility of Hg at 22°.

Pressure, kgm./cm.^{2}.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
Piez. No. 8.		
4690	0.1258	0.01720
5860	1441	2079
6980	1599	2453
1170	0437	0451
2350	0776	0898
3530	1044	1313
8080	1740	2784
9080	1863	3031
10430	2012	3389
*11640	2128	4101
11030	2070	3720
10130	1980	3257
5690	1416	2129
593	0245	0355
Piez. No. 10.		
10150	0.1982	0.03472
9130	1869	3145
8060	1740	2848
6960	1596	2478
Piez. No. 10 (*cont.*).		
5840	0.1439	0.02132
4720	1264	1806
3570	1052	1378
2410	0787	0923
1210	0450	0472
1930	0657	0947
2950	0918	1087
4140	1160	1530
5350	1364	1855
6410	1521	2243
7520	1670	2599
8600	1806	2916
9740	1938	3218
10180	1985	3377
9150	1872	3106
8080	1766	2765
8200	1756	2984
5290	1355	1926
8290	1767	2887
9210	1878	3113

* Freezes.

where
$$\log a = 4.5819 - 10,$$
$$\log(-b) = 9.7569 - 20,$$

and applying to this computed value the correction given by the deviation curve of Figure 7.

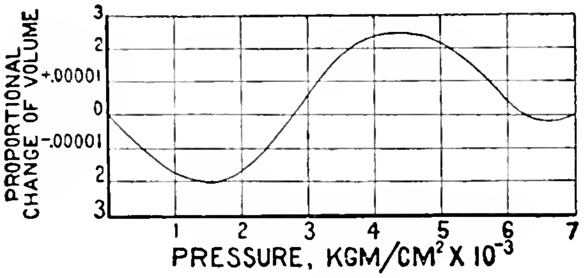

Figure 7. The deviation curve for the change of volume at 0°. This is to be used with the formula on page 373.

The data for 22° are shown in a corresponding set of tables and figures. The only difference is that here the parabola was used as the basis for both the first and the final deviation curves. Table IV. corresponds to Table I., Figure 8 to Figure 7, Table V. to Table II., and Table VI. to Table III. The final formula for computation at any pressure is

$$\Delta v = ap + bp^2,$$

where
$$\log a = 4.5911 - 10,$$
$$\log(-b) = 9.7782 - 20,$$

and the final deviation curve from this formula is given in Figure 8.

There are only a few previous determinations of the compressibility of mercury with which these results can be compared, and all of these are at comparatively low pressures, where the percentage accuracy of the above work is naturally less than at the higher pressures. The only way of making the comparison is to find what the compressibility given by the above two expressions would be at atmospheric pressure. The values found in this way from the above data are 0.0_5380 at 0° and 0.0_5395 at 22°.

The early work, done by Regnault,[21] Grassi,[22] Jamin,[23] Amaury et Descamps,[24] and Tait,[25] may be summarily ruled out as too inaccurate for the comparison. The earlier of these determinations were made

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[21] Regnault, Mém. Inst. de France, Six. Mem., **21**, 329–428 (1847).

[22] Grassi, Ann. de Chim. et Phys., **31**, 437–478 (1851).

[23] Jamin, C. R., **66**, 1104–1106 (1868).

[24] Amaury et Descamps, C. R., **68**, 1564–1565 (1869).

[25] Tait, Challenger Report (1889), Phys. and Chem., vol. II, p. 1–76.

before the theory of elasticity was well understood, and the work of Jamin, in particular, is a classical instance of how dangerous it is to follow native intuition where the stress and strain system is at all complicated. Jamin's results were 50 per cent too small. Of the more accurate work, Amagat[26] gives 0.0_5379 for the pressure range 0 to 50 kgm., at a temperature apparently unspecified in the original

TABLE IV.

ADJUSTMENT OF DATA — FINAL VALUES OF COMPRESSIBILITY OF Hg AT 22°.

Pressure. kgm./cm.^{2}.	Δv_{Hg} at 22°.			Calculated, $\Delta v = ap + bp^2$.	Deviation.	Final Value.
	No. 8.	No. 10.	Weighted Mean.			
1000	0.00389	0.00389	0.00389	0.00384	+0.00005	0.00389
2000	0766	0766	0766	0756	+10	0766
3000	1129	1131	1130	1116	+14	1130
4000	1482	1485	1483	1465	+18	1483
5000	1818	1823	1820	1800	+20	1820
6000	2141	2149	2144	2124	+20	2144
7000	2451	2461	2454	2436	+18	2454
8000	2746	2761	2751	2736	+15	2751
9000	3026	3044	3030	3024	+06	3030
10000	3290	3313	3297	3300	−03	3297
11000	3540	3568	3549	3564	−15	3549
12000	3776	3809	3787	3816	−29	3787
....	2	1	Wt.	....	....	....

Calculated values are by the formula

$$\Delta v = ap + bp^2$$
$$\log a = 4.5911 - 10$$
$$\log(-b) = 9.7782 - 20$$

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[26] Amagat, loc. cit.

paper. De Metz,[27] in quoting Amagat, however, gives 0.0_5379 as Amagat's value at 0°. The source from which this knowledge was obtained is not clear. Amagat's results, obtained with seven different piezometers, vary among themselves by 2 per cent. De Metz gives 0.0_5374 at 0° and a pressure range not over 50 kgm., as the mean of results with four piezometers differing among themselves by 5 per cent. De Metz also gives the temperature coefficient of compressibility. This is higher than the value found above, but is such as to bring de Metz's value at 22° up to 0.0_5394, almost identical with the present determination at that temperature. Lately Richards [28] has determined the compressibility to 500 kgm. He gives 0.0_5371 for the pressure range 0–500, at a temperature not specified, probably room temperature. Previous work by Richards, however, had given a value for the temperature coefficient of the mercury the same as that of the glass piezometer. This temperature coefficient is very much smaller than found above, producing a change from 0.0_53710 at 0° to 0.0_53724 at 20°.

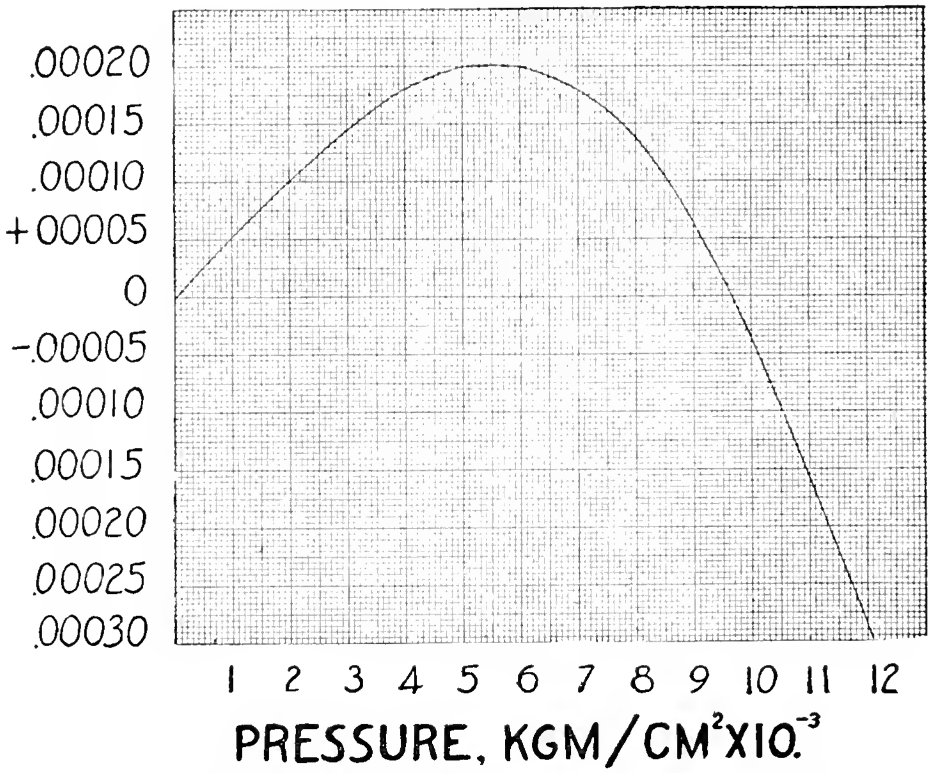

FIGURE 8. The deviation curve for the change of volume at 22°. This is to be used with the formula on page 376.

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[27] De Metz, loc. cit.

[28] Richards, loc. cit.

It is to be noticed, however, that Richards' value involves directly his own value for the compressibility of iron, which is almost certainly much too low. If the more probable value $0.0_6 58$ is used instead of Richards' value $0.0_6 38$, the value of Richards for mercury becomes $0.0_5 391$ at room temperature. The change of compressibility with pressure found by Richards is higher than that found above, dropping from 3.80 between 0 and 100 kgm. to 3.60 between 500 and 600 kgm. As mentioned in a previous paper, this is probably due to error in the pressure gauge. Carnazzi[29] has published data over a much wider pressure and temperature range than the other previous observers, up to 3000 kgm., and from 23° to 192°, but with less pretense to accuracy, as only two figures are given in the results. Carnazzi gives $0.0_5 37$ as the initial compressibility at 23°. Since Carnazzi's results are the only ones which give the change of compressibility with pressure over an at all wide pressure range, it may be permitted to anticipate a little in order to compare his results with the present ones. Carnazzi finds a drop in the compressibility of $0.0_6 4$ from 250 kgm. to 2750 kgm. at 23°, against $0.0_6 25$ of the present work. His change in the mean dilatation between 23° and 53° is from 181 at 0 pressure to 157 at 3000, against a change in the mean dilatation between 0° and 22° from 181 to 163 for the same pressures as found in the present work.

Finally, the results may be compared with the results of the previous paper.[30] It has been already stated that the method of the paper was open to question, but it should be remembered, as was stated at the time, that the primary object of that work was to find whether the compressibility of mercury showed any marked change over a pressure range from 0 to 6000, and that the data were obtained because of their bearing on another question. The accuracy was sufficient for the purpose in hand, and the employment of the method seems to have been justified in view of the very much greater speed and ease of manipulation. The initial compressibility at 20°, making correction as already explained for the erroneous value used for the compressibility of steel, was $0.0_5 375$.

Taken altogether, the agreement with the more accurate of the previous determinations is as satisfactory as could be expected: 380 at 0° against 379 of Amagat and 374 of de Metz, and 395 at 22° against 394 of de Metz and 391 of Richards.

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[29] Carnazzi, loc. cit.

[30] Bridgman, loc. cit.

Discussion of the Data.

These data may be used in mapping out the p-v-t surface, and for giving certain information about the thermodynamic behavior of liquid mercury under pressure. The proportional changes of volume given above were calculated in the usual way, by taking the volume under atmospheric pressure and at the temperature in question as the unit volume. To map the p-v-t surface, correction must be made for the change of volume with temperature at atmospheric pressure. Thus, if the volume when $p = 1$ and $t = 0°$ is taken as unity, the values given by the process just mentioned for Δv at 22° must be corrected by multiplying by the ratio of the volume at 22° and $p = 1$ to the volume at 0° and $p = 1$. The actual volume under different pressures, and at 0° and at 22° is given in Table V. In this the value for the total change of volume between 0° and 22° was taken as 0.00398, as given by the most recent work of Callendar and Moss[31] on the expansion of mercury. It appears from their work that the mean coefficient of expansion at 0° is 0.0001805, while the mean coefficient between 0° and 100° is 0.0001817. This gives for $\left(\frac{\partial^2 v}{\partial t^2}\right)_p$ the value 0.0_724, which is evidently beyond the accuracy of this work. That is, for the present purpose, over the temperature and pressure range involved, the isothermals may be assumed to be equally spaced. This is sufficiently accurate at atmospheric pressure, and all our experience with other more compressible liquids would lead us to expect it to be all the more nearly true at higher pressures.

TABLE V.

Volume of Hg at 0° and 22°.

Pressure. kgm./cm.².	Volume.	
	at 0°.	at 22°.
0	1.00000	1.00398
1000	0.99626	1.00007
2000	99261	0.99627
3000	98905	99264
4000	98561	98909
5000	98231	98571
6000	97914	98246
7000	97607	97934
8000		97637
9000		97356
10000		97088
11000		96835
12000		96596

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[31] Callendar and Moss, Proc. Roy. Soc. Lon., A, **84**, 595–597 (1911).

Figure 9 shows the compressibility at these two temperatures and different pressures. The compressibility plotted in Figure 9, is the

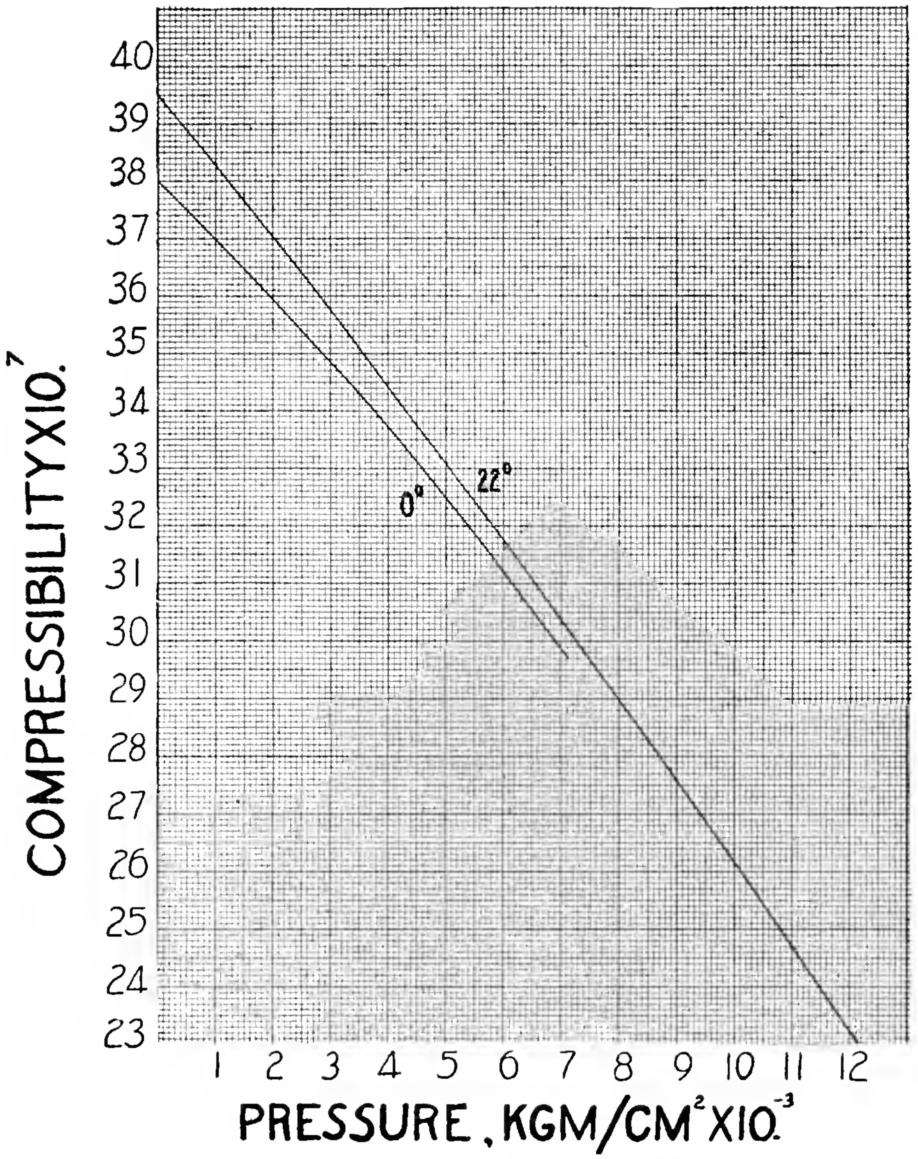

Figure 9. The compressibility of mercury at two different temperatures. This compressibility is the instantaneous compressibility $\left(\frac{\partial v}{\partial p}\right)_\tau$.

thermodynamic quantity $\left(\frac{\partial v}{\partial p}\right)_\tau$, which is slightly different from the ordinary meaning of compressibility as used above. It may be obtained at 0° directly from the parabolic formula and the deviation curve. At 22° the results obtained from the parabolic formula and the deviation curve are to be corrected by about 0.4 per cent for the increased initial volume at 22°. The results given in the figure are from smooth curves drawn through the points so determined. The compressibility is less at higher pressures, as it is universally for all liquids, and is greater at higher temperatures, as it is for everything except water. The decrease of compressibility with pressure is very nearly linear, but nevertheless shows a tendency to become more rapid at higher pressures, which is a little surprising. The decrease of compressibility with pressure is more rapid at the higher temperature. Whether the compressibilities at different temperatures would ever become sensibly equal cannot be determined because of the entrance of the solid phase.

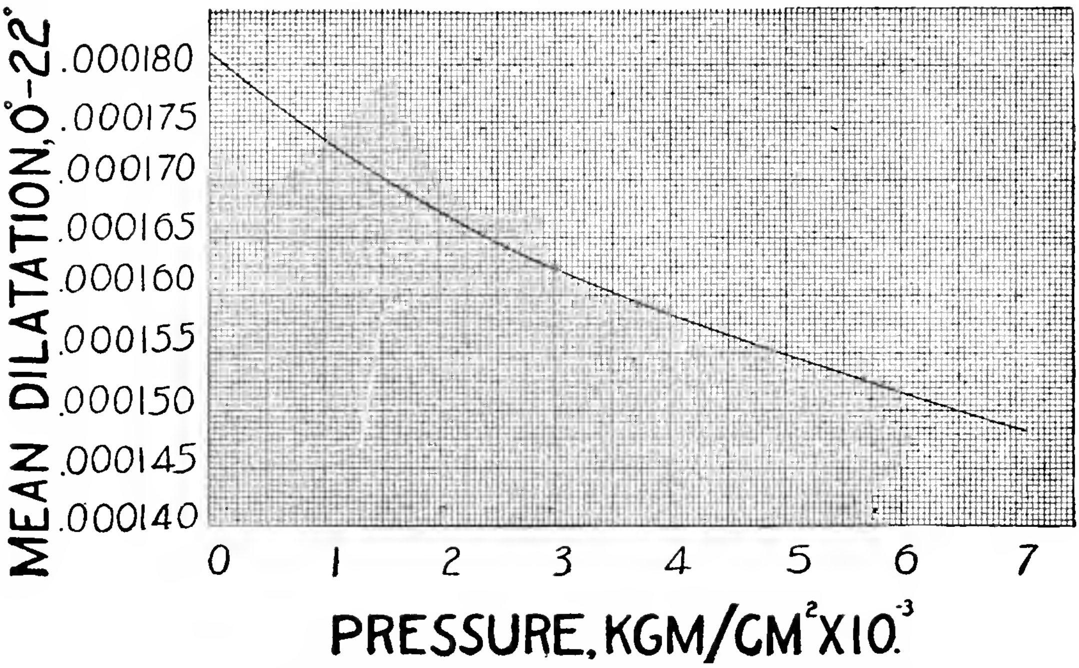

FIGURE 10. The mean dilatation per degree between 0° and 22° for mercury as a function of the pressure.

The dilatation of the mercury, or rather the derivative $\left(\frac{\partial v}{\partial \tau}\right)_p$, may be found from the distance apart of the isothermals at 0° and 22°. The results are shown in Figure 10. The dilatation becomes less at higher pressures, the rate of decrease also becoming less as one would expect.

The data so found, $\left(\frac{\partial v}{\partial \tau}\right)_p$ and $\left(\frac{\partial v}{\partial p}\right)_\tau$, are sufficient to give the difference of the specific heats at different pressures, for we have the relation,

$$C_p - C_v = -\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}$$

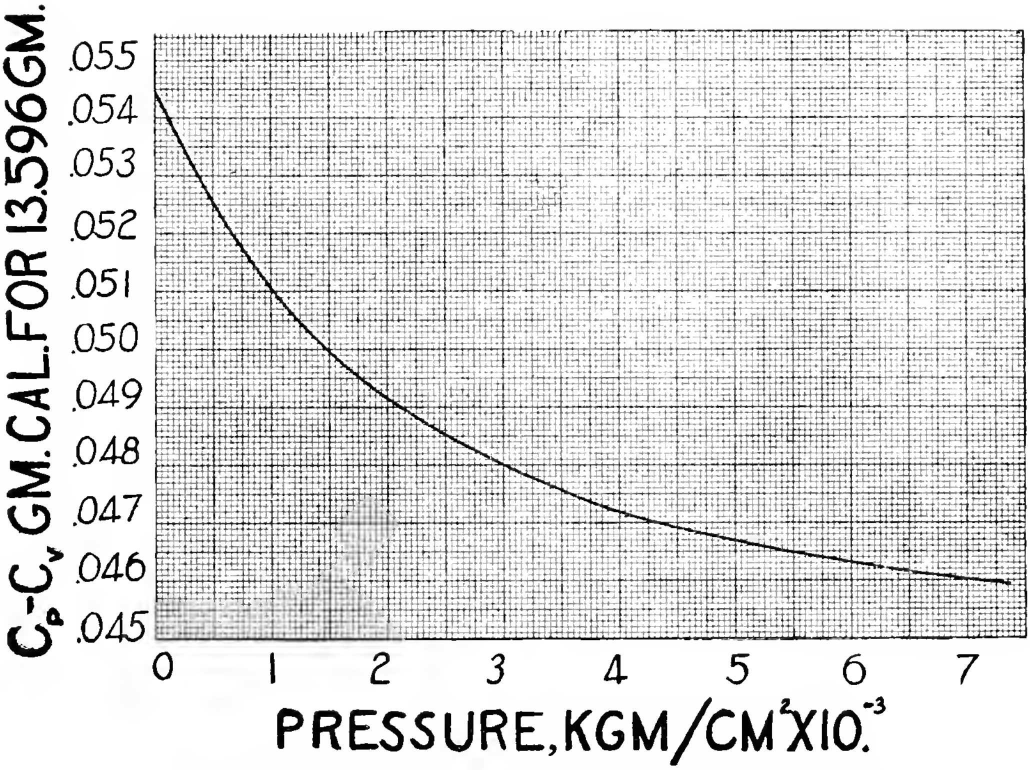

Figure 11. The difference of the specific heats as a function of the pressure in gm. cal. for a quantity of mercury occupying 1 cm.³ at 0° and atmospheric pressure.

The results in gm. cal. along the isothermal at 0° are given in Figure 11. The difference becomes less at high pressures, the rate of decrease itself decreasing rapidly. The behavior is thus different from that of water, which shows an increase.

The data are not sufficient to give the actual value of either specific heat along the isothermals, but we can find the initial rate of variation from the thermodynamic formula

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau \left(\frac{\partial^2 v}{\partial \tau^2}\right)_p.$$

The work of Callendar and Moss [32] gives at atmospheric pressure and 0°

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[32] Callendar and Moss, loc. cit.

$$-\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p = -273 \times 0.0_7 24$$
$$= -0.0_5 655,$$

C_p being expressed in ergs per cm.^{3} and p in dynes per cm.^{2}. Expressed in gm. cal. and kgm./cm.^{2} this becomes

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -0.0_6 154.$$

This variation is so small that we may assume it to remain constant over the pressure range here. This would give a total change of C_p of only 1/4 per cent for 7000 kgm. Probably the change is actually less than this. Table VI. shows the values of C_p calculated with this assumption, and also the values of C_v found from the already calculated values of $C_p - C_v$. It is seen that while C_p decreases with pressure, C_v increases, the increase being more rapid than the decrease. In computing the date of the table, the value of Barnes and Cooke[33] for C_p at atmospheric pressure and 0° was used, 0.03346 gm. cal. per gm., or 0.4549 gm. cal. per cm.^{3}.

TABLE VI.

C_p AND C_v FOR Hg AT 0°.

Pressure. $\frac{\text{kgm.}}{\text{cm.}^2}$	Specific Heat, gm. cal. for initially Unit Vol. (13.596 gm.)	
	C_p.	C_v.
0	0.4549	0.4003
1000	4547	4035
2000	4546	4056
3000	4544	4063
4000	4543	4073
5000	4541	4073
6000	4540	4077
7000	4538	4079

There are several other quantities of interest that may be deduced from the given data. One of these is the difference between the isothermal and the adiabatic compressibilities. We have the thermodynamic formula

$$\left(\frac{\partial v}{\partial p}\right)_\tau - \left(\frac{\partial v}{\partial p}\right)_\phi = -\frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2.$$

The results are shown in Figure 12. The adiabatic compressibility, therefore, on the isothermal $t = 0°$, decreases less rapidly than the isothermal compressibility.

Intimately connected with the adiabatic compressibility is the temperature effect of compression. For this we have

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[33] Barnes and Cooke, Phys. Rev., **16**, 65–71 (1903).

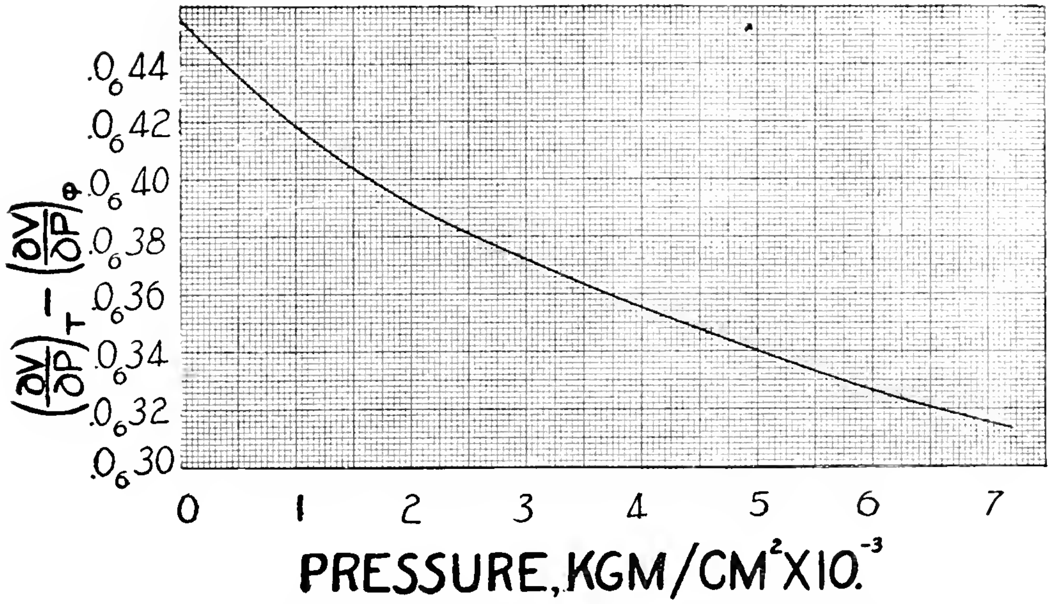

FIGURE 12. The difference between the isothermal and the adiabatic compressibilities as a function of the pressure.

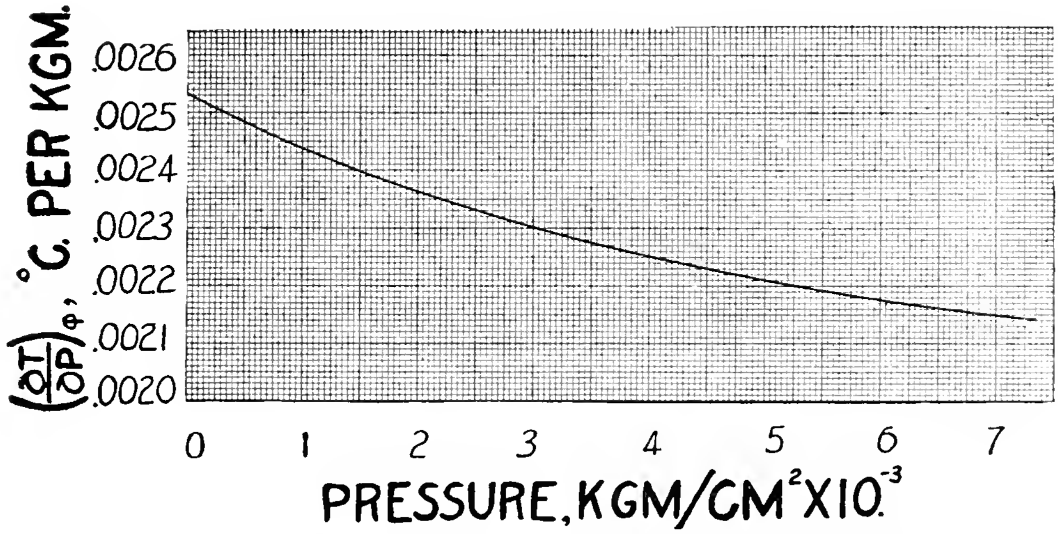

FIGURE 13. The heating effect of compression; that is, the rise of temperature in degrees centigrade for an adiabatic rise of pressure of 1 kgm.

$$\left(\frac{\partial \tau}{\partial p}\right)_\phi = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}.$$

The numerical values of this quantity are shown in Figure 13. The initial rise of temperature is, therefore, about 2°.5 for 1000 kgm. The rise of temperature becomes less at higher pressures, the rate of decrease also decreasing. The rise of temperature for 500 kgm. was found by actual experiment by Richards [34] to be 1°.2, agreeing essentially with above. The fact that this rise of temperature is less at high pressures might at first sight seem surprising, since the work done by the external pressure during a given pressure increase is increasing nearly proportionally to the pressure and the specific heats are nearly constant. It must be, therefore, that most of the work done by external pressure goes toward increasing the internal energy of the liquid, very little being left over to increase the temperature. That this is true is seen at once from the thermodynamic formula

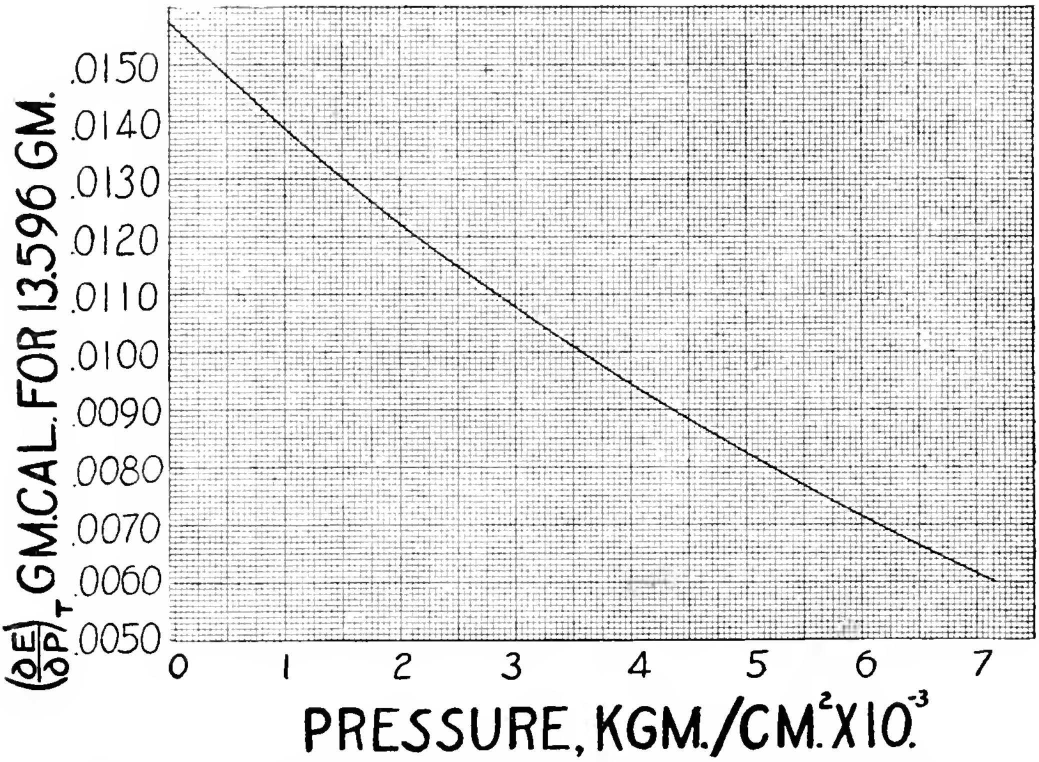

FIGURE 14. The rate of change of internal energy with pressure along an isothermal in gm. cal. for a quantity of mercury occupying 1 cm.^{3} at 0° and atmospheric pressure. Notice that the sign of the derivative is negative.

$$\left(\frac{\partial E}{\partial p}\right)_\phi = -p\left(\frac{\partial v}{\partial p}\right)_\phi,$$

which shows that the internal energy is increasing along an adiabatic, and at a rate very nearly proportional to the pressure. The internal energy decreases along an isothermal, however, as may be inferred from the value of the derivative given by

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[34] Richards, loc. cit. (1903), p. 40.

$$\left(\frac{\partial E}{\partial p}\right)_\tau = -\left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right],$$

and shown in Figure 14. The curvature of Figure 14 is so slight, however, that it seems probable that at a high enough pressure the derivative will vanish and then become positive, so that ultimately the internal energy will increase along an isothermal.

The Change of State Liquid–Solid.

The quantities involved thermodynamically in the passage of a substance from one phase to another at a given pressure and temperature are the change of volume and the latent heat. From these quantities the change of freezing temperature with pressure may be calculated by Clapeyron's equation, $\frac{d\tau}{dp} = \frac{\tau\Delta V}{\Delta H}$. But the experimental difficulties of determining the latent heat are almost prohibitive. This is because in order to withstand high pressures the mass of the steel containing vessel must be much greater than the mass of the substance under experiment. Another method of finding these quantities based on Clapeyron's equation was therefore used, as in practically all the work done previously in this field. If the course of the freezing curve is known, $\frac{d\tau}{dp}$ may be found at any point, which, together with the change of volume at this point and the temperature of transformation, gives the latent heat.

The data were obtained by three methods. The first gives simply the course of the freezing curve. This was found by measuring the electrical resistance at constant temperature as a function of the pressure, freezing being indicated by a sudden drop in the resistance to about one third its value for the liquid. The second method, by far the most important, gives both the melting pressure and the change of volume. It is the same as that used by Tammann,[35] and consists in measuring the volume as a function of the pressure at constant temperature. At the freezing pressure, the volume suddenly changes, so that by plotting volume against pressure, the point of discontinuity gives both the equilibrium pressure and the change of volume. The third method is concerned with a single isolated quantity on the freezing curve, the change of volume on freezing at atmospheric pressure. The existing data were not accurate enough, so this quantity had to

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[35] Tammann, loc. cit., p. 204.

be redetermined. The measurements were made by weighing mercury under CS_2, and plotting weight against temperature. Melting is accompanied by a sudden decrease in the displacement and so by a sudden increase in the apparent weight.

The Freezing Curve by Change of Resistance.

The points on this curve were obtained on two separate occasions; the fall of 1909, and January, 1911, and with two different pieces of apparatus. The data of 1909 are not as accurate as those of 1911, because the gauge was destroyed by an explosion before an entirely satisfactory calibration was made.

The details of the apparatus have been described elsewhere. The absolute gauge, against which the pressure measurements were made directly, has been described in a separate paper. The details of the glass capillary containing the mercury resistance, and the electrical connections with the details of the insulating plug have been described in the paper on the use of mercury as a standard of pressure. The pressure range employed there was only 6800 kgm./cm.^{2}; it has since been found that the same arrangement of apparatus is good to at least 12,000 kgm./cm.^{2}, the range of this paper. The measurements of electrical resistance were made by a null method on a Carey Foster bridge, exactly as in the preceding paper.

One slight change in the details of the measurements as made in 1911 should perhaps be noted, the employment of kerosene as the liquid surrounding the glass capillary instead of a mixture of glycerine and water. This avoids all possibility of short circuiting the terminals of the plug dipping into the mercury cups, and also avoids the necessity for carefully protecting these terminals. A light oil like kerosene is necessary since a heavy oil, such as ordinary lubricating oil, freezes at about 4000 kgm. at room temperature. It was found by independent experiment that at least up to 12,000 kgm. the kerosene does not become so stiff as to refuse to transmit the pressure hydrostatically.

The experimental procedure was the one which would naturally suggest itself, but there are a number of details of manipulation which were necessary to observe. The resistance was measured at appropriate intervals of pressure, the temperature being kept constant. After every increase of pressure it was necessary to wait 10 or 20 minutes for the dissipation of the heat of compression to the surrounding bath, which was kept constant to within 0°.01 with a thermostat. With increasing pressure it was never found possible to reach exactly the freezing pressure, but always the mark was overshot a little. It would have been impossible to land exactly on the mark, in the first place because of the mechanical difficulty of raising the pressure exactly the right amount, in the second place because of the initial effect of heat of compression which would keep the mercury liquid even if the pressure corresponding to the bath temperature were reached, and in the third place, because of the possibility of subcooling the liquid into the region of stability of the solid. With increasing pressure it was always necessary, therefore, to run past the point by from 200 to 400 kgm. Freezing was indicated by a sudden drop in the resistance. This drop was not instantaneous, but might continue for several minutes. Everything points to the spontaneous formation of a crystalline kernal at some point in the capillary, and then the advance of the surface of separation of solid and liquid through the capillary at a rate depending on the amount subcooling, etc.[36] Freezing, when it had once started, usually ran to completion. This was because the volume of the mercury was so small that the change of volume on passing to the solid state was not sufficient to lower the pressure to the equilibrium value. To find the equilibrium pressure, the pressure on the solid phase was lowered until the reaction to the liquid started, and then by rapid work at the pump the pressure was so adjusted that the resistance was in a state of unstable equilibrium, changes of pressure too small to measure on the gauge sufficing to produce a very large increase or decrease of resistance. With a little practice, one could keep the mercury in a partly melted condition for any desired length of time. This was necessary in order to avoid the effect of heat of compression, which might sometimes be so large as to mask the effect sought. The heat of compression of kerosene is so high that it is possible for a decrease of pressure in the kerosene to bring about a freezing of the mercury, the adiabatic drop of temperature with pressure for the kerosene being more rapid than the drop of pressure with temperature on the freezing curve of mercury. To be absolutely certain that there was no such effect the mercury was always kept in the partially melted condition for twenty minutes before recording the equilibrium pressure. To avoid any possibility of error from impurities absorbed by the mercury, pains were taken to find

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[36] To measure the rate of advance of the surface would have been interesting, but to be of value would have demanded some other disposition of apparatus from that used. Evidently the rate of advance of the surface depends more than anything else on the rate at which the heat of transformation is conducted away, which in turn will depend on the size of the glass capillary, and the thermal conductivity of the surrounding liquid. Any results obtained with the apparatus without modification would have had significance only for this piece of apparatus.

the equilibrium pressure with as little of the solid phase present as possible. This evidently avoids the large depression of the freezing point which would result from the concentration of impurities in the small remaining mass of liquid after the solid had nearly all separated out. The precaution was probably superfluous because the mercury was carefully purified to begin with, and no effect of such a nature was ever detected.

One other source of error was guarded against which was especially prominent in the earlier work of 1909. The fluid transmitting pressure from the lower cylinder, in which was the absolute gauge, to the upper cylinder, in which was the mercury, was a thick mixture of either molasses and glycerine or glucose and glycerine. It was necessary to use such a mixture in connection with the absolute gauge in order to avoid leak at the high pressures. But there is the disadvantage that the viscosity of either of these fluids increases so rapidly with pressure that high pressures are not transmitted immediately through the connecting pipe from the lower to the upper cylinder. This connecting pipe was 15 inches long and 1/16 inch internal diameter. That the pressure was transmitted slowly was shown by the fact that after pressure had been increased in the lower cylinder by advancing the piston, the absolute gauge in the lower cylinder indicated a fall of pressure for some minutes, while the change of mercury resistance in the upper cylinder indicated a corresponding rise, evidently due to the slow flow of liquid from the lower to the upper cylinder. The effect was troublesome only at the higher pressures, the pressure coefficient of the effect being very high, and was very much greater for the mixture of glycerine and molasses used in 1909 than for the glycerine and glucose of 1911. In the extreme case, glycerine and molasses at 12,000 kgm., it was necessary to wait two hours for the equalization of pressure. For most of the pressures used the effect disappeared more rapidly than the heat of compression. To avoid error from this effect, the decrease of resistance indicating freezing must come after an increase of pressure in the lower cylinder, and the converse increase of resistance after a decrease of pressure. The measurements were made with this in mind.

The temperature measurements above zero were made with a Tonnelot thermometer calibrated at the Bureau of Weights and Measures in Paris. Below zero the readings of 1911 were made with a toluol thermometer calibrated at the Reichsanstalt, and in 1909 with a mercury thermometer made by Green of New York, the zero correction for which was the only correction applied. In any case, the errors in the temperature readings were less than the possible error in the pressure. The temperature was kept constant with an ordinary thermostatic device; a stream of ice water, or for the lower temperatures a stream of $CaCl_2$ brine, running constantly into the bath, which was automatically heated with a Simplex heating coil when the temperature fell too low. The temperature did not vary more than 0°.01 during a run, whereas a change of 0°.05 is necessary to produce a change in the equilibrium pressure of 10 kgm. which was about the limit of accuracy of the gauge. The temperature range of the experiment was from —15° to +20°. Since the freezing curve as determined between +20° and —15° extra-

TABLE VII.

Freezing Pressure at Different Temperatures by the Method of Change of Electrical Resistance. Data of 1909.

Temp. °C.	Equilibrium Pressure, kgm. cm.².		Difference, kgm./cm.².
	Observed.	Calculated.	
+14.35	10720	10600	+120
+21.0	11860	11910	− 50
+16.8	10850	11060	−210
+10.06	9620	9730	−110
+16.25	11010	10960	+ 50
+ 4.04	8540	8530	+ 10
0.00	7730	7730	0
0.00	7730	7730	0
− 8.52	6060	6040	+ 20
−15.09	4730	4730	0
+ 9.68	9690	9660	+ 30
+21.42	12070	11990	+ 80

Calculated values by the formula

$$p = a(t + 38.85)$$

where $$a = \frac{7730}{38.85} = 198.9$$

polates almost linearly to the ordinary freezing point at —38°.8 and atmospheric pressure, it was not thought necessary to make the special effort demanded to run a thermostat at temperatures below —15°.

One other remote possibility of error was guarded against. The capillaries containing the mercury were fine, the bore being about 0.1 mm. It was thought barely possible that the curvature of the surface might be sufficient to produce a rise of internal pressure in the mercury sufficient to change slightly the external pressure required to hold liquid and solid in equilibrium. This effect was shown to be negligible by using two capillaries of different sizes, one three times the diameter of the other. The equilibrium pressure found at 0° with the larger capillary was 7680 kgm., and with the smaller 7660. The divergence is in the direction to be expected, but it is of the same order as the experimental discrepancies. The data of 1911 were ob-

TABLE VIII.

Freezing Pressure of Mercury at Different Temperatures by the Method of Change of Electrical Resistance. Data of 1911.

Temp. °C.	Equilibrium Pressure. kgm./cm.².		Difference kgm./cm.².
	Observed.	Calculated.	
4.95	8570	8660	−90
9.92	9640	9640	0
14.86	10600	10620	−20
19.98	11640	11630	+10
0.00	7680	7680	0
−14.40	4790	4830	−40
−9.70	5630	5760	−130
0.00	7660	7680	−20

Calculated values by the formula

$$p = a(t + 38°.85)$$

where
$$a = \frac{7680}{38.85} = 197.7$$

tained with the larger of the above mentioned capillaries; those of 1909 with one of intermediate size.

The actual data follow. Those for 1909 are in Table VII. and in Figure 15. The data are given in the order in which they were collected. The two determinations at the higher pressures after the run with regularly decreasing pressures were made, the one at 9°.68 to correct the obviously bad point determined first of all, and the one at 21°.4 to make sure that there had been no systematic error introduced after the regular decrease of pressure of the first points. In addition, the three points determined during the initial testing of the apparatus, before the thermostat was installed, are given at the very end. The temperature error here easily accounts for the discrepancies of these last three points. As was stated before, the gauge with which these determinations were made was destroyed before it could be satisfactorily calibrated. The data used in the reduction of the gauge readings were simply the measured dimensions of the gauge, which could not be determined with the requisite accuracy. The column showing the calculated pressure must be taken, therefore, as merely evidence showing the regularity of the results and slight departure from linearity, and not as giving accurately the absolute pressures.

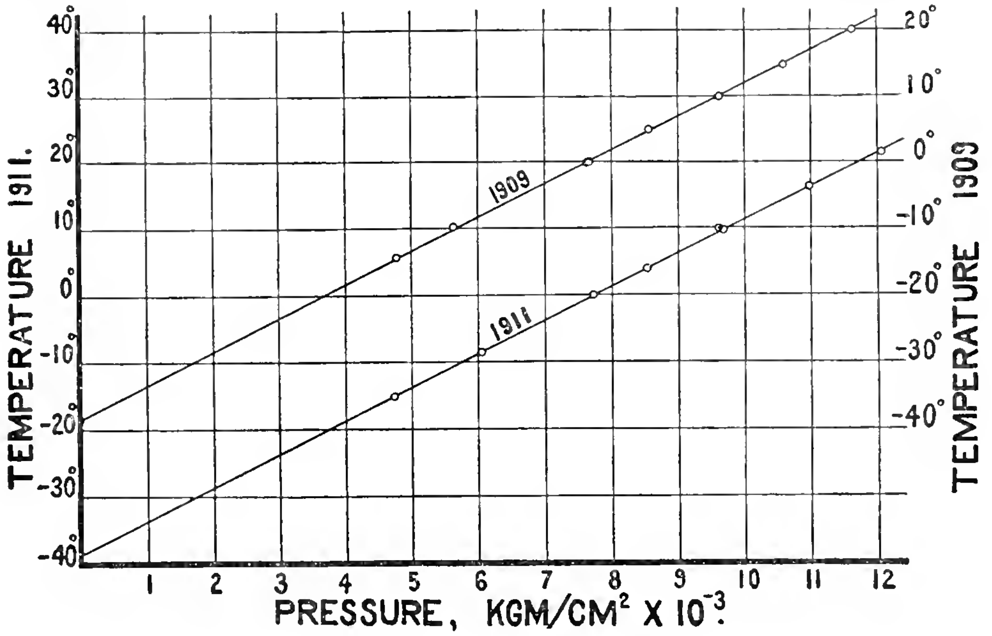

Figure 15. The melting curve of mercury by the change of resistance method.

Table VIII. and Figure 15 give the results of 1911. The method by which the results were calculated was the same combination of numerical computation with graphical construction already used in finding the compressibility. A straight line was passed through the point at 9640 and 9°.92, and the departure of the observed pressure values from those calculated by the linear relation plotted on a large scale. A smooth curve was then drawn through the midst of these points, and the final values calculated by applying to the smooth values the small correction determined from the smooth curve.

The points of 1911, except for the two bad ones mentioned above, lie on a smooth curve within the possible errors in reading the gauge. The departure from linearity, although slight, is pronounced in the direction of concavity toward the pressure axis, that is, less rapid rise of freezing temperature at the higher pressures.

There seems no reason why the points of 1909 are not just as valuable in indicating the manner of departure from linearity as those of 1911, since all the pressure readings are affected alike by the incomplete calibration of the gauge. The error in the gauge readings of 1909 is simply due to inaccurate knowledge of the cross-section. The following correction was applied, therefore, to the gauge constant of 1909. The best straight line through the points of 1911 was determined (graphically from the smooth correction curve) and also that through the points of 1909. The former gives a change of pressure of 197.1 kgm./cm.^{2} per degree rise of temperature ; the latter 199.2. The observed pressures of 1909 were all reduced in the ratio of 197.1 to 199.2. A smooth curve was then passed through these corrected values by the method described above. Finally, to determine the most probable departure of the freezing curve from linearity, the mean of the two correction curves, those for the data of 1909 and 1911, was taken. These curves differ nowhere by more than the possible errors in reading the pressure gauge. From this curve it is possible to find immediately the tangent to the melting curve at the origin.

Finally, all these results may be collected into the following form. At any given temperature the melting pressure is to be found by adding to the pressure given by the formula $p = 196.5\ (t + 38.85)$ the small correction term given graphically in Figure 16. The initial rise of pressure per degree rise of the freezing point is therefore 196.5 kgm./cm.^{2}; at 12,000 kgm. this has become only 1/2 per cent greater, so slight is the departure from linearity. The value of the initial slope, 196.5, has no more certainty than the single series of observations of 1911, but the departure from linearity shown in Figure 16 has the greater weight which should be given to the mean of two independent series of observations with different apparatus.

A number of data collected incidentally in the course of the work may be mentioned here, because they throw some light on certain properties of mercury under pressure, even if these are not the thermodynamic properties which are the particular subject of this paper.

The electrical resistance of the liquid mercury was usually measured over the entire range up to the freezing pressure. The matter of the electrical resistance of mercury under pressure has already been treated in a paper in which the pressure range was only 6800 kgm./cm.². The results obtained during the present work were pretty irregular, discrepancies of 1 or 2 per cent not being rare; but within the limits of error, the empirical formula given in the previous paper may be used by extrapolation up to the freezing pressure, at least within the present temperature range from — 15° to + 20°. The irregularities observed in the present work were without doubt due to the strains set up in the glass by the passage of the mercury from one state to the other. To reach the accuracy of which the measurements are susceptible it would be necessary to repeat the above resistance measurements, taking care never to push the pressure beyond the freezing value.

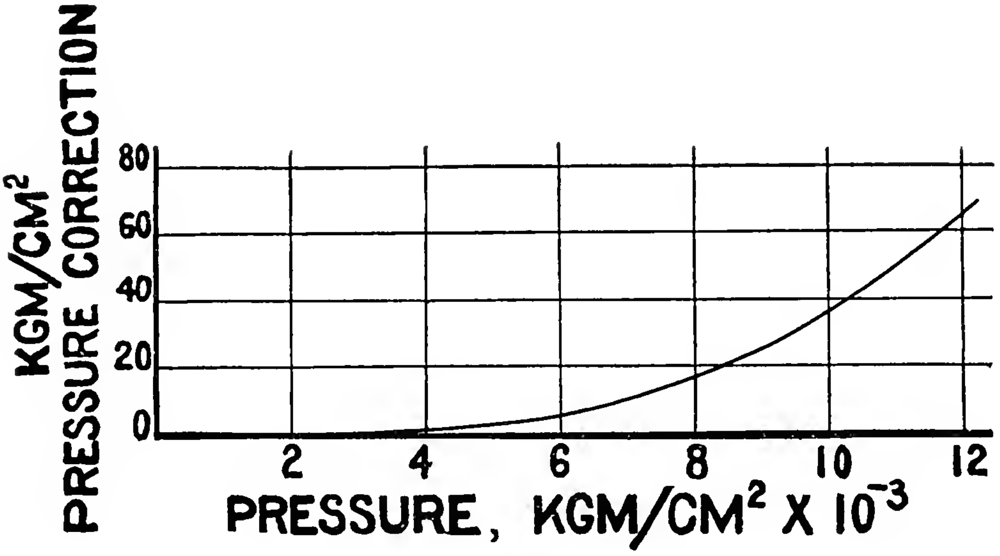

Figure 16. Departure of the melting curve of mercury from linearity. The initial slope is 196.5 kgm. for a rise of temperature of 1° C.

The electrical resistance of the solid mercury was also usually measured. These results cannot be expected to much more than indicate the order of the effect, for in addition to the comparatively small irregularities mentioned above, as due to elastic after-effects and hysteresis, comparatively large temporary alterations in the glass capillary are probably produced by the freezing of the mercury. The results are given in Table IX. *R* is the resistance of the mercury reduced by taking as unity the resistance of the liquid at atmospheric pressure and the corresponding temperature. *R* for the liquid was obtained by extrapolating beyond the freezing point to the pressure at which the resistance of the solid was measured. The resistance of the solid shows a distinct tendency to become less at the higher pressures and temperatures. The effect of temperature only would be to raise the resistance. The pressure coefficient of resistance must be negative, therefore, as for all other pure metals, and must have a value at least such that 200 kgm. increase of pressure produces a greater fall of resistance than 1° rise of temperature produces rise of resistance. This means that the pressure coefficient of the solid is greater than 0.0004/200 = 0.000002. The table also makes evident the tendency of the change of resistance liquid-solid to become less at higher pressures and temperatures. This indicates that the effect of pressure on the resistance of the liquid is greater than the effect on the solid, as one would expect, although the reverse is true for the temperature effect. This enables an upper limit to be placed on the pressure coefficient of the solid, since the coefficient of the liquid is known. This upper limit is about ten times the lower limit set above. It hardly seems worth while to at-

TABLE IX.

CHANGE OF ELECTRICAL RESISTANCE WHEN MERCURY CHANGES FROM THE LIQUID TO THE SOLID AT VARIOUS PRESSURES.

Temp. °C.	Pressure, kgm./cm.².		Resistance in Terms of Resistance at Atmos. Pressure and Temp. of the Measurement.			
	Pressure on the Solid.	Freezing Pressure.	Solid.	Liquid.	Change.	Ratio.
16.2	10960	10870	0.211	0.761	0.550	3.61
14.3	10660	10490	247	764	517	3.09
10.0	9960	9640	234	777	543	3.48
4.0	9220	8450	251	791	540	3.15
0.0	7660	7650	264	817	553	3.09
0.0	7610	7650	241	816	575	3.39
−15.1	5450	4680	258	863	605	3.35

tempt to force the above very imperfect data to give more accurate results.

It may be mentioned, however, that the above results are fully as consistent as the results which have been obtained by previous observers for the electrical resistance of solid mercury at atmospheric pressure. Thus Weber [37] found the following values for the ratio of the conductivity of the solid mercury to that of the liquid out of which it is freezing: 3.2, 4.2, 3.9, 4.0, 3.5, 4.0. Taking the reciprocals so as to compare with the above form, these become 0.31, 0.24, 0.26, 0.29, 0.25; different measurements of the same quantity. Cailletet and Bouty [38] give the single number 0.24, while Grunmach in his first paper [39] gives 0.67 and redetermines it in a later paper [40] as 0.40. The high values of Grunmach are doubtless to be explained by the formation of cracks in the mercury when freezing. This error can hardly come in the present work. In explanation of the other outstanding discrepancies, the fact does not seem to have been sufficiently considered that mercury freezes into crystals which may have different conductivities in different directions. It is known that the conductivity of bismuth, for example, may change by 60 per cent in different directions, and that of iron glance by 100 per cent. It is to be expected, therefore, that the particular form of vessel in which the mercury is frozen, by influencing the position in which the crystals tend to separate out, would have an effect on the apparent change of resistance on freezing.[41]

Finally, mention may be made of an unsuccessful attempt to get the heat of transformation from these same resistance measurements. The idea was to measure the depression of the freezing point occasioned by dissolving some metallic impurity in the mercury, the commencing of freezing being indicated by a kink in the curve giving resistance as a function of the pressure. The depression of the freezing point gives the heat of transformation by a well known formula. The difficulty with the method is that there is no metal which gives a depression of

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[37] Weber, Wied. Ann., **25**, 245–252 (1885), and **36**, 587–591 (1888).

[38] Cailletet et Bouty, C. R., **100**, 1188 (1885).

[39] Grunmach, Wied. Ann., **35**, 764–772 (1888).

[40] Grunmach, Wied. Ann., **37**, 508–515 (1889).

[41] Since the writing of this paper Onnes (Kon. Akad. Wet. Proc., **4**, **113–115** (1911)) has given data from which the ratio of the resistance of solid to liquid mercury may be found to be 0.237. This value was computed by the author from the values given in Science Abstracts for the resistance of a given quantity of mercury (172.7 ohms at 0°C., and 39.7 ohms in the solid state at the melting temperature).

the freezing point sufficiently large to give the desired accuracy. Few metals depress the freezing point at all, and those which do show a eutectic point 1° or 2° below the normal. In a preliminary testing out of this idea, the resistance of a 5 per cent Cd amalgam was measured at 21°.5. Beginning at between 1000 and 2000 kgm. the pressure coefficient was found abnormally large over the pressure range up to and including 12,000 kgm., which is the freezing pressure of pure mercury at 21°.5. The time required in reaching equilibrium was also abnormally long. Both these facts indicate the separating out of some component from the amalgam. Between 12,000 and 13,000, this process of separation seemed to have been completed, and from 13,000 to 13,500 the behaviour was entirely normal. The explanation is simple. The effect of pressure is to raise the entire melting diagram Hg—Cd, the Hg end more than the Cd end. (See Figure 17.) This raising is presumably accompanied by a shifting of the proportions of the two metals present in the eutectic mixture. The initial temperature and proportion of the two metals present in the amalgam may be represented by the point A (in this case $t = 21°.5$ and $x = 5$ per cent), but when the pressure has risen sufficiently to bring the melting curve up to A, with further rise of pressure A slides along the rising curve, always at con-

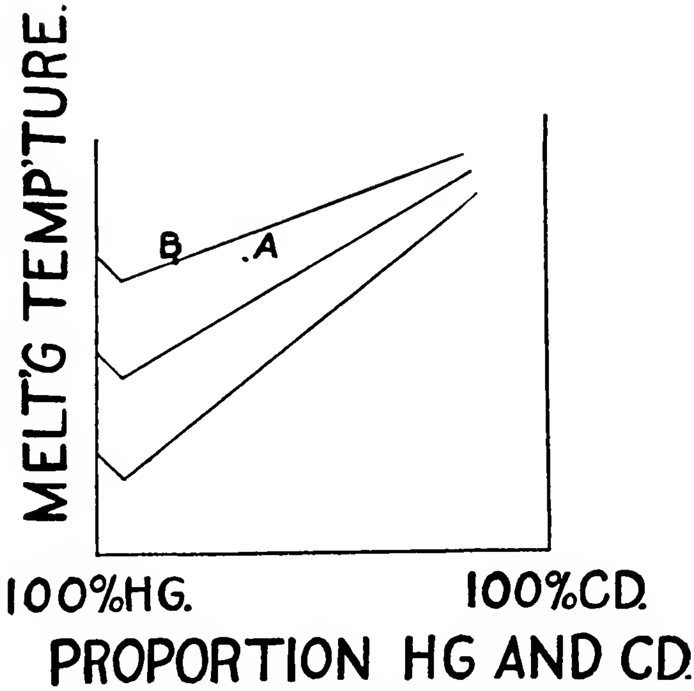

FIGURE 17. Showing the raising of the melting curve of mixtures of mercury and cadmium with increasing pressure.

stant temperature, shown by the point B on the highest melting curve of the diagram, until the eutectic point is reached, where complete solidification sets in. This takes place at a pressure slightly higher than the normal freezing pressure for the pure mercury, as shown experimentally above, but the precise amount will depend on the unknown way in which the proportions of the eutectic mixture have changed. To obtain the data desired by this method, A must initially lie to the left of the eutectic point corresponding to the particular freezing pressure instead of to the right, as in the diagram. The results evidently cannot be accurate, and it was therefore not thought worth while to push the investigation further at this time, particularly since the destruction of the gauge mentioned before came as the direct result of the high pressure reached above. An investigation of the change of eutectic proportions under pressure would make an interesting research for its own sake.

The Equilibrium Data by the Change of Volume Method.

The method was essentially that of Tammann, and gives both the change of volume and the pressure at a given temperature. It consists in measuring the displacement of the piston by which pressure is produced as a function of the pressure. Freezing is indicated by an interruption of the regular rise of pressure with advance of the piston. It is at once obvious that an absolute essential for the success of the method, and at the same time the hardest condition to maintain under high pressures, is the entire freedom from leak of the moving piston and the other parts of the apparatus. Tammann found this trouble at pressures above 2000 kgm./cm.^{2}, and avoided it in part by using a very heavy oil for transmitting pressure. In this present work a new packing device was adopted which secured entire freedom from leak even with so thin a fluid as kerosene or mercury. Data will be given in support of this.

The data needed at any point in addition to the equilibrium pressure and temperature are the amount of the advance of the piston during constant pressure, the quantity of liquid involved in the change, and the cross-section of the advancing piston. The first two may evidently be measured directly, but the last changes with pressure by an amount not susceptible to direct measurement. Here, as in all pressure measurements, the distortion of the containing vessel enters as a disturbing factor. But it should be pointed out that here the effect of the distortion is a minimum. It has been quite impossible up to the present to make direct determinations of compressibility, for example, by this method, because the changes of volume of the liquid are accompanied by unknown changes of volume of the same order in the containing vessel. But here, where the changes take place at constant pressure, the vessel remains constant during the change, and the only distortion which need be taken into account at all is the change of area of the cylinder, a change which is easy to calculate, and which furthermore never in the present work rose above 2 per cent of the total effect. To make this matter clearer, take the example of water. A pressure sufficient to change the volume of water by 20 per cent might introduce a change of about 2 per cent in the volume of the very heavy cylinders of this present work. This change of 2 per cent takes no account of the change of volume introduced by the compression of the packing of the various connecting pipes, etc., which are necessary if the pressure is to be measured at all accurately. This change due to the tightening of the packing is evidently incalculable, but may presumably be as large as the other effect. The change of volume as indicated by the advance of the piston is affected, therefore, by a quantity which may very reasonably be supposed to be 4 per cent on 20 per cent, that is, 1/5 of the total effect measured. Compare this with the change of volume during freezing at constant pressure. Here the change of volume of the rest of the vessel and the packing plays no part whatever, the only correction is 2 per cent for the change in cross-section of the cylinder. That is, a correction of 2 per cent which may be approximately determined, against a wholly unknown correction of 20 per cent. It should be remarked, however, that if once the compressibility of the water has been determined in some other way, it may be used in an apparatus of this form to determine the unknown distortion, and so the compressibility of other liquids may be determined.

Description of Apparatus.

The apparatus consisted essentially of two cylinders, connected by a piece of very heavy nickel steel tubing 12 inches long. The upper cylinder was placed in a hydraulic press, and the pressure was produced in this by a piston forced down by the ram of the press. The amount of motion of the piston was measured with a micrometer screw reading to 0.0001 inch. There were no valves in any part of the apparatus, as it is difficult to make these capable of withstanding high pressures. The apparatus was initially filled entirely full of liquid after the air had been exhausted with an air pump, and the piston was then introduced into the upper cylinder. The dimensions of the various parts were chosen so that the maximum pressure desired could be obtained with a single stroke. This upper cylinder was freely exposed to the air of the room, with no special device to keep the temperature at any definite value.

The lower cylinder contained the mercury, the subject of the experiment, and was surrounded by a bath kept at constant temperature by a thermostat. The mercury was contained in a cylindrical steel shell fitting loosely the hole in the cylinder. The same kerosene which entirely filled all other parts of the apparatus and transmitted pressure from the upper to the lower cylinder also entirely surrounded the walls of the shell containing the mercury. This arrangement was necessary, because if the mercury had been allowed to come in contact with the walls of the cylinder, the steel would have become amalgamated, and the cylinder speedily ruptured. Whereas, the steel shell in which the mercury was contained being surrounded on the outside by kerosene, and so being subjected to a purely hydrostatic pressure equal all over, experienced no amalgamation whatever.[42]

Screwed into the bottom of this lower cylinder, directly immersed in the kerosene and so subjected to the same pressure as the mercury, was an insulating plug carrying a coil of manganin wire with which the pressure was measured.

The procedure was as follows: After filling the apparatus with kerosene, the thermostat was raised around it and adjusted to the temperature desired. When a steady state was reached, the resistance of the manganin coil was read on the Carey Foster bridge, thus giving the pressure zero. The piston was then introduced into the upper cylinder, and pressure increased to a value a few hundred atmospheres short of the freezing pressure at the temperature of the thermostat. After pressure equilibrium had been attained by dissipation of the heat of compression, the pressure was read from the resistance of the manganin coil and the position of the piston was read with the micrometer. Two readings of the resistance of the manganin were made corresponding to the two positions of the eight-point switch of the Carey Foster bridge. These readings were made before and after reading the position of the piston. Since the circuits were non-inductive, the bridge could be used with the galvanometer circuit permanently closed. These two readings are, therefore, really two independent readings of the pressure, and agreement between them is indicative of the attainment of pressure equilibrium. It was not necessary to take any such precautions in measuring the position of the piston, for the

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[42] See These Proceedings, No. 14, 1911, for a discussion of the amalgamation of steel under high pressures.

friction of the packing prevented all motion after the initial increase of pressure.

The above procedure, reading of pressure and piston position, was repeated at appropriate pressure intervals up to several hundred or perhaps a thousand kgm. beyond the freezing pressure. On plotting piston displacement against pressure, the freezing is shown by a discontinuity in the curve. Similar readings were also made on release of pressure, and so another value for the change of volume found. On releasing pressure the discontinuity is more sudden than with increasing pressure, because it is impossible to superheat the crystalline solid on decreasing pressure, but the liquid may be subcooled on increasing pressure. Because of this, and for another reason to be explained later connected with the distortion of the steel, the value found with decreasing pressure was without exception accepted as the correct value.

In the use of this apparatus and in the calculation of the data, there are numerous corrections or disturbing factors which will now be considered in detail.

Leak. — As already stated, the most obvious and apparently the greatest difficulty with the method, particularly at high pressures, is the question of leak. It might perhaps be possible to correct for this as was done sometimes by Tammann by weighing the quantity of liquid escaping past the piston in a given time, but this correction would always be unsatisfactory in cases where, as here, the total motion of the piston during freezing is small (0.2 inch) and many extend over an hour or more. It has been stated that there was absolutely no leak. This was proved by the fact that the piston and upper end of the packing, when removed from the cylinder after the end of an experiment, were always perfectly dry, even though the total time over which pressure has been applied might reach into several days, as it did on several occasions. That there was no leak in any other part of the apparatus was proved by the self-consistency of the results as well as by special experiment. On one occasion pressure was left at 7500 over night, temperature being kept constant with a bath of ice and water, and in the morning had not dropped by as much as the smallest amount perceptible with the manganin resistance, namely 2 kgm./cm.^{2}.

The effect of leak, if there were one, would be to make the values of Δv during increase larger, and during decrease smaller. The values did actually in the great majority of cases disagree in this way. That this was not due to leak will be evident from a discussion of

Elastic After-Effects. — In the ordinary sense of the word, elastic after-effects, as is indicated by the name, are purely elastic phenomena, complete recovery after any application of stress always occurring, provided time enough is allowed. There are also other effects of somewhat the same general character, such as hysteresis, not usually included in the name. But there will be included in this discussion any effect in virtue of which the strain is not a single valued function of the stress only. The general nature and interpretation of these effects is still obscure, but there are a few facts which are well known. For instance, in all ordinary testing of materials it is first necessary to accommodate the metal to the particular stress conditions of the moment. The strain under a given stress is not the same the first time the stress is applied as the second, and not until the application of the stress a number of times does the strain come to depend always in the same way on the stress. Even after complete accommodation has been attained, the material may continue to show elastic after-effects, that is, continued yield after the application, or continued recovery after the release or stress. Or it may also show hysteresis. These effects become increasingly important as the magnitude of the stress is increased, or as the character of the stress changes from one uniform throughout the mass to one changing from point to point. The effects become most important of all when the material itself has become non-homogeneous by the exceeding of the elastic limit in some places while the remaining parts are without permanent deformation.

Various effects of just this kind are to be expected in these experiments, and may perhaps be fairly large in comparison with the usual magnitude of the effects, because of the wide range of stress here employed. It should be pointed out that one advantage of this method, namely, that the elastic deformation of the vessels does not enter the results, is in part offset by the various effects of the kind mentioned here, because in virtue of them the volume of the containing vessel may change while freezing or melting is going on at constant pressure. Furthermore, these effects, which are themselves intrinsically small, may appear with magnified effect in the result. Thus the actual change of volume of the mercury during freezing is about 1 per cent of the total internal volume of the containing vessel, so that a change of volume of 1/100 per cent of the containing vessel produced by elastic after-effects during freezing will appear in the result magnified to 1 per cent. As a matter of fact, there were found discrepancies between the values under increasing and decreasing pressure amounting in the worst case to 3 per cent.

It was possible, however, by an examination of the discrepancies themselves and by a brief consideration of the method of experiment to select from these the most probably accurate results. During the course of an experiment, the stress history of the steel in its bearing on this effect was as follows. Pressure was pushed to a value somewhat short of the freezing pressure, the readings were made, and then pressure increased again, etc., until the subcooled region had been entered far enough for freezing to begin. This first stage might occupy an hour. The second stage was that of approximately constant pressure during freezing, which might require from an hour to an hour and a half. During the third stage, pressure was increased a few hundred atmospheres beyond the freezing pressure, held at the maximum for a while, and then decreased to the melting point again. This occupied another hour. The fourth stage, melting at constant pressure, ran more rapidly than freezing, but might consume an hour. Finally a few readings below the freezing pressure, rarely more than half an hour. It is to be noticed that during melting the pressure has been held in the immediate neighborhood of the maximum for some hours, and that this melting pressure is only slightly removed from the maximum, whereas during freezing, the stress has just been increased over nearly the entire range and the time for accommodation has been much shorter. All our experience with elastic after-effects would lead us to predict that during melting these effects would be very much less important than during freezing. We would furthermore predict that the change of volume found during freezing would be greater than that during melting, for the piston must advance to compensate for the increasing volume of the steel vessels as well as for the decreased volume of the mercury.

These conclusions were verified by the data. The values found during melting were always self-consistent, lying on a smooth curve, and could be repeated. But those found during freezing might vary wildly within the 3 per cent limit mentioned above. Furthermore, the inconsistent results were always larger than the consistent ones, provided that the procedure was as described above. There seemed to be no connection between the duration of the pressure and the amount of the discrepancy.

We already have evidence enough to make it extremely probable that the discrepancy was not due to leak, although it is of the right sign. But the fact that the discrepancy is reversed in sign so as to indicate a leak in instead of a leak out, if the stress is applied differently from above, renders certain the conclusion that the effect is not due to a leak. The succession of points on the melting curve, the procedure in getting one of which was described above, was in general obtained by starting at low temperatures and pressures and working up to the higher values. Each maximum pressure, then, was higher than the preceding maximum. But if the preceding maximum was higher than the following one, the discrepancy was reversed in sign, the values during freezing being too low, while those during melting still lay on the same smooth curve as before. This certainly cannot be due to leak. Neither is it in accord with the general nature of other elastic after-effects at low pressures. But other experience of this same general nature at these high pressures indicates that this is probably the general nature of the effect at high pressures. It is as if the subsequent application of pressure, and possibly the change of temperature also, changes somewhat the position of the molecules, like shaking a magnet, so that they become free again to resume their natural elastic recovery from the previous greater maximum. One experiment with a hollow steel cylinder subjected to external hydrostatic pressure strikingly suggested the same general explanation. This cylinder had been previously subjected to a pressure many times beyond the elastic limit, so that the metal had flowed toward the center, decreasing the internal volume. On removing the pressure there was some slight elastic recovery of the internal volume, but not nearly as much as was to be expected. But the next increase of external pressure produced in the initial stages a very marked increase of internal volume, instead of a decrease, the natural effect of the pressure. It must be that in some way the pressure loosened up the molecules so that they were free to resume their natural recovery.

Other slight differences suggest also that these discrepancies are of the general nature of elastic after-effects. Because of breakage, several different pieces of apparatus were used. The discrepancy was always greatest with the thickest-walled vessels. It has been observed several times in other connections that elastic after-effects are greater with the greater mass of metal, because this allows greater heterogeneity of strain and greater volume in which to store the effect, with consequent longer time of recovery. At a given pressure the effect in a new piece of apparatus was smaller before it had been subjected to the greatest maximum than it was at this same pressure after being so subjected to the maximum. In general, the effect was likely to increase with time, showing fatigue of the metal. In one case, in the similar measurements on water, to be described elsewhere, rupture of the vessel was foreshadowed by an increase of the effect beyond 3 per cent.

There may be some slight effect of permanent set mixed up with the above effects. An undoubted set was always very distinctly obvious after the first application of the greatest maximum. This application was usually made in a preliminary test in order to season the apparatus before the measurements were undertaken. This applies particularly to those three or four occasions after the lower cylinder had been broken. The seasoning of the upper cylinder was done more carefully, and is described elsewhere. The set must have been nearly all removed by this seasoning, but any subsequent set would still affect only those results for increasing pressure.

In view of all these considerations, the course actually adopted seems justified; namely, to retain only those values found during melting, that is, during decreasing pressure. In consequence, in some two or three of these last determinations, and in many of those on water, the experimental determination with increasing pressure was entirely omitted.

Elastic Deformation. — It has already been stated that the only way in which elastic deformation, that is, a deformation depending only on the pressure, enters, is in the correction for the change of cross-section of the upper cylinder. Although the value finally adopted for this correction is small, only 1.3 per cent at 10,000 kgm./cm.^{2}, still it must be admitted that the greatest uncertainty in the work is precisely in determining this correction. The difficulty comes because of the very high pressure employed, which renders doubtful the calculation by the ordinary theory of elasticity. If the maximum pressure used in the experiment, 12,000 kgm., were the greatest pressure involved, the case would not be so doubtful, because the elastic limit of the steel is not greatly exceeded here. Indeed, if it were possible to harden the steel uniformly throughout its mass, reaching to a depth of 1 1/2 inches, the elastic limit would not be reached until about 15,000 kgm., and there would not be much question in applying the ordinary equations of elasticity. But it is impossible to raise the elastic limit throughout the metal by quenching, and the interior of the cylinder always shows some set at 12,000. Since the accuracy of the whole method depends on accurate knowledge of the cross-section it was necessary to remove every vestige of set in this part of the apparatus. This was done by subjecting the cylinder initially for five or six hours to a pressure of 24,000 kgm. This was sufficient to stretch the inside of the cylinder from its initial value of 1/2 inch to nearly 9/16 inch. The cylinder was then reamed out to 9/16 inch for its entire length, and this was the form in which it was finally used. The effectiveness of the treatment is shown by the fact that the cylinder has shown no further change of so much as 0.0001 inch on the internal diameter.

The present condition of the cylinder is therefore far from one of a state of ease; there are certainly internal strains. But it should be noticed that this fact in itself is not sufficient to destroy the applicability of the equations of elasticity. Provided only that the metal shows no further set after the first application, and that strain remains proportional to stress, any stress will produce the same additional strain as the same stress applied from a state of ease. The long interval of time for which the maximum pressure was exerted, and the large excess of this pressure over any subsequent pressure, make it exceedingly probable that such a state has actually been reached. The residual stress in the cylinder is then of exactly the same nature as the stress in a gun with shrunk-on hoops, and the deformation may be calculated by the ordinary theory. It may be mentioned, in support of this position, that measurements have been made of the external elastic deformation of another such cylinder of the same steel up to 10,000 kgm., showing agreement with the accepted theory to at least 5 per cent, with no trace of hysteresis.

The calculation of the actual deformation of the cylinder according to the elastic theory would be impossible because of the indeterminate nature of the boundary conditions. An approximate solution only can be obtained, in which the end effects are neglected altogether. This solution is nevertheless probably accurate enough, because the end effect in other similar cases in which the rigorous solution is known has been shown to be negligible. It is well to remember in considering the validity of these approximations that the maximum value of the correction at the highest pressure is only 1.6 per cent.

The internal diameter of the cylinder does not expand uniformly under pressure. The expansion may be supposed to have its greatest value at points removed from the position of the piston by at most a few diameters. The expansion throughout the greater length of the cylinder is constant, therefore, and equal to the value it would have in a cylinder infinitely long and of the same radial dimensions. But for a short distance beyond the head of the piston the expansion varies from its maximum value to a value which may be shown to become half this maximum at the piston itself. Now if we suppose that the cylinder is so long that as the piston moves at constant pressure (during freezing or melting) the locality of transition in dimensions travels bodily with the piston, then a moment's consideration shows that the volume swept out by the piston is equal to the length of stroke multiplied by the area of the cylinder at its locality of maximum distortion. The assumption does not seem forced in view of the fact that the length of the cylinder is between ten and fifteen diameters.

The formula for the displacement under these conditions may be found in any book on elasticity. We have

$$\Delta b = \frac{bP}{a^2 - b^2}\left(\frac{a^2}{2\mu} + \frac{2b^2}{3\kappa} \cdot \frac{4\mu + 3\kappa}{12\mu}\right),$$

where b is the internal and a the external radius, μ the shearing modulus, and κ the compressibility modulus.

a was measured directly from the outside of the cylinder and was 3.536 cm.; b was found from a measurement of the plug at the end of the piston after this plug had been forced to conform to the hole by the application of high pressure. It has been already stated that no change in b could be detected during the course of the experiments of so much as 0.00004 cm. b was found to be 0.7183 cm. μ and κ were found by the ordinary equations of elasticity from Young's modulus, taken as 2×10^6 kgm./cm.^{2}, and Poisson's ratio, taken as 0.28. These quantities vary only slightly in different grades of steel. The values of μ and κ calculated in this way were found to be 7.81×10^5 and 15.2×10^6 respectively. Substituting in the formula gives directly

$$\Delta b = 0.00491 \text{ cm. for } 10{,}000 \text{ kgm./cm.}^2.$$

Whence the change of area, $\Delta A = \dfrac{2 \times 0.00491}{.7183}$

$$= 1.35 \text{ per cent for } 10{,}000 \text{ kgm./cm.}^2.$$

Temperature Corrections. — There are a variety of temperature corrections to be considered; those which are to be met in any physical measurement, and those which were peculiar to this particular work. The ordinary corrections concern only the reading of the temperatures and may be dismissed with a few words. Temperature about the lower cylinder was maintained constant to 0°.01 with a thermostat. Above zero this temperature was read with a Tonnelot thermometer calibrated at the Bureau of Weights and Measures in Paris. The correction for the zero was determined, but it was not necessary to apply any of the other corrections. Readings on this are probably accurate to 0°.01. Below zero, readings were made on a toluol thermometer, graduated to 0°.1, and calibrated at the Reichsanstalt. In addition to the corrections of the Reichsanstalt, the zero correction was applied. This is accurate to 0°.1, which corresponds to the accuracy of the pressure measurements.

Of the corrections peculiar to this work, the temperature effect on the pressure readings was the simplest. The manganin resistance coil with which pressure was measured was placed in the lower cylinder with the mercury, and so was exposed to the same changes of temperature. It has already been shown in the paper on the gauge, that within the temperature limits of this work the pressure coefficient of resistance is constant. The only temperature effect is on the total resistance of the coil, which, therefore, merely displaces the zero. This zero was usually redetermined directly at every temperature, but in a few cases where it was inconvenient to release the pressure to zero between two sets of readings at different temperatures a calculated correction was applied. This correction was determined from an independent measurement of the temperature coefficient of the zero of one of the four manganin coils with which pressure was measured. These four coils were made from contiguous pieces of the same piece of wire. The greatest change of the zero from this effect amounts to 400 kgm. between − 20° and 0°. Above zero the correction becomes very much smaller, as this particular kind of manganin shows a maximum resistance at 28°. It will be noticed that it was necessary to keep the bath temperature constant to only 0°.5, in order to remain within the errors of the pressure readings.

By far the most serious correction is due to the fact that the lower cylinder with the mercury under experiment is at one temperature, while the upper cylinder where the measurements of the change of volume are made is at another temperature, the temperature of the room. It is readily seen that the change of volume during melting, for example, as measured by the displacement of the piston of the upper cylinder, will be in error by the expansion at constant pressure of the liquid kerosene on passing from the temperature of the lower to that of the upper cylinder. This error has the same sign during both melting and freezing. The change of volume so measured will be too large if the lower cylinder is colder than the upper, and too small in the reverse case. The correction evidently becomes rapidly larger with the increase in the difference of temperature, but because thermal dilatation becomes less with increasing pressure, this correction fortunately becomes smaller at high pressures, where it is harder to determine. The maximum value for the correction in this work was 2 per cent over the range + 20° to − 20°.

This correction seems to have been entirely overlooked by Tammann. It might very possibly amount at the maximum to over 10 per cent for temperature ranges over 100° such as he employed. The effect of the correction will not be to change at all his co-ordinates of the melting curve, but might possibly modify somewhat the way in which Δv apparently tends toward zero at high temperatures and pressures. This latter point has some theoretical significance in Tammann's theory of solid-liquid.

The correction had to be determined by direct experiment, as there were no data by which it could be calculated. The discussion, which is somewhat long and involved, will be given in the following separate section.

The Thermal Dilatation of Kerosene at Constant Pressure.

Since the accuracy desired was not very high, the maximum value of the correction being 2 per cent, a procedure was adopted which was rapid, but not accurate enough to employ in determining this quantity as a physical constant interesting in itself. The method consisted essentially in filling the entire apparatus with kerosene, lower as well as upper cylinder, immersing the lower cylinder in the constant temperature bath, and plotting piston displacement against pressure. Then the lower cylinder was allowed to come to room temperature, and again the piston displacement and the corresponding pressures noted. The difference of displacement at the two temperatures gives the change of volume of the kerosene which was in the lower cylinder on expanding from the one temperature to the other. It is to be noticed that this gives the thermal dilatation of a quantity of kerosene of unknown mass but of known volume. To find the dilatation as ordinarily defined, we should require the compressibility, so that we might know the original volume of the kerosene which at the given pressure completely filled the lower cylinder. But the data as given by the experiment are exactly the data needed in making the correction. For suppose the change of volume of the mercury on melting at a certain temperature and pressure is approximately 1 cm.^{3}. We require to know how much this 1 cm.^{3} of displaced kerosene has changed in volume on passing from one temperature to another at constant pressure, and we are not interested at all in the original volume of this 1 cm.^{3} of kerosene.

The procedure as roughly outlined above is evidently liable to a multitude of errors. It is exactly similar to the corresponding method of obtaining compressibilities against which objections were made in the introduction. But it is to be said in extenuation that the correction is small, and that the maximum correction comes at the low pressure where the objections of the introduction have little weight. The correction at $-20°$ of 2 per cent corresponds to only 3500 kgm. At this pressure and with a cylinder seasoned by exposing to 24,000 kgm. there need be no hesitation even in applying the method to accurate determinations of the compressibility. The correction at 0° and 7500 kgm. has already dropped to 0.6 per cent.

The corrections to apply in determining this maximum correction of 2 per cent are the corrections on the volume of the lower cylinder brought about by the changes in temperature and pressure. The volume was found by weighing the lower cylinder when full of mercury. To be subtracted from this volume was the volume of a copper block inserted to reduce to manageableness the total quantity of the kerosene, and the volume of the manganin pressure gauge. The volume occupied by the kerosene increases with pressure both because of the stretching of the cylinder and the shrinking of the copper and the manganin gauge. The stretching of the cylinder was calculated by the theory of elasticity as outlined above. A slight modification of the formula is necessary because the cylinder carries the end thrust of the pressure. The total correction for the stretching of the cylinder is 1.4 per cent at 10,000 kgm. The effect of the copper and the small quantity of mica washers in the insulating plug were assumed to be represented by the compressibility 0.0_51, the compressibility of the copper alone being 0.0_69. This correction amounts to 0.5 per cent at 10,000. Together, the two effects produce a total change on the effective volume of kerosene of 1.00 cm.^{3} per 10,000 kgm., on an initial volume of 28.6 cm.^{3}. The correction for the thermal dilatation of the lower cylinder was found from the known dilatation of steel at ordinary pressures, assuming it to be independent of pressure.

In making the actual measurements, endeavor was made to avoid as far as possible the small effect of mechanical hysteresis. The set of readings at —15°, for example, was obtained as follows. The piston displacement was measured with increase of pressure from 3500 to 5800 kgm. with the lower cylinder at +20°; the lower cylinder was then cooled to —15°, and the displacement measured from 5800 back to 3500; and finally the lower cylinder was warmed again to +20° and the displacement measured from 3500 to 5800. The difference between the second curve and the mean of the first and the third, which differed only very slightly, gives at any one pressure the expansion of the corresponding amount of kerosene on passing from —15° to +20°, since the temperature of the upper cylinder was also +20°. This difference was found for a number of pressures for the range 3500 to 5800, and a smooth curve drawn through these differences. From this curve was taken the difference corresponding to the freezing pressure of mercury at —15°. This process was performed for four temperatures, —20°, 15°, —7°, and 0°, and four points were thus determined on the correction curve. It was not necessary to obtain other points above 0° on the curve, because the correction was already small at 0° and the other end of the curve is fixed by definition as passing through the value zero at 20°. Through these five points, —20° to 20°, another smooth curve was drawn, giving at any temperature the piston displacement when the amount of kerosene in the lower cylinder passes from that temperature to +20° at the pressure corresponding to the freezing pressure of mercury at that temperature. Finally this curve gave the required percentage correction curve by translating piston displacements into volumes and dividing by the volume of the kerosene in the lower cylinder at the corresponding pressure as already determined. The correction curve actually used is shown in Figure 18. It is obtained by combining with this temperature correction the correction already determined for the elastic deformation of the upper cylinder.

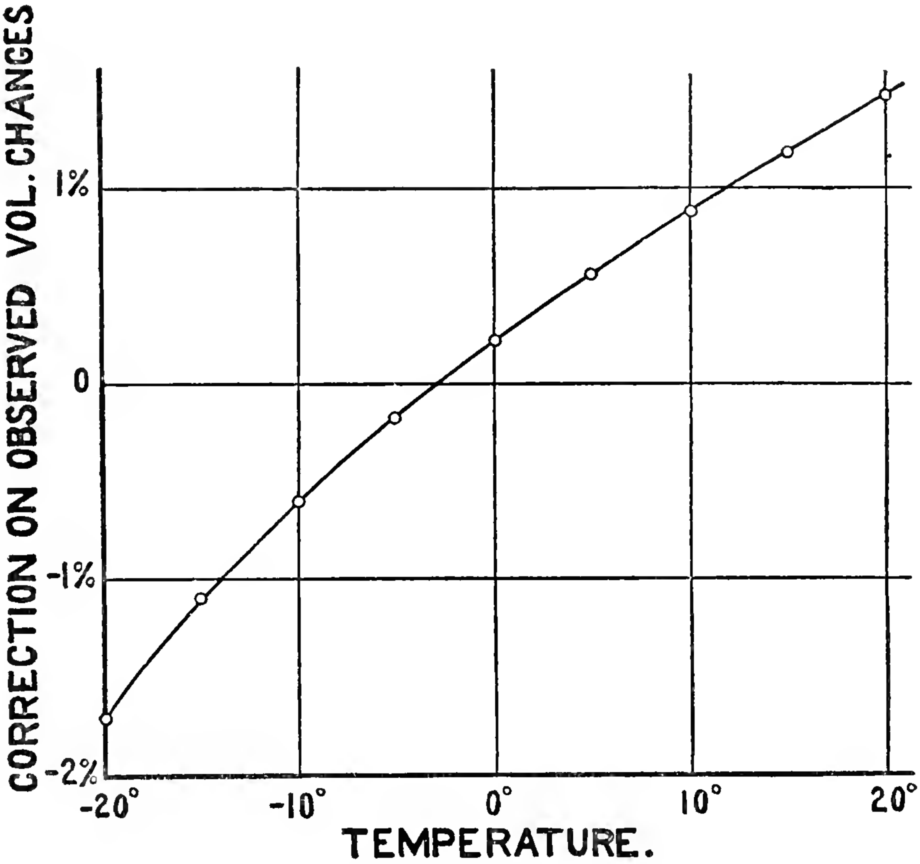

FIGURE 18. The corrections due to the thermal dilatation of the transmitting liquid and the elastic deformation of the cylinder to be applied to the directly measured change of liquid mercury when it passes to the solid state.

The correction curve so determined is not linear, the values being 2.0 per cent at -20°, 0.65 per cent at 0°, and 0 at +20°. The departure from linearity is evidently due to the decreasing dilatation of the kerosene under high pressures.

Temperature Correction for the Upper Cylinder. — In the form of apparatus used in this experiment there is one other small correction because the upper cylinder is exposed to the slightly varying room temperature. If the room temperature changes during freezing, the observed change of volume is evidently incorrect by the thermal expansion at the particular pressure of the total quantity of kerosene in the upper cylinder. The temperature changes were usually very slight. They were made still smaller at the cylinder itself by enveloping this in a large mass of cotton batting. The temperature of the cylinder was read with a thermometer directly in contact with it. The correction demands an approximate knowledge of the quantity of kerosene in the upper cylinder, which was obtained by measurement of the position of the piston. The thermal dilatation of the kerosene at any given temperature was found from the correction curve already described, making the justifiable assumption that at constant pressure the dilatation is sensibly constant over the temperature range. The maximum correction was at —20°, where the dilatation is a maximum, and where the temperature variation, 0°.7, happened also to be a maximum. The correction here was 0.5 per cent. Above 10° the correction was entirely negligible.

Possible Change of State of the Transmitting Liquid. — The effect of any freezing of the kerosene with contraction during the freezing of the mercury would be to make the change of volume appear too large. This possibility was entirely eliminated, however, incidentally by the measurements determining the thermal dilatation of the kerosene. At any given temperature these measurements extended considerably beyond the freezing pressure of the mercury, and no evidence of a change of state with change of volume was found.

Measurements of the Piston Displacement.—These measurements were made with a Brown and Sharpe micrometer reading to 0.0001 inches. The measurements were made between a point on the head of the advancing ram which drives the piston and a fixed point on the frame of the press against which the cylinder is pressed. There are two possibilities of error here. One, the most serious, is warping of the entire frame of the press. Such an effect was detected and may give rise to discrepancies of 0.002 inch over the entire stroke of 4 inches. It was obviated by making four measurements of every displacement between four pairs of points at the four corners of the frame of the press. The second error may come from elastic deformation of the parts of the press between the head of the ram and the fixed point on the frame, so that the measured change of length does not give the actual piston displacement. The effect, which is in any event small, was obviated by taking advantage of the fact that there is considerable friction in the packings. In virtue of this it is possible to vary the pressure on the low pressure end of the ram over a considerable range without producing motion of the piston, and so without altering the high pressure. Now it is the pressure on the low pressure end which produces distortion in the frame of the press, the cylinder at the high pressure end taking up in itself the effects of the high pressure. The effect of distortion in the frame was avoided, therefore, by adjusting the low pressure before every measurement of displacement to the same constant value for all values of the high pressure in the immediate neighborhood of the freezing point.

The Pressure Measurements. — The method of measuring these high pressures, with a discussion of the various sources of error has been given in another paper. Briefly, the pressures were obtained from the measured change of resistance of a coil of manganin wire immersed directly in the kerosene of the pressure chamber which contained the mercury under investigation. The coils, four of which were used during this investigation, were each calibrated separately against an absolute gauge. These were capable of reproducing the gauge with as much accuracy as the gauge itself could be read, which was about 8 kgm./cm.^{2}.

The Data.

The actual determinations by this method extended over about two months, from Oct. 13 to Dec. 3, 1910. In all, eleven points were determined, from −20° to +18°, both with increasing and decreasing pressure. The measurements were sandwiched in between similar ones on water which are to be described in another paper. The apparatus was taken apart and set up a great number of times, both in the course of the ordinary manipulations attending the experiment and in making those changes necessary because of the piecemeal explosion of various parts of the apparatus. There were at least five such explosions during the experiment; two lower cylinders being burst, two upper cylinders, and one connecting pipe. The accuracy of the work is spoken for by the fact that determinations with all these different groupings of apparatus, including change of the pressure measuring coils, gave points lying on the same curve. This does not appear so strikingly from the actual data given, but it must be remembered that by far the greater number of measurements during this time were made on water, where the same independence of the particular piece of apparatus is also shown. The first five measurements on mercury were made with different combinations of apparatus; the last six were made with the same set up. The equilibrium pressures found in all eleven sets of readings are equally worthy of acceptance, but the volume measurements of the first five must be discarded because the effect of changes of room temperature was not sufficiently recognized at the time, and no correction was applied for it. The data of the same period for water, however, where the total change of volume is larger and the correction of less account, give consistent values for the change of volume also.

First for the equilibrium pressure. This was ordinarily found at only two points, one with increasing and the other with decreasing pressure, but in order to make sure that this equilibrium pressure was a perfectly definite quantity, independent of the quantity of mercury melted, equilibrium was found, during the first two or three runs, with various proportions of the solid melted. This is shown in Figure 19 (Oct. 13), where the piston displacement is plotted against pressure. The vertical part of the curve shows the period of transition. The equilibrium pressure thus appears to be the same whether the freezing is nearly complete or only just begun. It is possible to get much

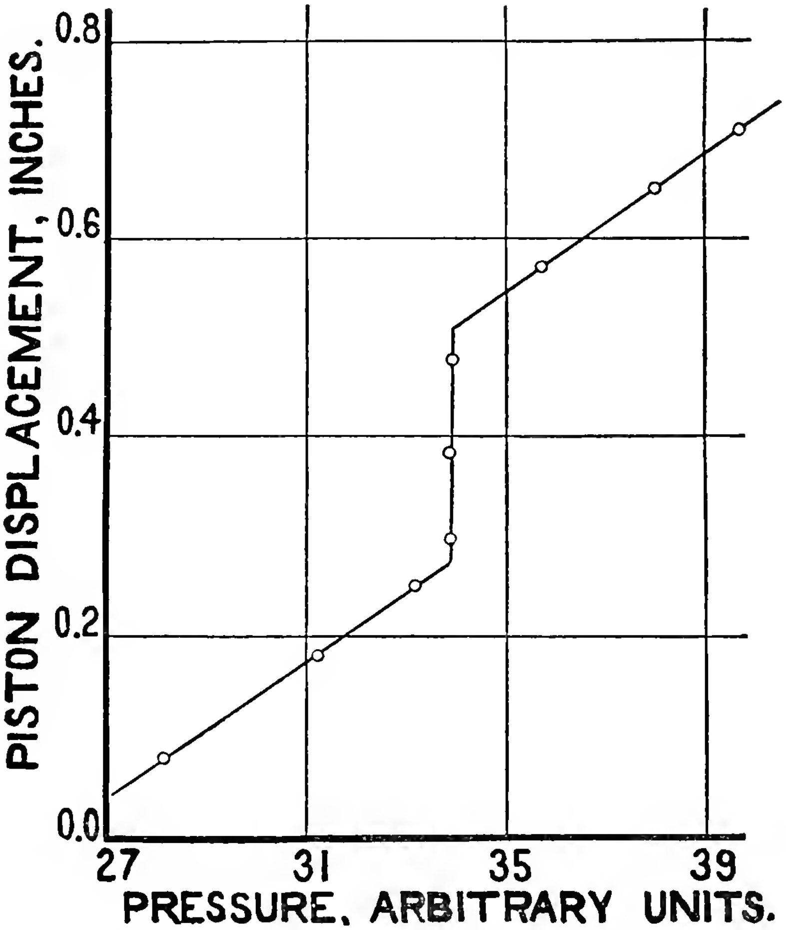

Figure 19. Shows the discontinuity in the piston displacement during freezing. (One division on the pressure axis corresponds to 900 kgm.)

closer to the upper corner of the curve, as will be shown in the magnified diagram later, but the lower corner cannot be approached very much more closely, because of the subcooling of the liquid mercury.

The data are collected in Table X. and shown in Figure 20. These data can be subjected to a calculation exactly like that used for the equilibrium points found by the change of resistance method. A straight line was passed through the midst of the points, the deviations from this line plotted on a large scale, and the best smooth curve drawn through the deviations. The calculated values were obtained from this smooth deviation curve and the original straight line. The points are not so regular here as for the determination by the change of resistance method, and the best smooth curve is open to greater question. The deviations from linearity are nearly twice that found by the resistance method, namely 140 against 60 kgm. at 12,000. This has

TABLE X.

FREEZING PRESSURE OF MERCURY AT DIFFERENT TEMPERATURES BY THE METHOD OF CHANGE OF VOLUME.

Temp. C.	Pressure, kgm., cm.².			
	Observed during Increase.	Observed during Decrease.	Observed Average.	Calculated [Linear Relation + Deviation Curve].
0.00	7570	7550	7560	7620
6.37	8905	8895	8900	8890
12.87	10230	10210	10220	10180
18.45	11360	11340	11350	11340
12.88	10130	10150	10140	10180
−19.9	3660	3660	3660	3700
− 9.8	5610	5570	5590	5680
0.00	7590	7590	7590	7620
9.16	9455	9445	9450	9440
16.4	10910	10910	10910	10900
5.23	8650	8670	8660	8680

as a result that the tangent at the origin as determined here gives a rise of pressure of 195.5 kgm./cm.^{2} per degree, against 196.5 found before, a difference of 1/2 per cent. The two series are not really so much different as this would indicate, because the smaller initial slope of this present series is unduly influenced by the very evident greater irregularity of the low-temperature points, and is compensated for by the greater departure from linearity. If we are willing to admit that the departure from linearity of the resistance measurements is probably more nearly correct, and apply this departure to the seven determinations by the present method above zero, we shall find as the average slope 196.3 kgm./cm.^{2} at the origin, agreeing within 1/10 per cent of the former value. In the rest of the work of this paper the best value for the slope at the origin will be taken as 196.4 kgm./cm.^{2} per degree, and the departure from linearity given by the resistance measurements will be taken as most probably correct.

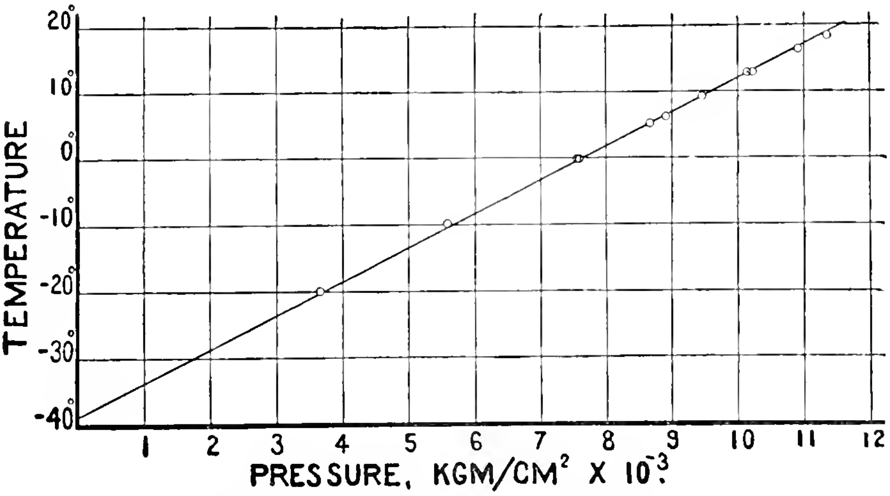

FIGURE 20. The equilibrium curve of liquid and solid mercury obtained by the change of volume method.

The changes of volume corresponding to these equilibrium pressures were all determined with the same set up of apparatus as already explained. These results are given in Table XI., and plotted against temperature on an enlarged scale in Figure 21. The observed values were obtained graphically from figures like Figure 19, drawn on a very much enlarged scale. For this purpose, it was not necessary to plot the actual pressures, but the position of the slider on the bridge wire on which the resistance measurements were made was used instead. This enables smaller changes of pressure to be measured with accuracy than could be done in the other way. The absolute gauge against which the calibration of the resistance was made has a limit of sensitiveness of about 8 kgm./cm.^{2}, while the resistance measurements are sensitive to about 2 kgm. The scale of the graphical construction was so enlarged that 1 cm. on the bridge wire goes into 5 cm. on the diagram, and 0.01 inch piston displacement into 1 cm. on the diagram.

TABLE XI.

Change of Volume of Mercury on Freezing as a Function of the Freezing Temperature.

Temp. °C.	Δv, cm.^{3} per gm.		
	Observed.	Corrected (1).	Corrected (2) final.
−19.9	0.002533	0.002503	0.002515
− 9.8	2498	2487	2492
0.0	2448	2458	2454
5.23	2410	2426	2426
9.16	2376	2399	2399
16.40	2315	2348	2348

Ordinarily four points were found on the curve both above and below the transition point, covering a range of from 500 to 700 kgm. in both directions. Over this range, and within the errors of reading, the curve connecting piston displacement with the position of the slider on the bridge wire was almost without exception linear, and was drawn in with a ruler. There was no tendency whatever for either corner of the melting curve to be rounded off, indicating that the change of state takes place at a single definite temperature and pressure, and affording the best possible evidence of the sufficient purity of the mercury. To this fact of absolutely sharp freezing is to be attributed the self-consistency of the results. With water, where there is some slight rounding off of the corners, the results are not so self-consistent, although the total change of volume is larger.

The process of correction applied to the observed values is shown in the table in two steps so as to give an idea of the magnitude of the corrections. In column (1) the corrections for the thermal dilatation of the kerosene on passing from the lower to the upper cylinder and the correction for the elastic deformation of the upper cylinder are both applied. In the second and finally corrected column, the additional correction for the variation of room temperature is applied. The sign of this correction changes with the direction of variation. As appears from the figure, these points are self-consistent, lying on a smooth curve to at least the order of accuracy given above, 1 part in 2500, except the point at 9° which is only 1/10 per cent out. The total displacement of the piston during freezing was about 0.2 inch, the quantity of mercury used being in the neighborhood of 350 gm. To obtain the above accuracy, therefore, it was necessary to take advantage of the utmost capacity of the micrometer, making all the readings to 0.0001 inch. That the single measurements do enjoy this degree of accuracy is made evident by a later very much enlarged figure drawn for the purpose of showing the impossibility of subcooling.

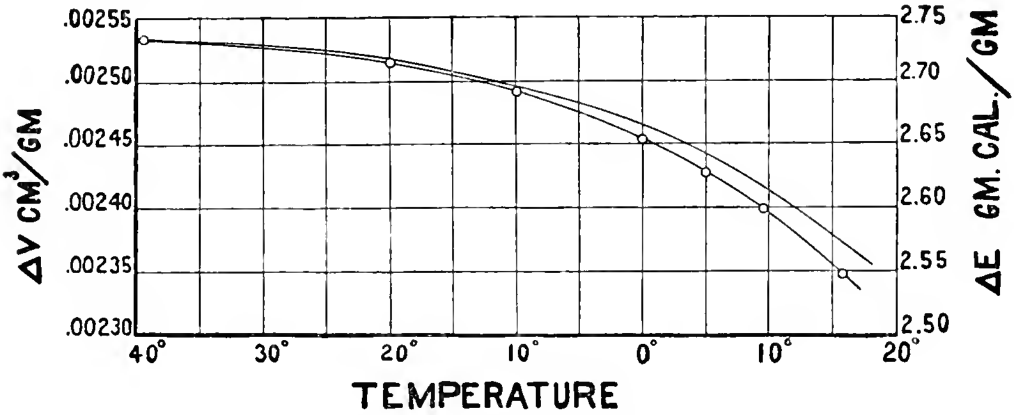

Figure 21. Shows the change of volume and of internal energy on passing from the liquid to the solid. The change of volume curve was directly observed, and the experimental points are indicated. The change of energy curve was calculated from the other data.

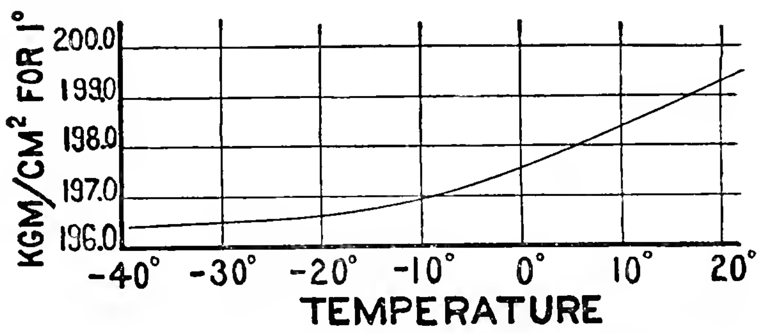

Figure 22. Shows the slope of the freezing curve as a function of the equilibrium temperature.

It is not claimed, however, that the absolute values at the high pressures have quite so much accuracy as this self-consistency would indicate, since probably the correction for the distortion of the upper cylinder leaves room for greater uncertainty than this.

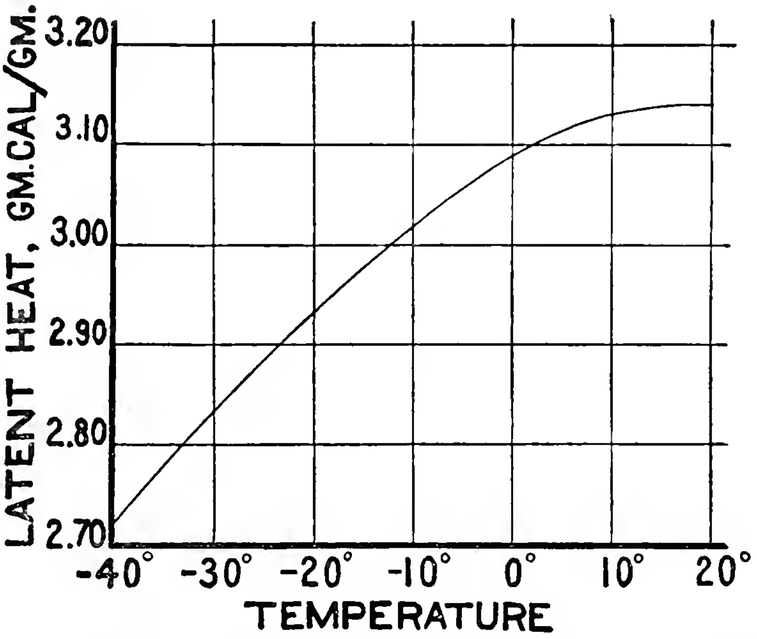

Figure 23. The latent heat of solid mercury as a function of the equilibrium temperature.

It is gratifying to notice that the point determined at atmospheric pressure by an entirely different method agrees perfectly with the points found above, making the accuracy of both determinations very probable.

From these data the latent heat of transformation may be found at every point of the melting curve by Clapeyron's equation,

$$\Delta H = \tau \Delta v \frac{dp}{d\tau} \cdot$$

ΔH was calculated from this equation at intervals of 10° from $-40°$ to $+20°$. $\frac{dp}{d\tau}$ was found by adding to the constant value 196.4 kgm. per degree the correction found from the graphically constructed slope of the curve showing the departure of the curve from linearity. The results of this graphical construction are shown in Figure 22. The absolute zero in the calculation was taken as $-273°.1$ C. The results in mean gm. cal. per gm. of mercury are shown in Figure 23 and Table XII.

The rise of ΔH to a probable maximum is the most interesting feature. The course of this curve is to be explained by the increasingly rapid drop of ΔV at high pressures, this drop finally becoming more rapid than the increase in $\frac{dp}{d\tau}$ and in the absolute temperature.

TABLE XII.

Change of Latent Heat on the Freezing Curve of Hg.

Temperature.		Δv cm.^{3} per gm.	$\frac{dp}{dt}$ gm./cm.^{2}.	Latent Heat mean gm. cal. per gm.
°C.	Abs.			
−40	233.1	0.002535	196400	2.720
−30	243.1	2526	196500	2.828
−20	253.1	2515	196600	2.939
−10	263.1	2492	196900	3.025
0	273.1	2454	197600	3.103
+10	283.1	2393	198350	3.149
+20	293.1	2311	199300	3.163

It will be noticed here, as for the change of volume, that the curve does not give the usually quoted value for the heat of transformation at −38°.85, but here also it seems that there is considerable chance for error in the previous value. The value always given is 2.82, which was obtained by Person[43] in 1847. As far as can be discovered, this is the only determination of this quantity which has ever been published. Person's method consisted essentially in dropping the frozen mercury at a temperature of about −42° into the water or turpentine of a calorimeter, and noting the fall of temperature. The usual corrections for radiation and the heat capacity of the vessel were applied. The actual heat given to the calorimeter was the sum of the heat given out by the solid in cooling to the transformation point, the heat of transformation, and the heat of the liquid in warming to the temperature of the calorimeter. The value $C_p = 0.0333$ was assumed to hold for the liquid over the temperature range. This is probably nearly correct, but the assumption that C_p for the solid is the same as

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[43] Person, Ann. de Chim. et Phys., **24**, 257–261 (1848).

for the liquid is probably open to greater question. The error introduced by this cannot be very large, however, because of the small temperature range over which the solid cooled. By far the greatest possibility of error seems to be in the simple measurement of temperature. The thermometry of low temperatures must have been in a chaotic state at the time, judging by the values given by Person for known fixed temperatures. He gives the value on the air thermometer of the melting point of mercury as —41°. This point is now known to be —38°.85. He furthermore states that his alcohol thermometer read higher than a mercury thermometer at —20°. No statement whatever is made as to the corrections applied to the readings of this alcohol thermometer. If, however, he did apply the correction of the mercury thermometer to the alcohol thermometer, then there is still the possibility of great variation between —20° and —40°. The consistent behavior of three calibrated alcohol thermometers which have been used in this present work indicates a possibility of error of as much as 3 per cent between —20° and —40°.

Person made three determinations of the latent heat, giving 2.77, 2.86, and 2.83, mean 2.82, as against 2.735 found above. The use of this latter value seems to be justified, therefore, in preference to that of Person.

Person's value for the latent heat has entered directly into the determination by Regnault[44] in 1849 of the specific heat of solid mercury. Again the value of Regnault is apparently the only value which we have of this quantity. The method of Regnault was exactly the same as that of Person, except that the mercury was initially at —77°.7, so that the heat given out by the solid in cooling to the melting point was a very appreciable part of the total heat given out. Incidentally Regnault's temperature measurement was very probably at fault as well as Person's, for he gives —40° as the melting point of mercury. Regnault made two determinations of the mean specific heat from —77°.7 to the melting point, giving 0.0314 and 0.325. Evidently the effect of a smaller latent heat of melting would be to give a larger specific heat to the solid. Substituting the value found above produces a change of 6.5 per cent in the values given by Regnault, giving 0.0334 and 0.0346 respectively, mean 0.0340.

The data used in determining the change of volume may also be used to give evidence on one point for which they were not intended. The slope of the curve plotting piston displacement against pressure is evidently going to be different above and below the melting point be-

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[44] Regnault, Ann. de Chim. et Phys., **26**, 268–278 (1849).

cause of the difference in compressibility between the solid and the liquid mercury. The compressibility of mercury is small in any event, and here the greater part of the piston displacement is used in compressing the kerosene, so that only rough values can be expected from the small difference. There is the further complication of the drift in the temperature of the room. The slope does show a distinct tendency to be less when the solid state is present, but the change is irregular. It can be said, however, that the compressibility of the solid at the freezing point is less than that of the liquid, the difference being in the neighborhood of 10 per cent.

THE CHANGE OF VOLUME OF MERCURY ON FREEZING AT ATMOSPHERIC PRESSURE.

It has already been stated that the necessity for redetermining the change of volume at atmospheric pressure arose from the probable inaccuracy of the previously accepted value (0.00260 cm.^{3} per gm.). The inaccuracy of this number was first suspected when a set of values found for Δv at different pressures, consistent among themselves to 1/25 per cent, did not extrapolate to within 2 per cent of 0.00260. Investigation showed that the value 0.00260 is not a direct experimental determination, but is obtained from the difference between the density of the solid, as found by one observer, and the density of the liquid as given by another. Since the change of volume is only about 3 per cent of the total volume, the density of both solid and liquid must be known with an accuracy of sixty times the accuracy desired in the change of volume. The following short discussion of these previous experimental determinations will make clear that there are here possibilities of error of fully the indicated magnitude.

The value of the density of the solid seems to be open to by far the most serious question. The commonly accepted value, in fact the only value with any claim to accuracy at all, was given by Professor Mallet [45] of the University of Virginia. The method consisted in freezing a weighed quantity of mercury in a glass bulb, and then determining the quantity of alcohol necessary to fill the bulb to a fixed mark. The largest possibility of error seems to be in determining the volume of the bulb at the freezing temperature of mercury. This was found from the quantity of mercury filling it at 0° and 100°, using Regnault's value for the dilatation of mercury, and extrapolating back to the freezing point. No account at all was taken of the possibility of per-

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[45] Mallet, Proc. Roy. Soc. Lon., **26**, 71 (1877).

manent changes of volume of the glass bulb after subjecting to 100°. That there is such an effect, very noticeable, is shown by the change of zero of glass thermometers after subjecting to a high temperature. No mention is made of the kind of glass; if it were an American lead glass, the effect would be comparatively large. The final value for the density of the solid as given by Mallet was 14.1932. This is the mean of three values, 14.1948, 14.1920, and 14.1929.

The density of liquid mercury at the freezing temperature is given in Landolt and Börnstein's tables as coming from Vicentini and Omodei,[46] but the value given by them is as a matter of fact quoted from a paper of Ayrton and Perry.[47] Their method consisted in reading simultaneously the same temperatures between 0° and —38°.85 with a mercury in glass thermometer and an air thermometer. The readings of one plotted against the other are stated to be "very nearly linear," from which the conclusion is drawn that the dilatation of mercury between 0° and —38°.85 has the same constant value as that found by Regnault to hold between 0° and +100°. The density at —38°.85 is then calculated from the known density at 0°. No statement whatever is made as to the degree of accuracy attained, or even as to the direction in which the plot of the air against the mercury thermometer departs from linearity. However, the fact that one of the conclusions drawn from the results is that mercury shows no maximum of density in the neighborhood of the freezing point analogous to water, suggests that the previous knowledge of this quantity was very imperfect indeed, and that the results of Ayrton and Perry themselves are not so accurate as necessary for the present purpose.

A direct determination of this change of volume with the same apparatus as was used at higher pressures and temperatures would have been possible, but inconvenient for several reasons. Chief of these was the difficulty of running a thermostat of the requisite size with sufficient constancy at this low temperature. Furthermore, if a result concordant with the others could be found by an entirely different method, the results by the two methods would mutually support each other, making any consistent error in either improbable.

The method used consisted in weighing a known quantity of mercury under CS_2 at different temperatures in the neighborhood of the melting point. The weight varies with the temperature. When the temperature passes through the melting temperature, the mercury melts with increase of volume, and the increased displacement causes a sudden

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[46] Vicentini and Omodei, Atti di Torino, **23**, 38–43 (1887–1888); and **22**, 28–17, 712–726.

[47] Ayrton and Perry, Phil. Mag., **22**, 325–327 (1886).

change in the weight equal in amount to the weight of the displaced CS_2, that is, equal to the weight of CS_2 of volume equal to the change of volume of the mercury. The only quantities directly concerned are the discontinuity of the weights and the density of the CS_2 at the point of discontinuity. It is not necessary to know even the temperature accurately. Any consistent device for indicating changes of temperature, so that the weight may be plotted as some continuous function of the temperature on either side of the melting point, is all that is required.

The temperature was indicated by the resistance of a coil of fine double silk covered iron wire, wound on a glass core 4 inches long and placed in kerosene inside a thin-walled brass tube, which was immersed directly in the CS_2 in which the weighings were made. The coil was not calibrated for absolute temperature, but the resistance could be measured with an accuracy corresponding to changes of temperature of 0°.002. In addition, the temperature was read on a toluol thermometer, graduated to 0°.1, which was also immersed in the bath. The readings of the thermometer were taken only to give a check on the readings of the resistance thermometer, since the thermometer readings were inaccurate because of varying parallax and the necessity of removing the thermometer partly from the bath in making the readings.

The cold CS_2 in which the mercury was weighed was contained in a cylindrical Dewar flask, 2 inches in diameter and 12 inches long. The inside of this was lined with a sheet of celluloid to protect the glass from being scratched, and inside this a tube of heavy copper tubing, 5/32 inch thick, to promote rapid equalization of the temperature. The most effective equalization of temperature, however, was provided by a small turbine stirrer, reaching the entire length of the flask. This was run constantly between readings, but was naturally stopped while a weighing was being made. The mercury was contained in a thin steel shell, 9/16 inch diameter, and 4 inches long, suspended by a fine iron wire (0.007 inch diameter), from the beam of a sensitive balance above. The quantity of mercury used was about 140 gm. It was possible to weigh this to 1/4 milligram, giving an accuracy on the discontinuity of weight on freezing, which was about 0.6 gm., of one part in 2000. In the respect of sensitiveness, the CS_2 is probably as convenient a liquid as could be found, because of the high density and very low viscosity and surface tension. Provision was made for warming the bath after each weighing by passing a current through a small heating coil immersed in the bath.

The experimental procedure was the natural one. The Dewar flask was first filled with CS_2 which had been cooled in another dish with

CO_2 snow and ether. In this was suspended the steel shell with the mercury, which had been previously frozen. The temperature was then raised to about —42°, and readings made at intervals of 0°.5. The spontaneous rise of temperature of the bath during a weighing was so small as to introduce no error. During warming, the weight increases linearly, due to the larger thermal expansion of the CS_2 than the mercury. Melting is indicated by a rapid drop in the weight of about 0.6 gm. This drop is not instantaneous, but may extend over 1°.5, showing temperature lag between the mercury and the bath while the heat of transformation is being absorbed. Completion of melting is indicated by resumption of the linear relation between weight and temperature. To find the discontinuity in the weight, it is merely necessary to extrapolate this straight line back to the point at which melting began.

There are only a few special precautions to observe. The most likely source of error is the formation of minute cracks in the mercury when freezing. To obviate this, the mercury was poured into the steel shell already filled with CS_2, so as to ensure filling of all the corners, and then frozen by placing merely the very bottom of the shell in the freezing mixture. Freezing took place very slowly and uniformly from the bottom, the surface of the finally frozen mercury being as perfectly convex as that of the liquid. Pains had to be taken to scrape away from time to time the minute quantities of ice condensing on the suspending wire. This wire was so fine that no correction whatever had to be applied for the slightly varying depths of immersion during the course of an experiment. Finally, it was necessary to determine the density of the CS_2 at the freezing temperature separately for each experiment. This arose from the fact that during the preliminary work a slight quantity of ether had been accidentally spilled into the CS_2, enough to decrease the density by 1 per cent. This gradually evaporated, producing a slow rise in the density of the CS_2 to a final steady value. The density was given directly by the loss of weight of the mercury and steel in the CS_2 at the freezing temperature. There seems no question whatever but that the density of the liquid mercury at the freezing point is known with the accuracy demanded here, 1 part in 2000, although there may be reasonable question as to whether its accuracy is 60 times greater, as it must be when used to give the change of volume by a subtraction. The steel shell was only a small part of the total weight, and its thermal dilatation is so well known and so small that there is no danger at all in calculating the density of the steel at −38°.85 from the experimentally measured density at room temperature. The accuracy of this procedure is vouched for by the fact that the density of the CS_2 when determined by weighing in it a solid steel cylinder agreed within 1 part in 13,000 with the value found by weighing in it the steel shell with the mercury.

Five preliminary determinations of the change of volume were made giving results varying from 0.00253 to 0.00257. The chief cause of inaccuracy in these preliminary results was the irregular behavoir of the resistance thermometer. This was due to the defective insulation of the enamelled wire used in these first experiments. Replacing the enamelled wire by silk-covered wire gave perfectly satisfactory results. Advantage was also taken of this preliminary work to modify slightly various details of apparatus and procedure.

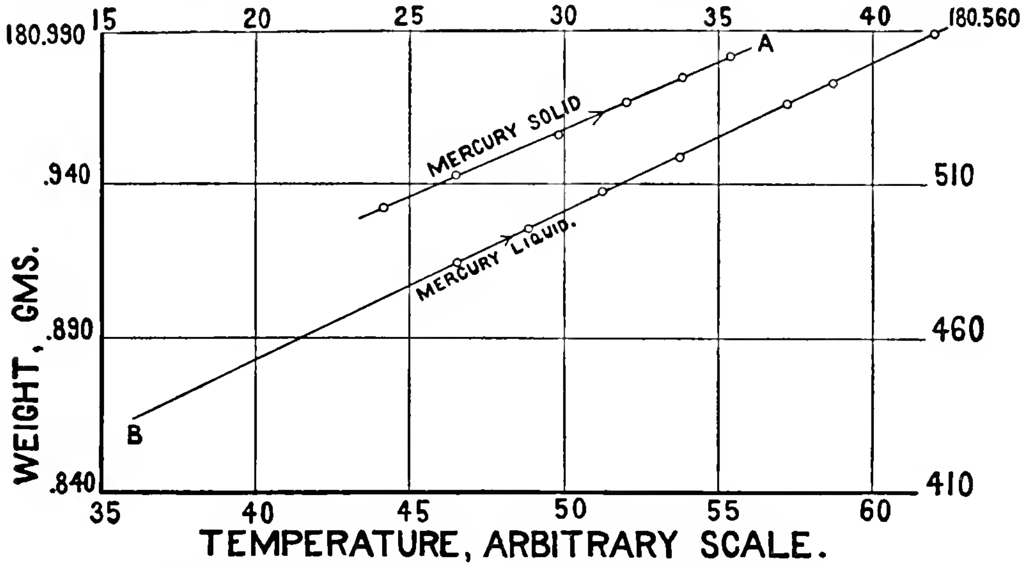

FIGURE 24. Shows the readings from which was found the change of volume when mercury melts at atmospheric pressure. The scale above and to the left refers to the solid mercury, and that below and to the right to the liquid. The point A indicates the beginning of melting, and the point B shows the completion of melting.

Three independent determinations of the change of volume were made with the final form of apparatus. The experimental points of one of these determinations are shown in Figure 24. The mercury was changed for each of these determinations, the total quantity being varied by 10 per cent. The three values found, using the iron resistance as the temperature indicator, were 0.002533, 0.002536, and 0.002532 cm.^{3} per gm. The same weighings plotted against the thermometer readings (it is to be remembered that this was done merely as a check) gave 0.002533, 0.002537, and 0.00252 respectively. The thermometer points of the last determination were very irregular.

The resistance points are to be taken as the correct ones, and the mean of the three determinations, 0.002534, is accepted as the best value. The departure from the previous value, 0.00260, is thus nearly 3 per cent.

This result may be used to give a more accurate value than that of Mallet for the density of the solid mercury at the freezing point. Assuming for the density of the liquid at the freezing point the value of Ayrton and Perry, 13.690, the density of the solid is found to be 14.182 as against 14.193 of Mallet.

This also enables a correction to be applied to the value of the coefficient of dilatation of solid mercury as found by Dewar.[48] He determined the density at —188°.7 (in liquid air) and from Mallet's value for the density at the freezing point calculated the coefficient of thermal dilatation to be 0.0000887 over the range from —38°.8 to —188°.7. Substituting the above value for that of Mallet gives 0.0000907. Dewar's value for the density of mercury at the temperature of liquid air seems open to question, however. All of Dewar's measurements of density at low temperatures depend on his value for the density of liquid oxygen, which he gives as 1.137. The measurements which he made on ice would seem to show a probable error here. The value for the thermal dilatation of ice over the range 0° to − 190° was found to be only half the known value from 0° to — 20°. So large a decrease seems hardly probable. A change in the fundamental constant so as to give a higher value to this dilatation would also give a higher value to the thermal dilatation of mercury. Furthermore, a change in this direction would bring Dewar's value for the dilatation of mercury into agreement with that of Grunmach,[49] namely, 0.000123 from — 38° to — 80°. This is apparently the only other value we have. But Grunmach used a dilatometer method in which he made no correction whatever for the effect of the glass envelope. The value obtained by him for the change of volume on freezing with the same apparatus is certainly wrong, namely, 5 per cent as against 3 per cent found above, and this one fact is enough to cast discredit on the rest of the work. There seems to be no value, therefore, which can be accepted at present with confidence for the thermal dilatation of the solid.

In view of the apparent uncertainty as to the value of the thermal dilatation of the solid, it may perhaps be allowed to force the above weighings to give what information they can on this point. It is not

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[48] Dewar, Proc. Roy. Soc. Lon., **70**, 237–246 (1902).

[49] Grunmach, Phys. ZS., **3**, 133–136 (1902).

expected that the value so obtained can do more than roughly indicate the probable value, since this use of the data was not contemplated in the original experiment. The information comes by observing at the melting point the change in the slope of the curve plotting weights against temperature. The slope is evidently connected with the various thermal dilatations.

The exact expression is found to be

$$\left(\frac{dW}{dt}\right)_1-\left(\frac{dW}{dt}\right)_2=\frac{dD_{CS_2}}{dt}\left[V_{Hg,2}-V_{Hg,1}\right]$$
$$-D_{CS_2}\left[\left(\frac{dV_{Hg}}{dt}\right)_1-\left(\frac{dV_{Hg}}{dt}\right)_2\right].$$

The subscript 1 refers to the liquid and 2 to the solid. D_{CS_2} is the density of the CS_2. The value $\frac{D_{CS_2}}{dt}$ was taken to be 0.0014. This amounts to assuming the value of the dilatation of CS_2 to be 0.001, which is the value given at 0° by Pierre's formula. There is room for considerable question here, but the term into which $\frac{D_{CS_2}}{dt}$ enters is only 10 per cent of the other term involving the dilatation of the liquid mercury.

Only the last two of the sets of weighings are available for this calculation, the CS_2 having then assumed an unvarying value for the density. The dilatation of the solid calculated from these two sets was 0.000165 and 0.000125, mean 0.00014. The value is extremely rough, but probably as good as either the value of Dewar or Grunmach.

These data also give a rough incidental determination of the density of CS_2 at $-38°.85$. This was found to be 1.3460. It has been already mentioned that this is probably slightly in error due to the presence of a slight impurity of ether, but the above value was the final value, and remained constant over two days, showing that what little ether there was had nearly all evaporated. The density as calculated by the third degree formula of Isid. Pierre is 1.3647.[50] The formula of Pierre is intended to hold only for the range 0° to 100°. The discrepancy suggests at any rate the danger of using the formula by extrapolation to considerable negative temperatures.

SUBCOOLING AND SUPERHEATING.

All these observations on the freezing and melting of mercury under pressure also show that one property which apparently holds without

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[50] Pierre, Ann. de Chim. et Phys. (3), **15**, 325 (1845).

exception at atmospheric pressure also holds under high pressure. This is the fact that it is impossible to superheat a crystalline phase with respect to the liquid phase, although the liquid may be subcooled, sometimes very considerably, with respect to the solid. Figure 25, drawn on a very large scale, shows this fact. At the lower corner the subcooling of the liquid with respect to the solid is shown, while at the upper corner, where the pressure is decreased on the solid phase, is shown the sharp change of state when the equilibrium pressure is overstepped. The slight irregularities in the points are due to errors of

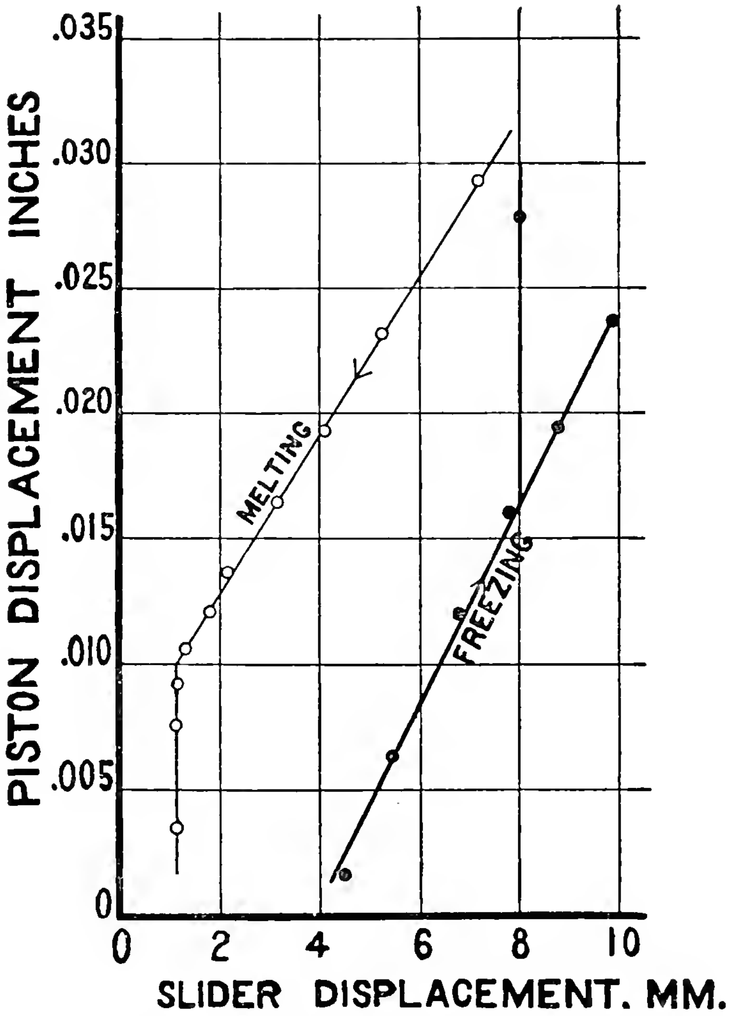

Figure 25. Shows on an enlarged scale the possibility of subcooling the liquid but the impossibility of superheating the solid. The two curves have been displaced, the one with respect to the other; the melting and freezing actually takes place at the same pressure. One division on the pressure axis corresponds to 40 kgm.

reading, the several points on the vertical part of the curve at decreasing pressure differing among themselves by only 0.05 mm. of bridge wire, better than the limit of reading, corresponding to pressure differences of 1 kgm./cm.^{2}. The points plotted are the mean of two readings, each to 0.1 mm. The same possibility of subcooling was found during measurements by the change of resistance method.

Attempts to measure the amount of subcooling would have had no absolute value, for its amount depends on many extraneous factors, such as the size and shape of the glass capillary, the presence of small particles of grit in the fluid transmitting pressure, and most important of all, the element of time. The greatest amount of subcooling found from the resistance measurements was 230 kgm. at 10°.2, equivalent to about 1°.1. The mercury remained liquid under these conditions for about 30 minutes, and did not freeze until the pressure was still further increased.

This impossibility of superheating a crystal has been shown to be so universally true that it is coming to be regarded in the light of a natural law. It holds whether the liquid melts with increase or decrease of volume. No satisfactory explanation has yet been given of the fact, however. Nearly all the explanations suggested, applicable at atmospheric pressure, have attempted to make it in some way a surface phenomenon, the melting beginning at the free surface and running in toward the interior. In view of the fact shown above that superheating is also impossible under very high pressures, it would seem somewhat doubtful whether this is the correct method of attack on the problem. Under high pressures the surface of separation between the solid and the surrounding liquid (mercury and kerosene, for example) cannot be thought of properly as a free surface. The molecules of mercury would seem no more free to assume their natural positions at this surface than they would in the interior of the mercury itself. This is particularly probable when it is remembered that the mercury melts with increase of volume.

Conclusion.

In this conclusion an attempt will be made to show what bearing the data may have on the theories of the liquid state and on our knowledge of the change of state liquid-solid. As giving the best general survey of all the data, a diagram is presented showing the isothermal lines for the liquid and the sudden change on passing to the solid state. (Plate.) The data from which this figure was constructed are shown in Table XIII. Within the accuracy of this work the isothermals may be taken as equi-spaced, as already explained. The first thing to strike one on looking at the diagram is that the effects are nearly constant over the entire range; the compressibility does not change markedly, nor does the dilatation, and the lines bounding the domain liquid-solid are nearly parallel. It is evident, therefore, that any reversal of the ordinary effects or the appearance of critical points must be far beyond the reach of the diagram. The diagram is competent to show only the initial trend of the various effects.

TABLE XIII.

Points on the Isothermals of Liquid Hg.
(Computed from Experimental Curves at 0° and 22°.)

Pressure, kgm./cm.^{2}.	Volume, cm.^{3}.					
	−30°.	−20°.	−10°.	0°.	+10°.	+20°.
0	0.99457	0.99638	0.99819	1.00000	1.00181	1.00362
1000	99207	99280	99553	0.99626	0.99799	0.99972
2000	98760	98927	99094	99261	99428	0.99593
3000	...	98581	98743	98905	99067	99232
4000	...	98245	98403	98561	98719	98877
5000	...	...	98077	98231	98385	98540
6000	...	...	97763	97914	98065	98216
7000	...	...	...	97607	97756	97904
8000	...	...	...	...	97461	97608
9000	...	...	...	...	97182	97327
10000	...	...	...	...	96915	97059
11000	...	...	...	...	...	96806
12000	...	...	...	...	...	96567
Change of vol. on freezing	0.03435	0.03418	0.03388	0.03337	0.03243	0.03142
Freezing pressure	1740	3710	5670	7640	9620	11600

For the liquid state the results are the same in general as those with which we are familiar for the more compressible liquids under lower pressures. The compressibility and the dilatation both decrease with rising pressure. This has as a consequence that the effect of rising temperature is as usual to increase the compressibility. The behavior of the specific heats is rather unusual, approximate constancy for C_p and increase of C_v with pressure. For water, $C_p - C_v$ increases instead of decreasing. As a little surprising, but not unusual, it may be mentioned that the internal energy decreases along an isothermal with increasing pressure, but increases, as is normal, along an adiabatic. This means that along an isothermal the attractive force between the molecules is still the dominant factor in the situation, even up to 12,000 kgm. At higher pressures a reversal of the effect is indicated, where the repulsion between the molecules would become the important part.

The data are more suggestive in the light they throw on the change from the liquid to the solid state. In this connection it may be useful to outline briefly the present state of the theory, and the points at issue.

For the change of state liquid-vapor, the physical facts have been worked out pretty fully until we now have a fairly definite understanding of the nature of the process. This increase of knowledge has come about almost entirely from the experimental side, the one thermodynamic relation not being of much assistance. In particular, the existence of the critical phenomena, and the possibility of the continuous passage from the liquid to the vapor were facts which were unexpected before the actual experimental proof. There is no thermodynamics which would predict the existence of such a point. Our present knowledge of the nature of the equilibrium between liquid and solid is in much the same state as the knowledge of the transformation liquid-vapor before the discovery of the critical point. The fundamental question as to whether a critical point exists or not is therefore of greatest immediate interest.

At present, both the most important theory of the equilibrium between solid and liquid and the most far reaching experimental work are due to Tammann.[51] The essential part of his theory, as opposed to Ostwald,[52] Poynting,[53] and others, is that for the transition solid-liquid there is no critical point like that for the transition liquid-vapor. The reason for this fundamental distinction is to be found in the essential similarity between a liquid and a vapor on the one hand, and the essen-

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[51] Tammann, loc. cit.

[52] Ostwald, Lehrbuch der Allgemeinen Chemie, II^{II}, Verwandtschaftslehre, p. 389 (Engelmann, Leipzig, 1902).

[53] Poynting, Phil. Mag. (5), **12**, 32 (1881).

tial dissimilarity between a liquid and a crystal on the other hand. The molecules in both the liquid and the vapor are thought of as arranged at random, "molekular-ungeordnet," the only difference between liquid and vapor lying in the average distance apart of the molecules. Once let the average distance apart of the molecules appropriate to the vapor and liquid become equal, as they do at the critical point, and all further distinction between the two phases vanishes. In particular, the heat of transformation vanishes as a consequence of the equality of the volumes. But for the two phases liquid-crystal, there is besides the distinction of density the further distinction that in the crystal the molecules are arranged in some sort of a framework in space. Equality of density of the two phases liquid and solid does not mean identity, because the crystal still preserves the regular arrangement of the molecules which cannot hold in the liquid. In consequence, the energy difference between the two phases need not become zero when the volume difference vanishes; that is, the heat of transformation does not vanish at the same time with the change of volume, and we do not have a critical point. Tammann goes further than simply to deny the existence of a critical point. He concludes from an examination of all the known data, chiefly his own experiments, that for substances of the ordinary type of freezing with decrease of volume, not only do the change of latent heat and the change of volume fail to pass through the value zero at the same time, but that the change of volume always becomes zero before the heat of transformation. It is then an immediate deduction from Clapeyron's equation that the melting curve has a maximum. That is, there exists for every substance a temperature so high that no pressure, however intense, will bring the point of transition as high as this temperature. Above this temperature the substance is always liquid. This is really the essential part of Tammann's theory of the shape of the equilibrium curve. It has been immediately seized upon by geologists, and made the basis of many speculations as to the state of the interior of the earth, the matter there being supposed fluid because the temperature is higher than the maximum.

The experimental evidence in support of this theory is meagre, the pressure reached by Tammann being sufficient only to show a curvature in the direction demanded by the presence of a maximum, and an initial decrease toward zero of the change of volume more rapid than the decrease of the latent heat. The only case in which Tammann claims to have found a maximum, for $Na_2SO_4 10H_2O$, must be ruled out because of the complication introduced in the equilibrium conditions by the water of crystallization.

The evidence of the present data of significance for this question as to the existence of either a critical point or a maximum are the slope of the freezing curve, the variation of volume, and the variation of the latent heat.

The freezing curve is concave toward the pressure axis, which is curvature in the direction demanded by the presence of a maximum. This direction of curvature is the same as that shown by all the melting curves of Tammann, who uses it as an argument tending to show the existence of a maximum. But the curves liquid-vapor also invariably show the same curvature, and here there is a critical point. It is also easy for a curve to run to infinite temperature and pressure, still being concave toward the pressure axis. The direction of curvature would seem to give absolutely no presumptive evidence, therefore, one way or the other.

The change of volume and the latent heat together may be considered. The change of volume alone invariably decreases with rising temperature. This merely means that the phase with the smaller volume is less compressible. Tammann's argument consists in showing that the change of volume decreases along the equilibrium curve, while the latent heat usually increases, or if it shows a decrease, the decrease is slight in comparison with the decrease in the change of volume. The change of volume becomes zero first, therefore, and we have a maximum freezing temperature.

The curves for ΔV and the latent heat of this present work on mercury have been already shown. ΔV decreases with rising temperature, as it does universally. The latent heat curve is the significant curve, because it increases apparently to a maximum and seems about to descend. Tammann's argument would be perfectly valid for the first 6000 or 7000 kgm., but at higher pressures this reversal of the latent heat curve invalidates the whole thing. There is no reason to anticipate that the decrease in ΔH beyond 11,000 might not be rapid enough to make it vanish with ΔV.

It is interesting in this connection to plot the difference of internal energy between the solid and the liquid against temperature. The difference is given by

$$\Delta E = \Delta H - p\Delta v.$$

ΔE shows the part of the heat of transformation which has been made potential inside the mass. The rest of this heat goes into performing mechanical work. The results are shown, with the steps of the calculation in Table XIV. and in Figure 21, in direct comparison with the changes of volume. The energy decreases from the start along the equilibrium curve in such a way that its ratio to Δv is nearly constant. There seems no particular reason why this is not as significant a quantity on the melting curve as the latent heat. It is true that it does not enter the equations so simply, but the behavior at the points of special interest on the melting curve is just as simple as that of ΔH. At the critical point, for example, if there is one, where Δv becomes zero, but $\frac{d\tau}{dp}$ remains finite, it is known that $\Delta H = 0$. In this case $\Delta E = 0$ also. If the melting curve shows a maximum, which is characterized by $\Delta v = 0$, and $\frac{dp}{d\tau} = 0$, then ΔH remains finite, as does also ΔE, which in this case equals ΔH. The trend of ΔE on the melting curve would seem therefore to be just as valuable an indication as the trend of ΔH as to the possible existence of a critical point or a maximum.

TABLE XIV.

The Change of Internal Energy of Mercury on Passing from the Liquid to the Solid at Different Temperatures.

Temp. °C.	Pressure, kgm./cm.².	Δv cm.³ per gm.	Work $(=p\Delta v)$ gm. cal.	Latent Heat.	ΔE $(\Delta H - p\Delta v)$ gm. cal. per gm.
−28.66	2000	0.002525	0.118	2.848	2.732
−18.48	4002	2512	.235	2.951	2.717
− 8.31	6005	2486	.350	3.041	2.693
+ 1.87	8018	2443	.459	3.114	2.657
+12.06	10034	2377	.557	3.154	2.599
+22.24	12064	2296	.649	3.165	2.516

The present data offer no evidence, therefore, as to the existence of a critical point, except to show that if there is one it must be at pressures higher than can be reached directly. The positive result is obtained, however, that at high pressures there is a reversal in the behavior of the latent heat such as to invalidate Tammann's argument for a maximum.

As opposed to Tammann's argument for the impossibility of the existence of a critical point solid-liquid, it may be shown that it is possible to conceive of a molecular mechanism by which the continuous passage from the "molekular ungeordnet" assemblage of the liquid to the regular arrangement of the crystal on a space framework may be accomplished. We may think of the molecules as cubes, for example, with intense centers of force at the corners. As the molecules wander past each other in the liquid state, there will be a tendency for them to linger with the edges or the faces in contact. If the time during which they so linger in symmetrical positions with respect to each other becomes appreciable with respect to the total time, we will have some approach to the properties of a crystal, the approach becoming closer as the time of contact becomes relatively greater. And entirely aside from the question of molecular structure, there seems no difficulty in conceiving that if the temperature and pressure are varied properly on a cubical crystal, for example, that the three elastic constants might so change with respect to each other that two of them should eventually become equal, giving the two distinctive constants of an isotropic body, and so continuous passage from a crystalline to an amorphous body.

Summary of Results.

Data have been collected in this paper sufficient to give the p-v-t surface of the liquid, and the location and magnitude of the discontinuity in this surface when the liquid freezes to the solid over a pressure range of 12,000 kgm./cm.^{2}, and a temperature range from $-38^\circ.85$ to $+20^\circ$. Tables of various quantities of thermodynamic interest are given for the liquid; such as the compressibility, the dilatation, the change in the specific heats, the adiabatic compressibility, the heat of compression, and the change in internal energy both along an isothermal and along an adiabatic. For the change liquid-solid the co-ordinates of the melting curve are given, the change of volume, and the latent heat. The results do not show any behavior in the liquid at high pressures opposite in character from that which would be predicted from their trend at lower pressures. But for the change solid-liquid, it seems that at high pressures there is a change in the trend of the latent heat which invalidates Tammann's argument for the existence of a maximum. If either a maximum or a critical point exist for the transition solid-liquid it is at pressures higher than are at present open to direct realization. Such a point could not well exist at less than 50,000 kgm./cm.^{2}.

Apart from the main work of the paper a number of other quantities relating to mercury have been determined, some of them very roughly, either by a direct calculation from the new data given here, or else by a recomputation from the data of others, using in this recomputation some of the improved values found here. These new quantities are: a more accurate value for the density of the solid at —38°.85, a rough value for the thermal dilatation and the compressibility of the solid, an improved value for the specific heat of the solid, the electrical resistance of the liquid up to the freezing pressure, and the resistance of the solid under pressure, including the pressure and the temperature coefficients.

Finally, the computations made necessary the determination of another quantity of interest in itself, namely, the compressibility of steel. This was determined up to 10,000 kgm. and at two temperatures, from which the temperature coefficient of compressibility is found.

Acknowledgement is here made of several liberal appropriations from the Rumford Fund of the American Academy of Arts and Sciences with which the expenses of this investigation were partially defrayed.

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OCTOBER, 1911.

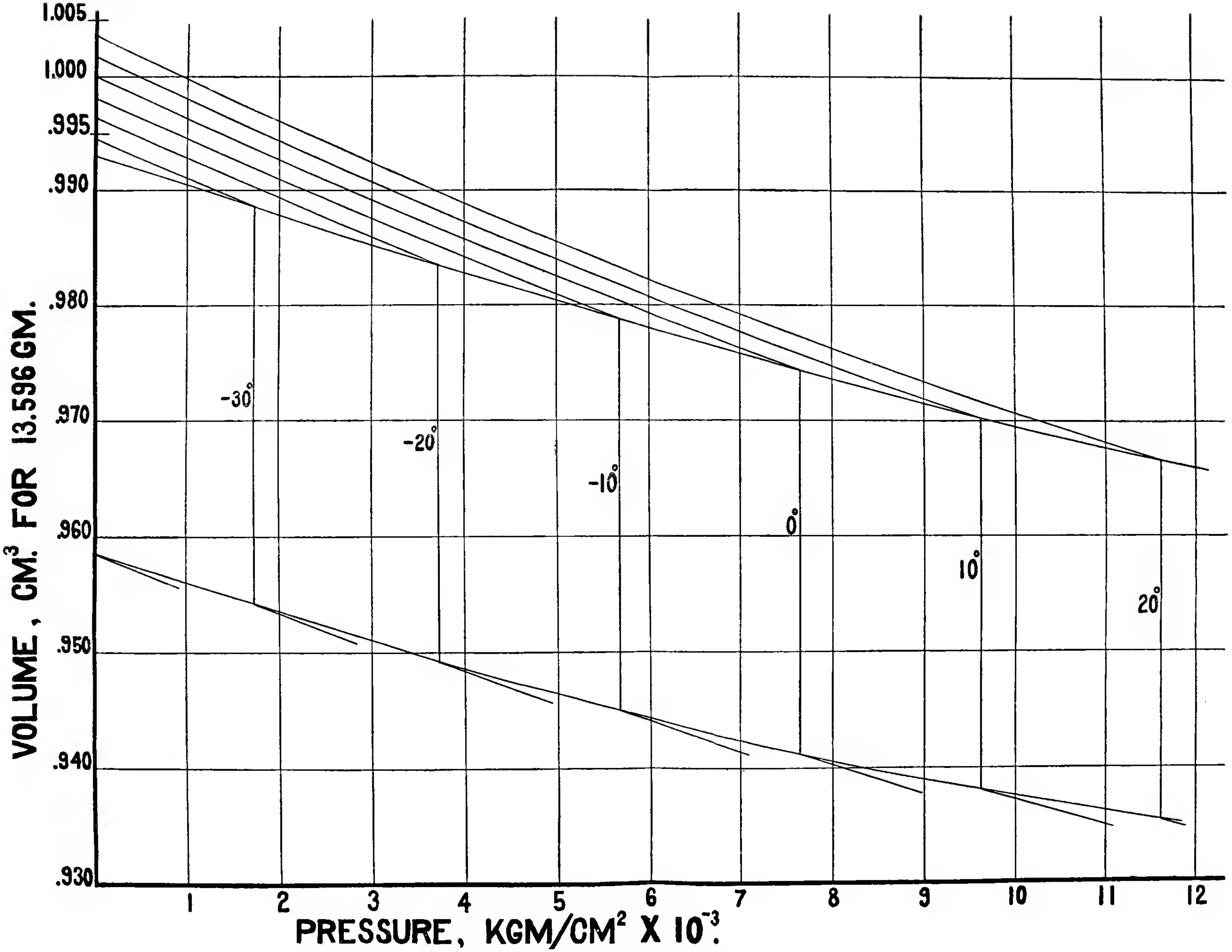

PLATE. Shows the isothermals at 10° intervals of liquid and solid mercury. The upper part of the diagram is for the liquid, the lower for the solid. The initial slope of the isothermals for the solid was not obtained by direct experiment, but was found approximately by a computation.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 13. — January, 1912.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

WATER, IN THE LIQUID AND FIVE SOLID FORMS, UNDER PRESSURE.

By P. W. Bridgman.

With Three Plates.

Investigations on Light and Heat made and published with Aid from the
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WATER, IN THE LIQUID AND FIVE SOLID FORMS, UNDER PRESSURE.

By P. W. Bridgman.

Presented by G. W. Pierce, October, 11, 1911. Received October 6, 1911.

Introduction.

The purpose of this paper is the same as that of the immediately preceding paper on mercury, — to indicate the nature of the fundamental facts which must be taken account of in any theory of liquids valid for high pressures, and to find something about the nature of the equilibrium between crystal and liquid. Both of these subjects are as yet practically untouched. All present theories of liquids are incompetent to explain known facts, and as for the theory of the equilibrium liquid-solid, even the fundamental facts are unknown. It seems, moreover, that these two subjects will find their best development side by side; one involves the other. Thus, any normal liquid may be made to crystallize by the application of high pressure. The internal forces producing crystallization must be present to some extent continuously in the liquid, modifying its behavior more and more as the crystallization point is approached. Yet no present theory of liquids takes account of these vector forces in the liquid which ultimately produce crystallization, but supposes instead that the force between molecules is uniform in every direction.

To be of significance the experimental study must be made over a comparatively wide pressure range, the order of the pressures being many fold greater than the pressures involved in the corresponding study of the liquid-vapor change. The results of this paper reach to 20,500 kgm./cm.^{2}, whereas the highest previous pressure under which water has been studied was only 3500 kgm.

As compared with mercury, the results for water are much more varied and richer in suggestion. It is well known that under ordinary conditions water is abnormal in many respects. The effect of high pressure is to wipe out this abnormality. The manner in which the abnormality disappears with increasing pressure is interesting. Beyond the disappearance of abnormality, the pressure has been pushed far enough to suggest in one or more particulars what the behavior of any liquid must be under very high pressures. The results with mercury did not suggest this so strongly, because the effect of pressure is much less on the properties of mercury than on those of water, so that to produce the effects peculiar to high pressure will require a much higher pressure for mercury than for water. Corresponding to the abnormal behavior of the liquid at low pressures, and probably connected with it, the solid also shows abnormal behavior at low pressures, appearing in no less than five allotropic forms. In addition to these five forms of ice with known regions of stability, there may possibly be two others with no domain of stability whatever. All of these forms, except ordinary ice, are more dense than water. With higher pressures, accompanying the return of the liquid to normality, the tendency of the solid to take new forms apparently disappears, the modification of ice stable at high pressures giving indications of being the last form, corresponding to the completely normal liquid. Here again the last form of ice has been studied over so wide a range as to suggest what may be the effects peculiar to high pressure for the equilibrium between any normal liquid and its solid.

The experimental study of the allotropic forms of ice involves the mapping of their regions of stability, by locating the transition curves, whether to the liquid or to some other solid form, and the measurement on these transition lines of the change of volume and the latent heat of transformation. Five of the six possible stable triple points have been found, and ten of the eleven possible stable transition lines of equilibrium have been followed. The sixth triple point and the eleventh equilibrium line lie at temperatures so low and at pressures so high that the slowness of the reaction makes them practically impossible to determine.

The methods used gave evidence on other points of interest, such as the variation in the reaction velocity with changes of temperature and pressure, the possibility of subcooling or superheating, and the compressibility and dilatation of the solid under pressure.

The data on these different curves are so numerous and bewildering in variety that there is considerable difficulty in choosing the order of presentation. This difficulty is increased by the fact that the paper itself was not planned from the beginning, but has been a growth. The first intention was to measure the isothermal compressibility of water at 0° and room temperature. The existence of a new modification of ice above 0° was not then suspected. When this was discovered in the course of the compressibility measurements, the plan of the paper was extended so as to take in the investigation of this new form of ice over the same temperature range as the compressibility determinations. The compressibility measurements were then completed and the investigation of this new form of ice taken up. This led into all the unsuspected complications of the equilibrium conditions between the five different forms of ice, which necessitated the expenditure of much more time than had been anticipated. It then became necessary, for the sake of completeness, to measure the compressibility of water in its region of existence as a liquid below 0°. During this work with the various modifications of ice, experimental familiarity with the possibilities of high pressure apparatus had been increasing, so that it became possible to extend the work on the ice first found to nearly twice the pressure range reached in the compressibility measurements. This is the state of the work as presented here. To be complete, the compressibility of water should now be redetermined over an increased temperature range corresponding to the increased pressure range, but this process of advancement might be continued indefinitely and a stop has to be made somewhere. For instance, it would probably be possible with the means now at hand to measure directly the compressibility and the dilatation of these various forms of ice, and also the adiabatic compressibility of the liquid. As it is, the pressures have been pushed far enough on both the liquid and the solid to indicate what the general nature of the effects for the highest pressures may be. The pressure required to indicate this is higher for the solid than for the liquid, so that the lack of complete parallelism between the results for the liquid and the solid is partly justified.

The order of presentation finally chosen arranges the subject matter in two parts. The first deals with the compressibility of the liquid at different temperatures. The second, by far the longer, gives the data for the different modifications of the solid, including the quantities involved in the transition solid-solid as well as in the transition solid-liquid. The order of presentation in the second part will be the natural order, proceeding systematically from the lower to the higher pressures.

This systematic order was not, as has been stated, the actual order of the experiment. The existence of another form of ice stable at high pressures and at temperatures above zero was first discovered by the anomalous results of the compressibility determinations. The existence of this form was then made certain by the measurement of the electrolytic conductivity of very dilute solutions, there being a change in the conductivity when the transition occurs. Not until then was the present method adopted by which the equilibrium pressure and change of volume were measured simultaneously, but even with this new method the curve was followed down, from high temperatures and pressures to lower temperatures and pressures. The domain of temperatures and pressures in which Tammann worked (up to 3500 kgm.) was approached with the distinct prejudice, therefore, that Tammann's work was incorrect, because there seemed no possible connection between the curves given by Tammann and the curves at the higher pressures. This prejudice makes more valuable, therefore, the essential verification of Tammann's work found at the low pressures. The expected discrepancy was avoided by the remarkable versatility of ice in appearing in different forms.

The experimental methods are in large part the same as those used in the preceding paper on mercury. Reference is made to that paper for detailed discussion. Where new methods have been necessary, discussion is given here in the appropriate place.

In presenting the data, the aim has been to give enough so that any one could, if he wished, check the computations for himself. Every one of the original observations, except those marred by obvious accidents, has been given. The table of contents should, however, enable one to omit the generally uninteresting discussion of details of methods and critical examination of data, and proceed to the discussion of the general results. In connection with the equilibrium of the different solid forms, it is suggested that some may find it clearer to read first the short history of the experiment, the description of the general nature of the experimental methods, and the description of the manner of appearance of the new forms of ice given first under the heading "The curve VI–L," and then under "The curve V–L."

CONTENTS.

THE COMPRESSIBILITY OF WATER.

A complete thermodynamic knowledge of any substance over any range of temperature and pressure is afforded by a knowledge of the characteristic equation of the substance over that range (that is, the relation connecting volume with temperature and pressure), and a knowledge of the specific heat along some curve of the pressure-temperature plane not an isothermal. For water, the specific heat is known in its dependence on temperature at atmospheric pressure, that is, along a line not an isothermal, so that theoretically all that is needed for a complete thermodynamic knowledge of water is the knowledge of the characteristic equation. This knowledge is evidently given by the change of volume with pressure along various isothermals, together with the change of volume along some line not an isothermal. Practically this means that the characteristic equation may be found by finding the isothermal compressibility at several different temperatures and combining with the known dilatation at atmospheric pressure.

It does not follow, however, that all the thermodynamic data are given with equal accuracy by the knowledge of these quantities. Thus the specific heat, which involves a second derivative of the p-v-t relation, can evidently be found much less accurately than the compressibility, for example. Therefore, while some hold is obtained by the data of this paper on all the thermodynamic quantities, some of these will be found more accurate than others.

Two methods were used in determining the compressibility. The first is the same as that used in determining the compressibility of mercury, and has already been fully described and critically discussed in the previous paper. Briefly, it consists in enclosing the water to be measured in a steel bottle, communicating at the upper end through a very fine channel with a mercury reservoir. The bottle and the reservoir are completely immersed in a fluid to which pressure is applied. The water contracts under pressure, mercury from the reservoir runs in to take its place, falls to the bottom of the bottle, and is weighed after pressure is removed. Compressibility was measured by this method at two temperatures, 0° and 22°, and the same method evidently might be used at any temperature above zero. Under pressure, however, water may exist as the liquid at temperatures considerably below zero, so that for a complete knowledge of the p-v-t surface of water, the volume must be measured throughout this extended region. The method just described is evidently not applicable here without a troublesome variation of both temperature and pressure together during a single measurement, and a second method was adopted.

The second method, which was used to obtain the changes of volume below zero, assumes as correct the compressibility at zero as found by the first method. The data given by this second method are the thermal dilatation from zero at constant pressure for a number of different pressures. Combined with the known volume at zero, this is evidently sufficient to give the volume at any temperature and pressure.

The apparatus used was the same as that already described in determining the data on the freezing curve of mercury, and consists of a lower cylinder placed in a thermostat, and an upper cylinder in which the pressure is produced by a moving piston. The water under experiment is placed in a cylindrical steel shell in the lower cylinder. The lower cylinder also contains the manganin resistance coil with which pressure is measured. The measurements of pressure by this method have been described in a previous paper. The remainder of the lower cylinder and the entire upper cylinder is filled with gasolene, by which pressure is transmitted to the water.

The experimental procedure was as follows. The temperature of the lower cylinder was maintained at some value below zero by the thermostat, and the pressure varied over the region of existence of water for this temperature. The piston displacement was plotted as a function of the pressure for this temperature. The temperature of the thermostat was then raised by a suitable amount, and the piston displacement found as a function of the pressure for this new temperature. This was done for four different temperatures, including zero. From these four curves, with the help of an interpolation for temperature, the piston displacement may be found for any temperature and pressure in the region of the liquid water below zero. This displacement was found at 5° intervals for several different pressures, increasing in steps of 800 kgm. At each pressure, therefore, the thermal dilatation may be found by taking the difference between the displacement at the desired temperature and zero.

If the experiment were performed in the simple manner described, evidently several very serious errors would be introduced. No account whatever has been taken of the thermal dilatation of the steel cylinder, which is not very large, or of the gasolene transmitting the pressure, which is comparatively more important. These two disturbing effects were corrected for by two auxiliary experiments. In the first, the lower cylinder was almost entirely filled with a cylinder of bessemer steel, and the displacement found for any temperature and pressure of the region in question, exactly as for water. In the second auxiliary experiment, the lower cylinder was entirely filled with gasolene, and the displacement found as before. In applying the correction, the entire interior of the apparatus may be thought of as consisting of two parts; one portion is that which would be occupied by the bessemer cylinder, and the second portion is all the rest, including the remainder of the lower cylinder and the upper cylinder. It is to be noticed that this "first part of the volume" is purely fictive: it need not be actually occupied by the bessemer. In the auxiliary experiment in which the lower cylinder is filled with gasolene, this "first part of the volume" is filled with gasolene; in the actual experiment with water, the "first part of the volume" is filled partly with the steel of the shell, partly with water, and partly with enough gasolene to make up the difference. The advantage in thus thinking of the volume as split up into two parts is that the second part remains the same in the three experiments. The displacement of the piston at constant pressure due to change of temperature of the thermostat will evidently include, for "the second part," the thermal dilatation of the cylinder, and what is important, will be independent of the position of the piston in the upper cylinder, since only the lower cylinder is involved in the change of temperature. By taking the difference of the apparent dilatations at constant pressure for the three experiments we shall obtain, therefore, two differences, from which the effect of the "second part of the volume" has been eliminated. These two differences involve the change of volume with temperature at constant pressure of the material occupying the same volume that the bessemer steel would have under the same conditions of temperature and pressure. The quantities entering into the two differences are, therefore, the thermal dilatation of bessemer steel, of gasolene, and of water at various pressures. Now the thermal dilatation of bessemer steel is very small comparatively, and is furthermore known to be little affected by changes of pressure. For the accuracy required in this work, therefore, the change of volume of the steel cylinder, both with temperature and pressure, may be assumed to be known. This leaves only two unknown quantities in the two differences mentioned above, so that either may be found. The thermal dilatation of the gasolene is found immediately from the difference of the displacements of the two auxiliary experiments. It should be noticed that the dilatation is used here in a sense slightly different from the usual one in thermodynamics. The quantity given here is the change in volume in cm.^{3} for 1° lowering of the temperature of the quantity of gasolene which at that pressure occupies 1 cm.^{3}. To find the change of volume of the quantity of gasolene which originally at 0° and atmospheric pressure occupied 1 cm.^{3} we should need to know in addition the compressibility of the gasolene. It is an advantage of the method that it is not necessary to know this compressibility. It is now obvious why a knowledge of the compressibility of water at 0° is necessary. The quantity of water is fixed. As the pressure is raised, the part of the "first part of the volume" occupied by the water decreases in a way known, because the compressibility is known, and the part occupied by the gasolene correspondingly increases. At any pressure, therefore, the number of cm.^{3} of gasolene concerned in the total dilatation of the "first part of the volume" is known, the dilatation per cm.^{3}, and so the total dilatation of the gasolene is also known, and therefore the remainder of the total dilatation due to the water is given immediately.

There are several minor corrections to be considered. The change of volume as given in cm.^{3} by the displacement of the piston involves directly the diameter of the piston. This changes with pressure. This correction has been already discussed in the mercury paper and found to be 1.35 per cent for 10,000 kgm. The magnitude is almost negligible for the present work, but the correction was nevertheless applied in making the computations. Furthermore, the volume swept out by the piston at constant pressure during a change of temperature of the lower cylinder does not represent accurately the change of volume of the material of the lower cylinder. This is due to the fact that the upper cylinder was kept at the constant temperature of 8° instead of 0°. For example, let us suppose that the contents of the lower cylinder expand 1 per cent when the temperature is raised from — 20° to 0°. This 1 per cent passes from the lower cylinder at 0° to the upper cylinder at 8°, and in so doing experiences an additional increase of volume due to the extra 8°. The error introduced by assuming the piston displacement to give the dilatation will be, therefore, in this example, about 0.5 per cent on the dilatation. This error was not corrected for in the present work, since the accuracy of the largest dilatation found, judging only from the number of significant figures, was not over 2 per cent.

One experimental source of error did require correction. This is due to the wearing away of the packing material of the piston by the enormous friction during the advance of the piston. The effect is evidently the same in its results as a leak, although there was absolutely no leak of the liquid and only this wearing away of the packing during actual motion of the piston. The effect was corrected for by making two runs at every temperature with increasing and decreasing pressure, and taking the mean. The discrepancy between the displacements during increasing and decreasing pressure gave the amount of wearing of the packing. This was of the order of 0.01 inch on a total stroke 3 inches. The maximum correction was 0.013 inch. This correction was applied to the next run at higher temperature. The correction so determined incidentally covers the effect of hysteresis, elastic after-working, or of viscous yield in the steel, all of which must be very small at these comparatively low pressures.

The method used in making the calculations from the data was a combination of arithmetic computation with graphical representation. The graphical representation alone would not have been accurate enough. This is because the changes of volume due to temperature are very small in comparison with those due to changes of pressure in the region in question, so that it was necessary to retain all the significant figures given by the measurements. Piston displacement was measured to 0.0001 inch on a total of 3 inches, but since the pressure measurements were sensitive to only 1 part in 3000, the displacement readings were retained only to 0.001 inch. The method was to pass the best parabola through the experimental points at the various constant temperatures; calculate the displacement given by the parabola at the pressure of the experiment; plot on an enlarged scale the difference between the observed displacement and the calculated displacement; pass a smooth curve through these difference points; and finally by combining the results given by the smooth deviation curve with the computed values on the parabola, to find the displacements at equal pressure intervals. This has the advantage of giving a curve perfectly smooth to the last of the significant figures. Curves thus obtained for the different temperatures were then combined by plotting the displacement corresponding to the same constant pressure against the temperatures of the different curves, and smooth curves were drawn through these points. This last step could be made entirely graphically, since the change of displacement with temperature at constant pressure is comparatively slight. From these two sets of smooth curves, the displacement for uniform pressure intervals of 800 kgm. and uniform temperature intervals of 5° was found over the entire region. These points were found in this way for each of the three experiments, that with water and the two auxiliary ones, and the difference of displacement at corresponding pressures and temperatures combined in the way already described.

The actual data above and below 0° follow. All the details of the calculation of the compressibility at 0° and 22° by the first method were the same as that used for determining the compressibility of mercury. In fact, the two determinations, compressibility of water and compressibility of mercury, were made at the same time and each involves the other. It is to be noticed that the various disturbing factors due to irregularities in the behavior of the steel bottle are much less important in the case of water than they were in the case of mercury. This is because of the higher compressibility of water as compared with that of the mercury. Nevertheless, the effect of these irregularities was distinctly felt here also, particularly if the pressure had been allowed to reach so high a value as to freeze the water. The best results were obtained with piezometers in which the water had never been allowed to freeze.

At 0°, four different piezometers were used, one before and after annealing, so that there are really five independent sets of determinations. Three independent points with a sixth piezometer, No. 1, were also found, but were not used in the computations, because this was the very first trial ever made of the method, and the piezometer had been badly strained by a pressure considerably beyond the freezing pressure, the existence of which was not then suspected. The actual data are given in Table I. To afford a comparison of the regularity of these results as against the values obtained for mercury, the actual points for the second best piezometer, No. 6, are shown plotted in Figure 1. If comparison be made with the mercury points it will be seen that these of Figure 1 are distinctly better. The changes of volume at even pressure intervals, obtained from smooth curves from the data of each of the five piezometers, is shown in Table II., together with the weighted means. Finally, the deviation of the weighted mean from a parabolic formula is plotted against pressure, and a smooth deviation curve drawn. In only two instances does the smooth deviation curve fail to pass through the points of the weighted mean. The value given by this smooth deviation curve is to be taken as the final value, and is also given in Table II. The change of volume is to

TABLE I.

Data for Compressibility of Water at 0°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.
Piez. No. 6.		Piez. No. 7.		Piez. No. 3.		Piez. No. 5′.	
2190	0.0795	2190	.0831	5270	0.1467	6810	0.1589
2970	0979	2970	0993	4520	1348	6090	1505
3740	1137	3740	1139	3750	1184	6810	1603
4500	1282	4500	1289	3000	1012	6800	1618
5270	1412	5270	1417	2220	0832	6070	1523
6020	1496	6020	1528	1450	0590	5340	1412
6760	1618	6760	1626	6050	1552	4540	1270
7110	1657	7110	1666	6770	1651	3770	1116
1420	0595	2960	0981	1000	0423	3020	1003
2180	0796	3740	1152	500	0221	2230	0806
2960	0995	6570	1636			1440	0564
3740	1152	6750	1605	Piez. No. 5.		1050	0421
6570	1624	6010	1524	1410	0.0568	1830	0667
6750	1629	5260	1416	2180	0776	2610	0919
6010	1547	4490	1290	3090	0989	3400	1052
5260	1429	3740	1139	3740	1265	4140	1208
4490	1301	2950	0978	4500	1265	4910	1366
3740	1151	2200	0786	5290	1391	5680	1457
2950	0985	1410	0547	5270	1365	Piez. No. 1.	
2200	0797	1000	0412	6030	1457		
1410	0561	500	0227	6760	1578	6750	0.1710
1000	0420			7500		6050	1501
500	0226					5260	1408

be found at every pressure by combining with the change of volume calculated by the formula

$$\Delta v = ap + bp^2,$$

where $\log a = 5.5942 - 10,$

and $\log(-b) = 1.3512 - 10,$

the small correction term given by the deviation curve of Figure 2.

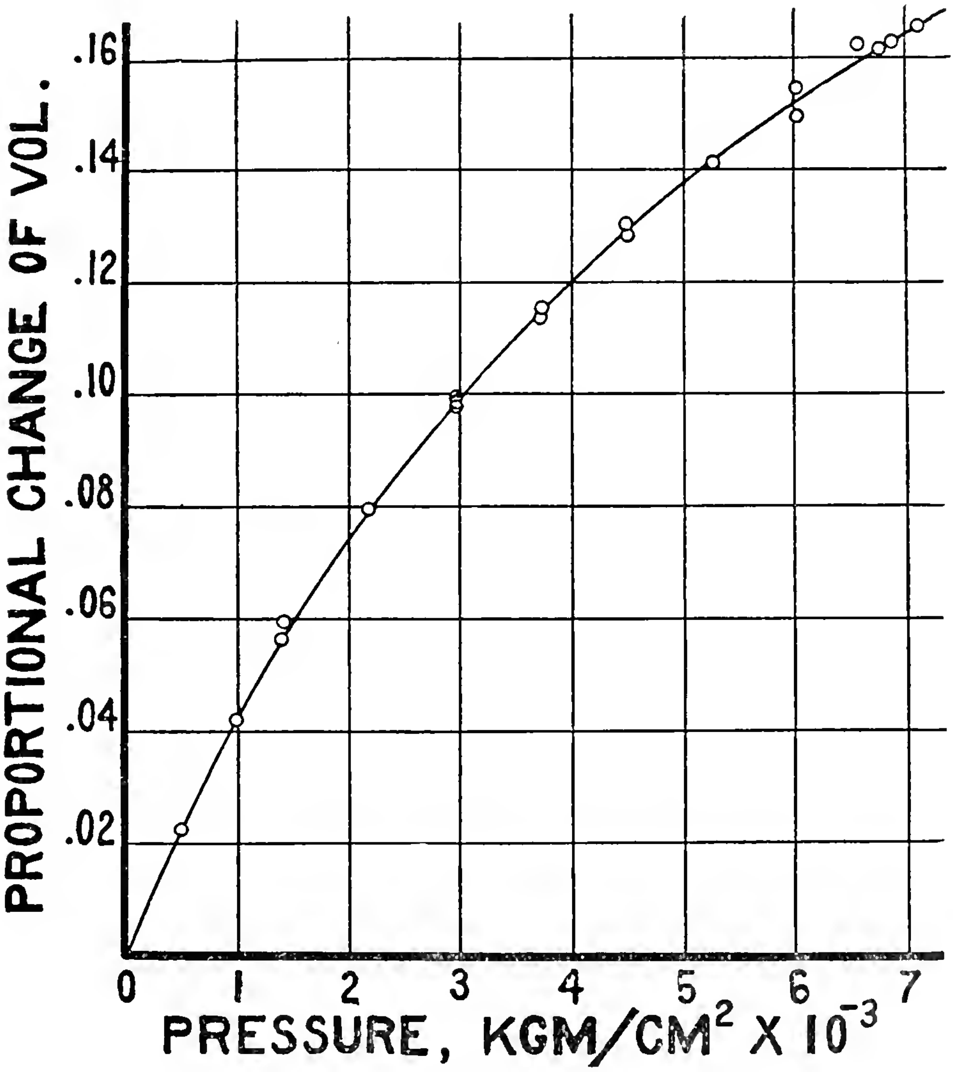

Figure 1. The change of volume of water at 0° C. as obtained with piezometer No. 6.

The data for 22° were obtained in exactly the same way. Only three piezometers were used here instead of five as at 0°. The results are slightly less irregular, owing to greater familiarity with the method and greater care exercised to keep the maximum pressure below the freezing pressure. The data are given in Table III.; the smoothed values for each piezometer, the weighted means, and the final values

TABLE II.

Compressibility of Water at 0°. Comparison of Best Results with Different Piezometers, Weighted Mean, and Final Values.

Pressure, kgm./cm.².	$\frac{\Delta v}{v_0}$.						
	No. 6.	No. 7.	No. 3.	No. 5.	No. 5′.	Weighted Mean.	Final Value.
500	0.0228	0.0222	0.0230	0.0230	0.0218	0.0224	0.0224
1000	0416	0408	0429	0409	0414	0414	0414
1500	0597	0586	0615	0605	0589	0593	0593
2000	0742	0721	0762	0736	0732	0732	0735
2500	0879	0859	0904	0860	0866	0869	0869
3000	0997	0992	1030	0967	0977	0994	0991
3500	1095	1099	1142	1068	1072	1097	1097
4000	1192	1193	1246	1168	1174	1195	1195
4500	1286	1288	1339	1253	1261	1287	1287
5000	1374	1375	1419	1333	1359	1374	1374
5500	1453	1454	1490	1407	1438	1452	1452
6000	1524	1523	1551	1474	1509	1520	1520
6500	1591	1589	1600	1541	1569	1586	1586
7000	1659	1652	1640	1600	1622	1644	1644
. . . .	.6	1.7	.4	.3	.4	Weight	. . . .

in Table IV. The change of volume at any pressure is to be found by combining with the value given by the formula

$$\Delta v = ap + bp^2,$$

where $\log a = 5.5139 - 10,$

and $\log(-b) = 1.1239 - 10,$

the correction given by the deviation curve of Figure 3. It is to be noticed that both of these formulas, for 0° and 22°, take as the unit of volume the volume which the given quantity of water occupies under unit pressure at 0° or 22° respectively. To find the change of volume of 1 gm. of water, a correction must be applied for thermal dilatation between 0° and 22°.

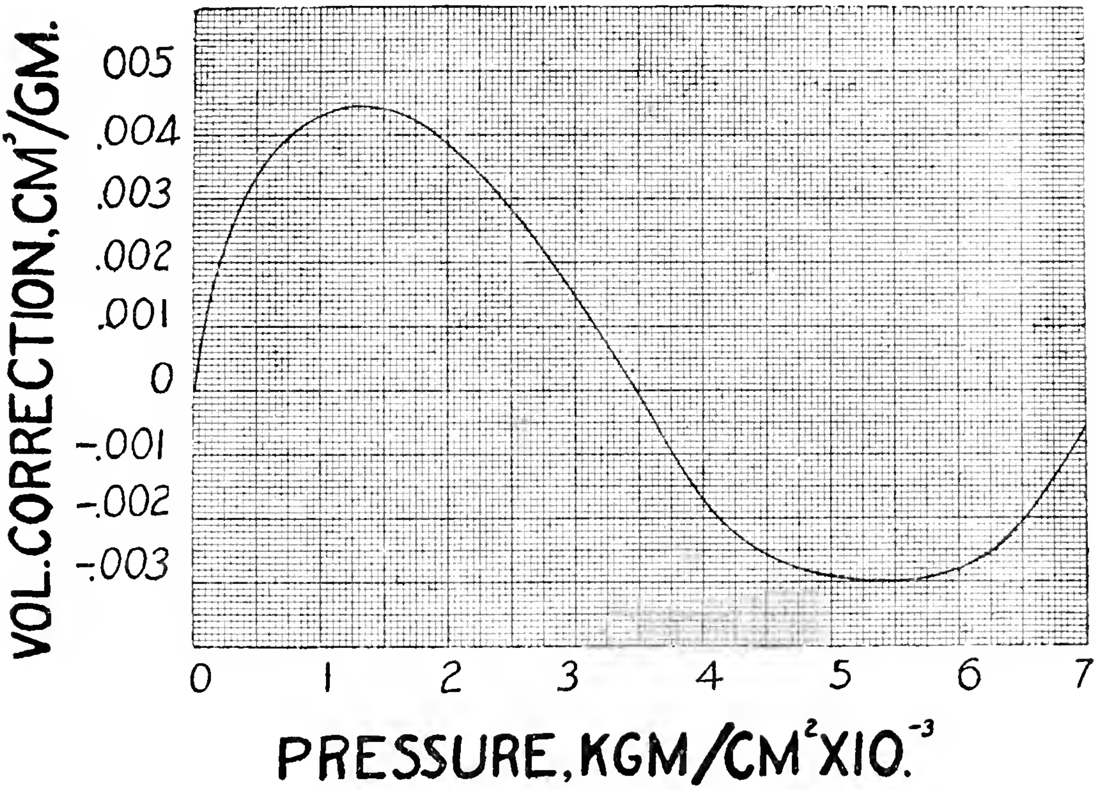

FIGURE 2. The deviation curve for water at 0°. This is to be used in combination with the formula on page 453 in determining the change of volume at 0° C.

These data may be compared with those of Amagat[1] (Table V.). In making this comparison, it must be borne in mind that this is a disproportionally severe test of these data. Values taken from the low end of a large range cannot be expected to show as small a percentage of error as will values obtained with apparatus designed only for this smaller range. In the present work very few actual experimental points were found below 1000 kgm.; the lower end of the curve is virtually an

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[1] Amagat, Ann. de Chim. et Phys. (6), **29**, 68–136, 505–574 (1893).

extrapolation to a known zero. The values of the present work are, with only one exception, lower than those of Amagat. The absolute value of the discrepancy becomes less at the higher pressures, as it should, since the comparison with the present values is made under more favorable conditions at the higher pressures. The fact that the absolute value of the discrepancy tends to become less, not greater, shows that the fundamental unit of pressure must be essentially the

TABLE III.

DATA FOR COMPRESSIBILITY OF H_2O AT 22°.

Pressure, kgm./cm.².	$\frac{\Delta v}{v_0}$.	Pressure, kgm./cm.².	$\frac{\Delta v}{v_0}$.
Piez. No. 6.		Piez. No. 7.	
1460	0.0522	1460	0.0537
2660	0853	2660	0836
3790	1101	3790	1060
4950	1288	4950	1311
6120	1470	6120	1470
7180	1615	7180	1614
8290	1732	8290	1730
		Piez. No. 9.	
3220	0981	3220	0.0978
2170	0732	2170	0730
4350	1206	4350	1202
9530	1889	9530	1999
10930	2041	10930	2046
12250	2619	12250	2612
5700	1458	5700	1469
6740	1571	6740	1612
7830	1706	7830	1754
495	0203	495	0204
995	0391	995	0403
6170	1493	6170	1488
8960	1839	8960	1832
10340	2394	10340	1983
11570	2634	11570	2147

same for the two determinations. Furthermore, the dilatation between 0° and 22°, as found by taking the difference of the compressions at 0° and 22°, is evidently going to show much less absolute difference for the two sets of determinations than the compressibilities, suggesting that the two sets are each consistent with themselves, since they show the same temperature effect.

TABLE IV.

COMPRESSIBILITY OF H_2O AT 22°. COMPARISON OF BEST RESULTS WITH DIFFERENT PIEZOMETERS, WEIGHTED MEAN, AND FINAL VALUES.

Pressure, kgm./cm.².	$\frac{\Delta v}{v_0}$.				
	No. 6.	No. 7.	No. 9.	Weighted Mean.	Final Value.
1000	0.0383	0.0379	0.0391	0.0383	0.0383
2000	0683	0667	0684	0679	0679
3000	0933	0914	0933	0928	0928
4000	1141	1123	1145	1137	1137
5000	1316	1304	1324	1314	1314
6000	1462	1460	1485	1465	1465
7000	1595	1594	1631	1600	1600
8000	1723	1702	1761	1728	1728
9000	1850		1885	1855	1855
10000	1963		2000	1967	1967
11000	2036		2078	2042	2042
	4	2	1	Weight.	

Since this paper was written, Parsons and Cook [2] have published data for the compressibility of a few liquids up to 4500 atmos. Their results for water at 4° are shown in Table V*a*. compared with the results of this paper. The agreement is closer than 1 per cent at

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[2] Parsons and Cook, Proc. Roy. Soc. A, **85**, 332–349 (1911).

the higher pressures. The results of Parsons and Cook differ from those of Amagat in the same direction as those found here and by about twice as much. The values given in the table as the result of the present work were calculated from the data of Table XXXI. on page 539.

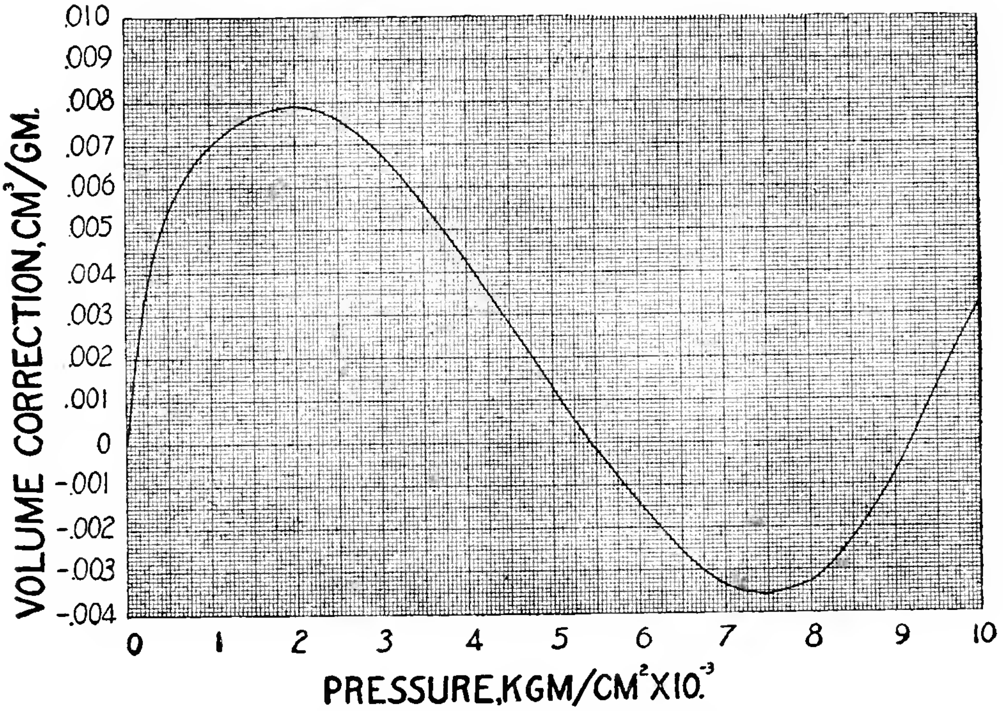

Figure 3. The deviation curve for water at 22°. This is to be used in combination with the formula on page 454 in determining the change of volume at 22°.

The results obtained by the second method below 0° next concern us. To give the original data would occupy so much space as to be out of the question. The methods and the details of the calculation have already been described. It is sufficient to give here some information about the actual data, and the probable accuracy. Four runs were made with water, at —15°.8, —10°.2, —5°.0, and 0°.0, and displacement and pressure measured at respectively 8, 10, 14, and 17 points. Each of these pressure measurements was the mean of two readings, and the displacement measurements the mean of four. The auxiliary experiment with the lower cylinder full of bessemer was also made at four temperatures: —17°.7, —12°.2, —6°.0, and 0°.0, and the number of points at these temperatures was 14, 15, 13, and 16 respectively. The auxiliary experiment with the lower cylinder full of gaso-

TABLE V.

Comparison of Results for Compressibility of Water with those of Amagat.

Pressure.		Δv.					
		At 0°.			At 22°.		
Atmos.	$\frac{\text{kgm.}}{\text{cm.}^2}$.	Amagat.	This Work.	δ.	Amagat.	This Work.	δ.
500	516	0.0237	0.0231	− 6	0.0216	0.0220	+ 4
1000	1033	0440	0425	−15	0402	0394	− 8
1500	1549	0611	0599	−12	0565	0552	−13
2000	2066	0763	0753	−10	0710	0697	−13
2500	2583	0898	0891	− 7	0839	0829	−10
3000	3099	1017	1013	− 4	0957	0950	− 7

TABLE V*a*.

Pressure.		ΔV at 4°.	
Atmospheres.	kgm./cm.^{2}.	Parsons and Cook.	This Work.
0	0	0.000	0.0000
500	516	0.022	0.0226
1000	1033	0.042	0.0418
1500	1549	0.059	0.0591
2000	2066	0.073	0.0742
2500	2583	0.086	0.0879
3000	3099	0.098	0.1002
3500	3615	0.109	0.1103
4000	4132	0.120	0.1203
4500	4648	0.130	0.1306

TABLE VI.

DILATATION OF WATER BELOW 0° — DISPLACEMENT OF PISTON AT REGULAR INTERVALS OF PRESSURE AND TEMPERATURE.

Pressure.		Piston Displacement, inches.				
Slider Displacement, cm.	$\frac{\text{kgm.}}{\text{cm.}^2}$.	−20°.	−15°.	−10°.	−5°.	0°.
		Lower cylinder full of water.				
3	800	....	0.642	0.636	0.627	0.623
6	1600	....	1.137	1.133	1.125	1.112
9	2400	1.542	1.533	1.521	1.508	1.483
12	3200	1.861	1.848	1.834	1.818	1.797
15	4000	2.126	2.118	2.108	2.093	2.073
18	4800	....	2.342	2.339	2.332	2.307
21	5600	....	....	....	2.544	2.521
24	6400	....	....	....	....	2.718
		Lower cylinder full of bessemer.				
3	800	0.427	0.423	0.419	0.415	0.411
6	1600	0.721	0.717	0.712	0.706	0.697
9	2400	0.936	0.932	0.927	0.920	0.912
12	3200	1.112	1.110	1.105	1.098	1.089
15	4000	1.268	1.265	1.262	1.257	1.251
18	4800	....	1.402	1.398	1.393	1.387
21	5600	....	....	1.524	1.520	1.516
24	6400	....	....	....	....	1.629
		Lower cylinder full of gasolene.				
3	800	0.904	0.884	0.855	0.818	0.762
6	1600	1.494	1.470	1.442	1.411	1.378
9	2400	1.916	1.893	1.867	1.838	1.805
12	3200	2.276	2.256	2.228	2.203	2.176
15	4000	2.554	2.538	2.520	2.499	2.473
18	4800	2.815	2.797	2.778	2.756	2.733
21	5600	3.036	3.023	3.008	2.991	2.971
24	6400	....	....	....	....	3.177

lene was made at only three temperatures: −15°.2, −7°.1, and 0°.0, with 16, 16, 16 points respectively. All of these points, with very few exceptions, lay on smooth curves consistently to 0.001 inch.

The results of the graphical computations of displacement and pressure at equispaced points are shown in Table VI. The displacement at zero pressure is arbitrary in these tables. The data of these tables, together with the quantities of steel, water, and gasolene, are sufficient to enable anyone to check up the computations. The weight of the steel cylinder filling the lower cylinder was 286.345 gm. The weight of the steel shell containing the water was 51.818 gm. The weight of the water was 26.775 gm. The density of steel was 7.840 at 17°, and it was assumed that the cubical dilatation of steel was 0.00036 and the cubical compressibility $0.0_{6}6$ in kgm./cm.^{2}. The volume in cm.^{3} of the bore of the upper cylinder, 1 inch long, was 4.117 cm.^{3}. With increasing pressure this increases 1.35 per cent for 10,000 kgm.

TABLE VII.

Dilatation of Water below 0° at Various Pressures.

Pressure, kgm./cm.^{2}.	Change of Volume in cm.^{3} per gm. on changing from Tabulated Temperature to 0°.				
	−20°.	−15°.	−10°.	−5°.	0°.
			−0.00173	−0.00057	0
800		−0.00015	00031	00062	0
1600	0.0000	0000	0000	0000	0
2400	0045	0038	0028	0017	0
3200	0052	0043	0029	0017	0
4000	0045	0040	0031	0017	0
4800		0034	0033	0022	0
5600				0023	0

The results of the computations from the data of these tables are given in Table VII. and Figure 4, showing the proportional change of the original volume at 0° and atmospheric pressure by which the water shrinks at various pressures on passing from 0° to the temperature listed.

From these results, both above and below 0°, the actual volume of the water for regular pressure and temperature intervals has been found and is given in Table XXXI. on page 539.

THE SOLID PHASES OF WATER — THEIR RELATION TO EACH OTHER AND TO THE LIQUID.

In order to present these data systematically and clearly, reference is made at once to the final equilibrium diagram for water and the solids given at the end of this paper. (Plate 1.) It may produce less confusion in referring to this diagram to state briefly the identical relations which must be satisfied in every such diagram. There are three of these relations. At every triple point the relative positions of the three equilibrium curves must be such that if any one is produced into the region of instability, it shall fall within the angle made by the other two. If one phase is carried into another by passing across an equilibrium line at constant pressure from a low to a high temperature, then the reaction runs with absorption of heat. And, if one phase is carried into another by passing across an equilibrium line at constant temperature from a low to a high pressure, the reaction runs with decrease of volume.

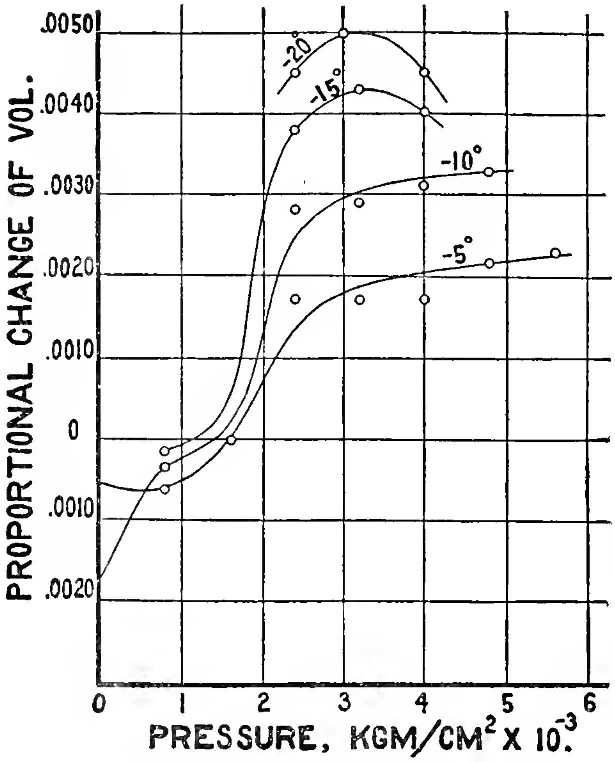

FIGURE 4. This shows as a function of the pressure the change of volume of water on passing at constant pressure from 0° to the temperature indicated on the curves.

The different branches of the curves will be taken up in order, beginning with I–L,[3] I–III, etc. The data to be given are the freezing pressure at any given temperature and the change of volume. From the relation between temperature and pressure on the freezing curve at different points, the slope may be found, and this, combined with the change of volume, gives the latent heat by Clapeyron's equation. The data are presented in this order: observed change of volume, calcu-

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[3] Throughout, the abbreviation L will be used in referring to the liquid.

lated slope, latent heat, and then other quantities of thermodynamic interest, such as the work done in passing from one form to the other, and the change of internal energy.

In the early part of this work up to 3500 kgm. constant reference will be made to Tammann,[4] since his are practically the only previous experiments on ice under pressure. It will be well, therefore, to briefly outline his work and show where it needs verification or completion. Tammann's work consisted essentially in following out the equilibrium curves without systematic measurements of the changes of volume. He discovered the existence of two new forms of ice (II and III), and studied their relations to water and ordinary ice (ice I). He obtained points on the equilibrium curves I–L, III–L, I–III, and I–II. The change of volume I–III and I–II was measured at a few points without any very great accuracy. The greatest possibility of question as to the results is in regard to the equilibrium curves I–III and I–II. Tammann found that these curves cross at —37° and 2200 kgm. Now it is necessary thermodynamically that a third equilibrium curve should start from the point of intersection of two equilibrium curves with a common phase. In this case the predicted equilibrium curve would be II–III. Tammann found no such curve and even maintained that no such curve was necessary, claiming that the thermodynamic argument was valid only when the two phases were present simultaneously, and that he had never been able experimentally to produce II and III together. The argument seems inadequate, however, and in this work the missing curve had been actually found. The other points of difference between this work and Tammann's are more or less minor in character ; there seems to be an error in Tammann's pressure measurements of 100 kgm. at 2000, and he found a curious point of inflection in the I–L curve, which does not seem actually to exist.

For convenience, the method used will be briefly outlined. It was essentially the same as that of Tammann, and consists in plotting the displacement of the piston by which pressure is produced against pressure. Change from one form to the other is accompanied by change of volume at constant pressure. This change of phase is shown, therefore, by a discontinuity in the curve piston-displacement vs. pressure. The pressure at the point of discontinuity gives the equilibrium pressure and the volume swept out by the piston, which is determined by the amount of the discontinuity, gives the change of volume on passing from one phase to the other. The water on which these experiments

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[4] Tammann, Kristallisieren und Schmelzen, pp. 315–344 (Barth, Leipzig, 1903).

were made was placed in a steel shell, open at the top, and completely surrounded by kerosene or gasolene by which pressure was transmitted. Pressure was measured by observing the change of resistance of a calibrated manganin wire immersed directly in the same chamber with the water. That the fluid transmitting pressure suffers no change of phase which is accompanied by change of volume within the limits of measurements was shown by direct experiment. Furthermore, that there is no reaction under pressure between the water and the oil, which are directly in contact, was shown by the sharpness of the freezing. See Figure 31, page 515. The effect of an impurity is to make the discontinuity less abrupt. In order to give additional evidence on this point, in the course of the experiments the water was placed in shells of steel or copper, directly in contact with kerosene or gasolene, in glass bulbs directly in contact with kerosene, and in a glass bulb with a mercury seal, the water coming in contact only with mercury and glass. The results in all cases were identical.

Three different forms of apparatus were used according to the temperature range. The first, for the middle range from –25° to +20°, was the same as that used in the work on mercury. It consisted essentially of two parts: an upper cylinder in which pressure was produced by an advancing plunger, communicating through a heavy tube with a lower cylinder containing the water under experiment and the pressure measuring coil. The lower cylinder was placed in a thermostat. The various sources of error and the corrections have been discussed in the paper on mercury. One correction had to be determined anew, since the values used in the mercury paper were not for a corresponding range of temperature and pressure. This is the correction for the thermal dilatation of the kerosene or gasolene which passes from the lower cylinder at the temperature of the experiment to the upper cylinder at the temperature of the room. The manner of determining this correction was the same as before. One correction applied to the results for mercury was avoided here, namely the correction for the variation in the room temperature. This was made unnecessary by a water jacket at constant temperature placed around the upper cylinder.

The second piece of apparatus, for temperatures from –20° to –80°, was essentially the same as the first, consisting of two parts. But the pressures for this temperature range are comparatively low, not reaching over 4000 kgm., so that it was possible to make the lower cylinder so small (1 inch o. d. by 8 inches long), that it could be placed in a thermos bottle. The connecting tube was also made much smaller so as to avoid conduction of heat into the thermos bottle. The method used in determining the change of volume had to be modified with this apparatus, since the reaction was so slow at the low temperatures. It will be described in detail later.

The third piece of apparatus for higher pressures and temperatures, 0° to 76° and 6000 to 20,500 kgm., consisted of only a single cylinder containing the water, the measuring coil, and the advancing piston. For these high pressures it was necessary to use only one piece of apparatus because of the impossibility of getting tubing to stand these high pressures over any extended time. The water was placed in a steel shell surrounded by kerosene as before. The cylinder, together with the lower part of the hydraulic press by which the piston was advanced, was placed in a thermostat. In this third form, therefore, the correction for the change of volume of the transmitting fluid on passing from one temperature to another is avoided. But at the higher pressures another correction is introduced because of the slow yield of the steel. This will be described in its place.

The data given for the ten equilibrium curves were all obtained independently of each other, at different times, with different fillings of the apparatus, and in a number of cases with different pieces of apparatus, either new pieces to replace those destroyed by explosions or pieces of a different type. The consistency of the data obtained under these various conditions is shown by the very close approximation with which the identical relations are satisfied by the independent data of the three curves at each of the three triple points.

At each triple point there are three independent checks. In the first place, the absolute values of the equilibrium pressures and temperatures are checked by the necessity for the three curves running together to a point. In the second place, the values of the change of volume are checked by the obvious condition that at the triple point I–II–III, for example, the change of volume I–II plus the change II–III must be equal to the change I–III. The third check is given by the condition for the latent heats analogous to that for the changes of volume. This third check involves, besides the values already given, the values of the slope of the three curves meeting at the triple point. This third check is the most difficult to meet and the most sensitive, as it is well known that the derivative of an experimental curve is subject to much greater error than the curve itself.

Such a triple check is afforded for the data of every one of the ten equilibrium curves at at least one point: Five of the curves are rendered still more secure by being tied down at both ends by a triple point, and the other end of a sixth curve, I–L, is checked by the already known data for 0°.

In the curves given for ΔV and the latent heat, the identical relations at the triple point were kept in view. In some cases the curve given does not seem to be the best possible through the individual points. The departure from the best curve was occasioned by the necessity of satisfying the identical relations at the triple point, and the amount of departure gives a pretty good criterion of the self-consistency of the data for the different curves.

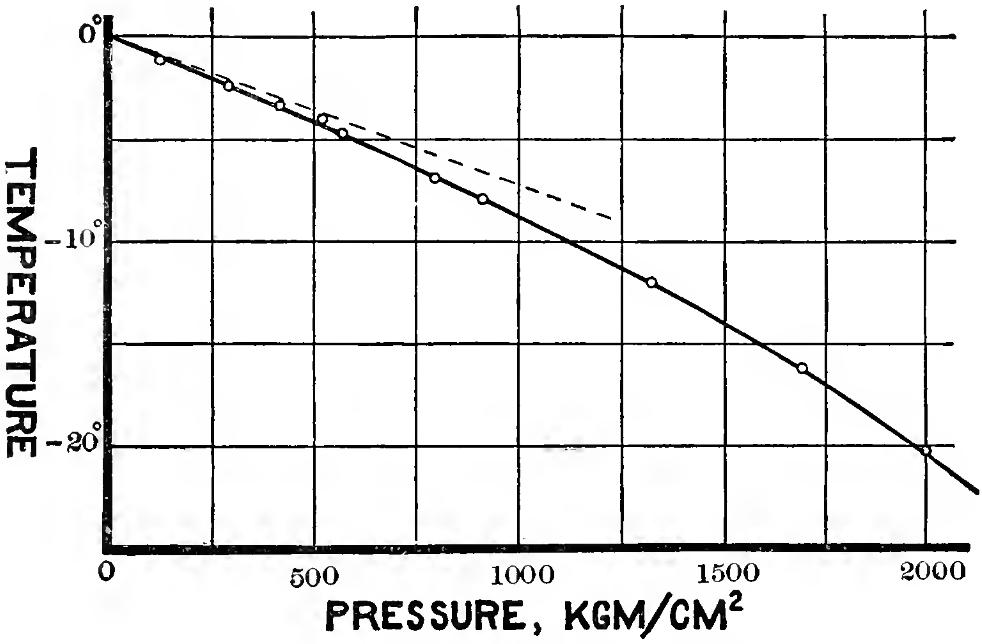

Figure 5. The freezing curve of ice I. The dotted line shows the slope at 0° computed by Clapeyron's equation.

The Curve I–L.

The points on this curve were obtained with the same apparatus as that used for mercury. No special discussion is necessary. The data were obtained on three separate occasions: February 2, February 23–24, and March 15, 1911. The equilibrium points are shown in Figure 5 and ΔV in Figure 6; the actual data are given in Table VIII. The first set is not accurate. It was taken only for fun one evening after the supply of $CaCl_2$ for running the thermostat had given out, so that the temperatures are not sufficiently accurate. These points are not shown in the diagram.

The second and third sets of readings give the equilibrium points determined with sufficient accuracy. The second set suffices to give the general shape of the entire curve, while the third set was taken with more pains at the lower pressures in order to test more definitely the existence of a point of inflection at —4° as found by Tammann. This third set was made with the apparatus directly connected to a Cailletet pump of the Société Genevoise, with a capacity of 1000 kg./cm.². As a check, the equilibrium pressures as given by the Bourdon gauge of this pump are tabulated as well as the pressures given by the manganin resistance. The slide wire of the Cary Foster bridge was especially changed for this experiment, so as to give greater sensitiveness in the measurements of resistance. The readings of the manganin gauge are to be accepted as more trustworthy than those of the Bourdon. Within the limits of accuracy of the readings, there seems to be no point of inflection on the equilibrium curve as found by Tammann, but the curvature is perfectly regular, increasing more and more rapidly at the lower temperatures and higher pressures. The point of inflection found by Tammann may very possibly be due to errors in the pressure measurements. His values for the pressures in the neighborhood of 2000 are nearly 100 kgm. higher than those found here. The effect of introducing such an error into the gauge readings at some point on

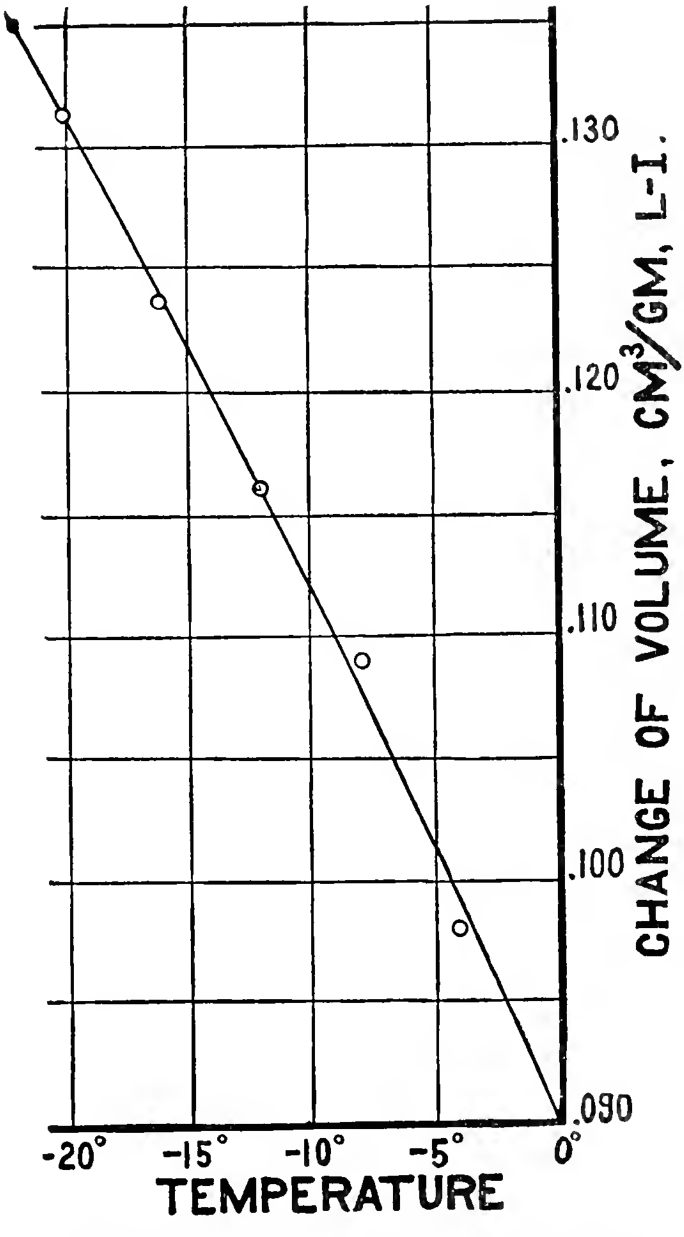

Figure 6. The change of volume when ice I melts to the liquid.

the way up would be to give exactly such a point of inflection as he found.

One check on the accuracy may be obtained from the known slope

TABLE VIII.

Data for the Equilibrium Curve Ice I–Water.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.².		Δv, cm.³ per gm.		
		From Resistance Measurement.	Bourdon Gauge.	Uncorrected.	Corrected for Dilatation of Gasolene.	Corrected for Distortion of Cylinder. (Final value.)
Feb. 2	−20.6	2100				
	−18.7	1890				
	−14.80	1580				
	−12.40	1370				
23	−20.15	2000		0.1337	0.1312	0.1316
	−16.15	1690		1257	1236	1238
24	−12.00	1320		1178	1160	1162
	− 7.9	910		1103	1090	1091
	− 4.0	520		0991	0980	0980
March 15	− 6.9	788	798			
	− 4.75	565	568			
	− 3.3	416	418			
	− 2.3	281	288			
	− 1.1	122	121			

at 0°, calculated by Clapeyron's equation from the known latent heat and the change of volume. This slope is given by the equation

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

Using the following values : $\Delta V = 0.0900$, $\tau = 273.1$, $\Delta H = 79.82$ gm. cal., 1 gm. cal. $= 42.66$ kgm. cm., we find

$$\frac{d\tau}{dp} = -\ 0.00722.$$

It is to be noticed that this value is lower than the calculated value usually given. This is because of the low value used for ΔV, which is taken from the most recent work of Leduc.[5] The effect of this change is to bring the calculated value into better agreement with experimental values. Thus Dewar[6] found recently for $\frac{d\tau}{dp}$, 0.0072. The slope at the origin as just calculated is shown by a dotted line in the diagram. The agreement is within the limits of error.

Even over this very low pressure range there are practically no other results to compare these with. Tammann is the only other observer who has gone to high enough pressures to find the direction of curvature of the curve, which agrees with that found here. Dewar has published results up to 250 kgm., and stated without publishing the data that the curve remains linear up to 700 kgm. The departure from linearity found above is about 6 per cent at 700. Several other accounts have been published of the effect of pressure on the freezing of ice, but the work has either been done only to a few atmospheres, or else the work to high pressures has been only qualitative, like that of Mousson.[7]

The second set of readings above gives the only determination of the change of volume made in the present work. The procedure in determining four of these five points was the same as that used for nearly all the other determinations with water as well as with mercury. This consists in plotting piston displacement against pressure during decreasing pressure. This has the advantage at higher pressures of almost entirely eliminating the effect of elastic after-effects in the containing vessel, but this procedure is less essential at lower pressures. For all ordinary substances this procedure means that the change of volume is measured during melting and has the advantage that it gives perfectly sharp values, it being impossible to overrun the melting curve. But here, due to the fact that ordinary ice is less dense than the liquid, the method gives the change of volume during freezing instead of melting, so that it is possible to considerably overshoot the mark before solidification sets in. The change of volume is so large during freezing, however, that this is no practical disadvantage, as it is with substances showing a smaller change of volume. The

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[5] Leduc, C. R., **142**, 149–151 (1906).

[6] Dewar, Proc. Roy. Soc. Lon., **30**, 533–538 (1880).

[7] Mousson, Pogg. Ann., **105**, 161–174 (1858).

fifth point of the above series was obtained in the inverse way, during melting, proceeding from low to high pressures. The pressure corresponding to —4° is so low that the elastic after-effect must be small, but still it is noteworthy that this point shows the greatest deviation from the straight line. This inverse procedure at —4° was necessary in this case because of the low pressures, the friction of the packing being so great that pressure could not be reduced sufficiently below the equilibrium pressure to induce solidification from the subcooled liquid when the regular procedure of running from high to low pressures was adopted.

The correction applied to the change of volume for the thermal dilatation of the gasolene (the fluid transmitting pressure in this set of experiments), was not determined directly at all points of the curve, but only at the two end points. At 0° the correction is 0.9 per cent, and at —22° is 2 per cent. The correction was assumed linear for intermediate points. It makes no difference within the limits of error whether temperature or pressure is taken as the independent variable of this linear relation, and there seems little probability that the error so introduced can exceed this 0.1 per cent. The tables give the values corrected both for the thermal dilatation of the gasolene and for the elastic deformation of the cylinder. This latter correction is 0.2 per cent at the maximum.

The values of ΔV are shown in Figure 6. The open circles are the observed points. The solid circle at —22° was not an observed point, but is the value required at the triple point by the conditions of consistency with the other data. In the ΔV diagrams for the other equilibrium curves the values at the triple points are indicated in the same way.

As an additional check on the values found here there is the known change of volume at 0° as found by other observers. The recent work of Leduc seems the most accurate. He gives for the value of the density of ice at 0°, 0.9176, from which the change of volume is found to be 0.0900 cm.^{3} per gm. The value of ΔV at 0° as found by Leduc is taken as the origin in the diagram. It is seen that the other points are perfectly consistent with this value, thus confirming the accuracy of the method. The relation connecting change of volume with temperature is nearly linear, the curve being slightly concave toward the temperature axis. Four of the points, including Leduc's, lie sensibly on the curve; one is 1 per cent too high, and the other 1.5 per cent too low.

This value of Leduc is higher than that of most other observers, but the discrepancy seems to be due to occluded air, which Leduc took particular pains to exclude. In these experiments in which the water was frozen under pressure, any dissolved air, naturally, can have only very little effect. Leduc's value, therefore, seems best for this comparison.

It will be well here to explain the sign convention used uniformly throughout the paper. A change of volume is taken as positive if the volume increases when the reaction runs in the indicated direction. Thus ΔV L–I is positive (water expands when it freezes to ordinary ice) but ΔV I–L is negative. Similarly the latent heat, ΔH, is positive when heat is absorbed during the reaction, and ΔE, the change of internal energy, is positive when the internal energy increases. ΔH for the reaction L–I is negative, but positive for I–L. In general, as already explained, ΔV is positive when the reaction runs from high to low pressure and ΔH is positive when the reaction runs from low to high temperatures.

TABLE IX.

Latent Heat, etc., on Equilibrium Curve Ice I–Water.

Temp. C.°.	Pressure, kgm./cm.².	Δv. cm.³/gm.	$\frac{dp}{dt}$.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. (Latent Heat) $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. (Change of internal Energy) $\frac{\text{gm. cal.}}{\text{gm.}}$.
			Directly from Curves.	Adjusted.			
−20	1970	−.1313	74.6	74.0	6.06	57.7	63.6
−15	1590	−.1218	86.0	84.8	4.52	62.5	67.0
−10	1130	−.1122	99.0	98.4	2.96	68.0	71.0
− 5	610	−.1016	116.0	115.5	1.45	73.7	75.1
0	0	−.0900	138.5	138.5	0.00	79.8	79.8

From the curves giving the equilibrium points and the changes of volume, the various data needed for computing the latent heat and the change of internal energy may be obtained. These are given in Table IX. for even temperature intervals. The values of ΔV were taken from the line drawn through the observed points. Two values of $\frac{dp}{dt}$ are tabulated. The first set of values was obtained by graphical construction from the equilibrium curve at different points, these values of $\frac{dp}{dt}$ plotted and a smooth curve drawn through them. The first tabulated values of $\frac{dp}{dt}$ are obtained from this smooth curve. With these values of $\frac{dp}{dt}$, ΔH was calculated. It was then necessary to adjust the values of ΔH slightly so as to satisfy the identical relations at the triple point. These new values of ΔH are tabulated. The change in the value of ΔH demands a corresponding change in the values of $\frac{dp}{dt}$ which are given in the second column. These latter values are to be taken as the most probable values. The difference between the two columns shows the amount of adjustment necessary, and gives an idea of the accuracy of the data. Of course, as already explained, the slope is very much more sensitive to slight errors than the observed values of p and t themselves. This same process of adjustment has been used on all the equilibrium curves. In some cases, where $\frac{dp}{d\tau}$ is very small, no change has been necessary. The data of Table IX. are shown graphically in Figure 7.

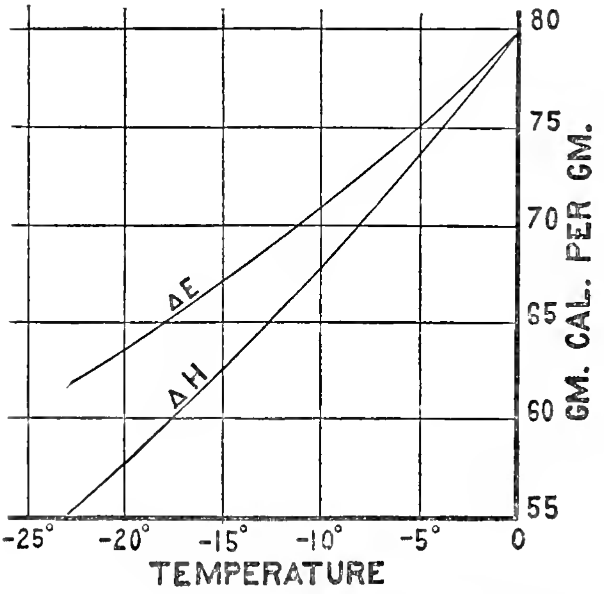

FIGURE 7. The latent heat and the change of internal energy on the I–L curve.

The data give some hold on the actual compressibility of the solid at different points on the equilibrium curve. At 0° this may be calculated without approximation from the observed data. The thermal dilatation and compressibility of water at 0°, and the thermal dilatation of ice at 0°, are already known. These present data give the change of ΔV with temperature and pressure on the equilibrium curve. These four quantities evidently suffice to determine the compressibility of the solid at 0°, for we have for small changes of p and t,

$$V_1(p,t) = V_1(0,0) + \left(\frac{\partial v_1}{\partial p}\right)_t dp + \left(\frac{\partial v_1}{\partial t}\right)_p dt,$$

$$V_2(p,t) = V_2(0,0) + \left(\frac{\partial v_2}{\partial p}\right)_t dp + \left(\frac{\partial v_2}{dt}\right)_p dt,$$

where the subscript (1) denotes the liquid and (2) the solid.

$$\Delta V(p,t) = V_2(p,t) - V_1(p,t) = \Delta V(0,0) + dp\left[\left(\frac{\partial v_2}{\partial p}\right)_t - \left(\frac{\partial v}{\partial p}\right)_\tau\right] + d\tau\left[\left(\frac{\partial v_2}{\partial t}\right)_p - \left(\frac{\partial v_1}{\partial \tau}\right)_p\right].$$

This holds for any values of *dp* and *dt*. On the equilibrium curve,

$$d\tau = \frac{d\tau}{dp}dp,$$

and we have

$$\frac{d\Delta V}{dp} = \frac{d\Delta V}{d\tau}\cdot\frac{d\tau}{dp} = -\left(\frac{\partial v_2}{\partial p}\right)_\tau + \left(\frac{\partial v_1}{\partial p}\right) + \frac{d\tau}{dp}\left[-\left(\frac{\partial v_2}{\partial \tau}\right)_p + \left(\frac{\partial v_1}{\partial \tau}\right)_p\right].$$

Everything in this equation is known except $\left(\frac{\partial v_2}{\partial p}\right)_\tau$.

We have $\left(\frac{\partial v_1}{\partial p}\right)_\tau = 0.0_452$ kgm./cm.^{2} (Amagat),

$$\left(\frac{\partial v_1}{\partial \tau}\right)_p = -\ 0.0_457,$$

$$\left(\frac{\partial v_2}{\partial \tau}\right)_p = +\ 0.0_3152 \text{ (Vincent),}^{8}$$

$$\frac{d\tau}{dp} = -\ 0.00722 \text{ [already computed; see p. 468].}$$

$$\frac{d\Delta V}{dt} = -\ 0.00200 \text{ [from these experiments].}$$

Substituting these values in the above expression, we find

$$\left(\frac{\partial v_2}{\partial p}\right)_\tau = -\ 0.0_436.$$

The compressibility of ice, with the larger volume, is therefore about 1/3 less than the compressibility of the liquid. There seem to be no published experimental data with which to compare this value.

The Curve I–III.

The existence of this new variety of ice, III, was discovered by Tammann, who obtained it by increasing the pressure on ordinary ice to about 2500 kgm. at temperatures between —22° and —60°. The nota-

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[8] Vincent, Phil. Trans. A, **198**, 463–481 (1902).

tion used here is the same as that used by Tammann. In the present work this variety of ice was found in another way, coming from high to low pressures at about −22°, and from the domain of stability of a variety of ice stable only at higher pressures. It was obtained first with the same apparatus as that used on the I–L curve. Two points on equilibrium curve I–III and two unsatisfactory measurements of the change of volume were made with this apparatus, but all the subsequent determinations were made with the apparatus especially designed for low temperatures. A short description of this new apparatus will not be out of place.

This had three different pressure chambers instead of only two as formerly. The upper cylinder in which pressure was produced by the advance of the piston was the same as that used before. This was jacketed with running water from a large tank, so as to be maintained at a constant temperature. Communicating directly with this, and exposed freely to the air of the room, was a block of nickel steel with provisions for three connections. In one of these holes for connections was placed the manganin resistance plug with which pressure was measured. No temperature correction had to be applied to the readings of this, therefore. The third connection in the block was to the cylinder containing the water to be experimented on. This cylinder was of hardened nickel steel, 8 inches long, 1 inch o. d., and 1/2 inch i. d. The water to be experimented on was placed directly in the cylinder, nearly filling it. The remainder of the cylinder was filled with gasolene communicating through the connecting block with the pressure-producing cylinder. Some hesitation was felt at first about allowing the water to completely fill the interior of the cylinder, instead of being placed in a cylinder exposed to pressure on all sides. Fear was felt that the water in freezing might so expand itself against the sides of the cylinder as to be able to support an appreciable stress, so that a hydrostatic pressure applied by means of the gasolene to the upper part of the frozen ice cylinder would not be transmitted uniformly to all parts of the mass of ice. In the first few experiments an attempt was made to avoid the possibility of the effect by providing means for the gasolene to penetrate to the neighborhood of all parts of the ice. This was done with a tube of very thin sheet copper, closed at the bottom, but open at the top to the gasolene, placed axially in the cylinder, and extending throughout the mass of water. The precaution proved needless, however, since there were no discrepancies to be ascribed to this cause when the device was omitted.

It was necessary to use gasolene as the transmitting fluid because of the low temperatures. Kerosene becomes too stiff to transmit pressure, and the gasolene itself gave evidence of considerable viscosity at the lower temperatures. Attempt was made to use a still lighter oil to avoid altogether this viscosity. Pentane was tried, but after a number of failures had to be abandoned. There is evidently some action under pressure between the pentane and either the water or the ice. The action seems to be one of solution. In every case water found its way sooner or later through the long connecting tube to the manganin resistance coil, where it short-circuited the coil, making measurements impossible.

The nickel steel cylinder containing the water was supported from above by means of the connecting pipe in a cylindrical Dewar flask, 2 inches diameter and 10 inches long. The low temperature was obtained with solid CO_2 and ether, or usually CO_2 and gasolene, this being much cheaper and giving nearly as low a temperature as the ether. No thermostatic regulation was used with the apparatus. The thermal insulation provided by the bath proved sufficient so that the slight amount of regulation necessary could be performed from time to time by hand, by dropping in small masses of solid CO_2. The bath liquid was stirred by blowing bubbles of air into it through a tube reaching to the bottom of the flask. It was possible with very little effort to keep the temperature constant to 1/2°, which was sufficient for most requirements, since in the region of these experiments the equilibrium pressure is affected only slightly by changes in temperature. Greater constancy of temperature was attained by the exercise of a little more care when this was necessary.

Temperature was measured with a nickel resistance thermometer. This was a coil of bare nickel wire wound in spiral grooves on a hard rubber cylinder, which was immersed in kerosene in a thin, tightly fitting tube of glass. The top of this tube was carefully stoppered to prevent the condensation of moisture around the leads. The glass tube, 3/8 inch o. d., was immersed directly in the temperature bath. The response to changes of temperature was always very prompt. The resistance of this wire was measured on the same bridge wire of the same Carey Foster bridge as that on which the measurements of the resistance of the manganin coil for pressure were made. Either the nickel or the manganin resistance, with the appropriate extension coils, could be connected with the bridge wire by two double-throw mercury switches in paraffin blocks. The temperature was ordinarily read both before and after the readings of pressure and piston displacement. The coil was calibrated by comparison at 0°, −50°, and −80° with a nickel resistance thermometer of Leeds and Northrup, which had been calibrated at the Bureau of Standards. The sensitiveness was sufficient to detect changes of 0°.03. The coil was tested for permanent changes, elastic after-effects, etc., by frequent calibrations in melting ice at 0°. That it was perfectly satisfactory is shown by the fact that the zero has not changed by 0°.03 since the coil was set up.

A special method for determining the change of volume at the low temperatures was made necessary by the extreme slowness of the reaction. At the higher temperatures, between −20° and −30°, the reaction runs rapidly enough so that the ordinary procedure is available, but at lower temperatures this is not possible. On one occasion, such an attempt was made at −70°. After four hours waiting at a pressure several hundred kgm. removed from the equilibrium pressure, the reaction had not yet shown any signs of drawing to completion, and the attempt was given up. The new method is made possible by the fact that the equilibrium pressure is very nearly constant. Figure 8 illustrates the method. The first part of the process consists in getting the change of volume by the ordinary method at some temperature where the reaction runs with convenient rapidity. This consists in measuring the piston displacement at constant temperature at several points on each side of the equilibrium line indicated at (1), (2), (3), (4), (5), (6). After reaching (6) the piston displacement is kept constant, but the temperature is reduced, the water now being in the form of ice III. The pressure is measured at several points with decreasing temperature until the point A is reached. The apparatus is so small that complete temperature equilibrium is attained in at most 5 minutes after changing the bath temperature. At the point A the pressure is reduced at constant temperature by changing the displacement, until the point B is reached, still to the right of the equilibrium line. From B, temperature

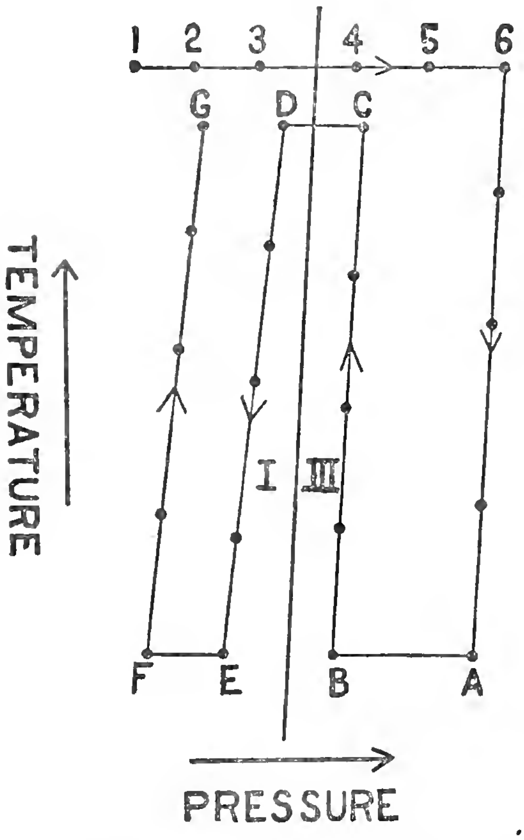

FIGURE 8. Shows the cycles described in finding the change of volume I–III.

is raised at constant displacement to the point C. Here the pressure is lowered to D, the reaction now running with sufficient speed because of the higher temperature. From D, two excursions to low and then back to high temperatures are made exactly as from (6), the water now being in the form of ice I. The result of all these manœuvres is that we have sufficient data to find the displacement corresponding to any temperature and pressure, and so the displacement on opposite sides of the equilibrium line corresponding to the two phases I and III. The difference of this displacement at any temperature is evidently the same as if the reaction had run at that temperature, but the slowness of the reaction is avoided. The change of volume is calculated directly from the difference of displacements as usual. It was in general necessary to measure the displacement at at least three points on each side of the equilibrium line, since the relation between displacement and pressure is not sufficiently linear to allow a linear extrapolation from two points to the equilibrium line. For greater security, four or five points were usually taken.

The data are such that they contain internal evidence of their self-consistency. After a complete cycle like the above, the starting point ought to be reached again, if there has been no change in the apparatus in the meantime. This condition was always approximately fulfilled, the piston returning within a few thousandths of an inch to the original position. Failure to return exactly to the starting point is probably due partly to elastic after-effects in the steel cylinders, and partly to wearing away of the rubber packing on the end of the piston. There was never any leak. The slight discrepancy was corrected for by assuming that it had grown uniformly with the time. It will be noticed that the cycle as described above is such that the effect of any such error is at a minimum, since the two paths nearest the equilibrium curve on either side were described in succession.

The method is applicable here because of the fact that the equilibrium lines run so nearly parallel to the lines of constant displacement that it is possible to approach very near to the equilibrium line over the entire range. The method evidently would not apply without modification to points on the I–L curve, for example.

The slowness of the reaction which made necessary a modified method of determining the change of volume is also evidently going to have its effect on the equilibrium determinations. At the low temperatures, the reaction runs so slowly that it requires a very long time for pressure to return to the equilibrium values, if it has once been changed. The behavior was such as to give the impression that the equilibrium pressure might never be reached, there being a domain of indifference within which the viscosity is sufficient to keep the reaction from running, even if the equilibrium conditions are not satisfied. This has been stated to be the fact by Tammann. The equilibrium points at the low temperatures were found by approaching as close as practicable to equilibrium from each side, and taking the mean. The tables of the actual data show how broad the band of indifference is and how rapidly it increases in breadth at the low temperatures.

For these determinations with this new piece of apparatus, ice III was usually obtained from ice I. The procedure was to freeze water to ice I at a low pressure, and then increase the pressure on ice I at a temperature in the neighborhood of —30°. It was always necessary to pass considerably beyond the transition curve before the reaction started. On several occasions at —28° the pressure was carried so far over the I–III curve as to arrive at the prolongation of the I–L curve, at which melting took place immediately, it never being possible to carry a solid into the domain of the liquid. I melts to the liquid even if the liquid is relatively unstable with respect to another solid phase. At the temperature —28° it was never possible to keep the unstable liquid long enough to make an accurate determination of the equilibrium pressure. The rough values fell within the limits of uncertainty on the smooth prolongation of the I–L curve. When the phase III did appear at temperatures above —30°, the reaction from I to III ran with explosive rapidity. Sometimes it was possible to hear a sharp click in the apparatus announcing the sudden change of volume.

Aside from the fact that it is possible to pass over the boundary line between two solid phases without the reaction running, the actual amount of possible trespassing has little significance. It is changed by alterations in the size and shape of the containing vessels, is affected by slight impurities, and most of all depends on the element of time. It may be mentioned, however, that under pressure the viscosity of the substances seems to be so great that mechanical shock has little if any part in starting the reaction, as it does under ordinary circumstances. It was never found possible to start a reaction from an unstable phase by smart blows on the outside of the apparatus with a hammer. This was tried both when the unstable phase was a solid and a liquid.

After the phase III had once been obtained, the other points on the equilibrium curve were obtained with decreasing temperature. At every new temperature, the piston was pushed in a little, the pressure then falling back to the equilibrium value, and then the piston was withdrawn slightly, pressure rising to the equilibrium value. The mean of these was taken as the equilibrium pressure. Sometimes at the higher temperatures, where the reaction velocity is high, equilib-

TABLE X.

Data for the Equilibrium Curve Ice I–Ice III.

Date, 1911.	Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. cm.^{3} gm. Corrected Value.	Date, 1911.	Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. cm.^{3} gm. Corrected Value.
Feb. 16	−22.80	2120	−0.1910	April 6	−52.5	2100^{-}	
	−25.25	2120	−0.1861		−50.0	2110^{+}	
Mar. 24	−32.0	2150^{-}			−62.0	2000^{-}	
	−31.7	2150^{+}			−61.2	2100^{+}	
	−24.7	$2110^{\pm}$			−32.8	2150^{-}	
Mar. 29	−33.8	2170^{-}			−32.6	2150^{+}	
	−28.7	2150^{+}			−26.5	$2120^{\pm}$	
	−26.7	2140^{V}		April 18	−27.6	2110^{+}	
	−23.5	2130^{V}			−22.4		−.1831
April 5	−33.4	2170^{+}			−29.1		.1903
	−33.0	2160^{-}			−35.7		.1966
	−28.1	$2150^{\pm}$			−41.7		.1948
	−23.1	$2140^{\pm}$			−49.6		.2018
	−21.5	$2140^{\pm}$			−56.6		.2042
April 6	−26.4	2120^{+}			−63.8		.2059
	−25.9	2100^{-}			−70.8		.2071
	−31.0	2110^{+}		April 20	−23.3	$2134^{\pm}$	
	−30.7	2110^{-}			−24.5	$2136^{\pm}$	
	−38.6	2120^{-}			−27.8	$2153^{\pm}$	
	−38.4	2130^{+}			−31.5	$2163^{\pm}$	
	−43.5	2130^{-}			−37.2	$2182^{\pm}$	
	−42.5	2150^{+}			−46.0	$2179^{\pm}$	

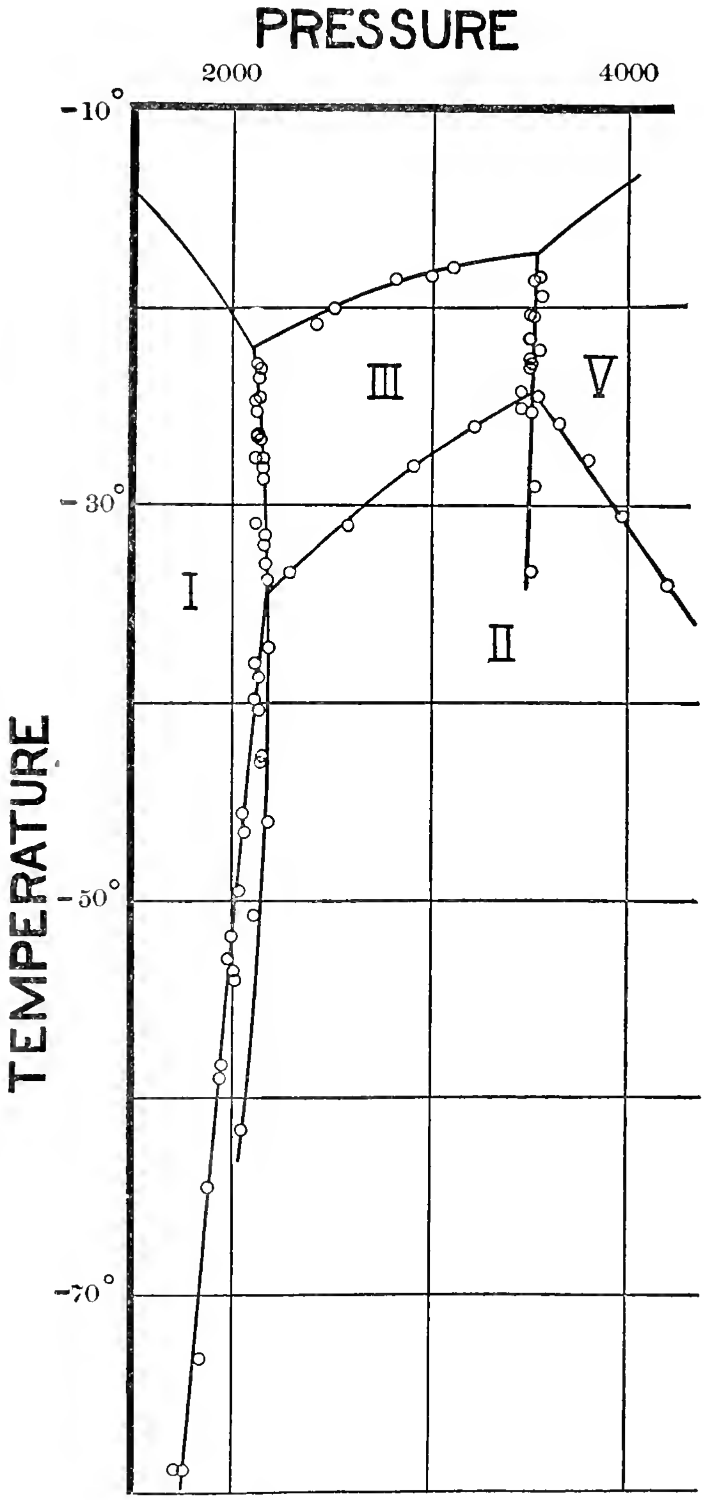

Figure 9. The various equilibrium curves between I, II, III, V, and the liquid.

rium was approached from only one side. By proceeding in this way from high to low temperatures, it was possible to prolong the curve considerably into the region of stability of II. A point was thus found at —62°.0, showing a subcooling of 28°. If the pressure had been increased on ice I at this temperature, ice II and not ice III would have separated out.

The actual data are given in Table X. Those of February 16 were obtained with the same apparatus as that used for the mercury; all the others with the smaller apparatus for lower temperatures. The plus or minus signs after the pressures show whether the value was approached from above or below. Three different manganin coils were used in making the measurements. The data of April 6 were obtained with a new coil which had not yet been sufficiently seasoned. For this reason the data of April 6 are slightly in error as to the absolute value of the pressure, but are competent to show the shape of the equilibrium curve. The data of April 20, taken with especial care to show the actual shape of the equilibrium curve, give more significant figures than one is entitled to for the absolute pressure, but the variation of pressure is accurately indicated by the figures given.

The equilibrium points are shown in Figure 9, in which are shown also the other equilibrium curves in the vicinity. The shape of the curve is given by the points of April 6 and 20, which agree, but the best value for the absolute pressure is to be given by the mean of the points at the upper end of the curve. On the same pressure and temperature scale as the complete diagram for ice and water this equilibrium curve appears nearly vertical, but on the scale shown here it is seen to have unmistakable curvature, being concave toward the temperature axis, and at one part parallel to that axis. At this point of parallelism, the latent heat of transformation is zero; above it is positive, below negative. This point is approximately at —40° and 2150 kgm.

The equilibrium curve I–III as found by Tammann shows the same general shape, concavity toward the temperature axis. But Tammann's vertical tangent is between —40° and —50°. The total change of pressure from the triple point at —22° to the maximum is practically the same, 50 kgm., but Tammann does not find so pronounced a curvature below the maximum as is found here. On the whole, however, the agreement in the shape of the curve as found in these two independent determinations is as good as could be expected, particularly when it is remembered that the discrepancies are at the low temperatures where the reaction runs very slowly. But the actual value of the pressure as found by Tammann at —22° is higher than that found here, 2200 against 2115. Tammann's pressure measurements were made with a Bourdon gauge, which is not accurate at high pressures. There are two pieces of evidence to show that Tammann's pressures may be wrong; the supposed inflection point on the I–L curve, which has been already mentioned, and the behavior of the I–III curve above the I–II–III triple point, which will be dealt with later.

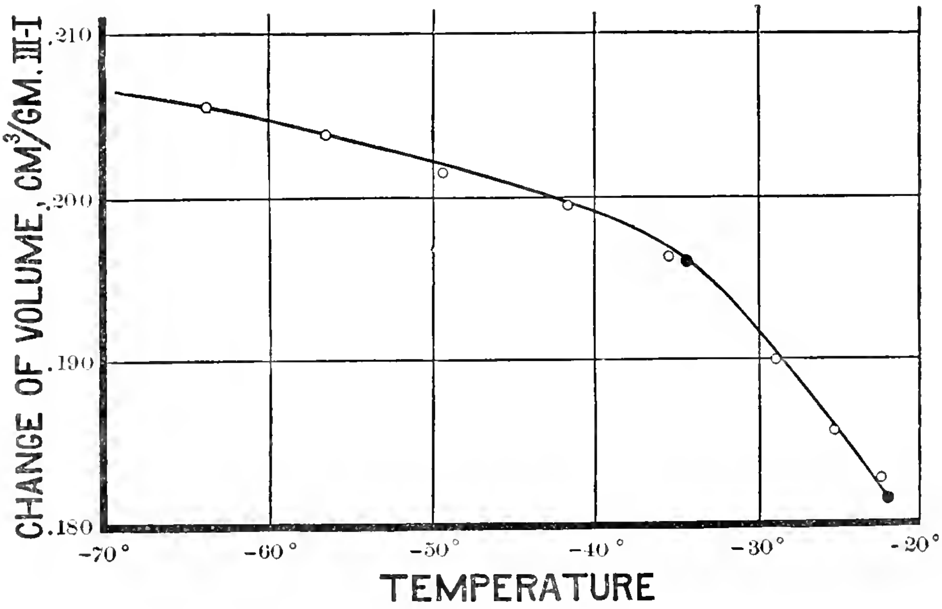

Figure 10. The change of volume III–I.

The values for the change of volume obtained on April 18 with the method described are given also in Table X., and shown in Figure 10. The most striking feature is the enormous value of the change, being about 20 per cent. The values extend into the unstable region over a temperature interval twice the interval of stability, which is from —22° to —35°. The values given have been corrected in the usual way for the elastic distortion of the cylinder and the thermal dilatation of the gasolene. Owing to the wide temperature range, this latter correction is unusually large, rising to 6 per cent at the lowest temperatures. The curve drawn through the points is forced a little so as to give consistent results at the triple points, at —22° passing about 1/4 per cent too low and at —35° 1/4 per cent too high.

The actual procedure in getting these change of volume points was not exactly the ideal one described above. Below —35°, III is unstable, and the reaction to II might run at any time. The path 6 A (Figure 8) was described successfully and two points found on the lower end of BC before the reaction to II ran. On raising the temperature above the II–III curve, the reaction ran back to III, so that at C the phase present was III, as it should be. The line 6 A was perfectly straight; it was assumed, therefore, that the line CB would also have been perfectly straight if it had been possible to trace it out for its entire length.

TABLE XI.

Latent Heat, etc., on Equilibrium Curve Ice I–Ice III.

Temp. C.°.	Pressure, kgm./cm.^{2}.	Δv. cm.^{3}/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−60	2117	.2049	5.4	10.13	−5.5	4.6
−50	2160	.2023	2.0	10.24	−2.1	8.1
−40	2178	.1992	−0.6	10.17	+0.7	10.9
−30	2156	.1919	−3.2	9.69	3.5	13.2
−20	2103	.1773	−5.3	8.74	5.6	14.3

The upper ends of the lines of equal volume for the phase I, that is, the lines ED and FG above the triple point at −35°, bear less and less to the right, and at their extreme upper ends are actually bearing to the left. This would mean a negative thermal dilatation for ice I at these temperatures. The effect deserves to be investigated for its own sake. The effect is so slight as to make very little difference for the purposes of this paper, however, and it was not investigated further. That there may be such an effect is borne out by the rather sharp change in the curvature of the ΔV curve at the triple point −35°, while the accuracy of the ΔV curve is made very probable by the closeness with which it checks at the two triple points. Pettersson[9] claims to have found that ordinary ice at atmospheric pressure shows a negative dilatation between −35° and −25°.

Table XI. gives the values taken from the equilibrium and the change of volume curves for the various quantities involved in the determination of the latent heat and the change of energy. The values of ΔE and ΔH are shown graphically in Figure 11. The internal energy of III is greater than that of I, and practically all this change of energy comes from the mechanical work absorbed when I

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[9] Pettersson, Vega Expedition, vol. 2 (1883).

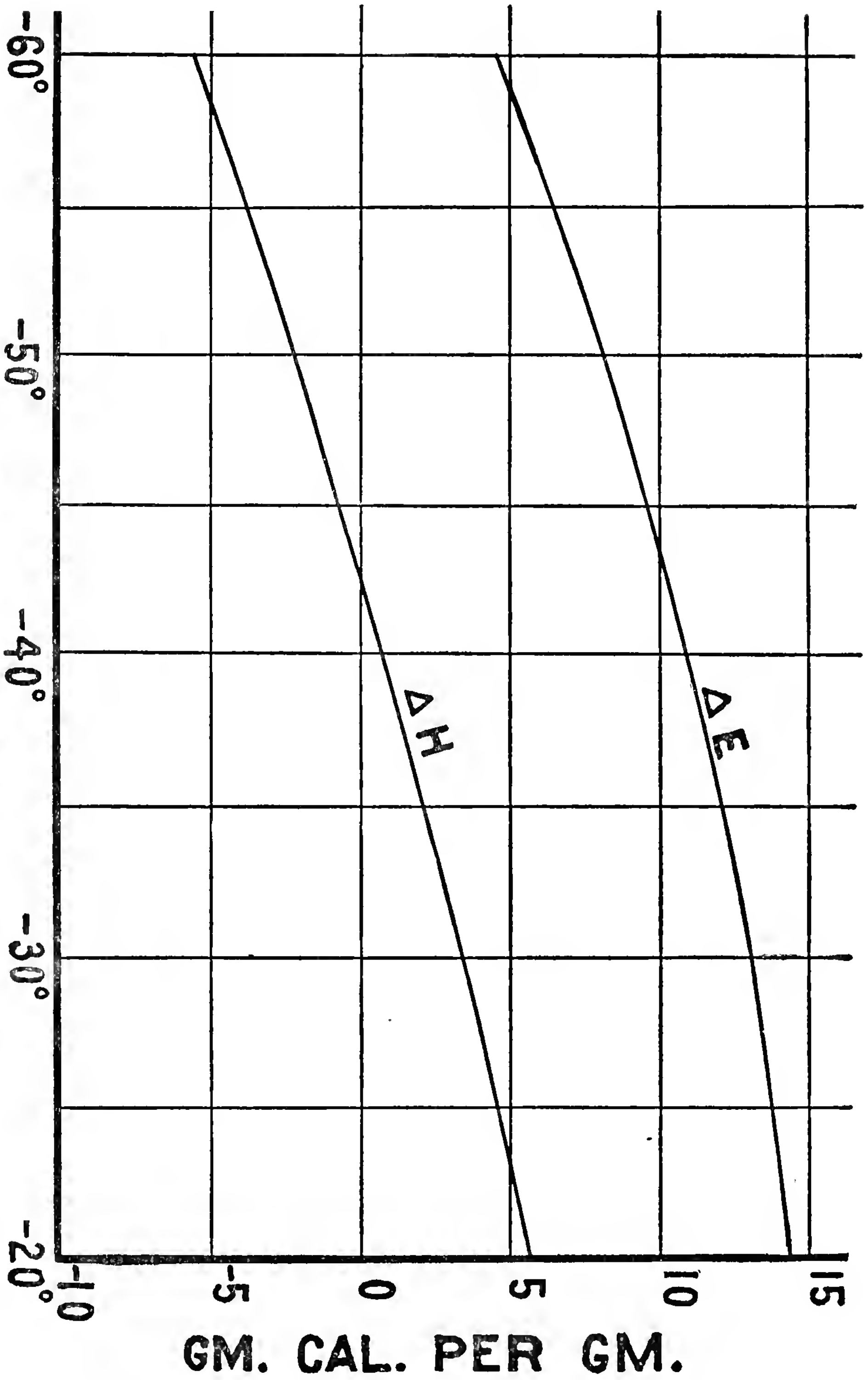

FIGURE 11. Shows the latent heat and the change of internal energy when I passes to III.

passes to III. The latent heat is small; above −40° I absorbs heat on passing to III, below −40° it gives out heat.

The Curve III–L.

The points on this curve were more difficult to obtain accurately than those on any of the other nine equilibrium curves. This is because of the extreme slowness of the reaction, accounted for in part by the comparatively small change of volume and the large heat of reaction. This does not prevent, however, a fairly accurate knowledge of the properties of the curve, since the curve is short, reaching over only 1500 kgm., and it is tied down by a triple point at either end.

TABLE XII.

Data for the Equilibrium Curve Ice III–Water.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.².	ΔV cm.³/gm. Corrected Value.
Feb. 1	−18.55	2820	
	−20.00	2510	
	−17.95	3110	
Feb. 16	−18.40	3000	.0301
March 2	−20.80	2420	.0373

The apparatus used for this curve was that of the mercury determinations, temperature being kept constant with a thermostat. This was necessary because of the great effect of temperature on the equilibrium pressure on this curve.

Five points on the equilibrium curve were obtained, and two on the change of volume curve. These are shown in Table XII. and Figures 9 and 12. The equilibrium points are satisfac-

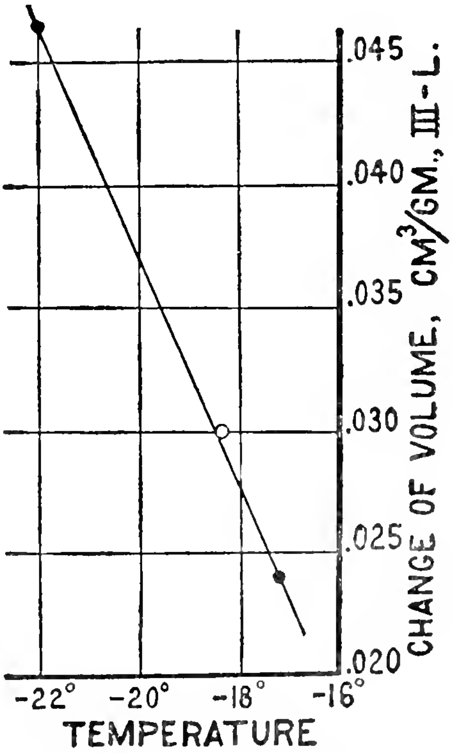

Figure 12. The change of volume when III passes to the liquid.

tory enough. The greatest difficulty was found with the Δ V points. These are evidently irregular, but with the two other known points on the curve at the triple points, the curve itself cannot be far from that drawn. The relation between temperature and change of volume was assumed linear within the limits of error.

TABLE XIII.

Latent Heat, etc., on the Equilibrium Curve Ice III–Water.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. $\frac{\text{cm.}^3}{\text{gm.}}$.	dp/dt.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal}}{\text{gm.}}$.
			Directly from Curves.	Adjusted.			
−22.0	2115	0.0466	180	186	2.31	50.9	48.6
−20.0	2510	.0371	240	246	2.18	54.1	51.9
−18.5	2910	.0301	326	320	2.05	57.4	55.4
−17.0	3530	.0231	450	443	1.90	61.4	59.5

Three points on this equilibrium curve were found by Tammann. The shape of his curve agrees with that found here within the limits of error, but the absolute values of the pressure found by Tammann are higher than those given, as already explained. Tammann gives no values for Δ V on this curve.

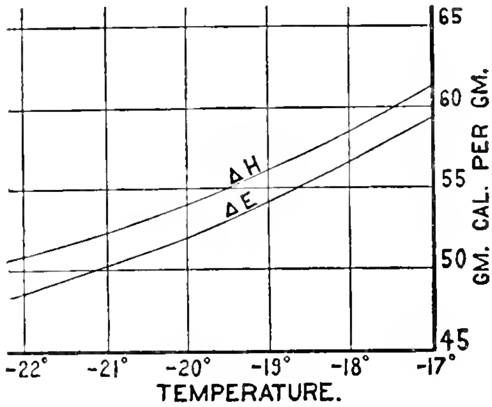

Figure 13. The latent heat and the change of internal energy when III passes to the liquid.

The values deduced from these curves for ΔH and ΔE are given in Table XIII. and in Figure 13. Very slight changes in the coordinates of points on the equilibrium curve make enormous changes in the value of the slope and ΔH. Thus, raising the upper triple point from —17°.2 to —17°.0 changed the calculated value of ΔH from 94 to 64. This latter value is taken as the more nearly correct, because it checks with the other values at the triple point, even though the V–L curve has to be slightly raised to pass through the point.

The Curve I–II.

We return now to the curve meeting the I–III curve at the lower temperatures, the I–II curve. The points on this curve were found with the low temperature piece of apparatus.

The data, shown in Table XIV., were obtained on five separate occasions with three different manganin resistance coils. The first three sets, on March 24, 29, and April 5, were obtained before the points on the I–III curve were obtained at the low temperatures.

The whole investigation at the low temperatures was approached with the prejudice that Tammann must have been wrong. In particular, the existence of two separate modifications of ice, II and III, with only slightly different properties, was thought to be explicable by some instrumental error. This prejudice was strengthened by Tammann's failure to find the triple point I–II–III, or any points on the melting curve of II, although he must have passed over this curve if there were such a one. His failure to find the II–L curve was difficult to explain because the reaction from solid to liquid always runs, and in this case the accompanying change of volume is fairly high. The work of the first three days still further strengthened the impression of error in Tammann's work. It showed conclusively that there was a modification of ice different from III in equilibrium with I at low temperatures, but seemed to show that this was not the variety supposed by Tammann. The points of the three days all lay on the same curve, which was headed exactly for the intersection of the I–L and the V–L curves both prolonged into the region of stability of III. It seemed probable, therefore, that Tammann's II was nothing but our V in the unstable region.

The determinations of these two days were made with two different coils, one a well seasoned one that had been maltreated in many explosions, and the other a brand new one. After several days' work suspicion was drawn to these coils and they were checked by measuring with them the equilibrium pressure on other already well established curves. Both on the I–III curve and the III–V curve they gave results consistent with each other but about 100 kgm. higher than the previous values. There seems no reason to doubt, therefore, that these coils were both in error and, by a stroke of luck, by the same amount. This disposed definitely of the idea that the new ice was V subcooled. The values tabulated are corrected by this quantity 100 kgm. There seems no reason why these readings should be entirely discarded; they

TABLE XIV.

Data for the Equilibrium Curve Ice I–Ice II.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
March 25	−64.7	1960	April 5	−63.7	1910^+	
	−66.8	1950		−53.6	2000^+	
	−65.2	1960		−52.2	1970^-	
	−59.2	1900^-	April 6	−69.5	2020^+	
	−58.7	1980^+		−76.5	1670^-	
	−52.1	1980^-		−58.7	1900^-	
	−51.5	2020^+		−58.0	2000^+	
	−45.7	2040^-		−50.0	2010^-	
	−45.5	2060^+		−49.0	2060^+	
	−38.0	$2110^\pm$		−40.1	2100^-	
March 29	−78.8	1690^-		−39.5	2120^+	
		1840^+		−53.4	2000^-	
	−54.1	1990^-		−54.5	2040^+	
	−53.0	2030^+	April 18	−36.9	$2110^\pm$	
	−46.7	2050		−35.7		0.2187
	−46.4	2070		−41.7		.2172
	−40.8	2130^-		−49.6		.2169
	−40.0	2130^+		−56.6		.2159
April 5	−78.8	1780^+		−63.8		.2154
		1640^-		−70.8		.2145
	−65.6	1850^-		−78.0		.2145

seem perfectly satisfactory in giving the shape of the equilibrium curve, on which the pressure varies only slightly, even if the absolute value of the pressure is somewhat high.

The last set of determinations on April 6 and 18 were with still another coil, a comparatively new one, but one which had been sufficiently seasoned. This coil gave readings consistent with the previous values on the I–III and II–V curves, and gave the same shape for the curve as that found with the two previous coils. There seems to be no question but that these are the correct values.

This variety of ice was obtained by increasing the pressure on I at low temperatures. The temperatures used here ranged from —65° to —80°. At —80° it is possible to run as much as 1000 kgm. beyond the transition curve before the reaction begins to run. Even so far removed from equilibrium as this, the reaction runs slowly and never seems to run to completion. The table shows the discrepancies in the stationary pressures when approached from above and below. The other points on the curve were obtained with regularly increasing temperature after the lowest. The temperature was raised as high as —23° to get the last point. The succession of points found in this way lie on a curve running nearly linearly with increasing temperature and pressure up to about —35°, where it turns and proceeds upwards nearly vertically. This verifies the form found for the curve by Tammann. This curve as found by Tammann crossed his I–III curve. Tammann advances as an argument against there being a true triple point at the point of intersection the experimental fact that it was possible to start with II at low temperatures, to proceed along the equilibrium curve with increasing temperature across the I–III curve into the supposed region of stability of III, and then to retrace one's steps, following down the original curve into the region of II where the two curves I–III and II–III are unmistakably different. This possibility, surprising as it seems, was verified also by direct experiment. The points of April 6 at —40° and —53° on the I–II curve were separated by points at —32°.5 and —26°.5, which are in the supposed region of stability of III.

The whole mystery is cleared up by the discovery of the II–III equilibrium curve. It may be permitted to anticipate the results as they were found on this curve in so far as they are needed to explain the curious facts found on the I–II curve. In the first place, the existence of the II–III curve puts beyond question the fact that there are two varieties of ice, II and III. The point of intersection of the II–III curve with the I–II and the II–III curves is at —35°, the triple point. This point is also the point at which the change in direction of the supposed I–II curve was found. Above this point the modification II passes into the modification III. The absolute regularity with which this turning point was found, both here and by Tammann, is to be explained by the experimental fact that it is impossible to superheat II with respect to III. In the course of these experiments it has never been possible to carry II the slightest distance into the region of III, the reaction running as inevitably as the reaction from a solid to a liquid when the solid is heated to the melting point. Furthermore this reaction, when it does run, runs with great velocity, since the temperatures are sufficiently high. The change is furthermore accompanied by a comparatively small change of volume. This evidently accounts for the curve having been overlooked by Tammann. The supposed crossing of the two curves I–II and I–III found by Tammann is to be explained by slight errors in the pressure measurements. The greatest difference between the curves is 30 kgm. This is the second bit of evidence alluded to on p. 482, that Tammann's absolute pressure measurements may be in error. The turning point of the curve found by Tammann is at the same temperature as that found here, —35°. The impossibility of superheating II also explains Tammann's inability to find points on the II–L curve. Apparently it is impossible to reach this. II appears to be surrounded on all sides by other solid phases.

The behavior of III with respect to II is not the reverse of II with respect to III. It is possible to subcool III greatly with respect to II. The amount of subcooling possible depends on a variety of factors. One of the most important of these is the interval of time which has elapsed since the water had previously existed in the form II. It is a fact verified repeatedly on all the other curves as well as on this particular one, that it is very much easier to obtain a phase after it has once been present in the apparatus. Thus it is possible to subcool III at least as far as —70° with respect to II, provided that II has never been formed. But if II has been formed previously, the reaction from III to II is very likely to run on passing from the III to the II region. This explains why it is possible to move up along the II–I curve, pass to the I–III curve, and then on decreasing temperature pass again to the I–III curve.

The points obtained experimentally have been classified with these facts in view. The points of March 25, 29, and April 5 obtained at temperatures above —35° after coming from lower temperatures on the I–II curve have been listed on the I–III curve in the tables.

The points are plotted in Figure 9. These points are the mean of the points found with increasing and decreasing pressures at temperatures very close to each other. Within the limits of error the points lie on a straight line. The two lowest points are irregular because of the extreme slowness of the reaction. It is interesting to notice that the line as drawn is heading straight for the absolute zero, the equilibrium pressure becoming zero at this temperature. Because of the slowness of the reaction it would be well nigh impossible to verify this conjecture experimentally. Except for the constant pressure error already mentioned, the curve as found by Tammann is of approximately the same shape as that found here. These figures give a drop in the

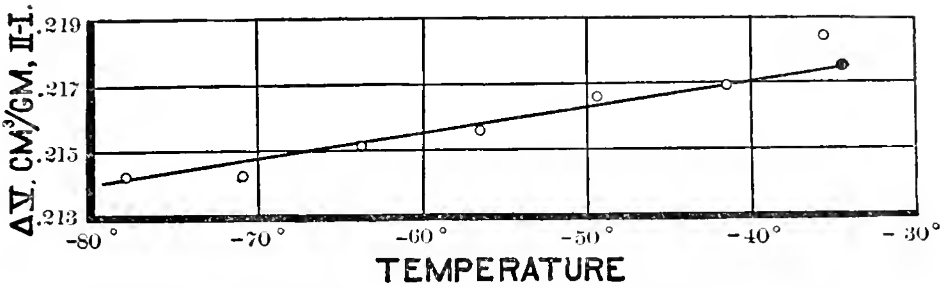

FIGURE 14. The change of volume when II passes to I.

equilibrium pressure of 360 kgm. between —40° and —80°, whereas Tammann gives 340 kgm. Tammann does not draw the line as straight, however, but prefers to make it slightly concave toward the temperature axis. This would bring the equilibrium temperature at atmospheric pressure up somewhat higher than the absolute zero.

The changes of volume, found by the method already described, are given in Table XIV., and shown graphically in Figure 14. Because of the fairly large difference in slope between the equilibrium curve and the lines of equal volume, the actual cycles described in measuring ΔV did not have the exact location shown in Figure 8. The lower parts of both DE and GF, which were fairly close together, projected over the equilibrium line into the region of stability of II. The upper end of the line CB was managed so as to just clear reaching into the region of I. This evidently introduces no essential error, since the compressibility and dilatation of one phase do not change on passing into the region of another. The difference merely means a somewhat wider extrapolation to determine the displacement on the equilibrium curve corresponding to the phase II, but this disadvantage is offset by the fact that what was an extrapolation for the phase I has now become an interpolation.

The change of volume is seen to be linear with temperature (or pressure) within a maximum error of 1/2 per cent. Only one point, that at —35.7°, shows a discrepancy as much as this, the average departure from linearity being in the neighborhood of 1/8 per cent.

Tammann gives three values for the change of volume which he lists as I-II, and two values listed as I-III. One of the supposed I-II values is above −35°, however, so that this must now be tabulated as I–III. He finds for I–II at −76°, 0.171 cm.^{3}/gm., and at −55°, 0.180. These

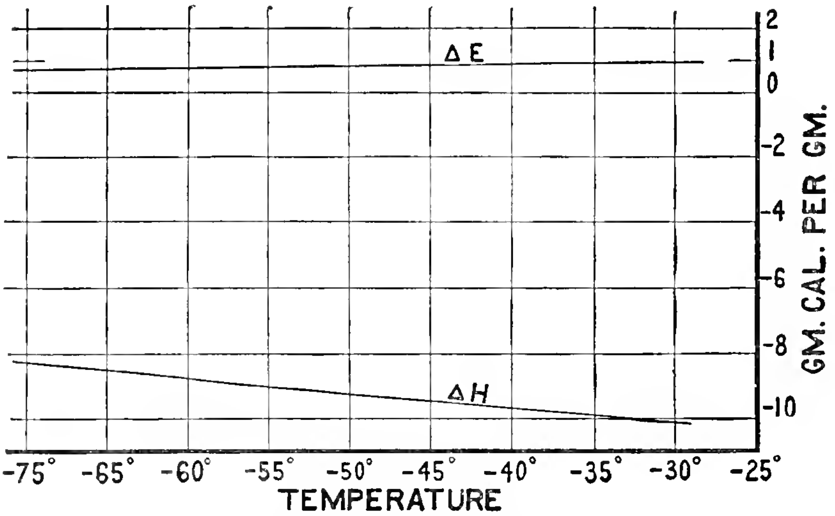

Figure 15. The latent heat and the change of internal energy when I passes to II.

values are considerably lower than the values found here. Tammann appears to have overlooked entirely the correction for the thermal dilatation of the fluid transmitting pressure; the effect of applying this correction would be to bring his values still lower. Tammann's results do agree with the present ones in showing an increase in the change of volume at higher temperatures, but Tammann finds a rate of increase

TABLE XV.

Latent Heat, etc., on Equilibrium Curve Ice I–Ice II.

Temp. C.°.	Pressure, kgm./cm.^{2}.	Δv. cm.^{3}/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−75	1794	0.2146	8.35	9.02	−8.31	0.71
−65	1886	.2154	8.35	9.52	−8.77	0.75
−55	1980	.2162	8.35	10.03	−9.22	0.81
−45	2072	.2170	8.35	10.54	−9.68	0.86
−35	2164	.2177	8.35	11.06	−10.15	0.91

four times that found here. Tammann states concerning his own data that his temperature coefficient is in all probability too high. His value at —33.5° for the supposed change I–II, but really for I–III, is 0.193 cm./gm. This agrees exactly with the value found here at the same temperature for the known change I–III, giving another bit of evidence from Tammann' s own data that above —35° II changes spontaneously to III. Tammann's value for the change I–III at —45° is 0.192, giving a temperature coefficient of the opposite sign from that found here. The actual values for the I–III change agree much better with the values found here than for the I–II change. The present values for I–III are 0.1904 at —32.5° and 0.2005 at —45°.

The data taken from these two curves needed in the calculation of ΔH and ΔE are shown in Table XV. and Figure 15. I gives out heat on passing to II and absorbs work. The work is greater than the heat, so that the internal energy increases on passing from I to II.

The Curve II–III.

This has been already stated to have been the curve overlooked by Tammann, but demanded thermodynamically. The discovery of it places beyond question the essential difference between the two varieties of ice II and III. The change of volume on this curve is very slight, so that it is easy to overlook it altogether, as did Tammann. A special method had to be used here in determining these equilibrium points. It is the reverse of the usual method. The usual method consists in changing the piston displacement and so the pressure at constant temperature. Change of phase is indicated by change of displacement with constant pressure. In the modification of the method used here, the displacement is kept constant and the temperature changed. The resulting change of pressure is plotted as a function of the temperature. Change of phase, accompanied by a slight change of volume, is indicated by a discontinuity in the direction of the temperature-pressure line.

At any given temperature during this change of phase there is only one corresponding pressure, the equilibrium pressure, unlike the former method, where the piston displacement may have any value within a considerable range corresponding to the same pressure and temperature. The change of volume is so slight that the interval of discontinuity in the direction of the temperature-pressure line extended over only 1° and 100 kgm. The method was made practicable by two things, the smallness of the containing cylinder, resulting in a very rapid attainment of temperature equilibrium, and the fact already noted, that it is impossible to superheat II with respect to III. Evidently if it had been necessary to superheat II even a single degree in order to start the reaction, the change of volume would not have been sufficient to carry the pressure automatically back to the equilibrium value, and the reaction would have run to completion.

The procedure in getting the points was to start with II at some pressure and temperature below the equilibrium line, and to raise the temperature by small intervals. Arrival at the equilibrium line was shown by an abnormally large rise of pressure. This pressure and the corresponding temperature gave one point on the equilibrium line. The reaction was not allowed to run to completion, because of the difficulty of recovering II after it has once been changed to III, but the pressure was immediately raised from the equilibrium pressure, bringing the material back into the region of stability of II, and causing the reverse reaction III–II to run to completion. Another equilibrium point was then found starting with this higher pressure.

The job was a rather fussy one because of the narrowness of the critical temperature interval. The temperature had to be maintained by dropping solid CO_2 into the Dewar flask, and some little practice was necessary before satisfactory results were obtained. Determinations of the curve were made on three occasions. The first two sets confirm the last set, but sufficient adeptness had not yet been attained with the method, and the points were discarded.

The final points, four in number, are shown in Table XVI. and Figure 9. The curve rises with increasing pressure from lower to higher temperature and is convex upward ; it is terminated at either end by triple points, at the lower end by the point I–II–III, and at the upper end by the point II–III–V. This curve is new ; there are no previous results with which to compare it.

The change of volume determinations were made also with a slightly modified method. The usual method of measuring piston displacement at constant temperature would have been available if the measurements had been made with decreasing pressure from the region of II to that of III, but the method was undesirable practically for two reasons. There was the difficulty of maintaining the temperature in the Dewar flask constant for a sufficiently long interval of time by hand, and there was the necessity of running down to the very lowest temperatures in order to recover II for the next determination after the reaction to III had been allowed to run to completion. This would have required much time and would have been very wasteful of solid CO_2.

The method used was a modification of that used in finding the I–II and the I–III points, namely, measurement of pressure as a function of temperature at constant displacement. The changes II–III and II–V were measured at the same time, so that some anticipation is necessary in describing the method. The diagram (Figure 16) illustrates sufficiently the paths described. The start was made at the point A with the phase II. The approximately vertical lines show the paths at constant displacement on which the pressure, temperature, and displacement are all known. The dotted lines show the connecting paths on which it was not necessary to know these values. The result of describing all these paths is to give a knowledge of the displacement corresponding to any pressure and temperature in either the region of stability of II or III or V. The discontinuity of displacement on the three equilibrium curves can be found immediately, and so the change of volume. It is to be noticed that the paths are described in such an order that one can easily apply the very small correction for wearing away of the packing or for viscous yield in the steel. The final point B is for the

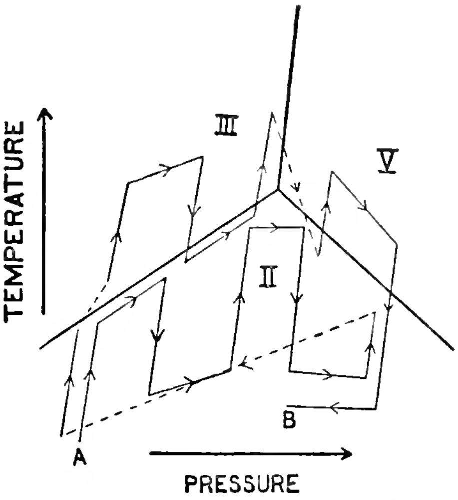

Figure 16. Shows the cycles described in finding the changes of volume II–III and II–V.

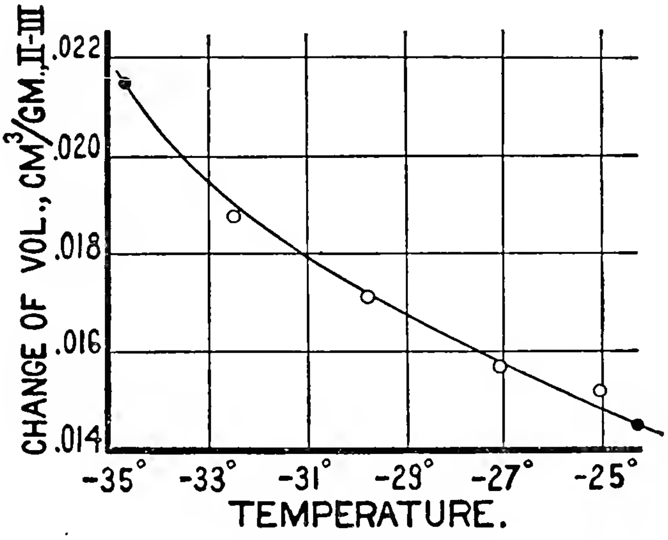

Figure 17. The change of volume when II passes to III.

phase II. The diagram illustrates the impossibility of carrying II into the region of stability of either III or V, but the possibility of subcooling both III and V into the region of II.

TABLE XVI.

Data for the Equilibrium Curve Ice II–Ice III.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.².	ΔV. cm.³/gm. Corrected.
April 19	−33.4	2290	
	−31.0	2580	
	−28.0	2910	
	−26.0	3220	
April 20		2400	0.0188
		2710	.0171
		3050	.0157
		3390	.0152

The experimental values of ΔV so found are given in Table XVI. and Figure 17. The actual volume of II is seen to be less than that of III. The percentage discrepancy of two of the points may rise as high as 2 per cent, but this means only a comparatively slight absolute error, less than 1 part in 2000 on the original volume. The ΔV curve is convex toward the temperature axis which is unusual.

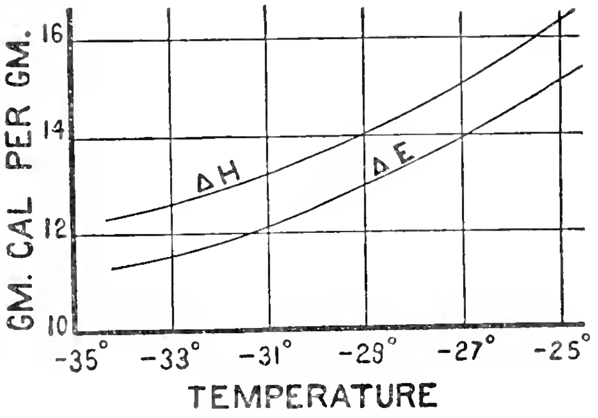

Figure 18. The latent heat and the change of internal energy when II passes to III.

The values for ΔH and ΔE deduced in the usual way are given in Table XVII. and Figure 18. III gives out heat on passing into II and absorbs work. But the mechanical work is comparatively small, so that the internal energy of II is less than that of III.

This completes the description of the equilibrium curves of the varieties of ice already known. This last curve had not been found before, and the rest of the curves to be described involve either one or two of the new varieties of ice found at higher pressures.

TABLE XVII.

LATENT HEAT, ETC., ON THE EQUILIBRIUM CURVE ICE II–ICE III.

Temp. C.°.	Pressure, kgm./cm.².	ΔV. cm.³/gm.	dp/dt.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
			From Curve.	Adjusted.			
−34.0	2230	0.0206	100	107	−1.08	12.4	11.3
−31.0	2530	.0179	125	130	−1.06	13.2	12.1
−28.0	2910	.0164	152	154	−1.12	14.5	13.4
−25.0	3370	.0148	184	189	−1.17	16.3	15.1

THE CURVE III–V.[10]

The points on this curve were usually obtained from above, coming from the region of stability of V into that of III. The reaction does not usually run of itself at temperatures above −25°; between −25° and −18° it is usually possible to reduce the pressure on V as far as the V–L curve, where V melts completely to water without the appearance of III. Below −25°, however, III is pretty certain to separate from V on passing slightly beyond the equilibrium curve. The points were usually obtained first at low temperatures and then at higher. Proceeding in this way it is easy to get the changes of volume also, although this did necessitate the reaction running to completion, because the reactions on this curve proved particularly sensitive to the previous appearance of the phase desired. If III and V had both been present recently, the reaction would run almost immediately, in either direction, at any temperature, on passing over the transition curve.

It has been already noticed that it is possible to carry both III and V down into the region of stability of II. Corresponding to this possibility we have the realization of the prolongation of the unstable curve III–V into the region of II. A point on this curve has been found at

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[10] For the notation V instead of IV for this new variety of ice, see p. 528.

—35°. The change in reaction velocity between III and V at different temperatures shows a greater and more striking change than that on any of the other curves. At the upper end, in the neighborhood of —20°, the velocity is explosive. It is possible to withdraw the piston by an amount corresponding to nearly the entire volume change of the reaction, and not be able to detect any change at all in the pressure, so rapidly does the change occur. While only 15° lower, at —35° the reaction runs so slowly that the attaining of complete equilibrium is a matter of several hours. This is the reason that the attempt was not made to prolong the equilibrium curve further. It is evident that we

TABLE XVIII.

Data for the Equilibrium Curve Ice III–Ice V.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected Value.
Feb. 1	−25.05	3460	
	−24.20	3460	
	−23.00	3500	
	−21.50	3500	
	−20.30	3500	
	−18.35	3500	
Feb. 16	−25.25	3510	0.0541
	−22.80	3510	547
	−20.40	3520	546
	−18.40	3550	547
April 20	−22.1	3549	
	−19.4	3559	
	−24.4	3542	
	−29.0	3527	
	−35.3	3514	
	−23.0	....	.0570

have here something entirely different from the mechanism of ordinary chemical reactions which produces change of reaction velocity with temperature. For chemical reactions the temperature coefficient of velocity is almost universally in the neighborhood of 100 per cent for 10°, a value enormously lower than that found here.

The actual determination of the equilibrium points was made on three occasions, February 1 and 16, and April 20. The first two were with the apparatus for the middle temperature range, that used with the mercury. These were made with the thermostat to keep the temperature constant. This apparatus was also used to give the changes of volume. The data of April 20 were taken with the low temperature apparatus. The particular object of this latter set was to obtain as accurately as possible the slope of the transformation curve, the previous data having shown that it was nearly vertical.

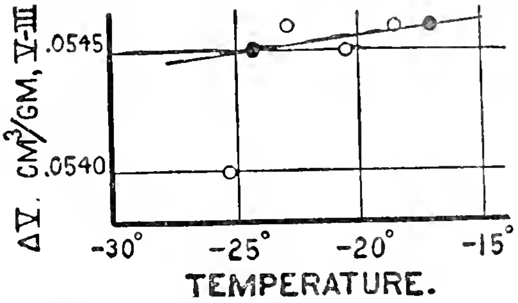

Figure. 19. The change of volume when V passes to III.

TABLE XIX.

Latent Heat, etc., on Equilibrium Curve, Ice III–Ice V.

Temperature, C.°.	Pressure, kgm./cm.².	ΔV. cm.³/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−35.0	3470	0.05446	2.75	4.43	−0.83	3.60
−30.0	3495	5454	2.75	4.46	−0.85	3.61
−25.0	3508	5461	2.75	4.49	−0.87	3.62
−20.0	3522	5469	2.75	4.51	−0.89	3.62

The equilibrium points are shown in Table XVIII. and Figure 9. The slope of the equilibrium curve is the slope given by the data of April 20, but the absolute value of the pressure as given by the mean of the other points is more likely to be correct. The equilibrium line is straight within the limits of error. The slope is in the same direction as for the curve I–II, but is less. There is no possibility of this line heading for the absolute zero.

The changes of volume, four in number and taken with the mercury apparatus, are given in Table XVIII. and Figure 19. The change is constant so far as could be judged from the points themselves, but the best values at the triple points would demand a slight decrease of this volume with decreasing temperature. In addition to the four points listed above, there is a fifth determination on April 20 by the method described on p. 495. This is higher by 4 per cent (0.2 per cent of the original volume) than the previous point. In view of the fact that the first four points very approximately satisfy the requirements at the triple points, there seems little doubt that they are the correct ones.

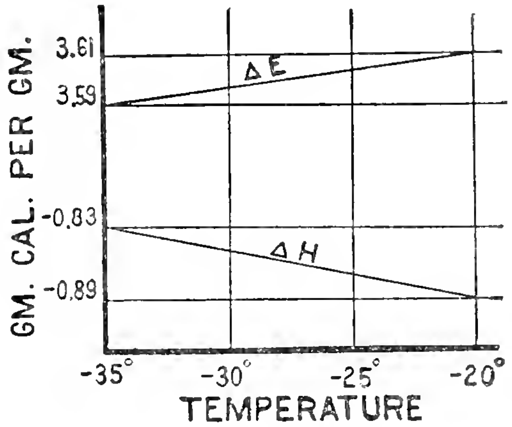

FIGURE 20. The latent heat and the change of internal energy when III passes to V.

The values of ΔH and ΔE calculated from these data are given in Table XIX. and Figure 20. III gives out heat on passing into V and absorbs work. The heat is very small, much less than the work, resulting in an increase of internal energy on passing from III to V.

THE CURVE II–V.

This curve has some of the properties of the II–III curve. It is characterized by small change of volume and by the fact that II passes into V immediately when the temperature is raised beyond the curve. The method of determining the points was the same as that of the II–III points. This was the last of all the equilibrium curves to be obtained. It was found after sufficient skill had been attained with the method, so that it was necessary to obtain the points only once. For this reason, the observation that it was impossible to heat II into the region of V was not tested by so many trials as the corresponding change II–III, and has therefore not quite so much probability of being absolutely true. The reaction velocity on this curve drops very much faster than it does on the II–III curve with decreasing temperature. This might, at lower temperatures, result in the apparent possibility of bringing II into the region of V, even if the reaction were actually running. This slowness of reaction makes very difficult the determination of the equilibrium points at the low temperatures, the determination being difficult enough anyway, because of the small change of volume. It would probably not be possible to extend this curve to very much lower temperatures than are given here. In partial explanation of the difference in the behavior of the reaction velocity with temperature on the two curves II–III and II–V, it is to be noticed that on the latter curve decreasing temperature is accompanied by increasing pressure, which of itself would tend to slow the reaction because of increasing viscosity, whereas on the former curve the retarding effect of decreasing temperature is offset by the accelerating effect of decreasing pressure.

TABLE XX.

Data for the Equilibrium Curve Ice II–Ice V.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
April 19	−34.00	4200	
	−30.50	3970	
	−27.7	3800	
	−25.8	3650	
April 20		3700	0.0408
		4000	406
		4280	398

The equilibrium points, four in number, are given in Table XX. and Figure 9. These points lie on a straight line, the temperature rising with falling pressure.

The change of volume points, obtained by the method already described for the II–III curve, are shown in Table XX. and Figure 21. The change is sensibly constant on this curve. This means that the relation between compressibility and dilatation is such that the changes of temperature and pressure on the equilibrium curve produce the same change of volume in both II and V.

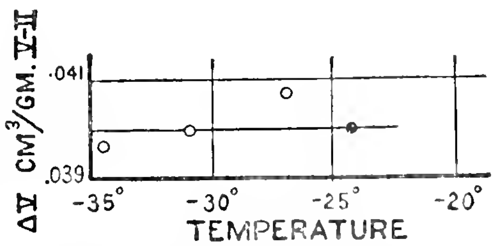

Figure 21. The change of volume when V passes to II.

The values of ΔH and ΔE, computed from these data, are given in Table XXI. and Figure 22. II absorbs heat on passing to V and absorbs work. The internal energy of V is greater, therefore, than that of II.

TABLE XXI.

Latent Heat, etc., on the Equilibrium Curve, Ice II–Ice V.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	dp/dt. From Curve.	dp/dt. Adjusted.	$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
−34.0	4200	0.0401	75.6	68.4	3.95	12.4	16.4
−31.0	4010	401	69.8	68.4	3.77	13.9	17.8
−28.0	3800	401	62.4	68.4	3.57	15.1	18.7
−25.0	3570	401	55.0	68.4	3.36	15.9	19.2

The Curve V–L.

V was the second variety of ice found in this present work, the first being that stable at higher pressures, namely VI. It seems worth while to give here a short account of the actual order of the experiments, as it illustrates well the capricious character of these reactions. Ice V was first found at −8°. An experiment was being run on the change of volume of ice VI when passing to water. Pressure was being decreased; it had passed over the equilibrium pressure and a sufficient interval of time had elapsed to allow the pressure to automatically restore itself to the equilibrium value. The change to V occurred without warning. By good fortune, a reading at the bridge was being made at the particular instant, so that the entire

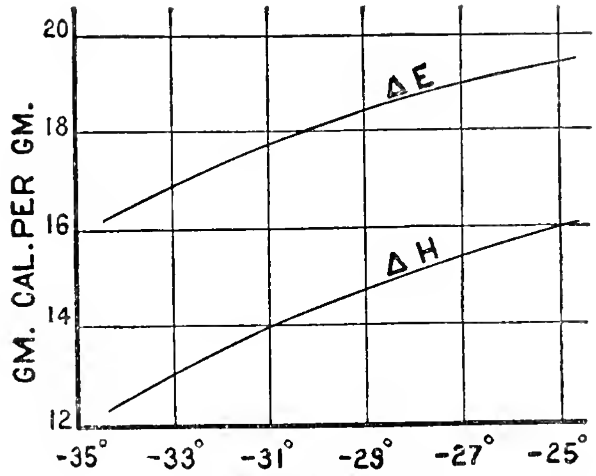

Figure 22. The latent heat and the change of internal energy when II passes to V.

process was observed. There was a sudden increase of pressure, followed by a slow fall past the equilibrium value VI–L to a final stationary value several hundred atmospheres lower down. This second stationary pressure had all the properties of a new equilibrium pressure, since the pressure was automatically restored to this value after withdrawal of the piston. After sufficient withdrawal of the piston, the pressure dropped in the normal way. The explanation, in view of the facts as they now appear with the complete diagram before one, is that ice VI at —8° was unstable. It had partly melted when it flashed suddenly into V with increase of volume and increase of pressure. The form V now found itself in the presence of water beyond the equilibrium curve. The water froze to V with decrease of pressure back to the equilibrium curve V–L. At the time, however, this explanation was adopted with considerable hesitation. No experience had been had of the very high reaction velocity possible between solids. After this set of readings, pressure was left at 2000 kgm. over night, the temperature gradually rising.

The next morning another run was made at —6°. The liquid froze to VI at —6° perfectly properly, with no trace of V. Pressure was increased considerably beyond the equilibrium value at —6° and then decreased. On the way down a new transformation point was found at pressures higher than either the VI–L curve or the supposed V–L curve. The new reaction ran with unusual velocity, equilibrium being attained in the time usually required for temperature equilibrium. On decreasing pressure further, the VI curve was passed over without incident, but a new equilibrium pressure was found lower down on the prolongation of the probable V–L curve of the day before. The explanation suggested itself that the upper transformation point was on the V–VI curve, the lower on the V–L curve. Some slight irregularities in the data made it desirable to dismount the apparatus after this run. During these experiments, the water had been enclosed in a glass bulb, as this was one of the series of experiments to detect if possible any effect of the transmitting liquid on the water. The glass bulb was found crushed to fragments, evidently because of the reaction between two solid phases with sudden increase of volume.

In the apparatus as set up next time, the glass bulb was discarded, therefore, and the water placed directly in a shell of copper. With this apparatus no trace whatever could be found of the new phase V. Measurements were made on the equilibrium and change of volume VI–L to temperatures as low as —20°. Lower temperatures could not be easily attained because of the trouble with the $CaCl_2$ cooling arrangements. The subject was then dropped for a couple of months;

in the meantime the data required for the mercury paper were finished.

On taking the matter up again, the only difference that presented itself between the two runs, one giving V and the other not, was that in the former run water had been in the presence of glass. The apparatus as set up again was made to differ from the former set up, therefore, only in the fact that splinters of Jena chemical glass were placed in the water, which was again included in a copper shell. The very first attempt at −10° was successful. Pressure was increased beyond the VI–L line, the reaction VI–L had started, and the equilibrium pressure had been reached, when the phase V put in an appearance, displacing VI. Briefly, the mere addition or subtraction of the fragments of glass appeared to be the determining factor. When it was desired to work on VI in the sub-cooled region, the glass was omitted; when V was desired, the glass was added. Even then the appearance of V was under surprising conditions. V was never formed directly out of the water, but always in the presence of the phase VI. Furthermore, V showed a preference for appearing only when VI, water, and glass were present together, usually during determinations of the equilibrium pressure VI–water, either during increasing or decreasing pressure. The facility with which V might replace VI was the source of some annoyance. Once a day's work was lost because V had successfully come in without being noticed. V might, however, form directly from the solid VI, as described above. All this holds only for the initial appearance of V, it being very much easier, as already explained, to produce it after it had appeared once. It was possible in this way to get V to separate directly from the liquid, if it had appeared recently before.

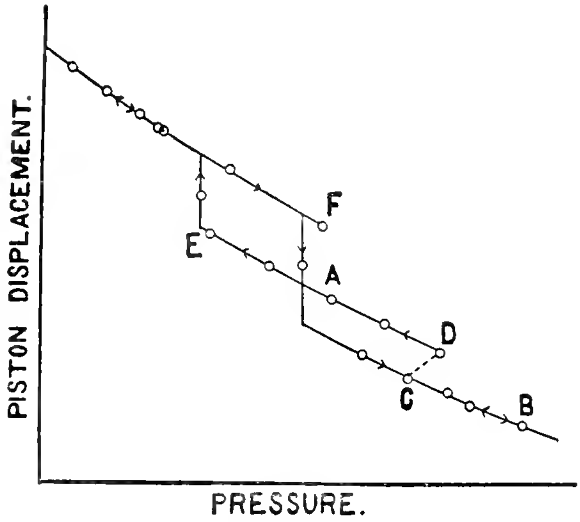

FIGURE 23. Shows the way in which V may appear. The dotted line C–D indicates the sudden transition from VI to V.

Figure 23, plotting piston displacement against pressure, shows well the way in which V might appear. With increasing pressure, the water froze regularly to VI, as shown at A. The point F shows the possibility of subcooling the water before the reaction starts. The pressure was then increased on the phase VI to the point B without incident. On decreasing pressure beyond C, VI suddenly changed to V with increase of pressure to D. This change took place so far beyond

TABLE XXII.

Data for the Equilibrium Curve Ice V–Water.

Date, 1910.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3} gm. Corrected.
Nov. 11	−7.8	4860	0.0541
14	−6.0	5200	0512
19	−8.9	4140(?)	
1911			
Jan. 30	−10.1	4490	0702
	−18.75	3420	
	−16.65	3680	
	−11.00	4440	
Jan. 31	−14.5	3910	
	− 4.0	. . . .	0578
Feb. 2	−20.6	3050	
3	− 2.0	5940	0552
4	−13.1	4030	0747
8	−15.45	3770	0765
	− 9.50	4600	0693
9	− 7.17	5010	0623
	− 4.3	5480	0586
	− 0.88	6120	
11	− 7.65	4890	0636
	− 4.60	5420	0587
	− 1.40	6020	0519
13	−10.8	4480	0693
	−10.5	4460	0663
	−14.2	3900	0724
14	−17.65	3460	0790
	−20.80	3040	0839
	−14.32	3780	0753
22	− 1.60	6040	0543

the equilibrium line that the change of volume VI–V was not sufficient to raise the pressure to the equilibrium value VI–V. From D, pressure was regularly reduced to E, the melting point of V. Beyond E, the curve of increasing pressure was retraced.

These remarks about the manner of appearance of V hold only for temperatures above —25°. At lower temperatures, V may be made to separate from the solid phases III or II without the presence of glass. In any event, V was the hardest of any of the solid forms to obtain, the only certain way being via II, which demanded lowering the apparatus to below —60°.

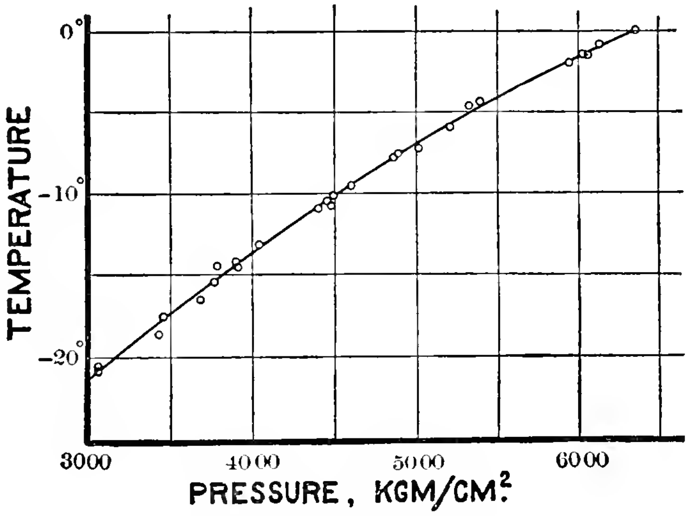

Figure 24. The freezing curve V–L.

The actual determination of the points on the V–L curve was made with the apparatus for the middle temperature range, temperature being kept constant as usual with a thermostat. The equilibrium points are shown in Table XXII. and plotted in Figure 24. As is seen, these points were obtained on a large number of occasions, with different pressure measuring coils, and with nearly all possible combinations of all the pieces of apparatus ever used with this general type of apparatus, part after part being replaced as it was destroyed by explosion. The lower part of the equilibrium line is a trifle high, still passing through a number of points, but not through the mean of all the points. This was demanded in order to obtain consistent values for the latent heat at the triple point L–III–V, the slope of the upper end of the III–L curve being extraordinarily sensitive to small changes, as already explained. The curve as given does not differ by over 0.2° from the best curve through the points for V–L alone. The curve as given extends to —21°, 4° into the region of stability of III. It is known, however, that it is possible to extend the curve as far as —25°. On one occasion a point was found here, but it is not sufficiently accurate to plot, owing to defective temperature control. The behavior at the upper end of the V–L curve is the exact opposite of that at the lower end. It was not found possible to prolong the equilibrium curve of V and L the slightest distance into the region of stability of VI, V always passing spontaneously into VI. This was tried several times; the reaction runs if the penetration into the VI region is even as slight as 1°.

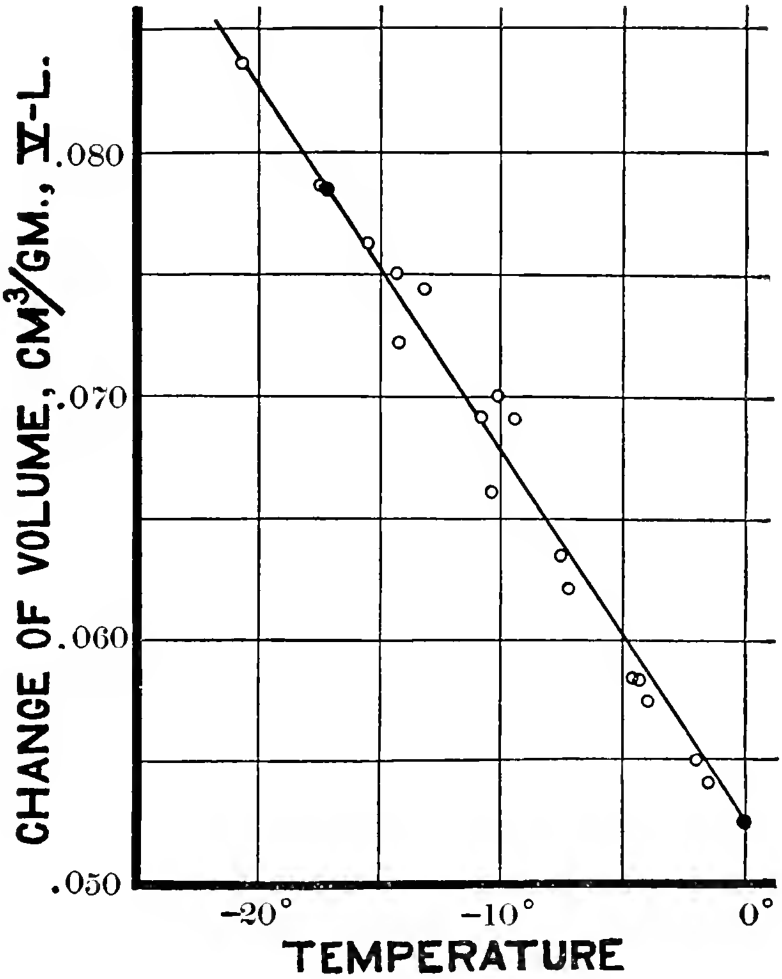

Figure 25. The change of volume when V passes to the liquid.

More or less trouble was found in determining the change of volume. When kerosene was used as the transmitting fluid, there seems to be some action below 0°, either between the water or the ice and the kerosene. This results in a slight rounding off of the corners of the displacement-pressure curve, so that the actual discontinuity is difficult to determine. This would point to a solution of the water in the kerosene. The rounding off of the corners is not enough to affect appreciably the equilibrium pressure. The effect was on the whole less marked when gasolene was used as the transmitting fluid. The change of volume points are given in the same table with the equilibrium points and also in Figure 25. All the data before February 10 were obtained with kerosene as the transmitting fluid; gasolene was used for the results obtained afterwards. The gasolene points are on the whole better, although the difference here is not sufficient to have necessitated the use of gasolene instead of kerosene. The changes of volume VI–L are much more affected by the transmitting fluid, below zero, than are the changes V–L. The first two values of November 11 and 14 are not plotted, since the design of the apparatus in the first few attempts was not good. Small portions of the water were likely to separate from the rest after a single freezing, so that unless the pressure was carried considerably beyond the freezing pressure, part of the water was likely to remain liquid, giving too low an apparent change of volume. The lowness of these first two points is to be explained in this way.

TABLE XXIII.

LATENT HEAT, ETC., ON THE EQUILIBRIUM CURVE, ICE V–WATER.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	$\frac{dp}{dt}$.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
			From Curve.	Adjusted.			
−20.0	3140	0.0828	123	123	−6.10	60.5	54.4
−15.0	3800	754	140	139	−6.72	63.4	56.7
−10.0	4510	679	160	157	−7.18	65.9	58.7
− 5.0	5440	603	184	180	−7.69	68.1	60.4
− 0.0	6360	527	210	208	−7.85	70.0	62.2

Within the limits of error, the relation between temperature and change of volume is linear. The lower end of the curve is about 1 per cent higher than what would be demanded by the points themselves. This was made necessary by the conditions at the critical point.

The values of ΔH and ΔE found from these data are given in Table XXIII. and Figure 26. Water gives out heat on passing into V, and absorbs work. The work is very much less than the heat, so that the internal energy of V is less than that of the liquid.

The Curve V–VI.

This is the last of the curves of equilibrium between two solid phases. The manner in which the curve was first found has been already described. The characteristics of this curve are the same as those of the other solid-solid curves; very high reaction velocity at the upper end, with enormously retarded reaction velocity at the lower temperatures. The slowing of the reaction was so great as to make impracticable the determination of points lower than −25°. Anomalous results obtained once or twice are to be explained by the slowness of the reaction velocity. The nature of the anomaly is shown in Figure 27, plotting piston displacement against pressure. It is as if there were two discontinuities, at A and B, and so two transition points. The explanation is probably as follows. The reaction from VI to V starts at the upper end of the steel shell. This reaction runs with increase of volume, so that the layer of the new ice V may form a protecting layer over the remainder of the old ice VI below. This protecting layer is capable of standing some appreciable stress at this high pressure and low temperature, so that changes of hydrostatic pressure do not reach the nest of

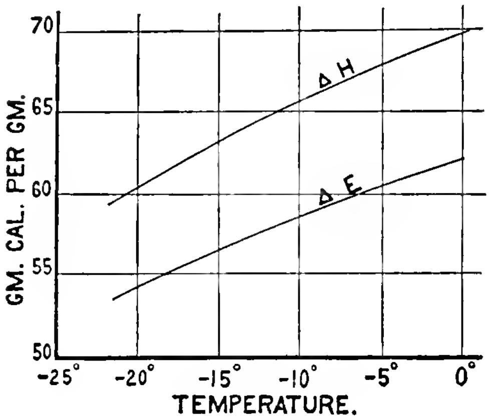

Figure 26. The latent heat and the change of internal energy when V passes to the liquid.

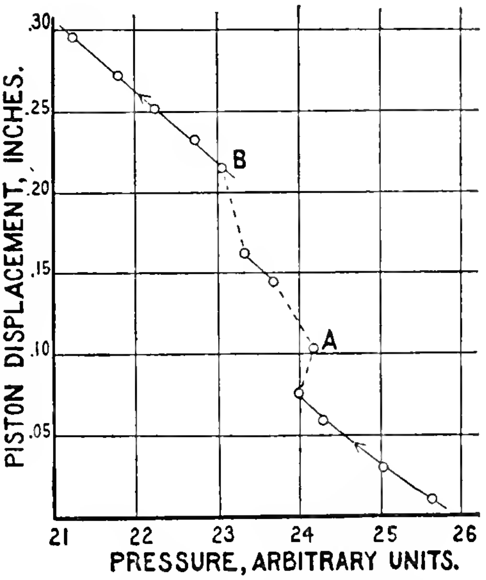

Figure 27. False equilibrium at low temperatures on the V–VI curve, due to the slowness of the reaction and the viscosity of the solids.

ice VI below, until the pressure has been reduced by an amount corresponding to the strength of the ice V. An exactly similar effect was found once on the III–V curve at —25°. That the ice in passing from one solid to another is capable of exerting considerable stress is shown by the occasional rupture of the steel shells containing the water.

TABLE XXIV.

DATA FOR THE EQUILIBRIUM CURVE, ICE V–ICE VI.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
Jan. 30	−10.10		0.0396
31	−14.5	6360	378
	− 4.1		400
Feb. 1	−16.60	6320	346
3	−18.1	6380	
	−24.65	6320	
	−22.70	6360	
	−19.90	6370	
	−12.05	6370	
	−12.08	6380	383
	− 2.00	6380	
4	−13.1	6360	396
20	−19.7	6360	386
	−16.8	6370	384
	−13.9	6370	384
21	−11.25	6370	386
22	− 8.15	6390	380
	− 5.00	6380	387
	− 1.60	6380	386

These were 9/16 inch o. d. and about 3/64 inch thickness of wall. In fact, it seems rather surprising that the effect did not prove troublesome on more than these two occasions.

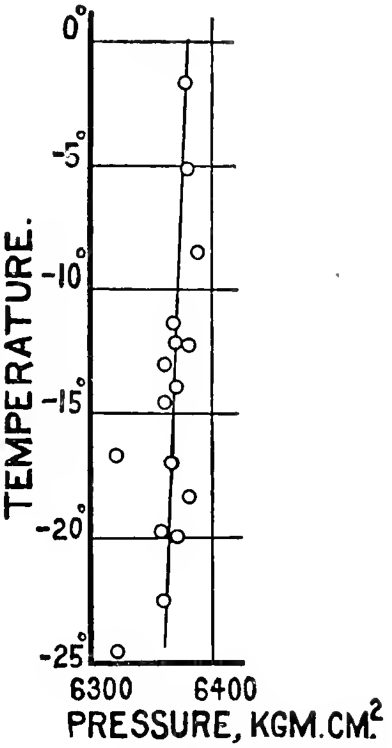

Figure 28. The equilibrium curve V–VI.

The regular apparatus for the middle temperature range was used in finding these points. Some skill in manipulation was necessary to arrive on the curve at all. The procedure was to start with the water impregnated with glass splinters and raise the pressure at a temperature somewhere between —10° and —20°. On sufficiently overpassing the unstable VI–L curve, VI would separate out. After some little while V would appear. With the first signs of its appearance, indicated by a rise of pressure, the pressure was increased as rapidly as possible, in a few seconds, to the V–VI curve, where the automatic change of volume was sufficient to ensure retaining of the equilibrium pressure after freezing of the remaining mass of liquid. This method of procedure was made necessary by the fact that at the temperatures at which it is easy to obtain V, it is possible to pass from either side of the V–VI curve into the region of instability on the other side, without the reaction running. At higher temperatures, nearer the triple point, it is not possible to carry V so far into the region of VI, corresponding to the fact already noted that at the triple point itself it is impossible to carry V any distance at all into the region of VI.

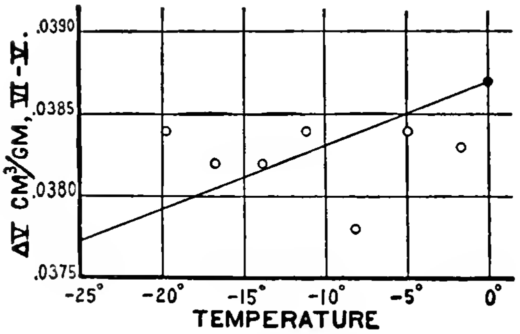

Figure 29. The change of volume when VI passes to V.

The equilibrium pressures and temperatures are shown in Table XXIV. and Figure 28. The equilibrium line is nearly at constant pressure, but there is an unmistakable though slight increase of pressure at the higher temperatures. Within the limits of error, the equilibrium curve is a straight line.

The change of volume points, obtained by the usual method of observing the piston displacement at constant temperature, are given in Table XXIV. and Figure 29, plotted on a very much enlarged scale.

TABLE XXV.

Latent Heat, etc., for the Equilibrium Curve, Ice V–Ice VI.

Temperature, C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	$\frac{dp}{dt}$.	$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
−20.0	6365	0.03809	.80	5.682	−0.181	5.50
−15.0	6370	3828	.80	5.716	−0.185	5.53
−10.0	6374	3847	.80	5.748	−0.190	5.55
− 5.0	6377	3866	.80	5.779	−0.195	5.58
0.0	6381	3886	.80	5.812	−0.199	5.61

Here again the points found before February 10 with kerosene as the transmitting fluid show much less regularity than the points obtained afterward with gasolene. The kerosene points have been omitted from the diagram. The effect may be due in part to the increased viscosity of the kerosene under pressure. Within the limits of error, the relation between V and temperature is linear, the change becoming less at lower temperatures as one would expect.

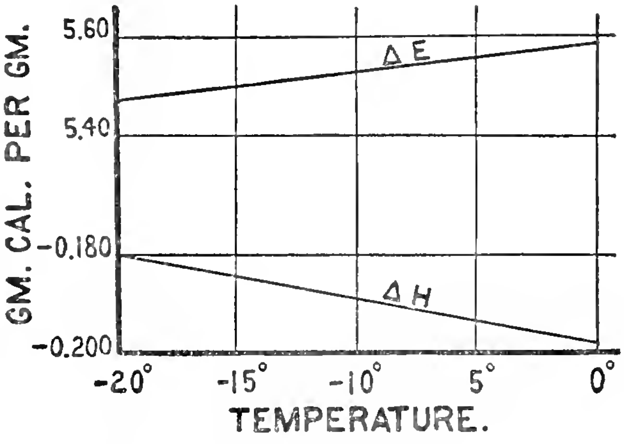

Figure 30. The latent heat and the change of internal energy when V passes to VI.

The missing triple point, mentioned at the beginning, is evidently given by the intersection of this line, V–VI, with the line II–V. This point is apparently situated at about —65° and 6300 kgm. Evidently the reaction velocity will be so slow at these temperatures and pressures that it would be hopeless to try to reach it. The missing equilibrium curve starting from this point is evidently II–VI. There is even less chance of realizing this than of getting down to the triple point, always assuming of course that some new variety of ice does not appear.

The values of the latent heat and the change of energy calculated in the usual way from the data are given in Table XXV. and Figure 30. The latent heat, owing to the approximate perpendicularity of the equilibrium curve, is almost vanishingly small. V gives out heat on passing to VI, but absorbs work. The heat is almost negligible compared with the work, so that the internal energy of VI is greater than that of V by nearly the amount of this work.

The Curve VI–L.

This modification of ice was the first one discovered in the present work, and has engaged more attention than any of the other forms. It has been studied over a pressure range of more than 16,000 kgm., nearly three times the pressure range of all the other modifications put together. So far as can be judged, this is the final form of the solid. This ice shows characteristics in its behavior different from any of the others, characteristics which are particularly significant for the theory of the solid-liquid states. In fact, this is the only modification stable over a pressure range wide enough to indicate what may be expected at still higher pressures, as yet unreached.

The manner in which this variety of ice was first found in the course of the measurements of compressibility has been already described in the introduction. The appearence of this ice resulted simply in an irregular disturbance at the upper end of the compressibility curve. It was evidently impossible to make any accurate measurements by this method of the freezing pressure or of the change of volume. All that could be stated about the freezing pressure was that it was less than a certain value, the maximum pressure reached during a run when there was a disturbance, and all that was known about the change of volume was that it was higher than a certain value, the discontinuity in the compressibility curve. The lower and upper limits so set on these quantities were found to be consistent with the more accurate values found later.

At the time that these disturbances were found no great confidence was felt in the explanation that the effect was really due to the freezing of the water. All of the compressibility measurements were made in the presence of mercury. Now it had been already found that mercury freezes under pressure, and at pressures very close to those actually found. At 0°, for instance, the freezing pressures of water and mercury, according to the final accurate determinations, are about 6400 and 7600 kgm. respectively, and these two transitions seemed much closer together in the preliminary work because it was necessary to superpress the water considerably before freezing begins, while the superpressure required for mercury is very small. It is true that there were very great quantitative difficulties in the way of supposing the effect due to the freezing of the mercury, but still the neighborhood of the mercury freezing point produced a sensation of disquietude.

In order to definitely rule out the possibility of complications from the neighborhood of the freezing point of mercury, a form of experiment was devised in which there was no mercury present. This was the experiment also briefly alluded to in the introduction on the electrolytic conductivity of water. The water was placed in a shell of steel or glass, and the conductivity measured between two concentric brass cylinders attached to the insulating plug and suspended in the water. The pressure chamber was filled with kerosene by which pressure was transmitted directly to the water. There was no mercury anywhere about it. The water was not absolutely pure, ordinary tap water being used, which was sufficiently conducting for the purpose. In one case distilled water with 1/10 per cent HCl was used. The resistance was measured with a Kohlrausch bridge and a telephone in the usual way. At high pressures there was unmistakable evidence of some sort of change. The electrolytic resistance at first decreased with rising pressure, passed through a flat minimum, rose slowly, and then very rapidly to several times the former value, the rapidity being such as to be almost equivalent to a discontinuity. This pressure of sudden rise was taken as the freezing pressure, since it would be natural to suspect the solid incapable of conducting. The pressure of transition was measured in this way at several temperatures. In all, three sets of readings were made with different forms of apparatus, and the last one six months after the first. In the last determination, the existence of the effect independent of the mercury having been already established, the water was enclosed in glass with a mercury seal, the more effectively to prevent absorption of impurities from the kerosene. The three sets of determinations gave perfectly consistent results. A brief statement as to the existence of a new variety of ice as proved by these experiments was published in the Physical Review, vol. 31, 1910, p. 606. The values as found by these measurements lie on a straight line, and agree with the possible limits found with the compressibility measurements, except that at the highest temperature, 22°, freezing had once been found to take place during the compressibility measurements at a pressure lower than that found here. This was disconcerting.

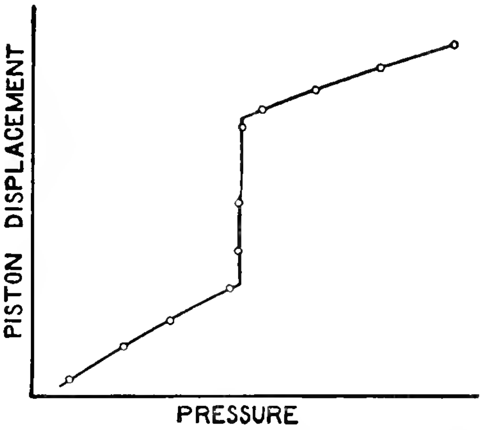

Figure 31. Shows the sharp change of volume during freezing.

The transition curve as found in this way did not give all the information needed for a complete statement of all the quantities involved in the change. A complete statement thermodynamically could be made if it were possible to measure also the change of volume during the change. This seemed at first sight of doubtful possibility. Tammann had made such measurements up to 2000 kgm., but had not been able to go much higher because of leak. As it was, even at 2000, a correction had to be applied for the leak, which was furthermore made as small as possible by the use of a heavy oil, such as castor oil. In the present work it was necessary to go to many times this pressure, the equilibrium pressure even at 0° being 6400 kgm. The difficulty was furthermore increased by the necessity for using some very light and mobile oil to transmit pressure, the castor oil freezing absolutely solid under such pressures as were to be used here. It was felt, therefore, to be a real step when it was found that the packing used in the previous high pressure work was entirely satisfactory when used for this purpose. It is possible with it to retain liquids as mobile as ether, CS_2, pentane, or mercury, absolutely without leak, up to the highest pressures attainable. Measurements of the change of volume have been made up to 15,500 kgm., and this limit was set by yield of the steel cylinders and not by failure of the packing. The readings of the piston obtained were consistent to a few ten thousandths of an inch. The only troublesome effect found with the packing was a slight wearing away by abrasion, owing to the enormous friction. This effect was troublesome only over a wide pressure range; for the limited motion of the piston during freezing or melting the effect was negligible.

It was also a part of the preliminary work to show that the freezing is sufficiently sharp to give trustworthy measurements of the change of volume. The presence of impurity in the water will be shown by a rounding off of the corners of the melting curve and by a change in the value of the equilibrium pressure with the relative proportions of liquid and solid present. Figure 31, chosen at random from the earlier measurements, shows the sharpness of freezing and the consequent freedom from impurity. In the majority of subsequent measurements, the question of absence of impurity having been settled, it was customary to find only one value for the equilibrium pressure, corresponding to a mixture varying from one third to two thirds liquid.

The equilibrium points obtained by the change of volume method were found to be consistently lower than the supposed transition points found by the method of change of resistance. There can be no question whatever but that the change of volume points are the correct ones. The cause of the discrepancy probably is the formation of the eutectic mixture of ice and salt.

Measurements made with the electrolytic conductivity method after the completion of the rest of the experiments, with the new apparatus giving also the piston displacements, showed that the flat minimum in the conductivity curve previously referred to occurs at nearly the pressure of the beginning of freezing. Evidently at first pure ice separates out, leaving the remaining liquid richer in whatever salt produces the conductivity. The total quantity of this salt remains nearly constant, but its concentration and so its association are increasing, so that on the whole we have a decrease in the conducting power. When the pressure has been carried so far that the concentration reaches the eutectic value, the solid salt separates out with the pure ice and we have the sudden jump in the resistance. That this was the case was also suggested by a fact observed once or twice when using water in glass with a mercury seal. This was that the sudden discontinuity might be either a short circuit or an open circuit. Evidently the short circuit is due to the penetration of the mercury through the mass of ice along the core left by the freezing of the pure ice to the walls of the tube.

The points on the VI–L curve were obtained with two different pieces of apparatus. The points between —20° and 20° were found with the apparatus already described as used for the middle temperature range. For the higher pressures, up to 20,500 kgm., another form was used. The particular point of weakness in the middle temperature apparatus is the connecting tube. The new form for the highest pressures was made in one piece, therefore. This has been already described as the third piece of apparatus. It is to be noticed that with this there is no correction necessary for the thermal dilatation of the transmitting fluid. These measurements to the highest pressures were made after the completion of all the others. It was confidently expected to find a new variety of ice, but none was found.

The pressure measurements with the high pressure apparatus were made in the usual way by measuring the resistance of a coil of manganin wire. This had been calibrated by comparison with an absolute gauge up to 13,000 kgm., which was about the limit of the gauge. The pressures above this were obtained by a linear extrapolation, therefore. There does not seem much danger in doing this in view of the fact that the relation is linear within 1/10 per cent up to 13,000.

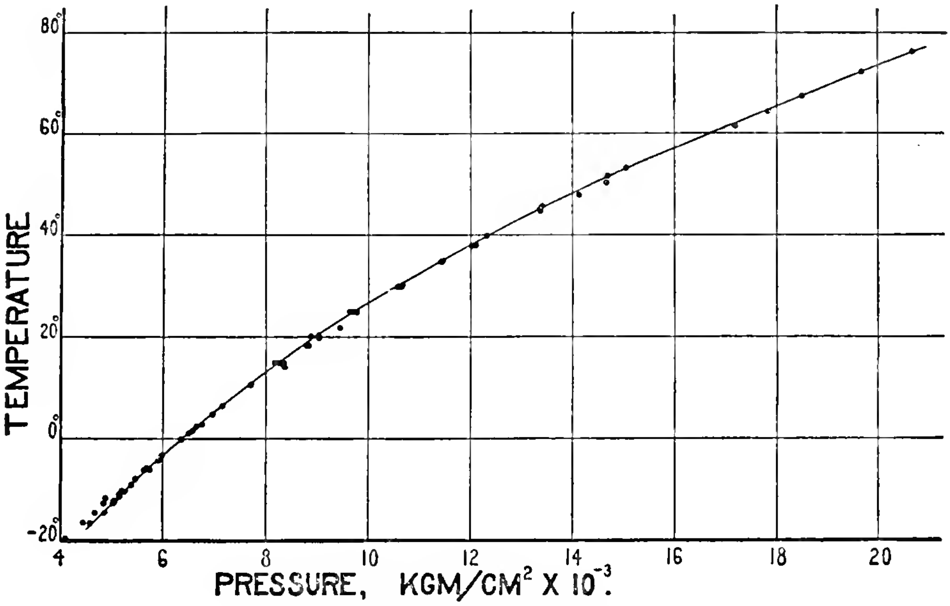

FIGURE 32. The freezing-curve VI–L.

For the middle temperature range the high pressure apparatus offers the advantage of fewer connections over that actually used. There are practical difficulties in the way of its use below 0°, however. It is necessary to submerge the entire lower end of the hydraulic press with the cylinder into the constant temperature bath. There is considerable flow of heat out of the bath along the heavy connecting bars of the press. It would for this reason have been difficult and expensive to have maintained temperatures below zero with the $CaCl_2$ solution. Points have, however, been obtained with the high pressure apparatus over the entire range above zero.

The equilibrium points are given in Table XXVI. and Figure 32. A greater variety of groupings of apparatus have been used for the points

TABLE XXVI.

DATA FOR THE EQUILIBRIUM CURVE ICE VI–WATER.

Date, 1910.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.	Date, 1911.	Temp. C.°.	Pressure, kgm. cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
Oct. 7	0.0	6380^{+}	0.0914	8	0.0	6360^{+}	916
		6360^{-}	0915			6360^{-}	906
8	0.0	6360^{+}	908	9	1.05	6500	
		6340^{-}	908		2.55	6660	
12	6.4	7170^{+}	876	March 3	−3.4	5970	908
		7150^{-}	880		−6.2	5630	943
15	14.0	8380^{+}		4	− 3.2	5990	923
18	15.0	8360^{+}			− 9.2		955
19	14.80	8330^{+}	798		−12.2	5040	1014
		8310	798	6	−10.4	5280	981
24	2194	9470^{+}	712		−11.3	5160	971
		9450^{-}	710		−12.5	5030	963
25	18.4	8840^{+}	776		−14.5	4870	978
Nov. 3	18.42	8800^{-}	758	April 28	30.0	10660	
4	10.63	7710^{+}	878		38.2	12120	
		7710^{-}	842		45.2	13360	
	2.90	6770^{-}	903	May 8	30.2	10680	0.0593
5	4.78	6960^{-}	888	9	38.0	12040	556
	1.65	6580	911		45.8	13410	
11	0.0	6360	916		53.4	15050	
	− 7.8	5470		13	38.4	12120	618
14	− 4.0	5910			48.0	14140	541
	− 4.2	5910	938		55.5	15670	566
17	−11.7	4890	853		61.6	17200	
18	−16.5	4440	900		67.5	18500	
	−19.6	4100	936	25	35.0	11450	647
19	0.0	6370	914		30.0	10590	671
	− 8.9	5390	994		25.0	9790	713
	− 6.0	$5630^{\pm}$	931^{+}	26	25.0	9680	705
			959^{-}		20.5	9050	758
21	−12.2	5080^{+}	1035		15.0	8260	795
		5050^{-}	1004		0.0	6350	928
22	−10.9	5160^{+}	959	29	0.0	6360	902
		5130^{-}	916		15.1	8180	797
Jan. 28 1911.	− 5.7	5650^{+}	997		20.1	8890	754
		5690^{-}	914	30	25.1	9650	707
30	−10.1	5200	1044		30.1	10450	676
	− 6.0	5750^{+}		31	35.0	11470	629
		5740^{-}			40.0	12330	590
31	−14.5	4680			45.0	13380	512
Feb. 1	−16.60	4590		June 1	45.0	13380	563
2	−12.75	4850		13	51.8	14700	516
7	0.0	6340^{+}	932		64.30	17840	
		6350^{-}	895		72.15	19670	
					76.35	20670	

on this curve than for any other. It was on this curve, for instance, that the test was made of the possibility of interaction between water and the substances in contact with it. The water was used in steel or copper or glass vessels, in contact with kerosene or gasolene or mercury. No difference in the equilibrium pressures could be found with any of these different forms of apparatus, but below zero it did seem desirable to use gasolene instead of kerosene. Figure 31 shows piston displacement aaainst pressure for one of the points on this line. The corners of the curve were seldom more rounded than here. The pressure measurements on this curve were made with six different manganin coils.

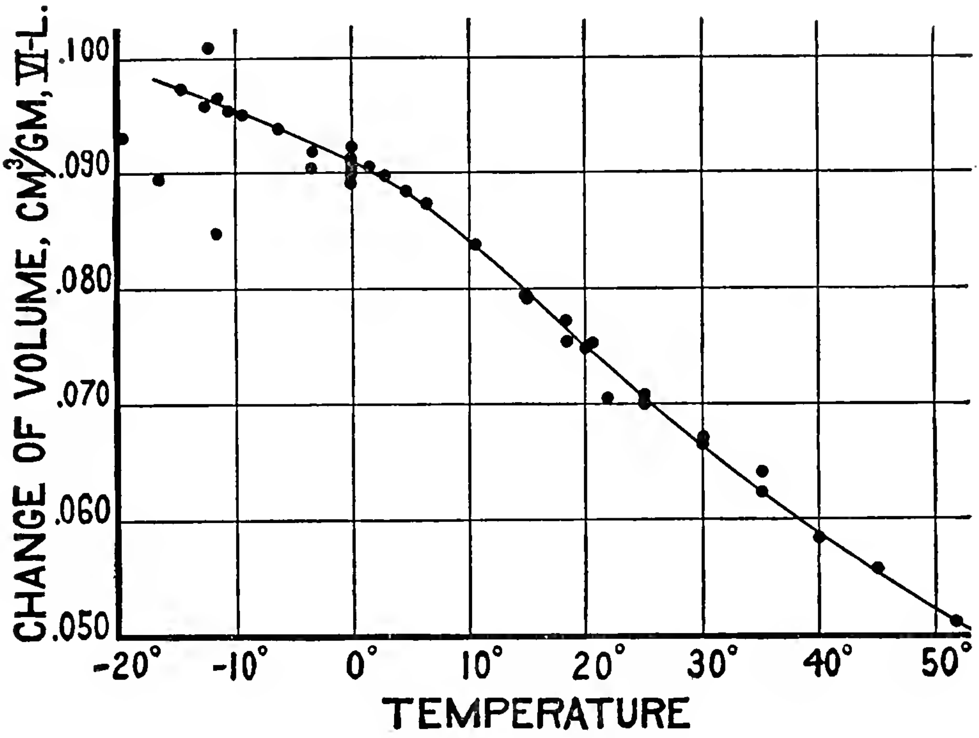

Figure 33. The change of volume when VI passes to the liquid.

Figure 32 shows that the equilibrium curve runs perfectly smoothly, without incident of any kind, from the lowest temperature of the subcooled region, —17°, to the highest temperature and pressure, 76° and 20,500 kgm. The curve is convex upward, like all the other curves of equilibrium between the liquid and the other solid forms of water. Attention is called to the five bad points lying off the equilibrium curve at the lower end.

The change of volume is shown in the same table with the equilibrium points, and graphically in Figure 33. All the values that were ever obtained have been given in the table, but not all these are plotted. In the earlier work, ΔV was found both during freezing and melting, that is, with increasing and decreasing pressure. In the paper on mercury a detailed discussion is given, showing why the values found during decreasing pressure are very likely to be in error. None of these values are plotted. When it has not been specifically stated in the table, the value has been obtained during decreasing pressure. Furthermore, all the points obtained with the kerosene as the transmitting fluid below 0° have been discarded from the figure, with the exception of the three low points to be mentioned later. Nearly all the other points found with the kerosene below zero lie above the curve given.

At the highest pressures there is an entirely new source of error which justifies the discarding of certain points. Before the explanation was found, considerable trouble was given by the points apparently lying on two distinct parallel curves. A succession of points on the low curve, not very regular, was first found, reaching up to 55°. The pressure was then pushed to 18,500 for an equilibrium point, and then after that, more change of volume points were found at lower pressures. These all lay on the high curve. Some of these points were determined three times with different fillings of the apparatus, giving almost identical results, and the measurements were extended back to 0° to compare with the results with the other piece of apparatus, giving approximate agreement here also. The high curve was then followed out again to higher temperatures, giving good points until at 45° the value jumped again to the low curve. The possibility of a new kind of ice was ruled out by the regularity of equilibrium points. Explanation was found in the viscous yield of the steel. This has the curious property of going on at a uniform rate during the time occupied by an experiment, not being asymptotic as one might expect. This yield had been carefully looked for at the lower pressures and not found. During the long course of the experiments so much practice had been obtained that during these last measurements the readings of pressure and piston displacement were made with almost clock-like regularity every six minutes. The yield was so slow as to be imperceptible during that interval of time, and the readings were made with such regularity that the effect was not discovered, as it otherwise would have been, by irregular points on the curve. Once the effect was discovered, it was found entirely competent to account for all observed discrepancies, since the melting occupies a fairly long time, between one and two hours. Another point at 45° was then found, applying a correction for the yield by noting its rate during the half hour before and after change of state. This corrected point lay consistently with the others on the high curve. Evidently the succession of high points found at the same pressures, as well as the previous low points, is to be explained by the seasoning effect of the maximum pressure of 18,500, which was applied between the two sets. The last low point is due to the passing to the viscous state again, after the seasoning effect had disappeared in time or had been overcome by too high a pressure. After the point at 45° another point was found at 52°, applying the correction for yield, and found to lie on the high curve consistently with the others. It did not seem worth while to attempt points at still higher pressures, because the correction becomes more difficult to apply at the high pressures, both because the yield is becoming more rapid, and because the yield does not remain uniform in time at the highest pressures.

TABLE XXVII.

Latent Heat, etc., on Equilibrium Curve Ice VI–Water.

Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm.	dp/dt. From Curve.	dp/dt. Adjusted.	$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$
−15.0	4790	0.0980	100.5	99.6	10.99	59.0	48.0
−10.0	5280	960	103.2	103.5	11.87	63.0	51.1
− 5.0	5810	938	112.4	113.8	12.77	67.1	54.3
0.0	6360	916	118.8	120.0	13.66	70.4	56.7
+ 5.0	7000	884	125.1	125.8	14.51	72.5	58.0
10.0	7640	844	132.0	132.7	15.13	74.4	59.3
15.0	8310	798	140.0	140.0	15.56	75.5	59.9
20.0	9000	751	148.3	148.5	15.84	76.6	60.8
30.0	10590	663	167.3	167.3	16.45	78.8	62.3
40.0	12390	590	189.0	188.7	17.14	81.7	64.6
50.0	14430	523	213.7	215.4	17.69	85.3	67.6
60.0	16690	477	243.0	242.9	18.68	90.5	71.8

The behavior of this cylinder is interesting from the point of view of elasticity. It shows the impossibility of obtaining perfect elasticity very much beyond the original elastic limit. This cylinder had been previously seasoned for use in this work by subjecting it for some hours to 28,000 kgm. The hole was then bored out from the original 7/16 inch to 1/2 inch. The 28,000 kgm. had produced a stretching at the inside from 7/16 inch to perhaps 15/32 inch. Even this high pressure did not completely do away with viscous yield at pressures as low as 10,500. Another interesting feature is the approximate constancy of the rate of yield over a pressure range of 5000 kgm., from 10,500 to 15,500, as shown by the fact that the low points are nearly all the same distance below the corresponding high points. This, too, bears out an observation made before, that elastic after-effects, hysteresis, yield, etc., are greater in larger masses of metal. This cylinder was 4 1/2 inches o. d. and 1/2 inch i. d. No such viscous yield was found in the cylinder with which the change of volume of mercury was measured up to 11,000. This cylinder was 3 inches o. d. and 9/16 inch i. d., and had been previously subjected to 24,000 kgm.

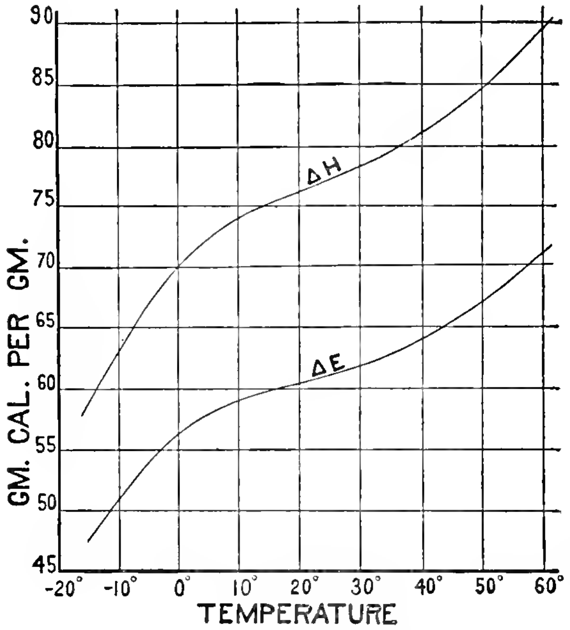

FIGURE 34. The latent heat and the change of internal energy when VI passes to the liquid.

In view of this yield, therefore, the values at the higher pressures which were evidently affected by this yield have not been included in the figure. The curve connecting ΔV with the temperature has a point of inflection, which is not shown by any of the other curves. This is of significance, as will be seen.

The values of ΔH and ΔE found in the ordinary way are shown in Table XXVII. and Figure 34. The point of inflection in both these curves is the particularly interesting feature. Water on passing to VI gives out heat and absorbs work. The work is less than the heat, so that the internal energy of VI is less than that of the liquid.

The data obtained with the high-pressure apparatus may be used to determine one other quantity which the other apparatus could not give, that is, the difference of compressibility between solid and liquid. This may evidently be found from the difference of slope above and below the melting point of the curves connecting piston displacement with pressure. If everything had been ideally perfect the other apparatus should have given it too, but the quantity to be determined is very small, and the irregularities introduced by the transmitting liquid passing from one vessel to another at a different temperature, which might not be perfectly constant, were so great as not to admit of any results of value. With the high-pressure cylinder, everything is in one piece, and there are fewer complications. The values obtained even with this are very irregular, but they are given as having some value in pointing out the direction of the effect at high pressures. The points are shown with sufficient accuracy in Figure 35. This shows a very rapid decrease in the difference of compressibility at high temperatures and pressures.

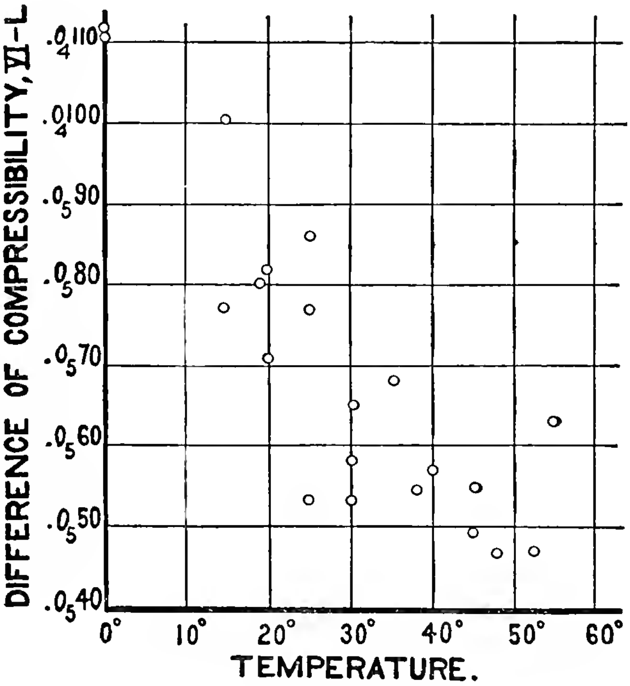

FIGURE 35. Showing the directly determined values for the difference of compressibility between VI and the liquid at various equilibrium temperatures.

This completes the presentation of the actual data. The points were determined separately, those on one equilibrium curve being independent of those on another. But the curves drawn through the points, particularly those for the latent heat and the change of volume, have not been in all cases the best curves through the points of the

TABLE XXVIII.

THE CO-ORDINATES AND CHANGE OF VOLUME AT THE TRIPLE POINTS.

Point.	Temp. C°.	Pressure, kgm./cm.².	ΔV. cm.³/gm.					
III–I–L	−22.0	2115	III–L	0.0466 (461)	L–I	0.1352	III–I	0.1818 (.1823)
II–III–I	−34.7	2170	II–III	0.0215 (208)	III–I	0.1963 (.1958)	II–I	0.2178
V–III–L	−17.0	3530	V–III	0.0547	III–L	0.0241	V–L	0.0788
V–II–III	−24.3	3510	V–II	0.0401 (408)	II–III	0.0145	V–III	0.0546
VI–V–L	+ 0.16	6380	VI–V	0.0389 (388)	V–L	0.0527 (522)	VI–L	0.0916

single equilibrium curves in question, but have been influenced by the behavior of the two neighboring curves meeting at the triple point. Some discussion of the way in which these data were adjusted at the triple points seems called for.

THE TRIPLE POINTS.

The equilibrium curves themselves were in all cases, except one, accurate enough so that the three curves met at the triple point naturally, without the slightest forcing. The one exception is the lower end of the V–L curve, already mentioned, where it seemed desirable to raise the lower end by 0°.2. Even this curve as thus raised is not actually inconsistent with the data. The values of the co-ordinates of the triple points are shown in Table XXVIII.

In selecting the best values for the change of volume, the greatest weight was attached to the curve which was evidently most self-consistent. The values on the other two curves were then so adjusted as to give consistent results with the least violence possible. The full details of the process are shown in the table, which gives the final values, and in parentheses the values found from the individual curves before this process of adjustment. The signs are so chosen that the change of volume is an increase when the reaction runs in the direction in which the symbols read. At every point, the sum of the two smaller changes is equal to the larger.

An adjustment was necessary in seven out of thirteen possibilities. The average adjustment was about 5 parts in 10,000; the maximum, 7 parts in 10,000 of the original volume. The points on the III–L curve were so difficult to obtain, as already explained, that the entire course of this curve was in large measure determined by the behavior at the two triple points at either end.

With regard to the values for the latent heat and the change of internal energy, there was room for more difference of opinion as to the best way of making the adjustment. The latent heat, given by the formula $\Delta H = T \Delta v \frac{dp}{dt}$, is seen to depend on the change of volume, already fixed, and on the slope of the equilibrium curve. The slope was determined graphically from the equilibrium curves. There is chance for considerable error here, and the possibility of introducing comparatively large changes into ΔH by a very slight raising or lowering of the equilibrium curve, too slight in all cases except that of III–L mentioned to introduce a perceptible change in the co-ordinates of the triple point. On the equilibrium curves solid-solid, which run approximately vertically, the latent heat is usually so small as to have very little effect in the adjustment. It was possible to determine this latent heat with a fair degree of accuracy, however, and so this was left without adjustment, the other values being adjusted so as to be consistent with it.

Evidently when the values of the latent heat are properly adjusted, the values of the internal energy will also be consistent, because these differ from the latent heat only by a quantity involving the change of volume, which is already consistent at the triple point.

The tables already given, under the equilibrium curves separately, enable an estimate to be formed of the amount of adjustment necessary. Two values are listed both for $\frac{dp}{dt}$ and ΔH. The first value of $\frac{dp}{dt}$ was obtained directly by graphical construction from the equilibrium curves, and from this the first value of ΔH was calculated directly, point by point. The final value given for ΔH is the value taken from smooth curves so drawn as to check at the triple points. From this final value of ΔH the final value of $\frac{dp}{dt}$ was calculated, and listed in the column of final values. Table XXIX. gives the values of ΔH at the triple points. The III–L curve is the only one that it was necessary to juggle with in any way, and this has already been explained. The symbols are so chosen that heat is absorbed when the reaction runs in the direction in which the symbols read. Thus, the heat I–L is given as 79.8. This means that heat is absorbed when I passes to water.

The changes of internal energy at the triple points are also given in Table XXIX. The positive sign means that the reaction runs in the direction indicated with increase of internal energy.

TABLE XXIX.

Latent Heat and Internal Energy at the Triple Points.

Point.	ΔH gm. cal./gm. (in the first lines). ΔE gm. cal./gm. (in the second lines).					
III-L-I	III-L	50.9 48.6	L-I	−56.1 −62.8	III-I	− 5.2 −14.2
II-III-I	II-III	12.3 11.2	III-I	− 2.2 −12.2	II-I	10.1 − 1.0
V-III-L	V-III	0.9 − 3.6	III-L	61.4 59.5	V-L	62.3 55.9
V-II-III	V-II	−16.0 −19.3	II-III	16.9 15.7	V-III	0.9 − 3.6
VI-V-L	VI-V	0.2 − 5.6	V-L	70.1 62.4	VI-L	70.3 56.8

There are several considerations of interest in connection with the diagram that are not directly concerned with the data as given. These are the questions as to our knowledge that these forms are actually solid, as to the possibility of other forms of ice, the possibility of existence of any form out of its region of stability, and the question of reaction velocity.

Are the Various Forms Really Solid?

This is the first question that naturally presents itself as to this work. The experimental evidence so far has merely been that there is a discontinuous change of volume; the new modifications have not been seen; it is impossible to take the pressure off and examine them, because they are unstable; why then are we justified in assuming that they are solids and not liquids? No direct evidence on this point has been collected in this work; the improbability of their being anything except solids seems so great as to make needless the special arrangement of apparatus necessary to give a direct proof. This was doubly needless, since Tammann has already given direct proof that II and III are solid.

The most striking evidence of Tammann is for III. Tammann cooled a steel cylinder containing ice III to the temperature of liquid air, then released the pressure and took ice III out and examined it. The temperature was so low that the reaction from III to I did not run immediately. III was solid and gradually changed to ice I with large increase of volume. In another experiment Tammann placed an electric contact maker in the water. Freezing to a solid was shown by the refusal of the contact maker to work, both for III and II.

That V and VI are also solid is made probable by two bits of evidence. In the first place, the reactions between V and III and V and VI are exactly similar to those between I and III and I and II. There is no mistaking the difference between a reaction solid-solid and liquid-solid. In the second place, when the reaction VI–V runs with increase of volume, the containing vessel, whether a glass bulb or a fairly heavy metal cylinder, may easily be destroyed. In this reaction V has the larger volume. It, then, must be solid, and probably VI also.

The possible crystalline forms of the different modifications seem to be impossible of direct observation. It would be possible to insert windows in the apparatus and look at all the forms, but this would probably give no information whatever. On several occasions the apparatus was opened and the cylinder of ice I, which had frozen under pressure, was removed. This was always a perfectly structureless, translucent mass, capable of giving no information whatever as to any of its crystalline properties.

Other Possible Forms of Ice.

In a recent paper Tammann[11] has stated the probable existence of a fourth variety of ice, very much like ordinary ice in its properties. The evidence for this was very meagre. Slight discrepancies found on the equilibrium curve I–L could be explained by it; also a momentary rise of pressure on one occasion after the fall of pressure proper to melting had begun. Seven successive attempts of Tammann to get the same effect again failed. It is evident that the discrepancies on the I–L curve might be due to pressure errors; a new manometer used by Tammann gave pressures 50 kgm. lower than the former one, and we have already seen that the crossing of the I–III and the I–II curves found by Tammann must be set down to pressure errors. Finally, Tammann states that ice IV may separate out from water when cooled

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[11] Tammann, ZS. Phys. Chem., **72**, 609–631 (1910).

to —7°. The fact that there is a different modification is shown by placing the ice so formed in a dilatometer, and warming slowly. At —2° there is a sudden increase of volume of about 1/10 per cent, followed by regular increase of volume and melting at 0°. The ice IV appears, therefore, to have a slightly less volume than ice I. In this experiment, sufficient attention does not seem to have been paid to the possibility of there being internal strains in the ice. It seems plausible that the water, freezing suddenly as it must at —7°, might so freeze as to produce a slight volume compression. On increasing temperature, this strain is relieved by the softening of the ice in the neighborhood of the melting point. This weakening of the ice near the melting point has been established by experiment. At high pressures it is undoubtedly true that internal strains may produce anomalous effects, as was found on at least two occasions.

Entirely apart from Tammann, however, there is independent experimental evidence of the possibility of two forms of ice, differing in density by 1/10 per cent, the amount found by Tammann. Two modern experimenters, Nichols[12] and Vincent,[13] as well as several previous observers, have each found that the density of ice may have either one of two distinct values. The difference seems to be connected with the manner of formation of the ice, whether natural or artificial. The natural ice, when kept for some time, tends to assume the value for the artificial ice. Barnes,[14] however, failed to verify the work of Nichols, and the most recent work of Leduc suggests that the discrepancies may possibly be due to dissolved air.

The question is as yet unsettled, with the probability, however, that the ice does not exist. In order to leave open the possibility of the establishment of its existence, however, the numeral IV has been reserved for this according to Tammann, and the first of the two new varieties found in this paper has been called V.

Besides this, there have appeared from time to time spasmodic notices concerning ice existing in crystalline forms other than the hexagonal. This is usually natural ice, which has been subjected to intense cold in the far north. None of these statements seem to have been subsequently verified, however.

In the course of the present work evidence was obtained as to the possibility of the existence of another form at high pressures. It seems

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[12] Nichols, Phys. Rev., **8** (Jan., 1899).

[13] Vincent, loc. cit.

[14] Barnes, Trans. Roy. Soc. Canada, **3**, Sect. III, 3–27 (1909), and Phys. Rev. (July, 1901).

probable that the five discrepant points found on the lower end of the VI–L curve may be due to the presence of some other form of ice than VI. These points were obtained on two separate occasions more than two months apart. Every one of the equilibrium points which have ever been obtained has been plotted in the diagrams, except a few where the temperature control was defective, and which have been mentioned. There are nowhere any points lying so far off the curve as these five. It seems hardly probable that the five worst points should have all been bunched in the same place, all lying consistently on a new curve. The probability of there being a new kind of ice is strengthened by the change of volume measurements made at these same points. These points are shown on Figure 33 for the change of volume VI–L. They lie far below the smooth curve, further than even the wildest of the discarded points, and they also lie consistently on another curve. The probability seems very strong for another modification of ice. This modification, if it does exist, is unstable in the locality found, V being a more stable form. Whether this new form has any region of stability at all is open to question; there is no necessity for it.

Whether there are still other forms stable at the highest pressures is of course a matter of pure conjecture. No inconsistencies were ever found suggesting in any way the existence of another form in the region studied. The domain of stability of ice VI as found is already five times more extensive than that of any of the other modifications. Furthermore, the course of the freezing curve and of the change of volume curve is such that both of these curves could be extended without difficulty to infinite pressures and temperatures. VI seems at any rate suited to be a final modification.

In this connection, some comment seems called for as to the possibility of predicting new forms. Of course it is well known that there is no such possibility from the equations of thermodynamics alone; the domain of existence of any form may be extended indefinitely in either direction without running into thermodynamic inconsistencies. But every substance, besides satisfying the identical relations of thermodynamics, also satisfies its own particular characteristic equation. This characteristic equation is determined by the special internal mechanism of the substance in question. It seems *a priori* possible that the approach of a new form should be heralded by some change in the mechanism, which should have its effect on the characteristic equation. But no such effect as this has been noticed. One substance may be extended across the boundary line into the unstable region beyond, with no appreciable change in either the compressibility or the dilatation, the two quantities determining the characteristic equation. And on an equilibrium line, the neighborhood of a triple point does not cast its shadow before, either by a change in the direction of the equilibrium line, or of the change of volume line, or of the curves of latent heat or internal energy. So far as the data presented in this paper are concerned, there seems to be no way of making the prediction. Nevertheless the conviction remains that if one had a complete description of the internal mechanism, it would be possible to find some criterion as to the possible stability of other configurations. What additional data are needed to give a sufficient knowledge of the mechanism? The question is an interesting one for investigation.

THE POSSIBILITY OF SUBCOOLING OR SUPERHEATING.

The facts regarding this subject have nearly all been mentioned incidentally in the course of the detailed description of the experiments. Although no observations of the possibility of subcooling or superheating were made separately for their own sake, yet the observations collected incidentally on this subject are nearly as numerous as all the other observations together. The effect was of course observed during every measurement of a change of volume, and frequently on other occasions. It was likely to be a very troublesome effect, preventing the appearance of the modification desired, so that at least sufficient familiarity had to be obtained with the slight regularities shown by the apparently confused mass of facts so that the modification of ice desired could be forced to appear.

First with regard to the solid phases. It has been found possible to go across nearly every one of the boundary lines into the region of instability on the other side. I has been found in the region of III and II; II in that of I (at low temperatures); III in that of I, II, and V; V in that of III, II, and VI; and VI in that of V. The only excursion of this kind which has not been found possible is that of II into the region of III or V. This latter reaction always ran immediately on passing the slightest amount into the neighboring country. For the other reactions no fixed limits could be set to the extent by which it was possible to overstep the boundary. The amount depends on the size and shape of the vessel, on the materials in contact with the ice, on the element of time, and on caprice. In general, however, the limits became narrower at high temperatures, as one would expect.

With regard to the passing from the solid to the liquid, the experience here is but a verification of the experience of everybody else; that it is impossible to superheat a crystalline phase with respect to the liquid. No good reason for this has ever been given, but no exception has ever been found, and it is coming to be regarded as a law of nature. One would think that if there were ever a chance to find an exception it would be here, where the materials are made viscous by the high pressure, and where the reaction must run with increase of volume against the pressure, doing considerable external work.

On the other hand, it is the easiest possible matter to subcool the liquid with respect to any one of the four solid phases bordering on the domain of the liquid. In fact, it is often a matter of some difficulty to start the reaction liquid-solid, superpressures of 1500 or 2000 kgm. being sometimes necessary. The amount of superpressure or subcooling necessary to start the reaction is again a matter of caprice. On the VI–L curve, however, where the greatest range was open to observation, there seemed to be in general a tendency for the subcooling to increase at high pressures.

In consequence of the possibility of carrying one phase into the region of another, it is possible to prolong certain of the equilibrium lines beyond the triple point into the region of instability beyond, thus realizing equilibrium points between two unstable phases. The equilibrium lines which have thus been extended are: I–L into the region of II, III–L into the region of I (by Tammann, not in the present work), III–L into the region of V, I–III into the region of II, III–V into the region of II, and VI–L into the region of V. It may also be possible to extend II–III into the region of I, although this was not tried. The only curves which it was found experimentally impossible to extend were II–III into V, II–V into III, and V–L into VI. There seems to be no obvious generalization about the possibility of extending these curves; everything seems to depend on the particular character of the substances in question. There was one plausible generalization from only two instances, which was missed by a very narrow margin, namely that it is impossible to extend a melting curve at the upper end into the region of another solid. The attempt always failed on the V–L curve, and until the very last day failed on the III–L curve. On this very last day, when the change of volume points II–III–V were being found, it was desired to pass from III to V. The greatest difficulty was experienced in doing this. Pressure was increased on III at about −20° to 4500, and the temperature then raised until III began to melt, thus spoiling the generalization. It was finally necessary to lower the temperature to −40° before V appeared. It is therefore conceivable that there are circumstances when V–L might be extended into VI, or II raised into the region of III or V.

It may be mentioned that at every triple point there is at least one equilibrium line which it has not been found possible to cross. At four of the five triple points there are two such lines, and at the fifth, I–II–III, the possibility of carrying II into the region of I was not tried. At three of the five points water is one of the substances, so that the statement is obviously true; at the other two points the solid II has the same relation to the solids above it that the solids above have to the liquid above them.

It was not found possible to extend any two of the curves so far into a region of instability as to give a triple point between three unstable phases, nor was the third unstable curve starting from this unstable triple point ever found. This third curve would have no region of stability whatever. The nearest approach to this was in the extensions of the III–L and VI–L curves. No especial attempt was made to realize such an unstable triple point, however, as it would have been a matter of considerable difficulty, but there seems no reason why such a point should not be found.

No such constancy was ever found in these subcooling experiments as to suggest the necessity of the existence of the metastable limit, as is claimed by many writers. With a particular piece of apparatus it may be possible to obtain fairly consistent results, but when the apparatus is being continually changed as it was here there seems to be no obvious regularity. There is no reason why there should be, if the formation of the nucleus of the new phase, which starts the reaction, is a matter of chance as seems likely. Owing, however, to the fact that there is at every triple point one equilibrium curve which it is not possible to cross, there are going to be lines reaching from every one of the triple points limiting the existence of one or more of the phases, which give the same impression as the metastable lines recently drawn by Tammann in the neighborhood of the triple point I–III–L for water, and also in the neighborhood of a triple point of phenol.[15]

In one respect the possible amount of subcooling showed great regularity and is of sufficient significance to deserve special mention. This is the fact, already noted, that a form is much more likely to appear again if it has appeared recently before. This fact was of great convenience in obtaining the change of volume points, because here one phase has to be allowed to be completely replaced by another, and the first phase is then wanted again in obtaining the second ΔV point. Very little difficulty was experienced in getting the desired form to appear under these circumstances. This was particularly true on the V–VI and the V–L curves, the modification V being the hardest to

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[15] Tammann, ZS. Phys. Chem., **75**, 75–80 (1910).

obtain initially. On the V–L curve a succession of ΔV points was obtained without difficulty, V always putting in an appearance when desired, separating directly from the liquid with very little subcooling, although V was never obtained directly from the liquid the first time, but only by way of VI after considerable subcooling. This ability of V to separate directly from the water could be retained for several hours at points removed 1000 or 2000 kgm. from the equilibrium curve. The ability was once retained over night, pressure not being far removed from the equilibrium curve. The disposition to react depends both on the element of time and on the amount by which pressure has been changed from the equilibrium value. This predisposition to react is lost if a third modification has intervened. Thus, on the occasion mentioned, when III was melted at 4500 kgm. in the endeavor to obtain V, only a half hour previously the reaction II–V had been running in either direction with the greatest facility. The subsequent conversion of II into III resulted in the complete loss of disposition of V to appear.

In explanation, there must be some structure in both the liquid and the solid not ordinarily accounted for, some nucleation or aggregation of the molecules left as a heritage from the previous modification, which is particularly adapted to fall back again into the old position. The possibility of such nuclei in the solid must show that the molecules in a crystal are not arranged in the absolutely symmetrical way usually thought of. The fact that these nuclei may persist for some time in the solid does not seem so surprising as the fact that they exist at all. For the liquid, the reverse is the case. The existence of nuclei might be expected; they are known to exist even in a gas, but that these nuclei may persist for some hours in an assemblage of molecules supposed to be in constant interchange with each other might not be expected at first. The disappearance of these nuclei is a matter of extraordinary slowness, considering the usual times involved in the motion of the molecules as a liquid. Doubtless the formation of these nuclei is intimately connected with the freezing of a liquid for the first time. The freezing can start only from one of these nuclei. The formation of one of these nuclei in an unimpregnated liquid is a matter of chance, and until the molecules do happen to fall together into the right position the freezing cannot start.

Reaction Velocity.

Here again no accurate measurements were made. The velocity depends on too many things to allow quantitative results of value without the expenditure of a great deal of time. These disturbing factors are such as the size and shape and material of the containing vessel, the rapidity of heat conduction, and the distance from the equilibrium line. But just as for the question of subcooling, so here, every measurement ever made, whether of the equilibrium pressure alone or of the change of volume, involved this matter of reaction velocity. One had to be sure before making a reading that the reaction had stopped running, and in the endeavor to waste no more time than was necessary the progress of the reaction was constantly watched, so as to make the reading as soon as possible after sensible equilibrium had been reached.

There are two distinct types of behavior of the reaction velocity, according as the reaction is between a solid and a liquid or between two solids. In general the reaction between solid and liquid was slower than between solid and solid. The time for the completion of the reaction liquid-solid was about two hours on the I–L, V–L, and lower end of the VI–L curve. No particular variation in this time was noticed from one end to the other of the I and V curves, but at the upper end of the VI–L curve, the velocity had been very appreciably accelerated, the time for completion of the reaction at the upper end being about one hour. On the III–L curve, as already mentioned, the reaction was very much slower. It was not practicable here to wait for the reaction to run to completion, but the equilibrium points were taken as the mean of values approached from above and below. This shows that the velocity depends on the form into which the water is transformed as well as on the heat of reaction, for the heat III–L is of the same magnitude as that of the neighboring modifications I and V. On all the curves the velocity seemed the same for melting as for freezing.

The most striking behavior of the reaction velocity is shown by the reaction solid-solid. The velocity ranges from explosive rapidity at the end near the triple point to such sluggishness 20° further down as to make further prolongation of the equilibrium curve out of the question. Of course the very low heat of reaction would lead one to expect, other things being equal, a high rate of transformation, but that the heat of reaction has practically nothing to do with it is shown by the enormous temperature coefficient of reaction velocity, while the heat of reaction is practically independent of temperature. The slowness of the reaction does not depend so much on the actual temperature as on the nearness of the triple point. Thus I–II is explosive at its triple point, −35°, while at −35° III–V is almost impossible; III–V is explosive at its own triple point, −17°, but at this temperature V–VI may take a couple of hours to run to completion.

The explanation does not suggest itself. The mere fact of such rapid reactions between solids is itself sufficiently surprising. It does not seem as if the mechanism could be the same as that of an ordinary chemical reaction. It is as if the molecules changed from one crystalline arrangement to another by snapping round on their axes, like the supposed molecular magnets of a piece of iron in a magnetic field. The high temperature effect is difficult to account for. Certainly no known viscosity effect has so high a temperature coefficient.

Some connection seems likely between this high velocity at the triple point and the impossibility of superheating a solid. There is no doubt but that at this point the molecules of the solid have a perfectly astounding possibility of motion. The passage to the liquid may still depend on the chance formation of nuclei in the solid, but the freedom of motion of the molecules in the solid may be so great as to secure the practically instantaneous formation of the proper grouping. This recalls the question proposed a few pages back as to the possibility of predicting the presence of a new phase from the behavior of a single other phase. Here we have a hint as to the possibility of predicting a third phase by an enormous reaction velocity between two others.

THE COMPRESSIBILITY OF THE DIFFERENT FORMS OF ICE.

These compressibilities have not, with one exception, been directly measured, but it is possible, nevertheless, to obtain some idea as to this magnitude for those varieties of ice which are anywhere in equilibrium with the liquid. This includes all the varieties except II. The compressibility of VI has been directly measured above 0°, and the initial compressibility of ice I has been computed. It has been already stated that the data do not possess the requisite accuracy to permit a direct determination of the compressibility of the other forms of ice. The approximate determination comes by finding the actual volume of the different kinds of ice along the equilibrium lines. The volume of water is known along these lines, and also the change of volume when the liquid passes into the solid, so that the actual volume of the solid may be obtained. This volume will change with temperature and pressure along the equilibrium line. The approximation to the compressibility is made by assuming that the change of volume due to changes in temperature along an equilibrium line is negligible compared with the change due to pressure. The error so introduced may be found at 0° for ice I at atmospheric pressure, where it is 3 per cent. Furthermore, at any point except in the immediate neighborhood of the origin, the thermal expansion of the ice is very probably less than that of the liquid with which it is in contact. This enables us to put an upper limit of 10 per cent as the probable error introduced by assuming all the change of volume along an equilibrium curve to be brought about by changes of pressure.

The complete values of the volume are shown in Table XXX., which gives the approximate compressibility along these curves. For comparison, the approximate compressibility of the water at the corresponding pressure and temperature is also given. In consequence of the change of volume due to temperature, the quantity listed as compressibility is too big on the ice I curve, and too small on the other curves which rise to higher temperatures with higher pressures. The compressibility of the ice is uniformly less than that of the water, as one would expect, varying from 1/3 to 2/3. On all the curves except the III–L curve, the compressibility shows a very marked decrease with rise of pressure, the decrease being more rapid proportionally for the liquid. The same decrease would probably also have been shown on the III–L curve, if it had been possible to make the measurements of the change of volume with greater accuracy. On the I–L curve, the change for a range of pressure of only 2000 kgm. is abnormally high. This might be accounted for by a negative temperature coefficient of expansion of ice at the lower end of the curve. The change of volume measurements I–III have already suggested this as a possibility. The change of compressibility with pressure is greatest at the low pressures, being particularly great in the region of instability of VI. In general, when one variety of ice replaces another, one would expect the new form stable at the higher pressures to show the lower compressibility, corresponding to the smaller volume; but this is certainly not true in the case V–VI, and probably not true when III replaces I. The compressibility of each modification seems to be a property inherent in that modification, depending probably on the symmetrical arrangement of molecules in the crystal, and not depending so directly on the volume.

As verifying these values very roughly, the directly determined difference of compressibility between L and VI has been shown in Figure 35. The values are evidently not of any great regularity. The only two points found below 15°, at 0°, are much too high. These would give a value for the compressibility at 0° of $.0_530$ as against $.0_56$ from the data above, $.0_56$ being too small. But in the region where the points are thicker, between 15° and 50°, the agreement is better, discrepancies being of the order of 0.0_51. These points run to higher pressures than the actual determinations of the compressibility of water, and do show strikingly the rapid decrease in the difference between the com-

TABLE XXX.

Volume and Approximate Compressibility of Ice on Equilibrium Curves.

Pressure, kgm./cm.².	Temp. C.°.	Vol. of Water cm.³/gm.	ΔV. cm.³/gm.	Vol. of Ice cm.³/gm.	Approx. Compressibility of Ice.	Compressibility of Water at Same Point.
			Ice I–Water.			
0	0	1.0000	0.0900	1.0900	0.0_435	0.0_452
500	− 4.1	0.9777	0998	1.0775		
1000	− 8.7	9588	1096	1.0684	0_416	37
1500	−14.0	9414	1201	1.0615		
2000	−20.3	9253	1318	1.0571	0_58	29
			Ice III–Water.			
2000	−22.5	0.9250	0.0476	0.8774	0.0_591	0.0_430
2500	−20.1	9099	373	8726		26
3000	−18.3	9874	286	8688		24
3500	−17.0	8867	231	8636		21
			Ice V–Water.			
3500	−17.0	0.8870	0.0785	0.8085		
4000	−13.6	8781	733	8048	0.0_572	0.0_4190
4500	−10.1	8694	681	8013		
5000	− 7.0	8610	634	7976	53	164
5500	− 4.2	8543	590	7953		
6000	− 1.6	8478	549	7929	47	140
6500	+ 0.6	8418	516	7902		
			Ice VI–Water.			
4500	−18.0	0.8689	0.0985	0.7705		
5000	−12.8	8604	968	7636	0.0_4102	0.0_4164
5500	− 7.7	8536	940	7596		
6000	− 3.2	8472	928	7544	0_572	140
6500	+ 1.1	8418	905	7513		
7000	5.0	8370	882	7488	55	126
8000	12.6	8271	816	7455	48	120
9000	19.5	8156	755	7401	43	110
10000	26.0	8055	697	7358	37	104

pressibility of water and VI with rising pressure. This point has some bearing on the discussion of the general nature of the change of state solid-liquid at high pressures.

Discussion of the Results.

So far in this paper merely the numerical results have been presented, without much discussion of their significance. For the liquid, the change of volume at different temperatures and pressures has been found, without discussing the shape of the p-v-t surface which these combine to give. For the solid states, the data have been presented for each variety of ice separately, without any consideration of the general features which may be common to all. The object of this discussion is to give a comprehensive survey of all the results, especially for the transition liquid-solid, and to point out the theoretical significance of these data at very high pressures.

For the liquid, the results will have their chief interest in showing how water passes from an abnormal liquid at low pressures to a normal one at high pressures. The data do not have so much suggestiveness for a theory of the liquid state as would those for some normal liquid, and in any case it would be dangerous to generalize from the behavior of a single substance, but the results at the higher pressures do suggest at least the nature of the effects to be expected in general at high pressures.

The results for the liquid at even temperature and pressure intervals have been collected in Table XXXI. In this table the smoothed results obtained separately above 0° and below 0° have been given without any attempt to smooth the values of either set so as to make connections with those of the other. But the fact that the two independent sets of determinations do run smoothly into each other makes probable the accuracy of the work. Above 7000 kgm. the value of the thermal dilatation used in computing the table was obtained by an extrapolation. This is probably good up to 10,000 kgm. in giving the actual volume at any temperature and pressure within the narrow range of existence of liquid water, but the use of the tables in any theoretical considerations demanding knowledge of the derivatives would be dangerous at the highest pressures. Above 3000 kgm., and indeed above 2000 kgm., the dilatation has been assumed to be independent of the temperature over the range of 22°, as has been sufficiently shown by the work of Amagat. For values below 2000 the variation of the dilatation as found by Amagat has been used in computing the table. Of course below 0° the variation of dilatation with temperature was given by the data of this paper.

TABLE XXXI.

The Volume of Water at Regular Pressure and Temperature Intervals.

Pressure, kgm./cm.²	Volume.									
	−20°.0.	−15°.0.	−10°.0.	−5°.0.	0°.0.	+5°.0.	+10°.0.	+15°.0.	+20°.0.	+25°.0.
0	....	....	1.0017	1.0006	1.0000	0.9999	1.0001	1.0007	1.0016	1.0028
500	....	....	9800	9783	9776	9782	9791	9800	9812	9825
1000	....	....	9606	9592	9586	9596	9609	9623	9638	9654
1500	....	9401	9413	9404	9407	9420	9435	9451	9467	9483
2000	9233	9240	9248	9257	9265	9281	9298	9315	9332	9349
2500	9083	9092	9102	9115	9131	9148	9166	9185	9203	9222
3000	8957	8966	8978	8991	9009	9026	9014	9063	9081	9100
3500	....	8860	8872	8884	8903	8923	8944	8964	8984	9005
4000	....	8764	8772	8784	8805	8823	8842	8860	8878	8897
4500	....	....	8680	8691	8713	8721	8749	8767	8785	8802
5000	....	....	8593	8604	8626	8643	8661	8678	8696	8714
5500	....	....	....	8531	8548	8565	8582	8599	8616	8633
6000	....	....	....	8464	8480	8496	8513	8529	8545	8561
6500	....	....	....	....	8414	8429	8444	8460	8475	8490
7000	....	....	....	....	8356	8370	8384	8398	8412	8426
7500	....	....	....	....	....	8309	8321	8334	8346	8358
8000	....	....	....	....	....	....	8262	8273	8284	8295
8500	....	....	....	....	....	....	....	8208	8218	8228
9000	....	....	....	....	....	....	....	8149	8157	8165
9500	....	....	....	....	....	....	....	....	8099	8106
10000	....	....	....	....	....	....	....	....	8046	8050

Before discussing the shape of the p-v-t surface as given by the determinations of compressibility, it may be well to review briefly the known behavior of water, especially with regard to the differences it shows when compared with ordinary liquids.

All ordinary liquids show a decreasing compressibility with rising pressure, the compressibility decreasing faster than the volume, and they also show an increasing compressibility with rising temperature. The mathematical equivalent of this last statement is that the thermal dilatation decreases with rising pressure. This normal behavior is exactly as we would expect if we regard the liquid as composed of nuclei of more or less invariable volume, separated by spaces which may be altered in size by pressure and temperature. It is not necessary for a qualitative understanding of the phenomena even to inquire whether these nuclei are subatomic or atomic; that is, whether the major part of the compression is given by the change of volume of the spaces between the atoms or by changes in volume of the atoms themselves.

For water the effects are anomalous. The compressibility decreases with rising pressure, as it does for everything else, but with rising temperature the compressibility at first becomes less, passes through a minimum, and then becomes greater again. This minimum is situated at about 50°. The position of the minimum is nearly independent of pressure but the minimum itself becomes less and less pronounced with rising pressure, and at 3000 kgm. has entirely disappeared. Corresponding to this anomalous behavior, the dilatation shows anomalous behavior with rising pressure, becoming greater with greater pressure at temperatures below 50°. It has been recognized by Amagat as possible, however, that at temperatures below 50° the dilatation would decrease with rising pressure at pressures sufficiently high. In the immediate neighborhood of 0° and atmospheric pressure, there are special anomalies connected with the maximum density point. In particular, the temperature of maximum density, which at atmospheric pressure is at about 4°, is depressed by rising pressure. This depression of the maximum density point is nearly linear with the pressure, and is so rapid that at 300 kgm. it has fallen below the freezing temperature at that pressure. So much has been shown by Amagat, [16] who worked up to 3000 kgm. The results may be briefly summed up in the statement that water, abnormal at low temperatures and pressures, tends to become normal at high temperatures and pressures.

Now consider the information given by the present data, examining

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[16] Amagat, loc. cit.

first the compressibility data above zero. Of course the rough facts already known appear immediately from an inspection of the figures. The compressibility decreases strikingly with rising pressure and is less at 22° than at 0°. Figure 36 shows the compressibility (= $\left(\frac{\partial v}{\partial p}\right)_T$) at 0° and 22°. At 10,000 kgm. it has decreased to 1/4 of its initial

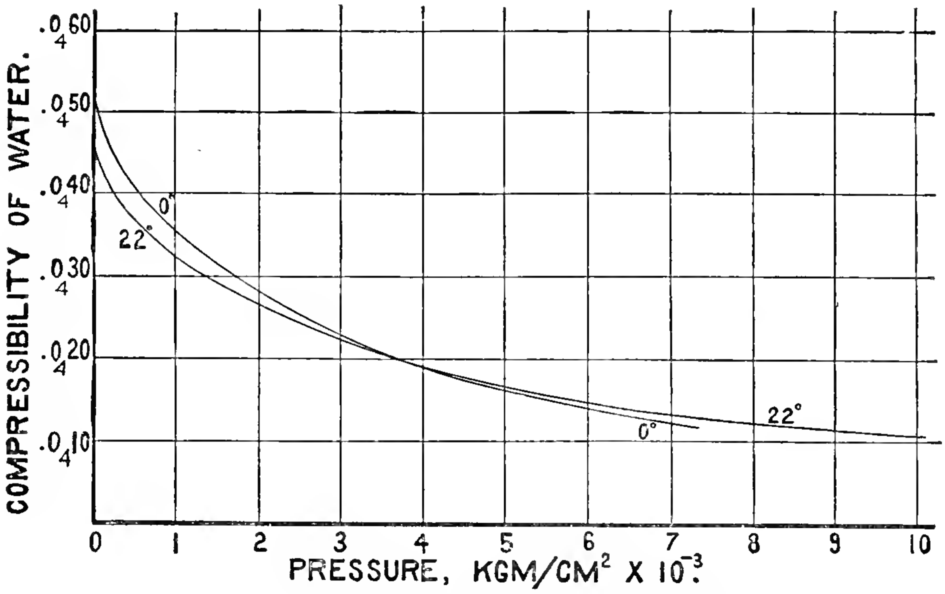

FIGURE 36. The compressibility $\left(\frac{\partial v}{\partial p}\right)_T$ of liquid water as a function of the pressure at 0° and 22°.

value. The figure shows also the crossing of the compressibility curves; at low pressures the compressibility at low temperatures is higher than it is at high temperatures, but with rising pressure the abnormality disappears, and beyond 4000 kgm. the compressibility is higher at the higher temperatures. The variation of thermal expansion between 0° and 22° is shown in Figure 37. This rises to a maximum at nearly 4000 kgm. and then falls again. The rise to the maximum is much more rapid than the fall away from it. This maximum verifies the surmise of Amagat that the dilatation at any temperature would ultimately decrease with rising pressure for pressures sufficiently high. The position of this maximum evidently corresponds to the crossing of the two compressibility curves at 0° and 22°, for we have

$$\frac{\partial}{\partial t}\left(\frac{\partial v}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial v}{\partial t}\right) = 0.$$

The usual explanation of the abnormalities shown by water at atmospheric pressure is on the basis of polymerization. The effect of decreasing temperature is to increase the polymerization. For the present purpose we may think of the molecule stable at higher temperatures as a single molecule and that at lower temperatures as a double molecule, although the latter is more probably triple and the former double. The double molecule must furthermore be thought of as occupying more than twice the volume of each of the single molecules of which it is composed. The effect of a decrease of temperature on volume is twofold: a decrease such as takes place in any normal liquid, and an increase due to the clustering of single molecules into double ones. This increase becomes increasingly rapid at low temperatures because of the increasingly rapid polymerization. At 4° it has become sufficiently rapid to neutralize the natural decrease, and at lower temperatures volume increases with falling temperature. The way in which polymerization is affected by pressure can best be discussed after reviewing the data below 0°.

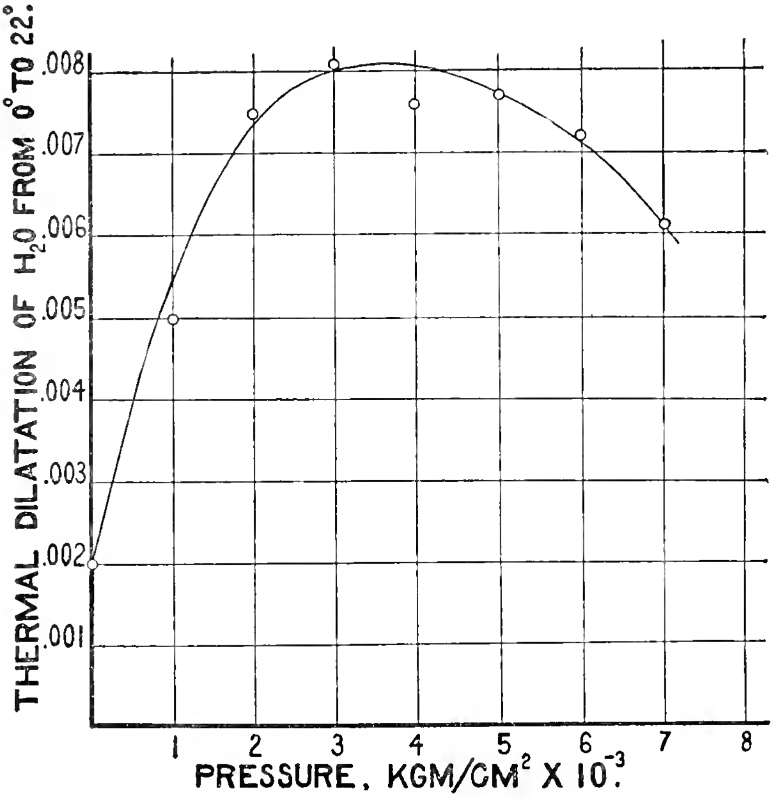

FIGURE 37. Shows the total change of volume of water between 0° and 22° as a function of the pressure.

The data below 0° show still more strikingly than those above 0°

the abnormality at low pressures followed by normal behavior at high pressures. No previous measurements seem to have been made within this region, although the principal effects are within the reach of previously attainable pressures. At atmospheric pressure the study of water at low temperatures is prevented by the accident of freezing. It will pay us, however, to imagine what would be the relation between temperature and volume on the present theory of polymerization if it were possible to subcool the water indefinitely. At high temperatures we evidently expect the water to behave normally, for its molecules are all single molecules of the same kind, and similarly at very low temperatures, where the molecules are all double molecules, we should expect the behavior to become normal again. The curve connecting volume with temperature for a normal liquid is of the form shown in Figure 38, the dilatation becoming more rapid at high temperatures. These considerations lead us to predict, therefore, a curve of the shape shown in Figure 39 for water. Experimentally it has been found possible to follow this only as far as —10°, not far enough to reach the first point of inflection. The effect of increasing pressure must be to change in some continuous way the curve of Figure 39 into that of Figure 38.

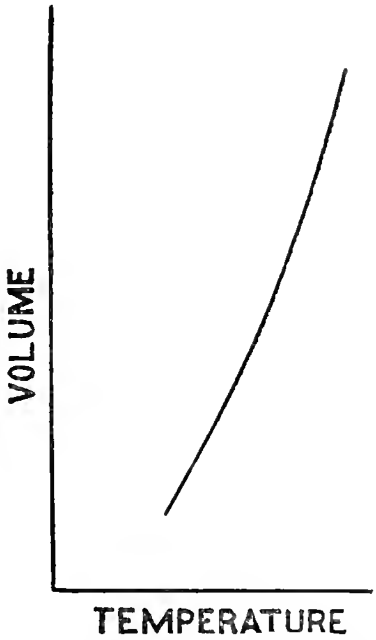

FIGURE 38. The relation between volume and temperature for a normal liquid.

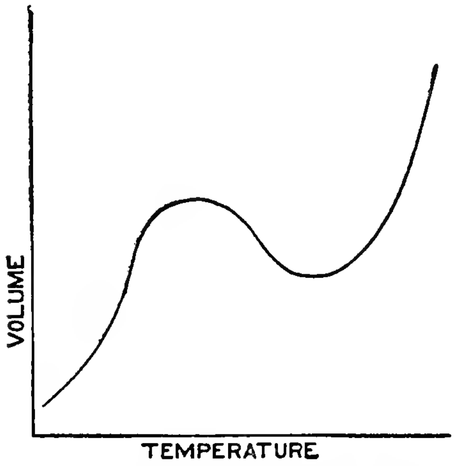

FIGURE 39. Hypothetical relation between volume and temperature for liquid water if it could be subcooled indefinitely without freezing.

The data indicate very strikingly the way in which the abnormality is effaced. Figure 40 shows this. In this figure the relation between volume and temperature for various constant pressures is plotted directly from the data of Table XXXI. Each separate curve is drawn to scale, but the curves for different pressures have been pushed together, so as to come within the limits of the drawing. The actual separation of the curves is about ten times that shown. The pressure and the value of the volume at 0° are indicated on each curve. The manner of transition from abnormal to normal is shown distinctly, and requires no comment. At 1500 kgm.

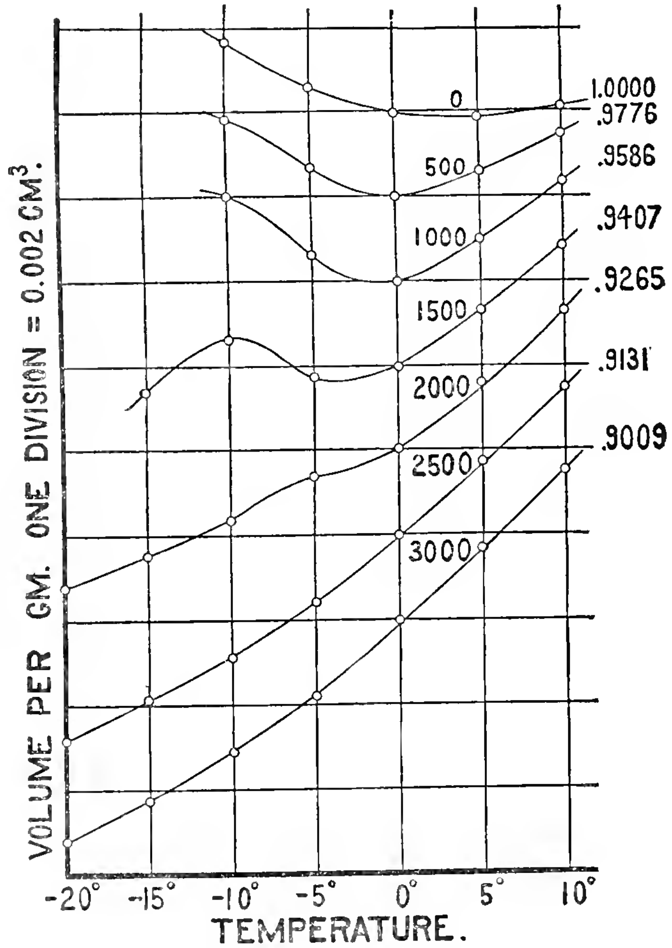

Figure 40. Curves showing the relation between volume and temperature of water for various constant pressures. The numbers in the body of the diagram show the constant pressure of each curve; the numbers to the right show the volume at 0° of the liquid at the indicated pressure. If drawn to scale the curves should be separated about ten times as much as shown.

we actually have realized a curve with both a minimum and maximum, like the conjectural curve at atmospheric pressure. The curves show one thing in connection with the previous experiments, namely, that the depression of the maximum density point with pressure cannot continue linear with pressure much beyond 300 kgm., the limit of the previous experiments, but the temperature of the maximum becomes nearly independent of the pressure until the maximum entirely disappears at higher pressures.

Figure 40 shows the results only to 3000 kgm. Up to this point the dilatation at 0° has been increasing with rising pressure. But the fact that the curves of Figure 4 pass through a maximum at about 3200 kgm. indicates a return to normal behavior. From here on the dilatation decreases with rising pressure. The position of this maximum evidently corresponds to the position of the maximum of the dilatation at 3700 kgm. found between 0° and 22°. One would expect some change in the position of the maximum toward lower pressures at lower temperatures, but even if there were none, the agreement is perhaps as good as could be expected when one considers how very small the experimental quantities are which are involved below 0°.

As far as 4000 kgm., the curves of Figure 4 have been in perfect accord with the manner of transition shown in Figure 40. Above 4000, however, if the curves are extrapolated in the direction in which they are heading, there will be new abnormalities. This extension is not actually possible physically, for the same reason that the hypothetical curve connecting volume and temperature at atmospheric pressure was not possible, namely because the water freezes. But the extension may be made, nevertheless, for the purposes of speculation. It is seen that this new abnormality at high pressures and low temperatures consists in a crossing of the lines again, so that at 5000 kgm., for instance, water would expand on passing from −15° to −20°, just as for water at 0° and atmospheric pressure. The explanation suggests itself that this new abnormality is due to the new variety of ice which is about to separate out, either V or VI. At any rate, the idea seems perfectly plausible that each of the forms III, V, and VI is a solid form of water in a different state of polymerization, and that this polymerization should be shown by anomalous effects in the liquid. There certainly seems to be a strong presumption raised for this possibility by the present data. A more accurate experimental investigation would be well worth making, but would require new methods and apparatus.

We now have enough material in the behavior of the curves both above and below 0° to see what the role of pressure in wiping out the abnormalities must be. The one significant fact is that the pressure wipes out the abnormalities where they stand, without any perceptible shifting of their temperatures. Thus above 0°, the temperature of minimum compressibility is very nearly constant at 50°, independent of the pressure. Increasing pressure merely makes this minimum at 50° less and less pronounced until it has entirely disappeared. And below 0° the abnormalities remain confined to the 15° or 20° below 0°, the effect of pressure being merely to smooth out the variation of curvature. Now this is distinctly what one would not expect at first. The usual explanation of the normalizing effect of pressure is to suppose that the amount of polymerization, the cause of the irregularities, is decreased by rising pressure. This is the assumption made by Röntgen[17] and Sutherland.[18] The effect of this evidently would be to displace the region of abnormality from high to low temperatures, which is what we have seen does not happen. The explanation is rather to be found in supposing that the pressure merely reduces the effects of polymerization uniformly at every temperature without necessarily reducing the amount. This means that the difference of volume between the double molecules and the two single molecules becomes rapidly less at higher pressures; in other words, that the double molecules possess an abnormally high compressibility. This seems an entirely plausible hypothesis in view of the abnormally large volume of the double molecules. At high pressures, then, the polymerization, even if it occurs, is unable to produce volume effects, and might as far as we are concerned be entirely neglected. There may be effects on the specific heats, which cannot be detected from the present data. The explanation of the various pressure effects on this basis is simple. The anomalous decrease of compressibility with rising temperature is due to the fact that at the higher temperatures the double molecules with abnormally high compressibility are becoming fewer. When pressure has become so high that there is no longer distinction between the associated and the dissociated molecules, the behavior of the liquid becomes normal. This explanation leaves entirely open the question as to whether pressure actually increases or decreases the amount of polymerization. One would naturally expect an increase. The explanation also leaves open the possibility of the polymerization being to several different groups, more complicated than doublets or triplets. This possibility is suggested by the appearance of the several allotropic forms of ice.

It is to be noticed that in assuming that the molecules are compressible we have not by any means assumed that the actual change of size of the molecules under pressure is the chief factor in the change of volume of the substance as a whole under pressure. In fact it is almost certainly true that the greater part of the total change of volume is due to the closing up of the spaces between the molecules. The substance as a whole may have a greater or less compressibility

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[17] Röntgen, Wied. Ann., **45**, 91–97 (1892).

[18] Sutherland, Phil. Mag., **50**, 460–489 (1900).

according as its structure is more or less compressible. Thus liquid water is more compressible than ice I, although it has the smaller volume and is composed of molecules which are themselves less compressible.

TABLE XXXII.

THE VOLUME OF WATER CALCULATED BY TUMLIRZ'S FORMULA COMPARED WITH EXPERIMENTS.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Volume. $\text{cm.}^3/\text{gm.}$					
	0°			22°		
	Tumlirz.	Experiment.	Difference.	Tumlirz.	Experiment.	Difference.
0	0.9964	1.0000	−.0036	1.0030	1.0020	+.0010
1000	9560	0.9586	+.0026	0.9629	0.9636	−.0007
2000	9237	9265	+.0028	9318	9340	−.0022
3000	8983	9009	+.0026	9067	9090	−.0023
4000	8778	8805	+.0027	8861	8881	−.0020
5000	8607	8626	+.0019	8690	8703	−.0013
6000	8464	8480	+.0016	8544	8552	−.0008
7000	8341	8356	+.0015	8419	8417	+.0002
8000				8311	8288	+.0023
9000				8216	8161	+.0055
10000				8132	8049	+.0083

With regard to the bearing of these data on the theory of liquids, the theory itself does not seem to be at present far enough advanced so that these data can settle definitely any crucial questions. In fact, there do not seem to be any clear cut questions waiting for settlement. Nearly all the work done so far on liquids has been in modifying van der Waals' equation by making assumptions which seem more or less plausible about the way in which the forces between the molecules, the distances between the molecules, or the energy of the molecules vary with the temperature and pressure, and the chief aim of all this activity seems to have been the production of an equation with as few constants as possible which should accurately represent the behavior of as many liquids as possible under changes of temperature and pressure.

The bearing of these data for water on the theory of liquids as developed in this way may be best shown by testing how well the equations already proposed are applicable by extrapolation over this wider pressure range. For this purpose we may choose the equation given by Tumlirz[19] as perhaps the best. Tumlirz has applied his formula to the data of all the liquids studied by Amagat over a pressure range of 3000 kgm. and a temperature range of 40° or 50°, with really remarkable agreement. Tumlirz's formula has the form

$$(p + P)(v - a) = RT,$$

where a and R are constants for any given substance, and P is a function of the temperature only, to be determined by experiment. The significance of the assumption evidently is that the covolume (proportional to the total volume of the molecules) is independent of pressure and temperature, and that the internal pressure P is not affected by changes of volume at constant temperature. The results calculated by Tumlirz's formula, and the actual experimental results are shown in Table XXXII. The constants used at 0° in the calculation are those given by Tumlirz. At 22°, P was found by interpolation from Tumlirz's values above and below to be 7152. At 0°, the agreement is fairly satisfactory, and the discrepancies are of the same order throughout the entire pressure range. The discrepancies are greatest at the low pressures, corresponding to the abnormal behavior of water here. At 22°, for the lower pressures, the discrepancy is about the same as at 0°, but the most interesting thing about these values at 22° is the very evident failure of the formula at high pressures. The values given by the formula for the compressibility become small too rapidly at the high pressures.

This question as to the behavior of the compressibility at high pressures is the first one that would occur to one as of significance for the theory of liquids at high pressures. That is, does the volume shrink toward a limiting value in the way indicated at low pressures, or is there some other effect introduced by the high pressure? The physical picture of the mechanism of the liquid suggesting this question is that of an assemblage of molecules with intervening spaces. Is the change of volume of the molecules themselves under pressure sufficient to produce an appreciable effect after the intervening spaces

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[19] Tumlirz, Sitzber. Wien, Bd. CXVIII, Abt. IIa (Feb., 1909), pp. 1–39.

have been shut up? The present conception of the atom as a planetary system of electrons would suggest that there are possibilities of enormous change of volume within the atom itself, and that the compression of the atom is going to continue uniform over a relatively enormous pressure and volume range, just as under ordinary circumstances a gas obeys Boyle's law for a relatively very great range of volume and pressure. The fact is that at high pressures the compressibility does remain larger than the formula of Tumlirz demands, whether this is due to a compressible atom or not. The same thing is shown also by the curve of Figure 36 giving compressibility against pressure. The tendency of this curve is to become asymptotic to some value greater than zero, the compressibility changing very slowly at high pressures. At 5000 kgm. the compressibility has dropped to 1/3 of its value at atmospheric pressure, while at 10,000 it is 2/3 of its value at 5000.

TABLE XXXIII.

Various Thermodynamic Properties of Water at 22°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$C_p - C_v$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	$\left(\frac{\partial E}{\partial p}\right)_t$ $\frac{\text{gm. cal.}}{\text{gm.}}$.	$\left(\frac{\partial v}{\partial p}\right)_\phi - \left(\frac{\partial v}{\partial p}\right)_\tau$.	$\left(\frac{\partial \tau}{\partial p}\right)_\phi$.
0	0.0079	−0.00159	0.0_637	0.0016
1000	164	−0.00117	54	19
2000	279	−0.00104	75	23
3000	430	−0.00104	95	26
4000	498	−0.00071	95	26
5000	517	−0.00049	85	24
6000	492	−0.00019	71	22
7000	417	+0.00019	54	19
8000	279	+0.00068	33	15

The compressibility curves for 0° and 22° also indicate one other thing that would be expected, that at sufficiently high pressures the compressibility will become independent of the temperature, or in other words, that the dilatation will approach a value, probably zero, independent of the pressure.

The data obtained for the liquid are sufficient to enable us to calculate certain other quantities of thermodynamic interest. Two of these, the difference of the specific heats and the change of internal energy along an isothermal, may be calculated directly from the given data. Two others, the adiabatic compressibility and the rise of temperature produced by compression, may be computed roughly, merely indicating the direction in which these quantities change under pressure.

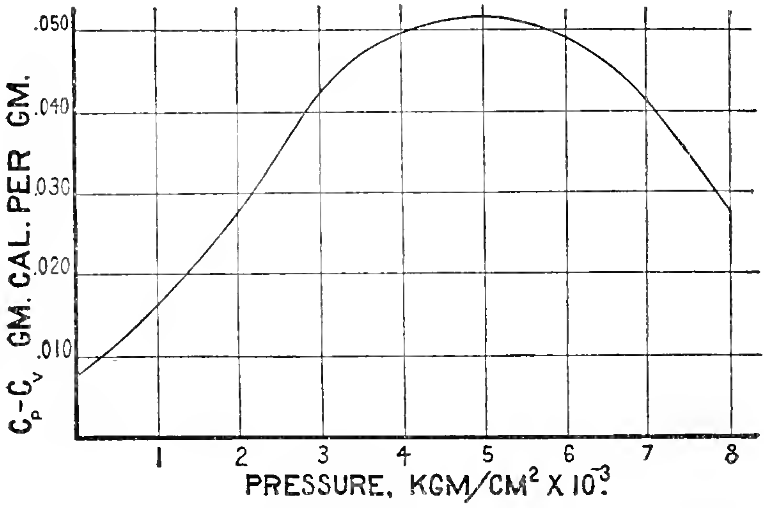

FIGURE 41. The mean difference of the specific heats of the liquid for the temperature range 0°–22°.

The difference of the specific heats is given by the formula

$$C_p - C_p = \frac{-\tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}.$$

The quantities entering this equation have been determined directly. The computed values for 22° are shown in Table XXXIII., and graphically in Figure 41. The general behavior is a rise to a maximum at 5000 and then a decrease. For a normal liquid $C_p - C_v$ probably decreases continuously with rising pressure. This has been shown to be the case for mercury in the previous paper. The significance of the maximum is, then, merely a repetition of the old story that at high pressure water loses its abnormality and becomes normal. The measurements have not been made to high enough pressures to show the reversal of curvature on the descending branch of the curve, which would show complete attainment of normality. The values of $C_p - C_v$

found here directly differ from those given by the formula of Tumlirz. This formula, used by extrapolation, would demand a continuous increase in the value of $C_p - C_v$ to infinite pressures, suggesting again that there is an effect entering at high pressures not taken account of or foreshadowed by the behavior at lower pressures.

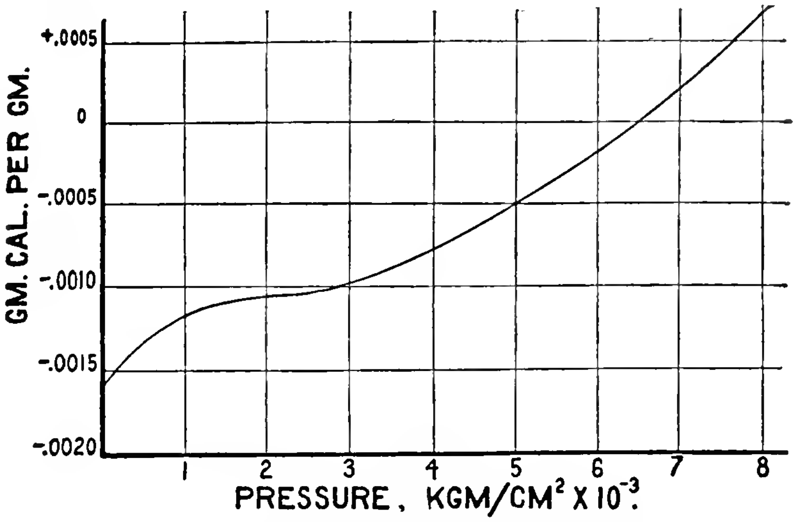

FIGURE 42. The change of internal energy of the liquid per kgm. rise of pressure along the isothermal at 22°.

The change of internal energy may also be found directly. For this we have the thermodynamic relation

$$\left(\frac{\partial E}{\partial p}\right)_\tau = -\left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right].$$

The computed values are shown in Table XXXIII. and Figure 42. Initially the internal energy decreases along an isothermal, but the rate of decrease becomes rapidly less with rising pressure, eventually changing sign, so that at the higher pressures the internal energy increases on an isothermal with increasing pressure. This means that initially the work done in compressing the water is more than lost by dissipation of the high heat of compression, but at higher pressures, the mechanical work per unit rise of pressure has increased so rapidly because of the high pressure that part of the mechanical work expended in compressing the water is retained as increased potential energy after temperature equilibrium has been restored. Except for a region of abnormal curvature, between 2000 and 5000, which is evidently due to the change from an abnormal to a normal liquid, the behavior of $\left(\frac{\partial E}{\partial p}\right)_\tau$ found here is probably typical for any liquid. For mercury, $\left(\frac{\partial E}{\partial p}\right)_\tau$ is initially negative, but it becomes greater algebraically with rising pressure, so that in the mercury paper it was suggested that probably at high enough pressures the energy would increase instead of decrease along an isothermal. Here we have an actual case where the pressure has been pushed far enough to secure this increase. This might have important applications to astrophysics or geophysics, since it shows the possibility of storing up very large amounts of energy in the interior of a star or the earth in virtue of the pressure alone, quite apart from the high temperatures.

Two other quantities of thermodynamic interest, the adiabatic compressibility and the temperature effect of compression, may be roughly approximated to. For these we have the formulae

$$\left(\frac{\partial v}{\partial p}\right)_\phi = \left(\frac{\partial v}{\partial p}\right)_\tau - \frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2,$$

and

$$\left(\frac{\partial \tau}{\partial p}\right)_\phi = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}.$$

Both of these involve the specific heat, which cannot be found from the data obtained, for the specific heat involves the temperature derivative of the dilatation by the well-known relation

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p.$$

Measurements of the compressibility at a number of temperatures would be necessary to obtain this. At high pressures, however, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ becomes less very rapidly. Amagat's data for water show that already at 3000 kgm. and for a temperature range at least from 0° to 30° $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ has vanished within the limits of accuracy. We may assume, then, that at high pressure C_p shows a very slow change. For the rough approximation given here, C_p was taken as constant at 0.9. Tumlirz found C_p at 2000 to be 0.86, but, as already remarked, his value is probably too low. The merely suggestive values for $\left(\frac{\partial v}{\partial p}\right)_\phi - \left(\frac{\partial v}{\partial p}\right)_\tau$ and $\left(\frac{\partial \tau}{\partial p}\right)_\phi$ calculated in this way are shown in Table

XXXIII. The difference between adiabatic and isothermal compressibility increases to a maximum and then decreases. The rise of temperature produced by the application of 1 kgm. pressure also increases and then decreases again. The normal behavior of both these quantities, as shown by mercury, is a continuous decrease, so that here again, we have an effect of the transition from abnormal to normal.

The quantities involved in the change of state from one form to another are shown collectively in the folder at the end, where the equilibrium curves, the change of volume curves, and the latent heat curves are plotted on the same scale for all the modifications. The fundamental question as to the change of state liquid-solid may be stated much more definitely than any fundamental question for the theory of liquids. This fundamental question is as to the ultimate behavior of the liquid-solid curve. Does it end abruptly, indicating a critical point for the transition solid-liquid as many have maintained, or does it rise to a maximum and then descend, as Tammann has claimed in combating the idea of a critical point, or does it merely continue rising indefinitely to infinite pressures and temperatures? Evidently none of these things have happened within the domain of the present diagram for water, nor have they happened in the low range up to 3000 or 4000 used before for any other liquid. The only hold we get on this question is by an extrapolation. In this we are very greatly helped by the behavior of the latent heat and the change of volume, for evidently an extrapolation of the equilibrium curve alone is absolutely incompetent to decide whether it is going to stop abruptly or not. But if this curve has an end or a maximum, then the latent heat and the change of volume must behave in a definite manner with respect to each other. At a critical point, the latent heat and the change of volume must vanish together, while at a maximum, the change of volume becomes zero, the latent heat remaining finite.

Tammann's argument for the probable existence of a maximum comes from observing the general trend of the latent heat and the change of volume on the equilibrium curve. Tammann could not make any very accurate measurements of the change of volume, but they were accurate enough to show that for the substances tried up to 2000 or 3000 kgm. the change of volume becomes less at high pressure, but the latent heat remains nearly constant. The change of volume is approximately linear with temperature on the equilibrium line. Whence by an extrapolation, Tammann concluded that the change of volume would pass through zero before the latent heat, and that therefore the equilibrium curve has a maximum. He has calculated the probable position of this maximum for a number of substances, assuming the melting curve to be a parabola, but this extrapolation is open to very great question. He himself remarks that at high pressures the equilibrium curves tend to show less curvature than one would expect from their behavior at low pressures.

The idea of a maximum seems opposed to our common-sense feeling of what to expect. If there is a maximum, it is possible by taking the substance through an isothermal cycle from the domain of the liquid into that of the solid and back into that of the liquid again to find a necessary connection between the compressibility of liquid and solid over a wide pressure range. This is unexpected in view of our present experience that there is no necessary connection between the properties of liquid and of solid. It is to be noticed that the nearest approach to a maximum found here, on the II–L curve, was neatly avoided by the appearance of another form of ice.

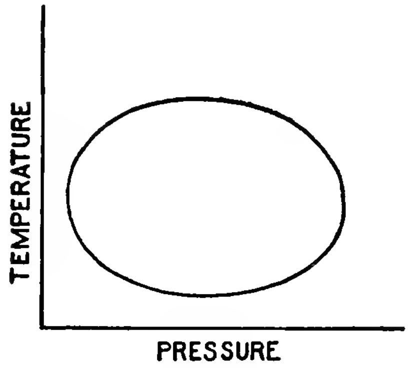

Figure 43. Tammann's complete equilibrium curve between liquid and crystal. The crystal is stable only within the closed region.

Proceeding from the probable existence of a maximum, Tammann has developed his well-known theory of the nature of the complete equilibrium curve between liquid and solid. The ideal curve (Figure 43) according to this theory is a closed curve, the crystalline solid having existence only in the interior of the curve. The complete curve may not be realizable for all substances, since part of the curve may fall at negative pressures or at temperatures below the absolute zero. As a matter of fact, only the two upper quadrants have been realized for known substances, and even then, no substance has been found in both the two upper quadrants. The upper left-hand quadrant is that for normal substances, while the upper right-hand quadrant shows the behavior of water and ice I.

We turn now to the evidence on these points afforded by the present work on water. First for the equilibrium curves alone. These all show curvature in the direction demanded by Tammann's complete diagram, on the I–L curve the fall of temperature becoming more rapid at higher pressures, and on the other curves the rise of temperature becoming less rapid with rising pressure. Except on the I–L curve, this behavior is just exactly what one would expect on nearly any conceivable theory, the effect of temperature becoming less at higher pressures. This is the behavior also on the liquid-vapor curve, which ends in a critical point. From the point of view of Tammann's theory, it is unfortunate that the form I gives place to III at higher pressures, for in the ideal diagram the behavior of I is the normal behavior at high pressure and that of III at low pressures, while here we have a form which should be adapted for the high pressures giving place at high pressure to one apparently appropriate to low pressures.

The change of volume curves next concern us. These also all show the general behavior demanded by Tammann's theory, the change of volume solid-liquid becoming algebraically less at high pressures. On the I–L curve this means that the change becomes numerically greater. The approximate reason of this has already appeared from the discussion of the compressibility of the solid to be merely that the solid is more incompressible than the liquid, whether it has the greater or smaller volume. The curvature of these change of volume curves is also everywhere, except for the curve VI–L, such as to suggest that the change of volume becomes zero at some finite temperature not very far removed from the temperatures actually reached.

The latent heat curves also bear out Tammann's point of view, for they all rise at the higher temperatures on the equilibrium curves. The direction of curvature of these latent heat curves appears to be governed by no such general rule as the change of volume curves, since the curve may be either concave or convex toward the temperature axis.

So far, for the forms of ice I, III, and V, which are stable at low pressures, everything seems as indicated by Tammann's theory. It should be remarked that the pressure range of existence of these forms is twice that reached before. It is on the VI–L curve, however, which reaches to much higher pressures, that we find the significant suggestion as to what to expect at still higher pressures. This suggestion comes from the change of volume curve, which shows a pronounced point of inflection in the neighborhood of 30°.[20] Below 30°, the curvature is like that for the other modifications at low pressures, indicating the vanishing of the change of volume at perhaps 50° or 60°, but beyond 30° the change of volume decreases less and less rapidly with rising temperature, with the possibility of becoming asymptotic.

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[20] With regard to the effect of probable experimental error at the high pressure it is to be said that the effect of this would be to make the inflection shown in the diagram appear less pronounced than it really is. The change of volume at high pressures is too low if anything, because in making the correction for the change in the bore of the cylinder under pressure it was assumed that the increase of bore is linear with pressure, whereas, if anything, it increases more rapidly at high pressures.

That is, at the high pressures there is no indication that the change of volume will ever become zero. This inflection in the volume curve is also mirrored by a corresponding inflection in the latent heat curve, which rises more and more rapidly at the upper end. Also this change of direction of the volume curve occupies the same general locality as the region on the compressibility curves for the liquid where the compressibility ceases to decrease as fast as one would expect from the behavior at low pressures. This behavior of the volume curve, together with that of the latent heat curve, shows in the first place that the latent heat and the change of volume do not vanish together, so that there can be no critical point, and in the second place, that the change of volume apparently will not vanish at any finite temperature, so that we will not have a maximum as supposed by Tammann, but the curve will rise instead to infinite pressures and temperatures.

Recently J. J. van Laar[21] has been developing a theory of the solid state which is more far reaching than that of Tammann, in that it attempts to show the actual mechanism which makes a liquid pass to the solid. This theory explains the solid state by the association of the simple molecules to molecular complexes. For the sake of simplicity, the theory has been developed for the case where the complexes are double molecules, although this restriction is not necessary. Given, then, a liquid in which both single and double molecules may exist, van Laar has found, by writing down the thermodynamic potential of the two kinds of molecules, how the dissociation of the double molecules into single molecules varies with pressure, volume, and temperature. Accompanying the dissociation is a change of volume, for the volume of the double molecule is not in general twice that of the two single molecules from which it comes. This change of volume, due to dissociation, is found to so modify van der Waals' equation, which is still supposed to hold for either kind of molecule separately, that an isotherm now has two maxima and two minima, instead of the single maximum and minimum of van der Waals' original equation. This evidently means the existence of a new phase, the solid, the equilibrium conditions of which are determined in the same way as the equilibrium conditions liquid-gas of the ordinary equation, by applying the condition that the work done in a reversible isothermal cycle is zero.

By detailed numerical computation, van Laar has shown how on this theory the equilibrium pressure solid-liquid changes with increasing temperature. The results are similar to those of Tammann in that a

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[21] van Laar, Proc. Amster., **11**, 765–780 (1909); **12**, 120–132, 133–141 (1909); **13**, 454–475, 636–649 (1910).

maximum melting temperature and a maximum melting pressure are both predicted. That is, in Figure 43, van Laar has the same maximum and the same right-hand vertical tangent as Tammann, but the results differ from Tammann's in that the minimum and the left-hand vertical tangent cannot exist, or at any rate if they do, they must always lie at temperatures below the absolute zero and at negative pressures.

These results of van Laar were obtained with the specific assumption that the actual volume of the molecules, and so the change of volume when a double molecule passes into two single molecules, is independent of temperature and pressure. This is almost certainly not the case. The value of the compressibility of water at high pressures, the way in which the abnormalities are smoothed out in the neighborhood of 0°, and the point of inflection in the ΔV curve for VI above 0°, all suggest most strongly that the assumption is not true, and furthermore that it is not approximately enough true to enable even the general character of the melting curve to be predicted at high pressures.

The conclusion of the whole matter seems to be that at high pressures, over 10,000 kgm. for water, we have a new effect appearing, probably connected with the compressibility of the atoms. This means that at high pressures the compressibility of the liquid and solid are going to become more and more nearly equal, which will have as a consequence that the equilibrium curve will continue rising indefinitely.

Besides the data just discussed for the liquid-solid curves, we have the corresponding data for the solid-solid curves. There is no theory at present of the equilibrium solid-solid, and the data here only bear out a remark of Roozeboom[22] that different allotropic solids would be expected to show every conceivable relation to each other. Two triple points between three solid phases had been found, I–II–III, and II–III–V. The first of these is of a type already known, but the second is of a type of which, according to Roozeboom, no examples have yet been discovered. This is Roozeboom's sixth type.[23] The equilibrium lines are for the most part straight, but this merely indicates that the compressibility and thermal dilatation of the solids are nearly constant over the range of temperature and pressure in question, as one might expect. The only curved equilibrium lines are I–III and II–III. In both of these III is involved. But it was to be expected *a priori* that III is a form of ice with more variable properties than the others, be-

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[22] Roozeboom, Die Heterogenen Gleichwichte, vol. 1, p. 206. (Vieweg, Braunchweig, 1901).

[23] Roozeboom, loc. cit. p. 202.

cause of the close approach of its equilibrium curve with water to a maximum. In general, the internal energy increases on passing from a solid stable at low pressures to the solid stable at higher pressures, but III–II is an exception. The most interesting features found for the equilibrium solid-solid are the probable passing of the I–II curve through the absolute zero, the enormous increase in reaction velocity on approaching a triple point, and the existence in one crystalline form of nuclei about which crystallization to another form may begin.

Acknowledgment is here made of several liberal appropriations from the Rumford Fund of the American Academy of Arts and Sciences, with which the expenses of this investigation were partially defrayed.

Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.,
October, 1912.

PLATE **1**.

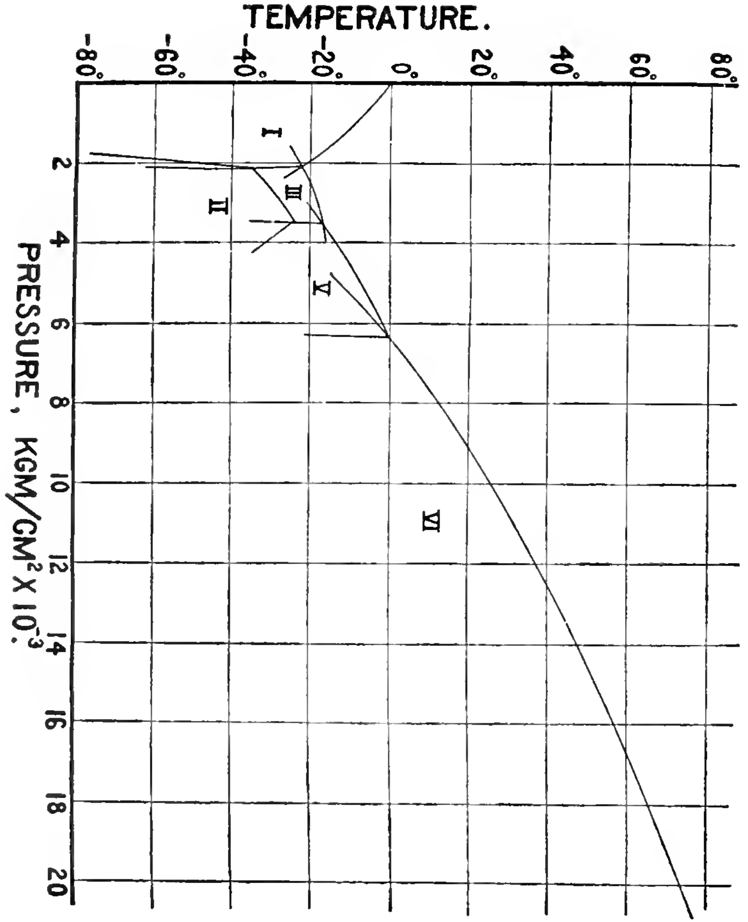
The equilibrium diagram between the liquid and the five solid modifications of water.

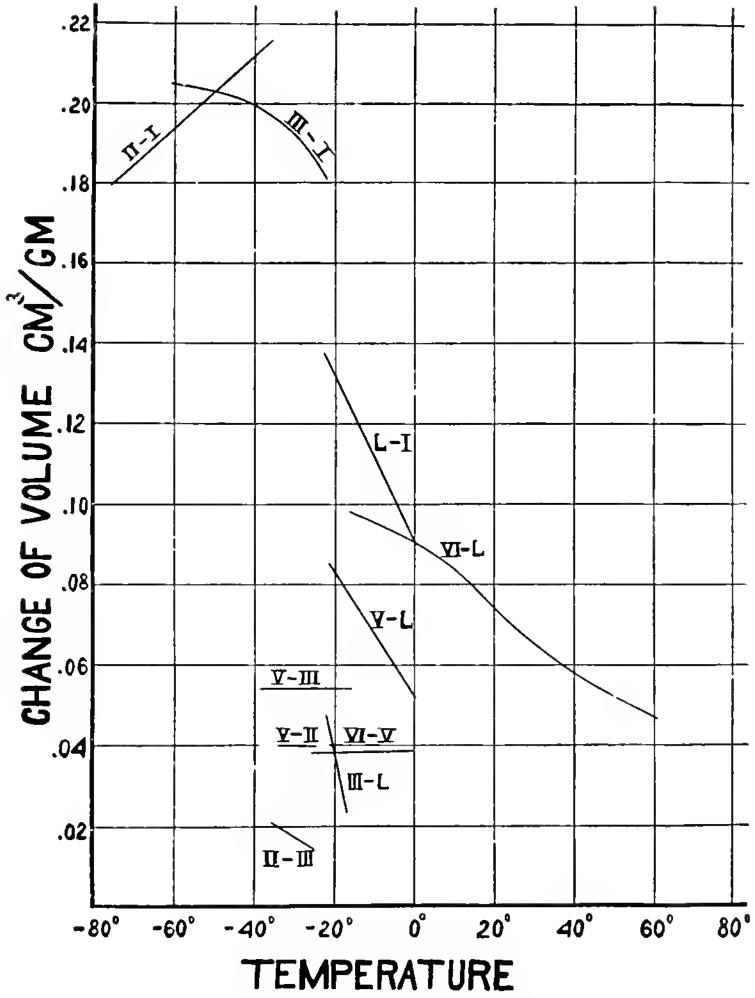
PLATE **2**.

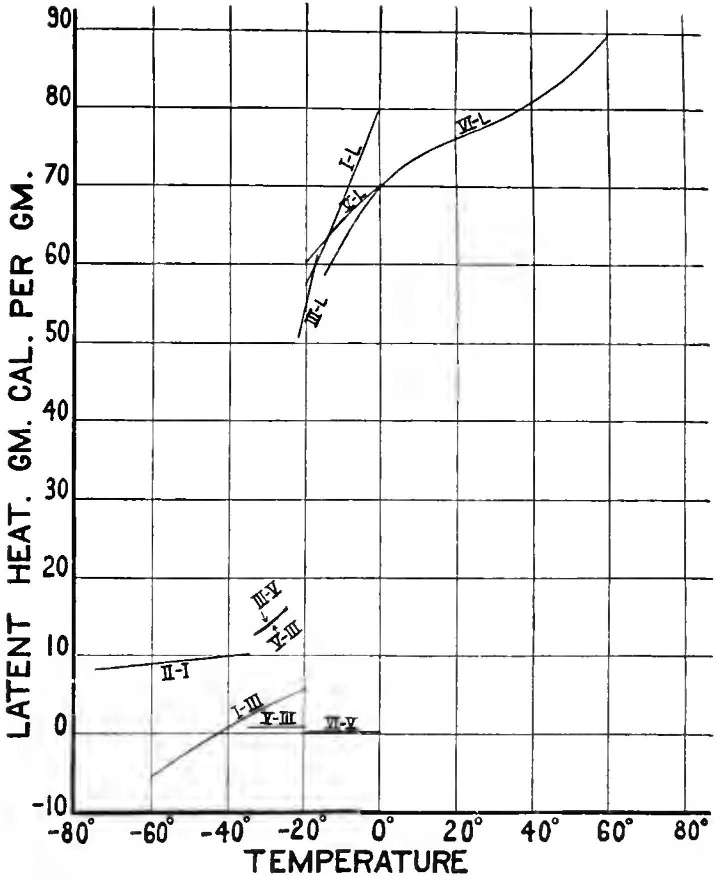
The change of volume when one modification passes to another under equilibrium conditions.

PLATE **3**.

The latent heat when one modification passes to another under equilibrium conditions.


TEMPERATURE.
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
PRESSURE, KGM/GM² X 10⁻³.
2
4
6
8
10
12
14
16
18
20
I
II
III
V
VI


CHANGE OF VOLUME CM³/GM
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
II-I
III-I
L-I
VI-L
V-L
V-III
V-II
VI-V
III-L
II-III
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
TEMPERATURE


LATENT HEAT. GM. CAL. PER GM.
90
80
70
60
50
40
30
20
10
0
-10
VI-L
I-L
V-L
III-L
III-V
V-III
II-I
I-III
V-III
VI-V
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
TEMPERATURE

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 14. — January, 1912.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON AN ELECTROMAGNETIC THEORY OF GRAVITATION.

By D. L. Webster.

ON AN ELECTROMAGNETIC THEORY OF GRAVITATION.

BY D. L. WEBSTER.

Presented by B. O. Peirce, November 8, 1911. Received November 8, 1911.

THE desirability of an electromagnetic theory of gravitation has been pointed out many times, by Maxwell,[1] Lorentz,[2] and others, who would assume that gravitation is due to a slight excess in the attraction of an electric charge for one of the opposite sign over its repulsion for an equal one of the same sign; and also by Einstein and his followers, who would have changes of gravitational attraction propagated with the velocity of light. But Maxwell and Lorentz had no proof of the truth of their theory, or reason for belief in it, other than that it might connect gravitation and electricity; and even Einstein had no proof, but only the fact that if the velocity were different from that of light, we should have a means of detecting absolute motion. The object of this paper is to give some reasons for belief in the electromagnetic theory, and to point out some of its most surprising results.

Objections have been raised against such a theory, principally on the ground that it would involve gravitational aberration like the aberration of light, but I hope to show that the electromagnetic theory involves no such consequences. Wiechert[3] and others have also objected on the ground that gravitation is essentially different from electrostatic force, especially in its ability to penetrate even the densest matter without appreciable change. But it may be proved, with no other assumption than that a dielectric affects electrostatic force only through the displacement of negatively charged particles within it, that the uniform gravitational permeability of all dielectrics is no argument against the electromagnetic theory. And it has been proved by Gans[4] that the equality of the gravitational permeabilities of vacuum and conductors is also consistent with such a theory.

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[1] Maxwell, Electricity and Magnetism, Vol. 1, p. 40.

[2] Versl. K. Ac. van Wet., **8**, 603 (1900); **8**, 616 (1900).

[3] Wiechert, Über die Relativitätsprincip und Äther, Phys. Zeitsch., **12**, 18–19.

[4] Phys. Zeitsch., **6**, 803.

Notation. — The notation used in this paper will be that of Gibbs, in which all vectors may be distinguished by being printed in Clarendon type, while scalars will be in italic type. Thus, **a** would be a vector, and a a scalar. The magnitude of any vector **a** will be denoted by $|\mathbf{a}|$.

The scalar product,

$$(\mathbf{a}_x\mathbf{b}_x + \mathbf{a}_y\mathbf{b}_y + \mathbf{a}_z\mathbf{b}_z),$$

of two vectors **a** and **b** will be denoted by $\mathbf{a}\cdot\mathbf{b}$; and their vector product,

$$\mathbf{i}\,(\mathbf{a}_y\mathbf{b}_z - \mathbf{a}_z\mathbf{b}_y) + \mathbf{j}\,(\mathbf{a}_z\mathbf{b}_x - \mathbf{a}_x\mathbf{b}_z) + \mathbf{k}\,(\mathbf{a}_x\mathbf{b}_y - \mathbf{a}_y\mathbf{b}_x),$$

by $\mathbf{a}\times\mathbf{b}$, where **i**, **j**, and **k** are the unit vectors in the directions of x, y, and z, respectively.

The symbol ∇ will be used for the operator,

$$\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right),$$

so that ∇a is the gradient of scalar a, a vector; $\nabla\cdot\mathbf{a}$ is the divergence of vector **a**, a scalar; and $\nabla\times\mathbf{a}$ is the curl of vector **a**, another vector.

The "mass" of a body must be understood to mean its mass as measured on a system of axes on which it is at rest; and similarly the density, which will be denoted by the letter ρ, will mean the limit of the ratio of the mass in a volume element to the volume of the element, with the above interpretation of the word mass. The mass of a body will, therefore, be a measure of the amount of matter, or "gravitational charge" in the body, which will be different for moving bodies from the "inertia" usually understood by the word mass.

Other Theories of Gravitation. — With this notation we may now examine the results of various methods by which we might imagine the changes of gravitational force to be propagated.

First, let us imagine, according to what I shall call "Theory I," that the changes of gravitational force due to any changes in the position of matter take place at the same instant at every point in space. In this case, if **g** is the gravitational force per unit mass at any point,

$$\mathbf{g} = k\nabla\iiint_{\infty}\frac{\rho}{r}\,d\tau = -k\iiint_{\infty}\frac{\rho}{r^2}\,\mathbf{r}_1 d\tau$$

where r is the distance from the volume element $d\tau$ to the point at which the integral is to be evaluated, $\mathbf{r}_1$ the unit vector in the direction from the element, and k the gravitation constant, $6.480 \times 10^{-8} \frac{\text{cm}^3}{\text{gm. sec.}^2}$. This assumption involves the existence of "absolute time" and instantaneous action at a distance, but is a possible hypothesis if these are possible.

The hypothesis which I shall call "Theory II" is the consequence of most of the mechanical explanations of gravitation, such as the well known Le Sage theory, and theories of attraction through the pressure of invisible radiation or through the pulsations of slightly compressible electrons in a less compressible fluid. According to this theory the attraction at any time t on any particle is determined by the matter that occupied each volume element at a time $\left(t - \frac{r}{C}\right)$, where C is some very large velocity, and r is, as above, the distance from the element. In this case, if we let $[\rho]$ equal the value of ρ in the element at this time, we have

$$\mathbf{g} = - k \iiint_{\infty} \frac{[\rho]}{r^2} \mathbf{r}_1 d\tau.$$

For "Theory III" let us suppose any particle moving uniformly to carry a perfectly symmetrical system of lines of force with it, so that at any instant the forces due to it at all equidistant points will have equal intensities and be directed exactly towards it. But if its motion is changed by an infinitesimal amount, let us suppose that the disturbance of the force is propagated with a velocity C relative to that of the particle at the time the change of its velocity takes place.

In this case,

$$\mathbf{g} = - k \iiint_{\infty} \frac{[\rho]'}{r'^2} \mathbf{r}_1' d\tau,$$

where r' is the distance at which the matter would have been at time t, that occupied the element $d\tau$ with density $[\rho]'$ at the time $\left(t - \frac{r'}{C}\right)$, if it had kept since that time the velocity it then had. We may also say

$$\mathbf{g} = - k \iiint_{\infty} \frac{[\rho]\mathbf{r}_1' d\tau}{r^2(1 + \mathbf{B}^2 - 2\mathbf{B} \cdot \mathbf{r}_1)'}$$

where $\mathbf{B}$ is the ratio of the velocity of the matter in the element $d\tau$ at the time $\left(t - \frac{r}{C}\right)$ to the velocity C.

For "Theory IV" let us assume that there is another vector **h** related to the vector **g** in the same way that magnetic force is related to electric, and that these vectors satisfy the set of equations:

$$\nabla \cdot \mathbf{g} = -4\pi\rho k$$

$$\nabla \cdot \mathbf{h} = 0$$

$$\nabla \times \mathbf{h} = \frac{\partial \mathbf{g}}{\partial (Ct)} - 4\pi\rho k \mathbf{B}$$

$$\nabla \times \mathbf{g} = -\frac{\partial \mathbf{h}}{\partial (Ct)}$$

$$\mathbf{f} = \mathbf{g} + \mathbf{B} \times \mathbf{h},$$

where **f** is the force per unit mass due to the gravitational force **g** and "gravimagnetic" force **h**. It will be noticed that these equations are very much like the electromagnetic equations:

$$\nabla \cdot \mathbf{E} = 4\pi\epsilon$$

$$\nabla \cdot \mathbf{H} = 0$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{E}}{\partial (ct)} + 4\pi\epsilon\boldsymbol{\beta}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{H}}{\partial (ct)}$$

$$\mathbf{F} = \mathbf{E} + \boldsymbol{\beta} \times \mathbf{H}$$

where **E** and **H** are electric and magnetic forces, ϵ the charge per unit volume, $\boldsymbol{\beta}$ the ratio of the velocity of the charge at any point to the velocity, c, of propagation of electromagnetic disturbances, and **F** the force per unit charge due to electric and magnetic forces.

If we assume with Einstein that there is no ether, and no universal or absolute time, we readily see that these theories are all inconsistent with this belief, with the single exception of the special case of Theory IV which we may call "Theory V," in which $C = c$. If, on the other hand, we assume the "conditional relativity principle," of Wiechert[5] and assume the existence of ether and absolute time, we see a wider range for Theory IV than that obtained by merely giving different values to C, in that Theory IV does not define any particular state of motion that may be assumed to be the state of absolute rest, and un-

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[5] Wiechert, Relativitätsprinzip und Äther, Phys. Zeitsch., **12**, 18–19.

less we make such a definition we have no single-valued definition of any of our time derivatives, even though we have a definition of absolute time. The physical significance of this statement is that, according to Theory IV, all gravitational disturbances must be propagated with a velocity C through an ether that is not necessarily at rest relative to the electromagnetic ether. Therefore to define Theory V completely in terms of Theory IV, we must say that the two ethers must be at rest relative to each other, and that the two velocities C and c must be equal.

Objection against Theories I–III. — If we now examine further the consequences of these theories, we shall see that Theory I, if not impossible, is highly improbable; and that Theory V is the only other that does not involve a continual increase of energy of any system of gravitating bodies.

Assuming the unconditional relativity principle, all but Theory V are, of course, impossible. But assuming the conditional relativity principle, we see that Theory I involves either instantaneous action through a medium that is also capable of propagation of disturbances with a finite velocity, or else it involves true "action at a distance." Also it has been shown by Wilkens[6] that the changes of the perihelion of Mercury and other astronomical phenomena, which are consistent with the electromagnetic theory, are inconsistent with Theory I.

These difficulties make it necessary to look for some other theory, such as II. But if we assume the truth of this theory, we must say that the components of a binary star revolving in circles about their centre of gravity will each be accelerated at time t by a force directed towards a point where the other was at time $\left(t - \frac{r}{C}\right)$; and this force will have a component in the direction of motion which is an infinitesimal, if C is allowed to become infinite, of the order of $|\mathbf{B}|$ for the other body. But no matter how large C may be, this component of the force will never be absolutely zero. Hence the ever increasing kinetic energy would tear any such system apart, even though the components were unequal and the orbits not circular; and even a rotating planet would increase its energy of rotation until it burst, and would continue increasing its energy forever, even after disruption; so that, if Theory II held, the earth and the whole solar system would have gone to pieces long ago and left not even the law of the conservation of energy for a vain consolation.

Theory III might be expected to remove this difficulty, but it does

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[6] Phys. Zeitsch., **7**, No. 23, 846.

not, though it does reduce the component of force in the direction of motion to an infinitesimal of the third order. For if we consider a system where A_1 and A_2 are the positions of the two masses m_1 and m_2, revolving in circular orbits at the time t, B_1 and B_2 their positions at the time $\left(t - \frac{C_1A_2}{C}\right)$ and $\left(t - \frac{C_2A_1}{C}\right)$, and C_1 and C_2 the positions they would have occupied if they had kept since the above-mentioned times the velocities they then had, we see that C_1 and B_1 must always lie on the same side of the line A_2A_1 produced. If the velocity C becomes infinite, the distances from C_1 and C_2 to the line A_1A_2 are obviously infinitesimals of the third order, but they can never be exactly zero; and hence there will always be a forward component of force that must ultimately produce the same disastrous results that we have seen in Theory II. Hence we see that Theories II and III are almost certainly false.

Theory IV. — Let us now suppose that Theory IV is correct, and examine its consequences. By Green's Theorem it may easily be proved that the gravitational energy liberated in scattering any distribution of gravitating matter to infinity is

$$-\frac{1}{8\pi k}\int\int_{\infty}\int \mathrm{g}^2 \, d\tau$$

if the matter is all at rest. But if the matter is in motion, we must add to this, to get the gravitational energy liberated in bringing it all to rest at infinity,

$$-\frac{1}{8\pi k}\int\int_{\infty}\int \mathrm{h}^2 \, d\tau.$$

And if the ratio of the velocity of matter at every point to that of light is the vector point function $\boldsymbol{\beta}$, the total kinetic energy in the universe is

$$\int\int_{\infty}\int \rho c^2 \left(R^{-1} - 1\right) d\tau$$

where $R = \sqrt{1 - \boldsymbol{\beta}^2}$. We may now assume as in the corresponding electromagnetic case, that the integrands in the above expressions actually represent the energy that would be removed in the scattering process from the volume elements for which they are evaluated, and hence that the energy in a region T of any distribution of matter acted upon only by gravitational forces is

$$\iiint_T \left\{\rho c^2 (R^{-1} - 1) - \frac{1}{8\pi k} (\mathbf{g}^2 + \mathbf{h}^2)\right\} d\tau.$$

While this assumption is not necessarily true for any finite region, it is certainly true in the limit for a sphere whose radius is allowed to become infinite.

Gravitational Radiation. — We may prove the following THEOREM :

If a distribution of matter is affected by forces of which none but those of gravitational origin do any work, the energy, E_s, within any closed surface, S, which neither matter nor electromagnetic energy enters or leaves, and which has a normal at every point, will increase or decrease at such a rate that

$$\frac{dE_s}{d(Ct)} = + \frac{1}{4\pi k} \iint_S \mathbf{g} \times \mathbf{h} \cdot \mathbf{dS}$$

where $\mathbf{dS}$ is the element of surface considered as a vector in the direction of the exterior normal.

The truth of this theorem depends on that of the above assumption about the energy in the region T, but it is certainly true for the infinite sphere.

The proof (like that of Poynting's theorem), is as follows : If T is the space within S,

$$E_s = \iiint_T \left\{\rho c^2 (R^{-1} - 1) - \frac{1}{8\pi k} (\mathbf{g}^2 + \mathbf{h}^2)\right\} d\tau$$

$$\frac{dE_s}{d(Ct)} = \iiint_T \left\{ \frac{\partial}{\partial (Ct)} [\rho c^2 (R^{-1} - 1)] - \right.$$
$$\left. \frac{1}{4\pi k} \left(\mathbf{g} \cdot \frac{\partial \mathbf{g}}{\partial (Ct)} + \mathbf{h} \cdot \frac{\partial \mathbf{h}}{\partial (Ct)} \right) \right\} d\tau$$

$$= \iiint_T \left\{ \frac{\partial}{\partial (Ct)} [\rho c^2 (R^{-1} - 1)] - \right.$$
$$\left. \frac{1}{4\pi} (\mathbf{g} \cdot \nabla \times \mathbf{h} - \mathbf{h} \cdot \nabla \times \mathbf{g}) - \rho \mathbf{g} \cdot \mathbf{B} \right\} d\tau.$$

But $\rho\mathbf{g}\cdot\mathbf{B}$ is the increase of kinetic energy per unit volume per unit Ct for a volume element moving with the matter in it; hence

$$\frac{dE_s}{d(Ct)} = \frac{1}{4\pi k}\iiint\limits_T (\mathbf{h}\cdot\nabla\times\mathbf{g} - \mathbf{g}\cdot\nabla\times\mathbf{h})\,d\tau$$

$$= \frac{1}{4\pi k}\iiint\limits_T \nabla\cdot(\mathbf{g}\times\mathbf{h})\,d\tau$$

$$= \frac{1}{4\pi k}\iiint\limits_T \mathbf{g}\times\mathbf{h}\cdot d\mathbf{S} \qquad \text{Q. E. D.}$$

To find the amount of negative gravitational energy radiated from an accelerated particle when it is at rest, we may make use of the result of the corresponding electrical case. In this case, if the charge on the electron is e, and the accleration is $\mathbf{a}$, and the unit vector in the direction from the electron to the point considered is $\mathbf{r}_1$, the electric force due to radiation at a distance r is

$$\mathbf{E} = -\frac{e}{c^2 r}\,\mathbf{a}_p,$$

where $\mathbf{a}_p$ is the component of $\mathbf{a}$ perpendicular to $\mathbf{r}_1$, and the magnetic force due to acceleration is

$$\mathbf{H} = +\frac{e}{c^2 r}\,\mathbf{a}\times\mathbf{r}_1 = \mathbf{r}_1\times\mathbf{E}.$$[7]

The magnitudes of these forces are seen to be equal, and the directions at right angles. For the corresponding gravitational case, we need only to change the signs of these expressions and substitute mk for e, and C for c, and we have

$$\mathbf{g} = \frac{mk}{C^2 r}\,\mathbf{a}_p,$$

$$\mathbf{h} = -\frac{mk}{C^2 r}\,\mathbf{a}\times\mathbf{r}_1 = \mathbf{r}_1\times\mathbf{g}.$$

We now see that

$$\mathbf{g}\times\mathbf{h} = \frac{m^2k^2\mathbf{r}_1}{C^4r^2}\,\mathbf{a}_p{}^2 = \frac{m^2k^2}{C^4r^2}\,(\mathbf{a}\times\mathbf{r}_1)^2\,\mathbf{r}_1.$$

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[7] For proof see Lorentz, "Theory of Electrons," Chapter 1.

But if we now have two particles with constant accelerations, oppositely directed, we see that the vectors $\mathbf{g}$ and $\mathbf{h}$ for one of the particles will have nearly opposite directions to the corresponding vectors for the other particle at points very far from the two masses. For such points we may then say the total gravitational force is

$$\begin{aligned}\mathbf{g} &= \frac{m_1 k}{C^2 r_1}\mathbf{a}_{p1} + \frac{m_2 k}{C^2 r_2}\mathbf{a}_{p2}\\ &= \frac{k}{C^2}\cdot\frac{m_1 r_2 \mathbf{a}_{p1} + m_2 r_1 \mathbf{a}_{p2}}{r_1 r_2}\\ &= \frac{k m_1}{C^2 r_1 r_2}\left(r_1 + \frac{\mathbf{a}_{p2}}{\mathbf{a}_{p1}}\cdot\frac{m_2}{m_1} r_2\right)\mathbf{a}_{p1}.\end{aligned}$$

The fraction $\mathbf{a}_{p2}/\mathbf{a}_{p1}$ will have a meaning only in a case where it is multiplied by a product of a scalar by $\mathbf{a}_{p1}$, or in a case where $\mathbf{a}_{p1}$ and $\mathbf{a}_{p2}$ have the same direction, as in the limit $r_1 = \infty$, when it will approach a scalar limit. Unless this limit is $-m_1/m_2$, $\mathbf{g}$ will be an infinitesimal of the order of $1/r_1$. But if $\lim \mathbf{a}_{p2}/\mathbf{a}_{p1} = -m_1/m_1$, then we readily see that $\mathbf{g}$ and $\mathbf{h}$ are both infinitesimals of the order of $1/r_1^2$ or of a higher order, and $\mathbf{g}\times\mathbf{h}$ is of the order of $1/r_1^4$ or higher. But this is possible for all directions only if $m_1\mathbf{a}_1 = -m_2\mathbf{a}_2$, and therefore in this case, and only in this case,

$$\lim_{r=\infty}\iint_S \mathbf{g}\times\mathbf{h}\cdot d\mathbf{S} = 0$$

where S is a sphere of radius r, surrounding the particles. Hence we see that there is no radiation of negative energy from a pair of uniformly accelerated particles momentarily at rest, if, and only if,

$$m_1\mathbf{a}_1 = -m_2\mathbf{a}_2.$$

Radiation from a Rotating Body. — Since Theory IV, with $C \neq c$, is inconsistent with the unconditional relativity principle, we must, in assuming the truth of it, assume the existence of an ether and an absolute system of simultaneity. But if now we assume that gravity is transmitted through an ether that is independent of the electromagnetic ether, and moving through it, we must assume the time to be the same absolute time in both cases, and the lengths to be measured in absolute units of length.

If, with these assumptions, we consider the motion of a body rotating, undisturbed by external influences, about an axis of symmetry that is at rest in the gravity ether, we may determine whether it can satisfy the condition

$$\frac{dE}{d(Ct)} = 0.$$

It might now be supposed that we could not do this by determining whether

$$m_1\mathbf{a}_1 = - m_2\mathbf{a}_2,$$

because the radiation from an accelerated electron already in motion is not the same as if it had the same acceleration when at rest. But it is obvious that, if we consider any direction making given angles with the directions of the velocity and acceleration, the ratio of the rate of radiation in that direction in the case with velocity to the corresponding rate in the case with no velocity is a function of only the magnitude of the velocity and the angle between the velocity and acceleration, and not a function of the charge or acceleration of the electron. Hence we see that, if we consider a case where the two variables that determine this ratio are the same for every point of the infinite sphere, we may then, and only then, say that there is no radiation of negative energy from a pair of uniformly accelerated gravitating particles if, and only if,

$$m_1\mathbf{a}_1 = - m_2\mathbf{a}_2.$$

Returning to our rotating body, which may be any solid, liquid, gas, or collection of very minute particles like Saturn's rings, provided only that all points in any ring of infinitesimal cross-section around the axis shall have the same density and the same constant angular velocity around it, we see that the condition that no energy shall be radiated to infinity from the body is that there shall be no radiation to infinity from any of these rings.

First let us assume that the axis is stationary in the gravity ether and perpendicular to the direction of motion of the electric ether through it, and let us see when this condition will be fulfilled. For simplicity let us consider first only the case of a collection of particles such as Saturn's rings or a rotating nebula with no internal forces but those of gravity. In such a case it is obvious from symmetry that if the inertia of a particle were proportional to its mass and independent of its velocity, the system could rotate indefinitely, preserving always its symmetry about the stationary axis, and, since the accelerations at opposite points would be equal, opposite, and constant, not radiating any energy. But since the inertias of two equal particles would be unequal when they were going in opposite directions not perpendicular to the direction of motion of the electric ether, we see that if the system were brought into the condition assumed above, the accelerations at opposite points would be unequal and there would be radiation. Hence to avoid radiation we must have the two ethers relatively at rest.

If we introduce internal forces other than those due to gravity, we make the problem much more complicated, but it is evident that the results would be of the same general nature, and that if the two ethers were relatively at rest there would be absolutely no radiation.

With this assumption of relative rest, we may now solve the problem of the radiation from such a collection of minute particles rotating about its axis, and at the same time moving through the ethers with a velocity comparable to that of light. From the similarity of the gravitational equations to the electromagnetic, we see that if we introduce a gravitational relativity principle, exactly like the electromagnetic relativity principle with C substituted for c in all formulas, the condition that two equal volume elements opposite to each other in the body shall not radiate negative energy to infinity is that the accelerations of the matter in them measured in the gravitational units of moving distance and local time shall be equal and opposite.

We may now suppose the particles to be brought into positions and velocities that appear at a certain instant of the gravitational local time of a system moving with the axis to be absolutely symmetrical about the axis. But since the equation "force equals rate of increase of momemtum," holds only when the electromagnetic units of local time and moving distance are used, we see that the accelerations of opposite particles are equal in the gravitational system only if all the corresponding units are equal, or if

$$C = c.$$

And we see also that if other internal forces are introduced, the problem is again more complicated, but that we have a similar result, that there is absolutely no radiation of negative energy from any body rotating about an axis of symmetry only with Theory V.

Radiation from two or more Gravitating Bodies. — If, however, we consider the more general case of two or more bodies moving under the action of no forces but those of gravity, we shall find a small amount of radiation even with Theory V. But this unavoidable radiation is very small, being in general for any pair of bodies less than the product obtained by multiplying the radiation from one of them alone by the square of the ratio of their relative velocity to the velocity of light. And we shall prove that while, for small bodies, this radiation is due only to the changes in the accelerations in the time required for propagation of radiations from one to the other, Theory IV involves radiations that may be larger than this in any desired ratio, and that are due to actual differences of mass acceleration.

To prove this, let us determine, from the equations of Theory IV, the accelerations of two masses, m_1 and m_2, moving through the gravity ether with equal opposite velocities parallel to that of the electric ether, and whose ratios to C are $\mathbf{B}_1$ and $\mathbf{B}_2$, let the direction of x be that of $\mathbf{B}_1$ and let us suppose the two particles to be moving so that m_2 is in the direction of the axis of y, at a distance a from m_1, at the instant considered. If now we let r_1 be the distance of any point from m_1, in a direction making an angle θ_1 with that of x, we have the gravitational force due to m_1, neglecting that due to radiation and change of $\mathbf{B}_1$ in time r_1/C, directed towards m_1 at every point, and of intensity

$$| \mathbf{g}_1 | = \frac{k m_1}{r_1^2} (1 - \mathbf{B}_1^2) (1 - \mathbf{B}_1^2 \sin^2 \theta_1)^{-\frac{3}{2}},$$

while the gravimagnetic force due to m_1 is

$$\mathbf{h}_1 = \mathbf{B}_1 \times \mathbf{g}_1.$$

These formulas may be proved by substitution in the equations of Theory IV, assuming $\mathbf{B}_1$ constant.

Therefore, neglecting radiated forces from m_1 and change of $\mathbf{B}_1$, the force acting on m_2 is

$$m_2 \mathbf{f}_2 = m_2 (\mathbf{g}_1 + \mathbf{B}_2 \times \mathbf{h}_1).$$

Therefore

$$m_2 \mathbf{a}_2 = - \mathbf{j} \frac{k m_1 m_2}{a^2} R_2 (1 - \mathbf{B}_1^2)^{-\frac{1}{2}} (1 - \mathbf{B}_2 \cdot \mathbf{B}_1).$$

Similarly

$$m_1 \mathbf{a}_1 = + \mathbf{j} \frac{k m_1 m_2}{a^2} R_1 (1 - \mathbf{B}_2^2)^{-\frac{1}{2}} (1 - \mathbf{B}_1 \cdot \mathbf{B}_2).$$

Since

$$\mathbf{B}_2 = - \mathbf{B}_1$$

we have

$$m_1 \mathbf{a}_1 = - m_2 \mathbf{a}_2$$

if, and only if,

$$R_1 = R_2,$$

or

$$\beta_1 = - \beta_2,$$

in which case the forces due to radiation are also equal and opposite.

Therefore to avoid continually increasing energy we must again have the two ethers at rest relative to each other.

Now let us consider a similar case where the centre of the line joining them is not at rest in the ether. Here we may again introduce the gravitational relativity principle and with the aid of the gravitational local time and auxiliary distance units thus defined, we may solve the problem exactly as we did the one above. But we now see that if the velocity of m_1 in the new system is in the direction of the velocity of the new system by the old, and if

$$\mathbf{B}_2' = -\,\mathbf{B}_1'$$

where primes denote measurement on the moving system, then, since the electromagnetic units of apparent distance and local time are different from the corresponding gravitational quantities,

$$\boldsymbol{\beta}_2' \neq \boldsymbol{\beta}_1', \quad \text{and} \quad R_2' \neq R_1'$$

unless

$$C = c.$$

It seems strange at first sight that Theory V is not overthrown by the same considerations that proved Theory III impossible even for the case of a rotating body. But the arguments used in that case do not apply here; because every particle in the body is affected at every instant by forces radiated from the other particles, and it is obvious from qualitative considerations that they will exert a backward force on the particle of the order of $|\,\boldsymbol{\beta}'^{3}\,|$ times the total force on it, and it is further evident from the fact that the radiation theorem proves that there is no gain of energy that this force must exactly balance the forward component of the non-radiational force.

Reasons for Preference of Electromagnetic Theory. — We now see that Theory V is the only theory we have examined, except the practically impossible Theory I, that does not involve an extremely improbable, continual increase of energy in any rotating planet, sun, or nebula. With such a continual increase of energy it is doubtful if the solar system could have been formed. Furthermore, Theory V is the one that involves the least radiation of negative energy, which we see is a destructive process, from such a system as the solar system is at present. Of course, we cannot prove that the solar system would yet have gone to pieces with more radiation than this, but we can say that if there had been enough additional radiation of this sort it would have.

We have, however, a much more convincing argument, for if we think of such laws as the law of the minimum possible loss of heat in electric currents, the principle of "Least Work" so useful in civil engineering, the principle of "Least Action" or "Hamilton's Principle" in dynamics of matter and of electricity, and many other laws of this sort, it seems highly probable that, if there must be destructive radiation of gravitational energy, the laws by which such radiation takes place should be those involving the least amount of it.

Another argument of the same general nature is furnished by the extreme simplicity of the fundamental equations of natural phenomena, such as the equations of electrodynamics, either in Maxwell's form or in terms of scalar and vector potentials, the equation for the flow of heat in a solid, and many others, that all combine to make us believe that, if there is one set of equations for gravity that are simpler than all other possible equations not involving improbable results, these are the ones that express the phenomena correctly. This argument of simplicity is all the more striking if we write the electromagnetic equations in the remarkably simple form that they assume when expressed in the four-dimensional vector analysis of Lewis.[8] This analysis gives us a set of gravitational equations of equal simplicity, if, but only if, we adopt the electromagnetic theory. And for Theory V we have not only a similar set of equations, but, when we consider their meaning, a simpler explanation of their fundamental causes than can readily be found with any other theory. With these considerations combined with the experimental evidence furnished by the planet Mercury, it seems as though we could hardly help believing in this theory.

To see what Theory V means we have only to consider the theory that matter is made up wholly of electrons and the corresponding positive charges. If now we suppose every positive charge at rest to repel every other positive charge with a weaker force than that with which it attracts an equal negative charge in the same relative position, the ratio of the difference between these forces to the attractive force being a very small number G, we see that every particle of matter at rest will attract every other particle with exactly the observed force if G is properly chosen. And if now we suppose that the magnetic force from a moving positive charge has a smaller effect on another moving positive charge than on an equal negative one with the same relative position and velocity, and that the ratio of the difference between them to the force between those of opposite signs is the same number G, the existence of the vector $\mathbf{h}$ is explained. But we must assume forces between two negative charges to be equal and opposite to those between positive and negative, for, as Gans[9] has shown, this set of assumptions

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[8] These Proceedings, **46**, No. 7, October, 1910.

[9] Gans, Phys. Zeitsch., **6**, No. 23, 803.

is the set which makes the gravitational permeability of any conductor equal to that of a vacuum. And we see, furthermore, that if electrostatic forces are to obey the principle of relativity, and the first of these assumptions is made, the second and the obedience of the force of gravity to the relativity principle are necessary consequences of the first.

By comparison of the electrostatic repulsion of two electrons, whose ratio of charge to inertia is 5.595×10^{-17}, with the gravitational attraction between two spheres, we would find that

$$G = 1.67 \times 10^{-42},$$

if the fundamental positive charge were similar to the negative electron.[10] This readily accounts for the fact that its existence has never been experimentally observed.

We may or may not, as we please, assume that this slight difference between the forces is produced by the same cause which produces the rest of the forces, but from the fact that it is transmitted through the same ether, with the same velocity, it seems most reasonable to assume that it is due to the same cause.

Consequences of this Theory, Negative Energy. — One of the most surprising facts about the electromagnetic theory of gravitation, and one with most surprising consequences, is the fact that we have to introduce the conception of negative energy, both potential and kinetic, distributed through the space around any gravitating matter. And by the term, "negative energy," we cannot mean a mere diminution of the positive energy in the space, as the following considerations will show.

First let us consider the energy radiated from an accelerated mass, whose inertia is balanced by the inertia of some mass at a great distance, so that the radiations of gravitational energy cannot interfere for a considerable time. We now see that during that time the transfer of energy across any element of surface **dS** per unit ct is

$$-\frac{1}{4\pi k}\mathbf{g}\times\mathbf{h}\cdot\mathbf{dS},$$

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[10] Since the inertia of an electric charge e on a sphere of radius a is proportional to e^2/a, G is different from the above value if the fundamental positive charge has not the same e/a as the electron, where a in this case is a sort of average radius of points in the electron or positive charge. But the fact that k is the same for all kinds of matter indicates that, if there is only one kind of positive electricity, with only one value of G, it must be collected in fundamental charges for all of which e/a is the same. Hence we have reason to believe that all atoms of positive electricity are probably alike.

but that if we draw two surface elements, $\mathbf{dS}_1$ and $\mathbf{dS}_2$, parallel to each other and perpendicular to the same line of the vector $\mathbf{g}\times\mathbf{h}$ at a distance dx apart, we see that, if $\mathbf{dS}_2$ is in the direction of $\mathbf{g}\times\mathbf{h}$ from $\mathbf{dS}_1$, the energy radiated from a mass that is accelerated for an infinitesimal time crosses $\mathbf{dS}_2$ at a time $\frac{dx}{c}$ units of time later than that at which it crosses $\mathbf{dS}_1$, so that the transfer is actually in the direction of $\mathbf{g}\times\mathbf{h}$. But such radiated energy has lost all connection with its source, and there is no positive energy radiated, hence it is negative energy that is transferred in the direction of $\mathbf{g}\times\mathbf{h}$ across these surfaces.

It is also interesting to notice that in the case of a mass moving with uniform velocity the vector $\mathbf{g}\times\mathbf{h}$ has the same direction as the motion at all points in the plane through this mass perpendicular to this direction. This also indicates that the mass carries negative energy with it as it moves. But if the mass is not charged with electricity, the electric and magnetic forces due to the electrons and corresponding positive charges within it are zero at points outside the mass. Therefore, the electromagnetic energy is wholly within it, and the external gravitational energy cannot be considered as a mere diminution of the electromagnetic energy on any theory that assumes the existence of positive energy only. To calculate the energy in terms of the electric and magnetic forces we must distinguish between the forces due to positive charges which we may call $\overset{+}{\mathbf{E}}$ and $\overset{+}{\mathbf{H}}$, and those due to negative charges, which we may call $\overset{-}{\mathbf{E}}$ and $\overset{-}{\mathbf{H}}$. In this case the total energy of the distribution is

$$\frac{1}{8\pi}\int\int_{\infty}\int\{(\mathbf{E}^2+\mathbf{H}^2)-\frac{1}{k}(\mathbf{g}^2+\mathbf{h}^2)\}\,d\tau,$$

$$=\frac{1}{8\pi}\int\int_{\infty}\int\{(1-G)\,(\overset{+}{\mathbf{E}}{}^2+\overset{+}{\mathbf{H}}{}^2)+(\overset{-}{\mathbf{E}}{}^2+\overset{-}{\mathbf{H}}{}^2)+2(\overset{+}{\mathbf{E}}\cdot\overset{-}{\mathbf{E}}+\overset{+}{\mathbf{H}}\cdot\overset{-}{\mathbf{H}})\}\,d\tau,$$

where we have exactly the same distribution of total energy in each element; and we have made a change only in assuming that the whole positive charge and whole negative charge have each a much larger amount of positive energy than the total energy of the system, but that negative mutual energy of the two distributions more than neutralizes their positive energy in all volume elements outside the mass, and fails to do so only within the mass.

Stresses in the Gravitational Field. — We have by no means yet exhausted the store of interesting facts connected with this negative energy. For the similarity of the gravitational equations to the electromagnetic tells us that we may expect gravitational energy to have inertia, like that of electromagnetic energy, and also that we may expect to find stresses in the gravitational field like those of the electromagnetic field. By the word "stress" I mean, of course, "force per unit area," but it must be thoroughly understood that "force" is defined merely as "that which produces acceleration in anything possessing inertia," so that the force must be thought of as accelerating the electromagnetic or gravitational energy of the medium rather than the medium itself, which is incapable of motion.

From the exact similarity of the gravitational field around a distribution of moving masses to the electromagnetic field around a similar distribution of charges constrained to move in similar paths, and from the fact that the mechanical forces of the fields in one case are exactly opposite to those in the other, we see that the stresses in the gravitational field are exactly opposite to those of the electromagnetic field. This gives us the following set of stresses: a pressure along the lines of $\mathbf{g}$ with a tension across them, each of intensity $\frac{\mathbf{g}^2}{8\pi k}$, equal to the negative energy per unit volume of the vector $\mathbf{g}$; and a pressure along the lines of $\mathbf{h}$ with a tension across them, each of intensity $\frac{\mathbf{h}^2}{8\pi k}$, equal to the negative energy per unit volume of the vector $\mathbf{h}$. These results look, at first sight, impossible, especially when we notice that these stresses have such enormous values as six hundred tons per square centimeter at the surface of the earth, and forty thousand tons per square centimeter on the sun; because it appears as if the forces in a static distribution would be in a state of unstable equilibrium, in which the least disturbance would cause the lines of force to crumple into a hopeless tangle, but it will appear presently that this is not the case at all.

Negative Inertia. — To see why not, we may again consider our corresponding electrical case, and consider the similarity of the vectors $\mathbf{E}\times\mathbf{H}$ and $\mathbf{g}\times\mathbf{h}$, which have exactly similar lines with proportional intensities at different points, and, what is most important, the same direction in every case. And, as Lorentz[11] proves, in space containing no matter, the force due to the stresses on the surface of any element $d\tau$ in an electromagnetic field is

$$\left(\frac{1}{4\pi c^2}\frac{\partial(\mathbf{E}\times\mathbf{H})}{\partial t}\,d\tau\right).$$

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[11] Lorentz, Theory of Electrons, chapter I, p. 23 et seq.

Therefore we see that in empty space in the gravitational field we have force due to the stresses on the surface of the element $d\tau$ equal to

$$\left(- \frac{1}{4\,\pi c^2 k} \frac{\partial (\mathbf{g} \times \mathbf{h})}{\partial t}\, d\tau \right).$$

But the vector $\mathbf{g} \times \mathbf{h}$ represents the rate of flow of negative energy per unit volume, and hence it appears that, if the stresses in the electromagnetic field accelerate positive energy with its ordinary inertia, the stresses in the gravitational field, which act against the acceleration, must accelerate negative energy with its *negative inertia.* It is now evident that since the system of stresses we have in the gravitational field would give unstable equilibrium in a set of lines of force with positive inertia, they give stable equilibrium in a similar set with negative inertia. And furthermore, it is evident that if we reverse the signs of both stress and inertia, as we do in changing from electromagnetic to gravitational conditions, the motions in free space of the negative gravitational energy will be exactly like those of the corresponding positive electromagnetic energy.

To see what effect this negative inertia of the gravitational field has upon the motion of any mass, we may consider its kinetic energy for different velocities. For a small sphere, either positively or negatively charged, and subject to the deformations required by the relativity principle, the electromagnetic energy for any velocity may be shown to be $\triangle mc^2 R^{-1}$, where $\triangle m$ is the electromagnetic inertia and $\triangle mc^2$ the electrostatic energy when it is at rest. If we now assume that matter is made up of minute electric charges, we see that if these charges are near enough to each other to have their fields of energy overlap to any appreciable extent, then if m is the sum of the inertias of the particles in a body when separated, and hence the gravitational mass of the whole body, the inertia of the whole body may be a different quantity m'. If the overlapping is that of fields of charges of opposite sign, it will make m' less than m, but if it is that of fields from those of the same sign, it will make m' greater than m. But if unbalanced effects of this sort could occur, it is evident that we could expect equal masses of different substances to have different inertias, and since these different inertias have never been observed, we may neglect such effects and say that the electromagnetic inertia of any body is the sum of the inertias of its component charges. This has been tacitly assumed in developing the theory, and we now see that it is a reasonable assumption.[12]

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[12] This assumption is inconsistent with the idea that positive electricity may be freely penetrable to negative electrons, as has sometimes been sup-

Since the body as a whole is subject to the same deformations with change of velocity, we may prove that if its gravitational energy when at rest is $-m_g c^2$, its gravitational energy when in motion will be $-m_g c^2 R^{-1}$, so that the effect of the negative inertia of the gravitational energy will be to reduce the total inertia in the ratio $1 : (1-m_g/m)$.

This result is so important that it is well to look at it also from the point of view of inertia as the property of resisting acceleration. In the case of a positively charged body which is accelerated, we see that every element of charge in it will radiate forces which have at all points outside the element components in the direction opposite to that of the acceleration. Therefore, during a constant acceleration each element will be acted upon by forces radiated from other elements which will hold it back by an amount proportional to the acceleration. But in the gravitational case the corresponding forces will act in the direction of the acceleration, and will therefore help, instead of hinder, the action of the accelerating force. And it will not be noticed that since these forces are inversely proportional to the distance between the elements, the inertias thus obtained will be inversely proportional to any dimension in two similar but unequal bodies with equal charges or masses. We also see that if we extend these considerations to cases of variable accelerations, the electromagnetic effects introduce the tendency to increase the rate of change of acceleration which has the effect of a force in the direction of this rate of the order of

$$\frac{e^2}{c^3}\frac{d\mathbf{a}}{dt}$$

and independent of the size of the body. Much use has been made of this in the theory of emission and absorption of light. We see, too, that the gravitational energy will introduce a similar force, whose ratio to that of the electromagnetic energy is not m_g/m.

It appears now, on account of these changes in the inertia of bodies by the gravitational energy, that we must modify the statements made above about the lack of radiation of negative energy from bodies moving under the action of gravitation. But the modification is not so great as might be supposed, because the case of the symmetrical body rotating on its axis of symmetry still involves no radiation, and the radiation in other cases is still less than what could be expected with other theories. Hence we see that in spite of this modification of the theory, the arguments for its preference over all others are still valid.

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posed ; but it is only one of many objections to this idea, so that the inconsistency need not cause much doubt as to the truth of the assumption.

To form an idea of the extent to which the inertia of a large mass is diminished by the gravitational energy, we may calculate the ratio m_g/m for a sphere of uniform density ρ and radius a. In such a case, at all external points whose distance is r the vector $\mathbf{g}$ has the intensity km/r^2, while at internal points its intensity is kmr/a^3. The energy is now

$$-m_g c^2 = -\frac{1}{8\pi k}\int_0^\infty 4\pi r^2 \mathbf{g}^2 dr,$$

which is readily shown to be

$$-\frac{3}{5}\frac{m^2 k}{a}.$$

Hence we see that

$$\frac{m_g}{m} = \frac{3}{5}\frac{mk}{c^2 a} = \frac{4\pi}{5}\cdot\frac{k\rho a^2}{c^2}.$$

For a sphere of homogeneous density and of size and mass equal to that of the sun, we have

$$m = 2.0 \times 10^{33},\quad a = 7.0 \times 10^{10},\quad k = 6.5 \times 10^{-8},\quad c^2 = 9.0 \times 10^{20},$$

so that
$$\frac{m_g}{m} = 1.2 \times 10^{-6}.$$

The inertia of the sun is therefore diminished by about one part in a million by the gravitational energy it possesses.

Consequences of Negative Inertia. — Small as it is, this minute diminution of inertia shows clearly the way to the ultimate condition of the universe. For we may imagine the sun and all the rest of the stars radiating their heat away as they drift through space, and having the supply renewed only by occasional collisions, each one of which combines the masses of the colliding bodies into a mass as great as both together, but with an inertia, after the heat of collision is lost,[13] not as great as the sum of those of the original masses. Thus a time will come when one of the masses formed by this process will have actually less inertia than one of the parts of which it is made up, and will readily be accelerated to enormous velocities by the least attractions. And at last there will be formed a tremendous mass, of the order of 10^9 times the mass of the sun, whose inertia will be nega-

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[13] Because heat is a form of motion of bodies with electromagnetic mass, we may consider it as electromagnetic energy, with inertia like that of any other such energy.

tive;[14] so that instead of being drawn towards its neighbors in space by their attractions it will appear to avoid them as if it were repelled, while they, being drawn towards it by its enormous attraction, will pursue it as it flees from them.

The more sluggish of them will soon be left far behind, but the livelier ones, with the least inertia, will draw nearer and nearer, until at last one will overtake it, *hit it from behind and slow it down.* By this process its negative inertia will be further increased, until it has collected to itself all matter with positive inertia within reach.

This process will be repeated in many different parts of the universe until at last all matter will be collected in enormous masses with negative inertia. They will then act as if they all had positive inertia but repelled each other, and, therefore, there will be no more collisions. But their heat will be lost by radiation, with no chance to renew the supply, and at last, if the present laws of nature still hold, the universe will be cold and dead forever.

Are all Forces Electromagnetic? — And now that we see that the reason gravitational forces obey the principle of relativity is the fact that they are really electromagnetic forces, and now we know from the Michelson-Morley experiment that all internal stresses in even the most rigid bodies obey the same principle, we may say that we have at last some evidence to show that all such stresses are of electromagnetic origin. And we may now say that the principle of relativity applies to all the laws of nature because it applies to all the laws of electromagnetic phenomena, and because all the laws of nature are laws of electromagnetic phenomena.

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[14] It might be supposed, at first sight, that just when the inertia became zero in the process of losing electromagnetic energy, the mass might have an infinite acceleration. But it will be noticed that the tendencies to resist change of acceleration, not being in the ratio $-m_0/m$, will not be equal and opposite, so that no such effects will occur.

Proceedings of the American Academy of Arts and Sciences.

VOL. XLVII. NO. 15. — JANUARY, 1912.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

BY GREGORY PAUL BAXTER, CHARLES JAMES MOORE AND ARTHUR CLARENCE BOYLSTON.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

SECOND PAPER. — THE ANALYSIS OF PHOSPHORUS TRIBROMIDE.

By Gregory Paul Baxter, Charles James Moore and Arthur Clarence Boylston.

Presented Dec. 13, 1911. Received Dec. 7, 1911.

In a recent investigation by Baxter and Jones [1] upon the atomic weight of phosphorus by the analysis of trisilver phosphate, the constant in question was found to have the value 31.04, if silver has the atomic weight 107.88, or 31.03 if silver is given the value 107.87. While this result is in good accord with those of most earlier experimenters in the same field, Ter Gazarian,[2] on the other hand, from the density of phosphine, has recently obtained a considerably lower value, 30.91. So large a difference as this obviously needs explanation, and the most promising method of solving the problem seemed to be to analyze some other compound of phosphorus.

In the research upon silver phosphate some uncertainty was introduced by the fact that the salt contains only 7.7 per cent of phosphorus, so that the percentage error in determining the molecular weight of silver phosphate is many times multiplied in the calculation of the atomic weight of phosphorus. In this respect phosphorus tribromide is somewhat better suited for the purpose, since it contains 11.5 per cent of phosphorus. Hence in spite of very considerable difficulties in the preparation of the tribromide in a pure state, and in its analysis, we were led to choose this substance for further investigation of the subject.

In outline the method followed was to synthesize phosphorus tribromide by the action of pure dry bromine on pure dry phosphorus

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[1] These Proceedings, **45**, 137 (1910); Jour. Amer. Chem. Soc., **32**, 298; Zeit. anorg. Chem., **66**, 97.

[2] Jour. de Chim. Phys., **7**, 337 (1909); **9**, 101 (1911).

in a vacuum. The product, which contained a slight excess of bromine, was fractionally distilled in a vacuum, and, as soon as the excess of bromine had been eliminated, various fractions were collected and analyzed for bromine in the usual way, after decomposition with water and oxidation of the phosphorous acid produced.

Purification of Materials.

Water. — All the water used in this research was prepared from the laboratory supply of distilled water by further distillation, first from an alkaline permanganate solution, and then a second time, after the addition of a trace of sulphuric acid, through a block tin condenser. No rubber or cork was used in the connection between the condenser tube and the Jena glass still.

Ammonia. — The best commercial ammonia was distilled into the purest water.

Nitric Acid. — C. P. concentrated acid was distilled through a platinum condenser, with rejection of the first two thirds of the distillate. It was always carefully tested in a nephelometer for traces of halogens.

Bromine.[3] — This substance was freed from all but a trace of chlorine by distillation from solution in a concentrated solution of potassium bromide. The product was next converted into potassium bromide by addition to a solution of recrystallized potassium oxalate. In order to remove iodine the solution of potassium bromide was boiled for some time, with the occasional addition of small amounts of the partially purified bromine which had been saved for this purpose. Toward the end of the boiling several small portions of potassium permanganate and sulphuric acid were added to remove last traces of iodine. Next the solution was evaporated to dryness and the dry salt was fused in a large platinum crucible to destroy organic matter. From the fused potassium bromide bromine was prepared as needed by solution in water and the addition of sufficient potassium permanganate and sulphuric acid to oxidize three fourths of the bromide. In this process the bromine was distilled a second time from a bromide, and since this bromide was already nearly pure, last traces of chlorine must have been eliminated from the product. The bromine was separated as far as possible from water, and was dried by resublimed phosphorus pentoxide, from which it was distilled imme-

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[3] For a discussion of methods for purifying bromine see Richards and Wells, These Proceedings, **41**, 440 (1906); Baxter, Ibid., **42**, 204 (1906); Jour. Amer. Chem. Soc., **28**, 1325; Zeit. anorg. Chem., **50**, 392.

diately before use. A quantity of bromine which had been thus treated was evaporated on a steam bath in a glass dish, which was then tested for residual phosphoric acid with negative results.

Phosphorus. — The method used for purifying the phosphorus was distillation with steam. In the case of the phosphorus from which the tribromide for the first series of analyses was prepared, the distillation was assisted by a current of carbon dioxide, and was not repeated. The phosphorus used for the second and third series of analyses was twice distilled with steam, the greater portion at atmospheric pressure, a small portion at reduced pressure, in an apparatus constructed wholly of glass. The purified material was preserved under water until used. Portions of these specimens were carefully tested for arsenic by the Berzelius-Marsh method and were found to contain less than one part in one million of the latter element. We are indebted to Mr. W. A. Boughton for carrying out these tests.

Silver. — Pure silver was prepared by methods which have already been found to be very effective. Since these methods have been described in detail several times in papers from this laboratory,[4] only a brief outline of the procedure is given here. Heterogeneous silver residues were reduced with zinc and sulphuric acid, and thoroughly washed with water. The metal was dissolved in nitric acid, and silver chloride was precipitated by a large excess of hydrochloric acid. After the precipitate had been washed it was dissolved in ammonia and reprecipitated with hydrochloric acid. The resulting chloride was reduced with alkaline sugar solution and the metal was fused on charcoal. After cleansing with sand and etching with nitric acid, the buttons were dissolved in nitric acid, and the metal was precipitated with pure ammonium formate. The thoroughly washed product was fused with a blowpipe on a crucible of the purest lime. Electrolytic deposition with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons followed, and the electrolytic crystals were fused in a current of pure hydrogen on a boat of the purest lime provided with compartments so that the resulting buttons weighed from two to ten grams. After the buttons had been etched with nitric acid until their surfaces were uniformly crystalline, they were thoroughly washed with ammonia and pure water, and finally heated to 400° in a vacuum. The pure silver was preserved in a desiccator over fused potassium hydroxide.

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[4] See especially Richards and Wells, Pub. Car. Inst., No. **28**, 16 (1905); Jour. Amer. Chem. Soc., **27**, 472; Zeit. anorg. Chem., **47**, 70.

Hydrogen Peroxide. — Merck's "Perhydrol," containing 30 per cent hydrogen peroxide, was found to be free from sulphuric acid and halogens and to leave no residue upon evaporation. Hence it was employed without further treatment.

Nitrogen. — Atmospheric nitrogen free from oxygen was obtained by Wanklyn's well-known method of passing air through very concentrated ammonia solution, and then over hot copper gauze in a hard glass tube. The excess of ammonia was removed by scrubbing with a dilute solution of sulphuric acid in three large gas-washing bottles. Since hydrogen is formed by the catalytic decomposition of a portion of the excess of ammonia, this impurity was oxidized in a hard glass tube filled with red hot copper oxide, and the gas was then dried in six towers filled with beads drenched with concentrated sulphuric acid and a long tube filled with resublimed phosphorus pentoxide. Finally the gas was passed through a third hard glass tube filled with hot copper to combine with any last trace of oxygen. The apparatus in which these operations were carried out was constructed entirely of glass with ground glass connections throughout.

Preparation of Phosphorus Tribromide.

Much time was consumed in finding a satisfactory method of preparing pure phosphorus tribromide. It was obvious at the outset that the substance must be rigorously protected from access of moisture, in order to avoid the formation of hydrobromic and phosphorous acids. This object was most simply gained by synthesizing the tribromide in a vacuum from bromine and phosphorus which were initially dry. But since phosphorus dissolves in its tribromide, and can not be readily separated from the latter substance by distillation, an excess of bromine was added at the beginning. Fortunately it was necessary to add only a slight excess of bromine, since a surprisingly small amount of phosphorus pentabromide can be detected in the tribromide by its darker color, especially at high temperatures. This dark color is undoubtedly due in large part to dissociation of the pentabromide into tribromide and bromine. The comparatively easy elimination of the pentabromide from the tribromide also depends upon this dissociation, for the free bromine can be removed by distillation in the first fractions.

At first the attempt was made to remove the excess of bromine by distillation from red phosphorus. But either the red phosphorus still contained traces of the yellow modification, or else the red modification dissolves in the tribromide and vaporizes with it when distilled (possibly as a lower bromide[5]). At any rate the tribromide prepared in this way contained far too little bromine, as was shown by the results of its analysis.

Much better results were obtained by simple distillation in a vacuum. Although the boiling point of the tribromide is thus much lowered, the dissociation of the pentabromide is sufficiently complete to secure rapid elimination of the excess of bromine. As stated before, the disappearance of the bromine can be followed by the color of the distillate and residue. If material is collected for analysis as soon as the bromine has apparently been eliminated it should yield at any rate a minimum value for the atomic weight of phosphorus, unless decomposition of the tribromide into a lower bromide occurs during the distillation. In the latter case, however, the composition of different fractions of distillate would probably not be constant.[1]

The synthesis of the tribromide was effected in an apparatus constructed entirely of glass shown in the figure on page 590. About fourteen grams of pure phosphorus were freed as completely as possible from water by cooling and pressing between folds of hardened filter paper. The phosphorus was weighed to a centigram and placed in the distilling flask D, which had previously been filled with nitrogen through the stopcock A. The flask was then fitted to the separating funnel B by means of a well ground and polished joint C, but it was not connected to the remainder of the apparatus at E, and the capillary tube F opened into the air.

In order to dry the phosphorus completely, the flask was surrounded with boiling water and for four hours a slow current of pure dry nitrogen was forced in at A and flowed out at the end of the constricted tube F. The melted phosphorus was agitated from time to time by shaking the flask in order to liberate any steam which might have been entangled mechanically and to bring new material to the surface of the phosphorus. During this operation a portion of the phosphorus distilled into the cool tube F, and a small amount was vaporized into the air. Probably, too, a small amount of acids of phosphorus was produced since slight oxidation of the phosphorus necessarily took place while it was being introduced into the flask. As soon as the phosphorus had been dried in this way, the end of the constricted tube F was sealed, the stopcock A was closed, and the flask, after being cooled, was exhausted as completely as possible through the stopcock S by means of the Töpler pump W. All the ground glass joints were made gas tight by means of a minimum quantity of syrupy phosphoric

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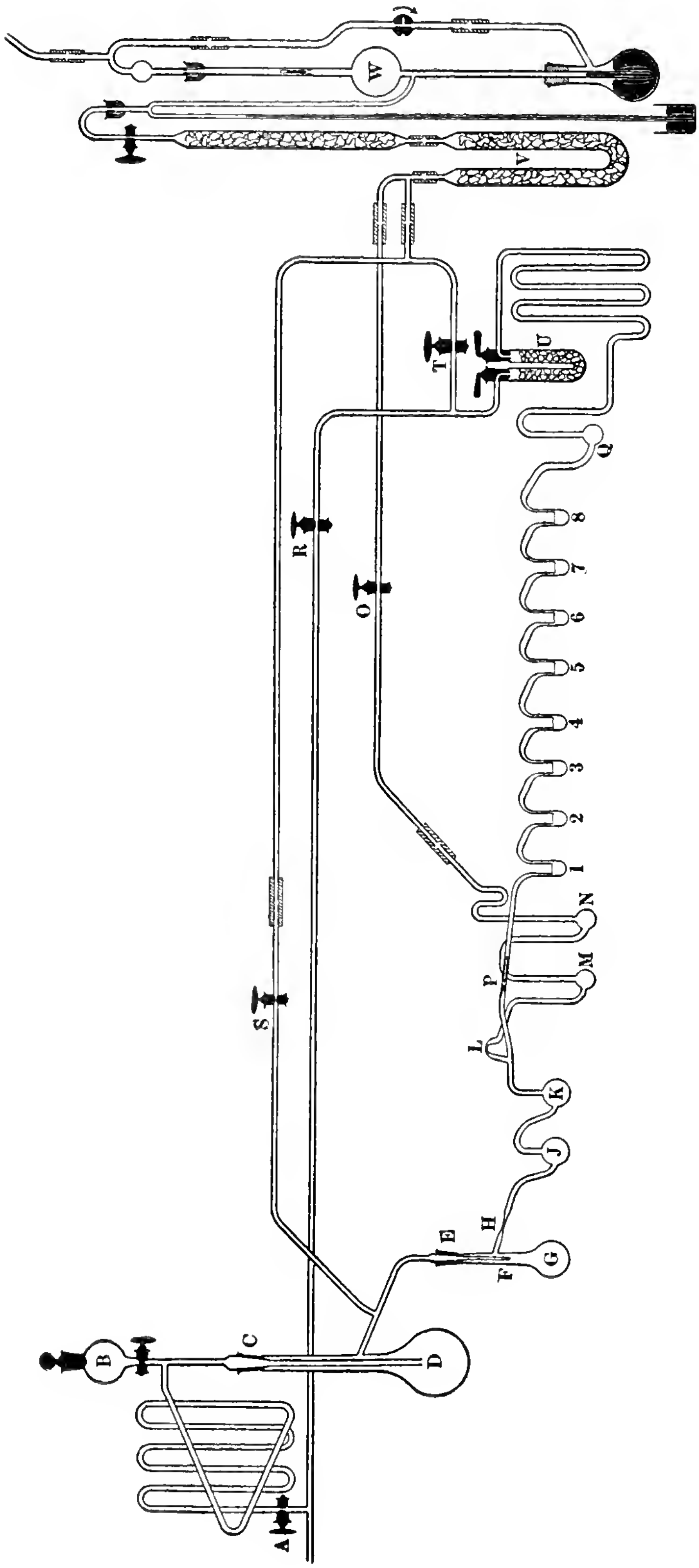
[5] Besson and Fournier, Compt. Rend., **150**, 120 (1910).


A
B
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D
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V
W

acid, and outside this, to prevent the absorption of moisture, soft paraffine was smeared.

Next the calculated amount of pure dry bromine was measured from a burette into the separatory funnel B and the funnel was stoppered. After cooling the flask containing the phosphorus with ice water to reduce the violence of the reaction, bromine was slowly admitted. The rapid evaporation of a portion of the bromine produced the solidification of the remainder. This solid bromine, upon falling into the flask, reacted violently with the phosphorus until a considerable amount of tribromide had been formed. As soon, however, as sufficient tribromide had been produced to dissolve the unchanged phosphorus the action became much less violent so that the bromine could be introduced more rapidly.

When nearly the theoretical amount of bromine had been used, the flask D was immersed in hot water in order to decompose a small amount of solid pentabromide which formed in the upper part of the flask. The bromine thus liberated diffused to the bottom of the flask where it combined with the residual phosphorus dissolved in the tribromide. More bromine was then admitted in very small portions until the warm tribromide acquired the reddish color which indicated an excess of bromine. The end of the reaction can be determined so sharply by the color that the excess of the bromine probably never amounted to more than a few hundredths of a gram, whereas nearly one hundred and twenty-five grams of bromine in all were used in each preparation.

When it was certain that an excess of bromine had been added, the flask D with the tribromide was surrounded with ice water and nitrogen was allowed to enter through A, until the pressure inside the flask was greater than atmospheric. The end of the tube F was then broken off, and the remainder of the apparatus, which had previously been filled with dry nitrogen, was attached by the gound joint E. The flasks D, G, J, K, M, and N were next exhausted through O, while the stopcocks A, R, S, and T were closed. In order to prevent access of bromine to the mercury of the Töpler pump, a **U**-tube V filled with fused potassium hydroxide was located between the pump and the remainder of the apparatus, and this **U**-tube was cooled with concentrated calcium chloride solution and ice.

During the fractional distillation of the tribromide to remove the excess of bromine it was highly desirable to protect the bulbs 1 to 8, in which the tribromide was eventually to be collected, from contact with the first fractions. This was effected by passing the first fractions through the side tube L into the bulbs M and N, while the bulbs 1 to 8 were cut off from the rest of the apparatus by the valve P. This valve was so perfectly made that it was nearly gas tight with no lubricant. Nevertheless, in addition, nitrogen was maintained at atmospheric pressure on the far side of the valve, so that the slight leakage produced a slow reverse current of nitrogen through the valve into the pump by way of the bulbs M and N.

Under as low a vacuum as could be obtained with the pump the tribromide was first distilled from D to G by surrounding D with boiling water and G with ice water. A small residual fraction was left in D, in order to make certain the elimination of phosphorus acids and possible oxybromide. During this distillation any phosphorus which had originally distilled into the tube F and still remained uncombined was converted into tribromide by the excess of bromine. A second similar distillation from G to J and K followed, with rejection of the last few grams in G. The material invariably contained an excess of bromine at this point. The capillary tube H was now sealed with a blowpipe and the flasks D and G were thus disconnected from the apparatus. Next the bulbs M and N were cooled with ice and the tribromide in J was boiled while the bulb K was gently warmed. The vapor from J in bubbling through the warm liquid in K carried with it all the excess of bromine in both bulbs. Furthermore it is probable that if the tribromide contained a trace of hydrobromic acid, the latter substance was eliminated at the same time as the bromine. The distillate collected in M and N as tri- and pentabromide. As soon as ten grams of material had been distilled from J and K the residue, amounting to considerably more than one hundred grams, was nearly colorless; nevertheless five times as much more was distilled into M and N before this part of the apparatus was sealed off at the capillary L. Thus when the stopcock O was closed, the impure distillate was entirely cut off from the remainder of the apparatus.

The bulbs 1 to 8 were then exhausted by opening the stopcocks of the U-tube U and at the point T, while R was closed. The U-tube contained resublimed phosphorus pentoxide to prevent the possibility of back diffusion of moisture into the bulbs. The valve P, into which a piece of soft iron had originally been sealed, could now be pulled from its seat by means of a magnet so that the bulbs J and K were connected with the pump through the bulbs 1 to 8.

In distilling the remainder of the tribromide into the small bulbs the one nearest the pump was filled first by surrounding it with ice water, while the other seven were immersed in beakers filled with boiling water. As soon as bulb 8 was three-fourths filled with material, bulb 7 was cooled with ice water, and so on until all were filled. All the residual material in J and K was distilled into bulb 1.

The train of bulbs 1 to 8 was next sealed off with a blowpipe at the capillaries, and the individual bulbs were separated from the connecting tubes by sealing the capillary tubes. Great care was taken in sealing the capillaries to avoid decomposing the tribromide, by first heating them gently to evaporate any tribromide with which they might be wet. There never was any sign of decomposition of the tribromide during this process.

The final samples of the tribromide were almost colorless when cold, but the very slight yellowish tint of the cold substance was materially increased by a rise in temperature. Since no difference in color could be detected between the first and last samples collected, it seems probable that phosphorus tribromide really possesses a slight yellowish tint.

Two series of samples of tribromide were distilled and sealed in bulbs from two different preparations of material. Ten fractions were collected in the first series and eight in the second.

In a third preparation the removal of the bromine was accelerated by distillation from metallic silver. The bulbs J and K were partly filled with fine electrolytic crystals of the purest silver which had been freed from moisture by ignition in a vacuum. After the tribromide had been distilled into J and K, and the excess of bromine had been distilled into M and N, the capillary tube L was sealed as described before. Then the bulbs J and K with the residual tribromide were warmed for some time with constant shaking before the tribromide was finally distilled into the collecting bulbs.

The Determination of the Weight of the Tribromide and its Analysis.

In the analysis of the tribromide it was first decomposed with water, and then the bromine was precipitated as silver bromide. The reducing effect of phosphorous acid upon silver salts is well known, so that the necessity was obvious of oxidizing the phosphorous acid. This operation was a somewhat delicate one, however, since the hydrobromic acid also is easily oxidized, with consequent loss of bromine. Hydrogen dioxide was eventually found to be the safest oxidizing agent, although its action on the phosphorous acid is not particularly rapid. In preliminary experiments the bulb of tribromide was broken under water and the oxidation was then effected by hydrogen peroxide in dilute nitric acid solution. In the final experiments the method of breaking the bulb under an ammoniacal solution of hydrogen dioxide was employed, since in this way the greater part of the oxidation was almost instantaneously effected. Then after some time the solution was acidified with nitric acid and allowed to stand for a further period. Even then it is probable that oxidation was not quite complete, for if the bromine is precipitated with any considerable excess of silver nitrate, even in the presence of much nitric acid, the silver bromide is perceptibly discolored. On the other hand, if the amount of silver salt used is very nearly equivalent to the bromide present, the precipitate retains its lemon-yellow color even when left for days under the solution.

Since the determination of the weight of the tribromide and its analysis are so intimately connected, they are described together.

The weight of the tribromide was found in each analysis by weighing the bulb with its contents, and then, after breaking the bulb, collecting and weighing the glass. The bulb was first carefully cleaned on the outside and dried, and left in a desiccator over sulphuric acid for at least twenty-four hours. Its weight in air was then found by substituting standardized weights for the bulb on the balance. The buoyant effect of the air was estimated by finding the volume of the bulb in the usual way from the loss in weight under water of known temperature. The conditions of the atmosphere were taken into account in calculating the buoyant effect of the air on the bulb and weights. Since the bulb was exhausted when sealed no correction is necessary for the space in the bulb not filled with liquid.

After the bulb had been weighed and its volume determined, it was placed in a 300 cc. thick-walled Erlenmeyer flask together with somewhat over one hundred cubic centimeters of redistilled ammonia and ten cubic centimeters of pure 30 per cent hydrogen dioxide. A glass stopper which had been very carefully ground into the neck of the flask, was inserted, and the flask was shaken violently enough to break the bulb. The heavy tribromide reacted quietly at the bottom of the aqueous solution, until at the end of about five minutes decomposition was complete. The flask was then allowed to stand twenty-four hours, with occasional shaking. This long standing was necessary to allow a small quantity of ammonium bromide fumes to be collected in the aqueous solution.

The flask, cooled to produce inward pressure, was next carefully opened and the solution was filtered into a three-liter ground-stoppered precipitating flask, while the particles of glass were collected upon a small filter paper. This filter was very thoroughly rinsed with pure water until the filtrate and washings amounted to about 1200 cc.

In order to find the weight of the glass the filter was burned at as low a temperature as possible in a weighed platinum crucible. When the weight of the glass, corrected to vacuum, was subtracted from the corrected weight of the bulb and the tribromide, the weight of the tribromide in vacuum was obtained.

In order to make sure that this method of finding the weight of the glass was a satisfactory one, it was tested by several blank experiments with bulbs containing no tribromide. These bulbs were first weighed in the air unsealed, and then were treated in exactly the same way as bulbs containing tribromide. In two cases the fragments of the bulbs were collected upon a weighed Gooch-Munroe-Neubauer crucible. In the first three, however, the glass was collected upon a small filter paper as in the analyses.

Weight of Bulb. grams.	Weight of Glass recovered. grams.	Difference. gram.
1.20098	1.20097	—0.00001
0.99814	0.99813	—0.00001
1.01851	1.01846	—0.00005
1.12986	1.12994	+0.00008
1.08438	1.08441	+0.00003

Since in every experiment the weight of the glass collected agrees with that of the bulb within 0.00008 gram and is never more than 0.00005 gram less than that of the bulb, it is evident that no important amount of glass is lost either by passing through the filter paper or by solution in the ammoniacal liquid.

The filtrate containing ammonium bromide was next acidified by the addition of about 40 cc. of concentrated nitric acid diluted to about 300 cc. Since bromine was sometimes temporarily set free during the addition of the acid, the acid solution was poured into the bromide through a thistle tube the stem of which extended to the bottom of the flask. Thus, although bromine might be set free at the dividing surface between the bromide and the nitric acid, no bromine ever reached the upper surface of the liquid, owing to unoxidized phosphorous compounds in the bromide solution. The thistle tube was thoroughly rinsed into the flask, the stopper of the flask was moistened and put in place, and the flask was gently agitated to mix the solutions. It was then allowed to stand for forty-eight hours. In no case was there any evidence that bromine was permanently set free by the nitric acid, for after the mixing of the solutions they were always colorless, and when the flasks were opened after two days' standing no odor of bromine could be detected, although 0.00001 gm. is readily perceptible in 3 liters of air.[6]

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[6] Baxter, Thorvaldson and Cobb, Jour. Amer. Chem. Soc., **33**, 329 (1911).

During the standing in acid solution the oxidation of the residual phosphorous acid progressed, but even at the end of the period it was not quite complete. Precipitation of the silver bromide immediately after acidification invariably resulted in darkened salt, but after forty-eight hours an apparently pure product was obtained, if no appreciable excess of silver was used.

The bromine in each sample was determined in two ways, first by finding the amount of silver necessary to combine with it, second, by weighing the silver bromide formed. Both determinations could be carried out with the same sample of tribromide.

A quantity of silver equivalent to the tribromide within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. After the silver solution had been freed from oxides of nitrogen by dilution and heating, about 40 cc. of concentrated nitric acid was added and the whole was diluted to a volume of about one liter. The silver solution was then quantitatively added to the bromide solution, with constant agitation, and the stoppered precipitating flask was allowed to stand for several days with occasional shaking. When the precipitate had coagulated and settled so completely that the supernatant liquid was apparently clear, portions of the solution were tested in a nephelometer[7] for excess of bromide or silver. As a matter of fact, bromide was always found in slight excess. The deficiency of silver, which was never more than a very few tenths of a milligram, was made up as nearly as could be estimated by means of a hundredth normal solution of silver nitrate. After thorough shaking and standing until the solution was perfectly clear, tests for excess of bromide or silver were again made. If necessary this process was repeated, until eventually the amounts of bromide and silver were equivalent. Owing to the slight solubility of silver bromide at this point the solution remained essentially clear, even in the nephelometer, when either bromide or silver solution was added.

The solution was now allowed to stand for a week with occasional shaking and then was tested again in the nephelometer. Usually a deficiency of one or two tenths of a milligram of silver was found, owing apparently to extraction of occluded soluble bromide from the silver bromide. This deficiency of silver was supplied and the solution was left for another week before being tested again, and this process was repeated until in the course of a week no further change in the solution took place. In a few analyses the solutions were tested over a

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[7] Richards and Wells, Amer. Chem. Jour., **31**, 235 (1904); **35**, 510 (1906).

period of four months, but in no case was an appreciable change in the end-point found after it had remained constant for a week. In most cases the final end-point was reached within two weeks.

This difficulty from occlusion by the silver bromide was unexpected since it has not been met to the same extent in other similar cases in this laboratory.[8] In fact, it was not discovered in this research until Analyses 1, 2, 5, 9, and 10 of Series I had been completed. After its discovery several unsuccessful attempts were made to eliminate the occlusion. In Analyses 6 and 19 the solutions of ammonium bromide and silver nitrate were each diluted to nearly four liters before precipitation. In these two analyses, on account of the large size of the precipitating vessel no attempt was made to collect the silver bromide, since the results of the comparison with silver were no different from those obtained in more dilute solution. Although occlusion of bromide seemed to be diminished in extent by this modification, the time necessary for the establishment of equilibrium was not materially lessened. Even in Analysis 6, where the bromide solution was added to the silver solution, the occluded substance seemed still to be a soluble bromide. Cooling the solutions to the temperature of ice water before precipitation seemed to accentuate the occlusion.

As soon as a permanent end-point had been reached, the precipitate was thoroughly washed by decantation with pure water and collected upon a weighed Gooch-Munroe-Neubauer crucible. The crucible and contents were heated gradually to nearly 200° and were kept at that temperature for eighteen hours or more. Then they were cooled and weighed by substitution for a similar counterpoise. In order to find the moisture retained by the dried precipitate it was transferred as rapidly and completely as possible to a small porcelain crucible which was immediately weighed with its cover. Then the silver bromide was fused by heating the small crucible contained inside a much larger one. During the solidification of the bromide the system was carefully rotated so that the fused bromide was stirred and caused to solidify in a thin layer. The loss in weight on fusion was then determined. This loss seldom amounted to more than 0.001 per cent of the weight of the salt. The fused bromide was always clear and light yellow, whereas an astonishingly small percentage of impurity is capable of producing perceptible darkening of the salt.

Since silver bromide possesses an appreciable solubility in water,[9] the

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[8] See, however, Richards and Staehler, Jour. Amer. Chem. Soc., **29**, 632 (1907); Ber. d. d. chem. Gesell., **39**, 3618.

[9] Böttger, Zeit. physik. Chem., **46**, 602 (1903), 0.00008 gm. per liter at 20°; Kohlrausch, Ibid., **50**, 536 (1905), 0.00011 gm. per liter at 21°.

SERIES I.

$PBr_3 : 3Ag$

Ag = 107.880 Br = 79.916

Number of Analysis.	Fraction of PBr$_3$.	Weight of PBr$_3$ in Vacuum.	Weight of Ag in Vacuum.	Deficiency of Ag.	Corrected Weight of Ag in Vacuum.	Ratio PBr$_3$: 3 Ag.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	grams.		
1	1	5.95293	7.11494	0.00010	7.11504	0.836668	31.031
2	2	4.71056	5.63017	0.00005	5.63022	0.836657	31.028
3	3	4.72373	5.64553	0.00030	5.64583	0.836676	31.034
4	4	6.47622	7.74048	0.00000	7.74048	0.836669	31.031
5	5	4.61956	5.52120	0.00020	5.52140	0.836665	31.030
6	8	7.62060	9.10809	0.00040	9.10849	0.836648	31.025
7	9	3.83321	4.58153	0.00010	4.58163	0.836648	31.025
8	10	4.72578	5.64800	0.00035	5.64835	0.836666	31.030
Average						0.836660	31.031

SERIES II.

$PBr_3 : 3Ag$

Ag = 107.880 Br = 79.916

Number of Analysis.	Fraction of PBr$_3$.	Weight of PBr$_3$ in Vacuum.	Weight of Ag in Vacuum.	Deficiency of Ag.	Corrected Weight of Ag in Vacuum.	Ratio PBr$_3$: 3 Ag.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	grams.		
16	1	3.21808	3.84619	0.00030	3.84649	0.836628	31.018
17	2	5.77604	6.90359	0.00020	6.90379	0.836648	31.025
18	5	5.51730	6.59400	0.00056	6.59456	0.836644	31.024
19	6	7.15048	8.54603	0.00050	8.54653	0.836653	31.026
20	7	7.94753	9.49900	0.00030	9.49930	0.836644	31.023
21	8	4.30924	5.15044	0.00030	5.15074	0.836625	31.018
Average						0.836640	31.022

SERIES I.

$PBr_3 : 3AgBr$.

Number of Analysis.	Fraction of PBr_3.	Weight of PBr_3 in Vacuum.	Weight of AgBr in Vacuum.	Loss on Fusion.	AgBr from Filtrate and Washings.	Corrected Wt. of AgBr in Vacuum.	Ratio $PBr_3 : 3 AgBr$.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	gram.	grams.		
9	1	5.95293	12.38515	0.00015	0.00060	12.38560	0.480633	31.035
10	2	4.71056	9.79992	0.00011	0.00077	9.80058	0.480641	31.039
11	3	4.72373	9.82782	0.00018	0.00066	9.82830	0.480624	31.031
12	4	6.47622	13.47392	0.00015	0.00051	13.47428	0.480636	31.036
13	5	4.61956	9.61089	0.00005	0.00059	9.61143	0.480632	31.034
14	9	3.83321	7.97524	0.00006	0.00045	7.97563	0.480615	31.025
15	10	4.72578	9.83205	0.00004	0.00060	9.83261	0.480623	31.029
Average							0.480629	31.033

SERIES II.

$PBr_3 : 3AgBr$.

Number of Analysis.	Fraction of PBr_3.	Weight of PBr_3 in Vacuum.	Weight of AgBr in Vacuum.	Loss on Fusion.	AgBr from Filtrate and Washings.	Corrected Wt. of AgBr. in Vacuum.	Ratio $PBr_3 : 3 AgBr$.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	gram.	grams.		
22	1	3.21808	6.69502	0.00015	0.00066	6.69553	0.480631	31.034
23	2	5.77604	12.01740	0.00030	0.00051	12.01761	0.480631	31.034
24	5	5.51730	11.47893	0.00014	0.00067	11.47946	0.480624	31.030
25	7	7.94753	16.53530	0.00032	0.00071	16.53569	0.480629	31.032
26	8	4.30924	8.96560	0.00024	0.00059	8.96595	0.480623	31.029
Average							0.480628	31.032

SERIES III.

$PBr_3 : 3AgBr$.

Ag = 107.880 Br = 79.916

Number of Analysis.	Fraction of PBr_3.	Weight of PBr_3 in Vacuum.	Weight of AgBr in Vacuum.	Loss on Fusion.	AgBr from Filtrate and Washings.	Corrected Wt. of AgBr in Vacuum.	Ratio $PBr_3 : 3AgBr$.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	gram.	grams.		
32	1	4.39626	9.14614	0.00018	0.00067	9.14663	0.480643	31.040
33	3	7.07758	14.72594	0.00017	0.00055	14.72642	0.480604	31.019
34	4	4.19854	8.73548	0.00020	0.00058	8.73586	0.480610	31.022
35	6	7.26540	15.11696	0.00020	0.00049	15.11725	0.480603	31.018
36	8	7.75072	16.12689	0.00032	0.00080	16.12737	0.480594	31.013
Average							0.480611	31.022
Average of Series I, II, and III							0.480623	31.029

SERIES III.

$PBr_3 : 3Ag$

Ag = 107.880 Br = 79.916

No. of Analysis.	Fraction of PBr_3.	Weight of PBr_3 in Vacuum.	Weight of Ag in Vacuum.	Deficiency of Ag.	Corrected Weight of Ag in Vacuum.	Ratio $PBr_3 : 3Ag$.	Atomic Weight of Phosphorus.
		grams.	grams.	gram.	grams.		
27	1	4.39626	5.25417	0.00030	5.25447	0.836671	31.032
28	3	7.07758	8.45917	0.00040	8.45957	0.836636	31.021
29	4	4.19854	5.01821	0.00030	5.01851	0.836611	31.013
30	6	7.26540	8.68375	0.00030	8.68405	0.836637	31.021
31	8	7.75072	9.26366	0.00040	9.26406	0.836644	31.023
Average						0.836640	31.022
Average of Series I, II, and III . .						0.836647	31.025

filtrate and wash waters were evaporated to small bulk, and after a slight precipitate of silicic acid had been removed by filtration, was diluted to 100 cc. Portions of the solution were then analyzed for silver by comparison in the nephelometer with standard silver nitrate solutions, after the addition of an excess of bromide. In each analysis the amount obtained in this way exceeds slightly the amount to be expected from the solubility of silver bromide, owing doubtless to colloidal silver bromide which escaped the crucibles. A correction for the silver found in this way, estimated as bromide, was added to the weight of the main mass of silver bromide.

The precipitating flask was rinsed with ammonia, and, if the solution was found to contain silver, the quantity was determined in a similar fashion in a nephelometer and a correction applied.

The preceding tables contain the results of all the analyses which met with no accidents. A considerable portion of the preliminary work on the methods of preparation and analysis was done by A. C. Boylston. The perfection of the apparatus and methods, and all the final preparations and analyses were made by C. J. Moore.

Weighings were made on a No. 10 Troemner balance sensitive to a very few hundredths of a milligram, while the gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.[10]

Vacuum corrections were applied as follows:

	Specific Gravity.	Vacuum Correction.
Weights	8.3	+0.000145
AgBr	6.47	+0.000041
Ag	10.49	−0.000030
Glass	2.5	+0.000335

The following table, which gives the ratio of silver used to silver bromide obtained in the same analysis, strengthens the view that the precautions taken to prevent reduction of the silver salts by the phosphorous compounds and occlusion by the silver bromide were effective.

Analyses.	Ag : AgBr.
1 and 9	0.574461
2 and 10	0.574478
3 and 11	0.574446
4 and 12	0.574463
5 and 13	0.574462
7 and 14	0.574454
8 and 15	0.574451
16 and 22	0.574486
17 and 23	0.574473
18 and 24	0.574466
20 and 25	0.574473
21 and 26	0.574478
27 and 32	0.574470
28 and 33	0.574448
29 and 34	0.574472
30 and 35	0.574446
31 and 36	0.574431
Average	0.574462

Although the average result is very slightly higher than the value which has already been shown by Baxter[11] to be the most probable

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[10] Jour. Amer. Chem. Soc., **22**, 144 (1900).

[11] These Proceedings, **42**, 201 (1906); Jour. Amer. Chem. Soc., **28**, 1322; Zeit. anorg. Chem., **50**, 389.

one, 0.574453, the difference, which is less than 0.002 per cent, is too small to be significant.

In examining critically the results recorded in the foregoing tables it should first of all be noted that a given percentage error in the experimental work is multiplied nine times in the calculation of the atomic weight of phosphorus. That is, an experimental error of one one-hundredth of a per cent affects the atomic weight of phosphorus by 0.027 unit. The highest value for the atomic weight of phosphorus in these tables is 31.040, the lowest 31.013, a difference corresponding exactly to one one-hundredth of a per cent in the experimental work. On the whole, however, the agreement of the results is better than this, since, of the thirty-six results, twenty-seven fall between the limits 31.035 and 31.021, a difference only half as large. In other words, the different specimens of material seem to be identical as far as the method is capable of testing this point.

In each series, if the first fraction, that of the highest number, 8 or 10, contained an excess of bromine, it would have yielded too low a result, while if decomposition occurred during the distillation, with the possible production of lower bromides of phosphorus, the residual fraction, 1, would have yielded too high a result. The only differences in each series, however, seem to be purely accidental. Furthermore, the three series yield average results in practical unanimity.

In the following table the final average of this research is compared with that of Baxter and Jones with silver phosphate:

	Ag = 107.88	Ag = 107.87	Ag = 107.86
PBr_3	31.027	31.024	31.021
Ag_3PO_4	31.04	31.03	31.02

SUMMARY OF RESULTS.

1. A method is described for the preparation of pure phosphorus tribromide.
2. It is shown that the precipitation of the halogen of phosphorus halides after decomposition with water, can safely be done only after the oxidation of the greater portion of the phosphorous acid produced.
3. A method is described for the determination of the bromine in phosphorus tribromide by comparison with silver and as silver bromide.
4. The molecular weight of phosphorus tribromide referred to silver 107.88 is found to be 270.775, whence phosphorus has the atomic weight 31.027. If silver is taken at 107.87, the atomic weight of

phosphorus becomes 31.024. These values agree very closely with those found by the analysis of silver phosphate by Baxter and Jones.

An attempt to prepare and analyze phosphorus trichloride in a similar manner is now under way in this laboratory.

We are particularly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

Cambridge, Mass.
December 1, 1911.

Proceedings of the American Academy of Arts and Sciences.
Vol. XLVII. No. 16. — March, 1912.

POLYCERELLA ZOOBOTRYON.

By W. M. Smallwood.

POLYCERELLA ZOOBOTRYON.[1]

By W. M. Smallwood.

Presented by E. L. Mark, October 12, 1911. Received December 30, 1911.

Contents.

I. External Characters.

In a previous paper (Smallwood, **:10**), the general external features of this new species (Figure 1) were described; a part of that description follows, as I desire to present at this time a complete account of the morphological characters of the species — the histology as well as the anatomy.

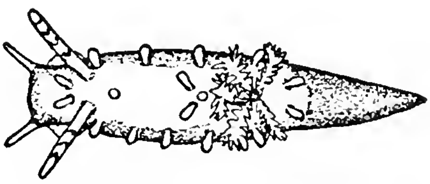

Figure 1. Polycerella zoobotryon, dorsal view. Magnified 8 diameters.

" Polycerella zoobotryon is a small nudibranch, from 5 to 6 mm. in length and 1 1/2 mm. wide. The body is thickest just anterior to the branchial plumes. The shape is much as in Polycera — elongated, narrow, and about as high as broad. Body compressed, smooth, sloping rather abruptly from the branchial plumes

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[1] Contributions from the Bermuda Biological Station for Research No. 24, and from the Zoölogical Laboratory of Syracuse University.

posteriorly until it merges into the long, pointed tail, which is much narrower and thinner than the body, and nearly one third the total length of the animal. The head is blunt and squarish. The tentacles are cylindrical, non-retractile, and one fourth the length of the rhinophores.

"The rhinophores are non-retractile, cylindrical, each having from three to six cup-like, equidistant folds on the posterior surface of its distal two-thirds.

"On the sides and dorsum of the body there are a number of short, clavate papillae, the tips of which are translucent. The number is not constant, but ranges from 16 to 19. Their distribution is as follows: — Of eight which are constant in position, two occupy the median plane, one of them behind the rhinophores about one sixth of the distance between base of branchial plumes and rhinophores, the other in front of the plumes about one fourth of the same distance. The remaining six are arranged in pairs near the median plane, one pair a little in front of the rhinophores and distant from each other about the thickness of a papilla; a second pair slightly in front of the posterior median papilla and a little further apart than the anterior pair; the third pair nearly as much behind the plumes as the posterior median papilla is in front of them; these are still further from each other.

"In addition to these eight papillae, there are on the dorsum near its lateral margins from eight to eleven papillae. There are four on each side, or four on one side and five on the other, or, finally, five on one side and six on the other.

"The ground color is whitish, mottled with light brown arranged in irregular splotches. A less abundant darker brown is disposed in streaks across the lighter brown. The foot is white and without any color markings. Its margin, as well as the tips of the papillae, is translucent.

"The foot is smooth and slightly notched anteriorly. The mouth is T-shaped [or a vertical slit]. The anal opening is subcentral in position, and the excretory orifice is just posterior to it, both being surrounded by the gills.

"The gills consist of four or five more or less irregularly branching plumes.

"When at rest, the body is shortened, the tentacles drop back alongside the body, and the rhinophores lie on the dorsum. The papillae, which are constantly in motion when the animal is crawling, are bent dorsally when it is at rest, and are often knobbed. Under a low power lens one can see the long cilia in motion. The animal assumes a variety of positions while in this resting state, and it frequently rests on its back. The foot may be fully expanded or much contracted. When the animal was placed in a weak solution of methylene-blue in sea-water, the cup-like folds on the rhinophores appeared as swellings, and after a few hours the lateral papillae and rhinophores were sloughed off.

"The eggs are laid in a cylindrical mass of jelly. The number varies from one hundred to three hundred in each mass. Each animal lays several egg-masses.

"The animals are very hardy, living in confinement for over six weeks."

II. The Systems of Organs.

The several systems of internal organs of Polycerella zoobotryon are so compactly grouped that it makes their interpretation difficult. The thin integument is rendered quite firm by the presence of numerous rod-shaped spicules. Between the integument and the various internal organs there is what remains unoccupied of the secondary body cavity, or coelom. In gross dissection one can recognize the anterior portion of the digestive system, consisting of the short buccal region, the dorsal suctorial bulb, and the ventral odontophore. The esophagus is distinguished with difficulty from the several reproductive ducts. The nerve collar of ganglia is so minute as to be made out only with fairly high powers of the dissecting microscope. Immediately posterior to the above organs lies the two-parted visceral mass, nearly concealed on the dorsal side of the liver and kidney chamber. The remaining portion of the secondary coelom is filled by the oval posterior visceral mass, which is composed of the liver and the hermaphroditic glands, bearing on their dorsal surface the stomach-intestine, kidney, and heart. The exact relationships of these several organs can be made out only by the aid of stained sections. Whole animals were fixed in either Hermann's fluid, Müller's fluid, or a picro-acetic mixture, the first two giving the best results. After remaining in Hermann's fluid for ten days, admirable adequately stained sections were secured, which have enabled me to make out some of the more perplexing conditions of the minute anatomy. Several specimens left in Hermann's fluid for three weeks were useless because they had become so brittle. Sections were made in the three principal planes of the body; these, together with dissections of several of the organs, have furnished the material for this study.

The observations on the living animal and the collection of the material were made in January, 1909, at the Bermuda Biological Station. I desire to express to the Director, Professor E. L. Mark, and to the local authorities my appreciation of the courtesies extended to me during this time.

1. *The Integument.*

The integument consists of an outer epidermal layer, the cells of which vary much in appearance, and a dermal layer of loosely united connective-tissue cells. The epidermis is strongly ciliated on the surface of the foot, and the cilia can be traced up the sides of the body, although here they are much shorter ; the dorsum is entirely destitute of cilia. The basal corpuscles at the base of the cilia are conspicuous. The pigment of the integument is deposited in roundish vaculated masses mostly at the inner ends of the epidermal cells. In the dorsum the epidermal cells are broad, short, and highly vacuolated, but in passing ventrally they gradually change to the elongated, cylindrical, richly cytoplasmic cells of the foot. The cells in the epidermis of the foot are fully twice as long as those on the back and are much crowded. The glands of the foot are simple, flask-shaped, multicellular glands having a small lumen. None of the epidermal cells of the foot appear to be glandular, as are many of those on the sides and dorsum, and on the rhinophores. The cells covering the gills constitute a thin columnar epithelium of a simple character. Histologically the foot is distinguished by a thicker epidermis, numerous glands, and a larger amount of connective tissue and irregularly shaped muscle cells.

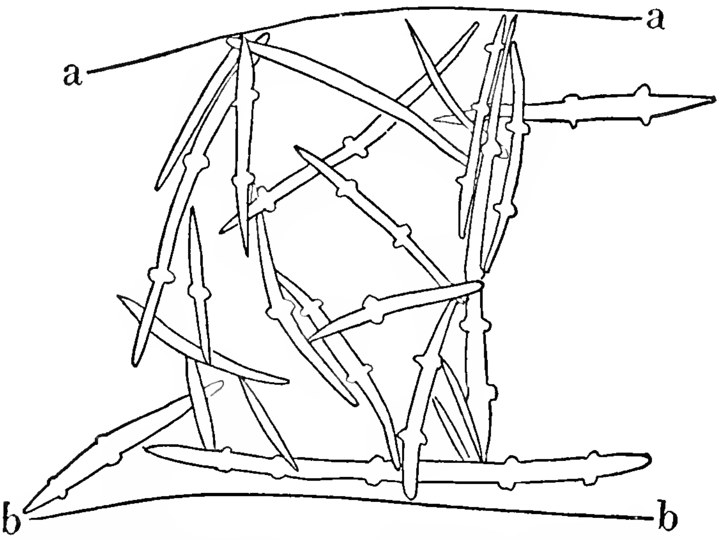

FIGURE 2. Spicules of the foot. *aa.bb.*, lateral margins of foot. Camera lucida, one inch ocular, and one-sixth inch objective. × 612.

The dermis contains numerous spicules, which vary in size from 15 to 60 micra in length and 1.4 to 3 micra in diameter. Each spicule is rounded at the ends and has a number of spiny enlargements. The largest spicules (Figure 2) are found in the foot. Their arrangement does not follow any plan, except that in the rhinophores and the several integumentary processes they are mostly parallel to one another.

2. *Anatomy of Digestive System.*

The mouth opens by a vertical slit directly into a short passage about 10 micra long, the buccal cavity (Figure 4, *cav. buc.*). The posterior part of this passage expands to form the pharynx, into the posterior end of which open three hollow organs; ventrally the anterior end of the radula sac (*sac. rad.*); more dorsally, the esophagus (*oes.*); and still more dorsally, the cavity of the suctorial bulb (*bb. suc.*). The walls of the buccal cavity are largely composed of muscles and have a thickness of 12–15 micra. The dorsal portion of the buccal cavity is directly continuous with the enlarged suctorial bulb, the wall of whose fundus often attains a thickness of 30 micra. The posterior wall is not more than one half as long as the anterior. The distance

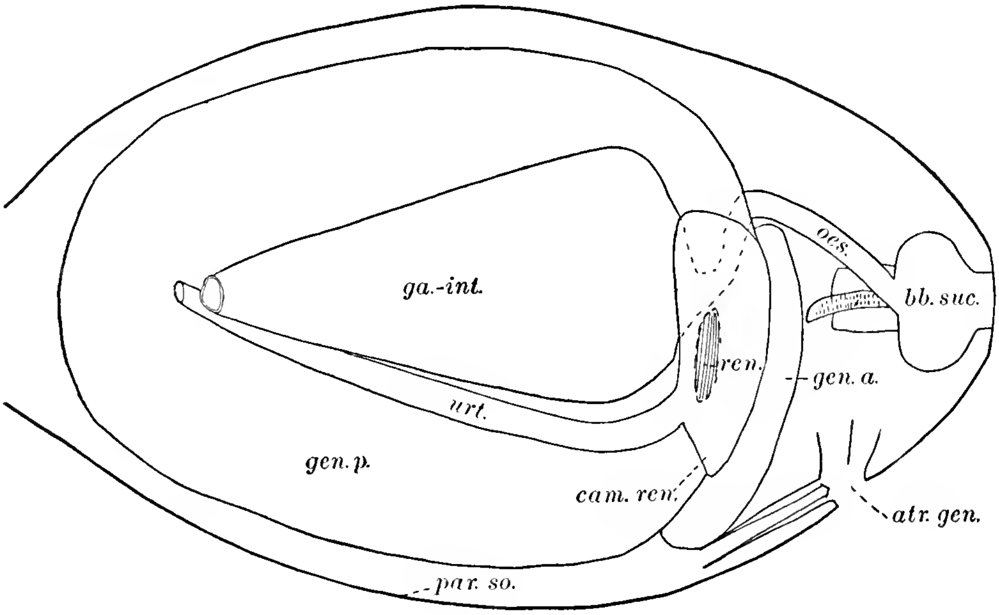

FIGURE 3. Diagram showing the general topographical relations of digestive, reproductive, and renal systems as seen from above. *atr.gen.*, genital atrium; *bb.suc.*, suctorial bulb; *cam.ren.*, kidney chamber; *ga.-int.*, stomach-intestine; *gen.a.*, anterior genital mass; *gen.p.*, posterior genital mass; *oes.*, esophagus; *par.so.*, body wall; *ren.*, kidney; *urt.*, ureter.

from the mouth opening to the most dorsal portion of the suctorial bulb is about 70 micra, the cavity of the bulb being 25 micra long (Figure 4). The suctorial bulb is often in contact with the nerve collar.

The radula is borne on a roundish muscular mass 13 micra in diameter. The radula sac is practically cylindrical and 12 micra in diameter (Figures 3, 4, *sac. rad.*); it projects 10 to 15 micra from the dorsal surface of the muscular mass. The total number of rows of teeth is 33–35, of which 18–20 are in the radula sac; in the posterior end of the sac are the beginnings of from 2–4 more rows. Each row contains eight teeth, the median tooth being absent, which gives the following formula 3–1–0–1–3. The first lateral tooth (Figure 5 l^1) is large and of a deep amber color; it is seven micra long and its greatest width is 1 1/2 micra. The lateral margin bears a wing-like projection 1/2 micron wide. The median edge of the distal half of the tooth is somewhat crenulated, producing the effect of a number of minute rounded teeth. This crenulated margin comes into close contact with the same region on the opposite tooth. Laterally there are three small teeth, the marginals; the first, though the largest of the three, is not more than 3 micra long and one micron wide; these

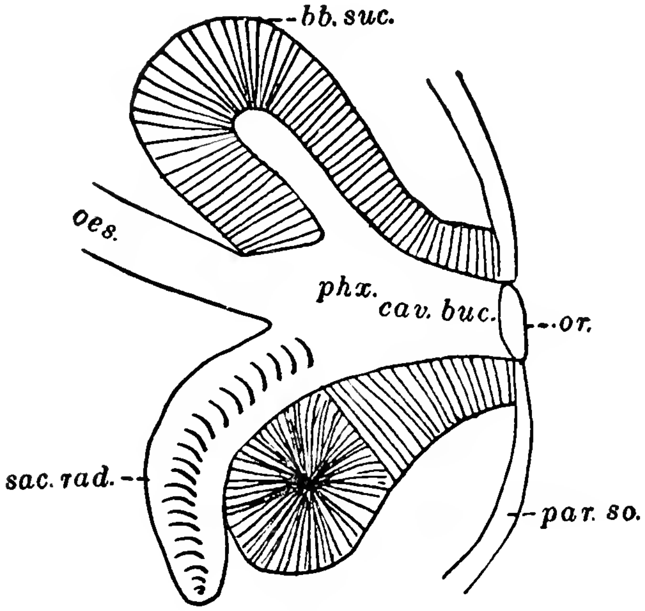

FIGURE 4. Diagram to show relation of organs to the pharynx. *bb.suc.*, suctorial bulb; *cav.buc.*, buccal cavity; *oes.*, esophagus; *or.*, mouth; *par.so.*, body wall; *phx.*, pharynx; *sac.rad.*, radula sac.

three marginals are not so deeply colored as the first lateral and have smooth outlines (Figure 5, l^{II}, l^{III}, l^{IV}).

Verrill ('**80**, p. 386) gives the characteristics of the radula of the genus Polycerella as follows: "Odontophore with six rows of teeth; median row absent; inner laterals large, curved, with three denticles; two outer rows much smaller, simple hook-shaped." Balch (**'99**, p. 150) gives for P. davenportii, "Radula almost as in P. emertonii Verrill ('**80–81**, p. 387; '**82**, p. 548), rhachidian tooth wanting; pleurae strongly hooked with accessory points, large; uncini two, sickle-shaped. Formula 2–1–0–1–2." The genus characters of the teeth should be modified, both in reference to the number of rows of teeth and to the shape of the outer laterals, so as to read as follows: — Odontophore with six to eight rows of teeth, median row absent, inner laterals large, slightly curved; outer rows much smaller, may or may not be curved.

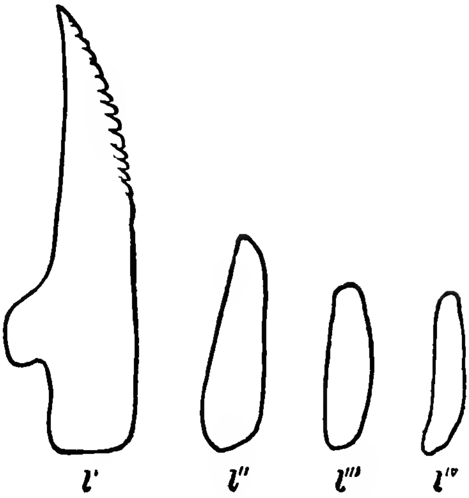

Figure 5. l^{I}, First lateral tooth; l^{II}, l^{III}, ll^{IV}, second, third, and fourth lateral teeth drawn under one-sixth in. objective and one in ocular, with the aid of a camera lucida.

The esophagus (Figures 3, 4, *oes.*), as it arises from the dorso-posterior angle of the pharynx, has a diameter of 15 micra, which it retains until it expands into the stomach. It passes dorsally and posteriorly 100 micra, until it reaches the anterior surface of the posterior genital mass, where it turns abruptly to the right, entering the liver and passing through it for a short distance. As it emerges from the liver, it expands into the stomach-intestine (Figure 3, *ga.-int.*), the anterior extremity of which is beneath the renal chamber. The stomach-intestine is dorsal to the posterior hermaphroditic mass, and it reaches its greatest width near its anterior end, becoming gradually smaller until the anal opening is reached. There is no differentiation into stomach and intestine. The stomach-intestine receives two separate bile ducts, each connected with an independent bile sac. The duct of the smaller sac opens into the floor of the anterior end of the stomach-intestine, while that from the much larger bile sac opens into the posterior third of the organ.

A single pair of salivary glands, each about 28 micra long and 12 micra in diameter, opens into the posterior part of the pharynx just anterior to the origin of the esophagus. Each gland is flask-shaped, the neck of the flask being only one half the diameter of its fundus. These glands are partly covered by the nerve collar. In the wall of the buccal tube there are a considerable number of small glands that open into the buccal cavity.

3. *Histology of Digestive System.*

The walls of the buccal cavity, the pharynx, and the suctorial bulb are lined with a firm, thin layer of chitin, which is as deeply colored as the first row of lateral teeth. In the suctorial bulb and the posterior region of the pharynx the chitin is thinner and less deeply colored.

The esophagus is lined for its entire length with a ciliated epithelium, which makes up about one half of the thickness of the wall, the remaining portion being made up of connective-tissue and muscle cells.

The wall of the stomach-intestine is composed of a thick inner epithelial layer, with a well marked basement membrane, and a very thin outer layer of muscle and connective tissue, which in many places is only one or two cells thick. The cells in the epithelial layer are large, but from the basement membrane to the free surface the distance is noticeably short. The free end of each cell is highly vacuolated; the nucleus is basal and surrounded by fine cytoplasmic granules. These cells show little variation in their appearance throughout the length of the stomach-intestine.

The cells of the salivary glands are quite uniform in size, possibly a little longer in the larger part of the gland. Each cell is nearly cylindrical; its nucleus is basal, and its cytoplasm finely and homogeneously granular.

4. *The Liver.*

The liver occupies more than one half of the posterior visceral mass; its anterior two-thirds is surrounded by the hermaphroditic gland (see infra), which extends inward some distance, though the liver lobules, lying between the germinal follicles, extend in many places to the surface. The posterior third of the visceral mass is composed entirely of the liver, which is made up of numerous racemose lobes, giving it a rather loose appearance. The lobules of the liver open by minute connecting ducts into one or the other of the two bile sacs, the greater number opening into the posterior one, which is much the larger.

The cells are stained brown in Hermann's fluid, owing to the action of the osmic acid on the granules surrounding the numerous, rather large vacuoles contained in each cell. The free ends of the liver cells are irregular in outline and the cavity of the lobe, which in the granular part of the liver they surround, is filled with the same granular cytoplasmic mass containing vacuoles, the cell apparently breaking down after it becomes filled with the hepatic secretion. The gland cells are long and irregularly flask-shaped, the neck being attached to the basement membrane (Figure 6, *f*). The liver cells apparently regenerate the portion which breaks down, as there are no small basal cells and the large nucleus near the base of the cell is surrounded by numerous compactly arranged cytoplasmic granules. In the minute ducts leading into the bile sac the cells are more regular and much shorter (Figure 6, *e*), while those lining the bile duct itself are ciliated.

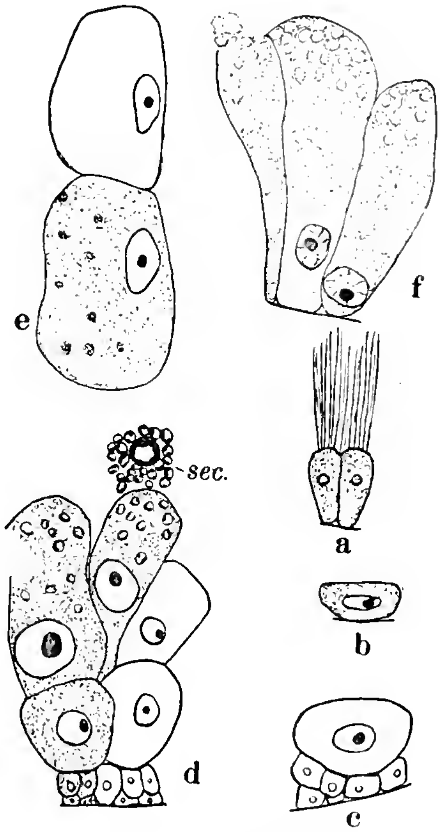

Figure 6. a, Ciliated cells from the mouth of the prostate duct; b, ordinary lining epithelial cells from prostate duct; c, cells from edge of glandular patch of prostate gland; d, cells of glandular patch of prostate gland; *sec.*, secretion; e, cells from duct leading from liver lobules; f, liver cells. All drawn with camera lucida, one inch ocular, and one-twelfth inch oil immersion objective. × 612.

5. *The Kidney.*

The nephridial organ (Figure 3, *ren.*) covers the upper surface of that portion of the posterior visceral mass which lies to the right of the esophagus and just anterior to the stomach. It does not extend down over the right side and usually does not exceed 40 micra in width. It consists of an irregular number of tubules immediately ventral to the pericardium. The cells are polygonal, their free ends being mostly transparent and apparently without concretions. A short duct connects the kidney with the real chamber (*cam. ren.*), which is a large bilobed sac. The dorsal lobe is 80 micra long, being much longer than the ventral lobe (50 micra). This large sac, 90 micra wide and 70 micra deep in its greatest extent, lies over the esophagus and projects beyond the anterior margin of the posterior genital mass (Figure 3, *cam. ren.*). On the floor of the renal chamber there is a fold which nearly fills the passage into the kidney and is covered with long cilia. There seems to be a minute pore through the wall of the renal chamber, in the region of the ciliated fold, which opens into the pericardium. The ureter of the kidney (Figure 3, *urt.*) is a small duct of uniform diameter, which follows the right contour of the stomach-intestine, and opens ventral to, and slightly at the left of, the anus.

6. *The Heart and Blood Gland.*

The blood gland is an irregular compact mass of minute round cells lying dorsal to the suctorial bulb and anterior to the nerve collar. The enlarged middle portion of the oviduct is often partly imbedded in this gland.

The heart consists of an anterior ventricle and a posterior auricle, the latter being partly divided. The pericardial cavity is nearly filled by the distended heart, the walls of which (Figure 7) are composed of connective-tissue cells and branching cells, which are interpreted as the contractile tissue of the heart because they are so similar to the evidently contractile cells of the foot. The blood passes to the various parts of the body through irregular sinuses, there being no clearly defined blood vessels apparent in my preparations. The fact that the cavities of the gills open directly into the secondary coelom is submitted as further evidence that there are no well defined blood vessels.

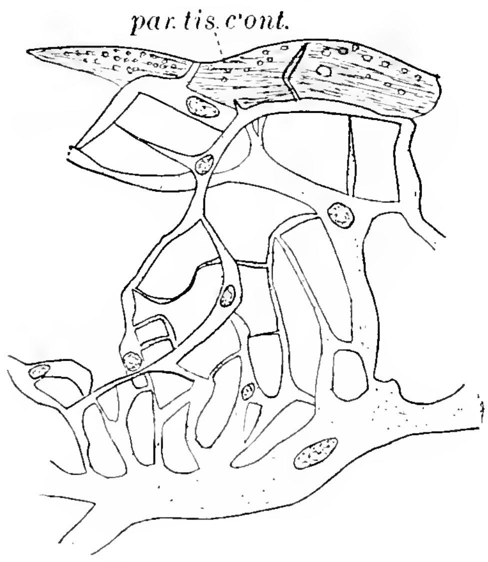

FIGURE 7. Edge of the ventricle of the heart showing the branching muscular cells. *par.tis.c'ont.*, connective-tissue wall. Camera lucida, one inch ocular and one-twelfth inch oil-immersion objective. × 612.

7. *Anatomy and Histology of the Reproductive System.*

The general features of the reproductive system are similar to those of most Nudibranchs. An hermaphroditic gland surrounds most of the liver, the two organs forming a conspicuous mass and nearly filling the posterior half of the secondary coelom. The hermaphroditic gland is usually designated as the posterior genital mass (Figure 3, *gen. p.*), the anterior genital mass (*gen. a.*) consisting of the albumen gland and the nidamental gland, which are united into one general body, and a prostate gland. The prostate gland lies posterior to the albumen and nidamental glands and is more conspicuous on the left side. The posterior genital mass projects forward over the dorsal aspect of the anterior genital mass, concealing about one half of it as seen from above. Into the genital atrium open the oviduct and receptaculum seminis close to each other and also the penis sac. The detailed relation of each duct to the posterior and anterior genital masses and to the genital trium is presented in the following paragraphs.

Posterior Genital Mass.

In the posterior genital mass the arrangement of the male and female portions does not follow any definite plan; the ultimate tissue from which the germ cells are derived is a columnar epithelium composed of short and broad cells. This epithelium is much folded, forming follicles which project inward toward the center of the genital mass. A cross section of the genital mass shows many knob-like regions of eggs and sperms projecting almost to the center of the mass. Between such projections the liver cells of the anterior region often extend to the surface. Elsewhere in the anterior two thirds of this genital mass the germinal follicles envelope the liver in a layer of varying thickness. Each follicle is exclusively occupied by growing eggs or sperm cells.

The sperm cells in the material collected in January seem to be mostly in a state of maturity, but the eggs exhibit all stages of development. The maturing eggs show in a clear manner the relation of the nucleus to the formation of deutoplasm. All stages from the young ova to the mature egg are seen in the same section. In the young ovum the cytoplasm is evenly and finely granular; as it increases in size, small spherical droplets appear in close contact with the nuclear membrane; as growth continues several rows of droplets are distinguishable surrounding the nucleus. In the more mature egg finger-like masses of these droplets extend from the nucleus toward the periphery of the cell; these continue to become more numerous until the early finely granular condition is obliterated. In Hermann's fixation these deutoplasmic droplets are of all shades from a deep brown to black, indicating that at least a considerable portion of their substance is of a fatty composition. Müller's fixation followed by the usual iron haematoxylin gives the best differentiation for the study of the growth of the deutoplasm.

The numerous follicles open into an irregular series of minute ducts, which are finally collected into the common hermaphroditic duct. Before taking up the course of this duct, it is necessary to describe the

Anterior Genital Mass.

The anterior genital mass consists, as already mentioned, of the mucous gland, the nidamental gland, and the prostate gland. The first two unite to form a simple, conspicuous mass, each gland consisting of a number of foldings of a greatly thickened epithelium. After fixation in Müller's fluid, it is not easy to distinguish between these two glands, as their tubules have no constant position or shape; but after fixation in Hermann's fluid the resulting differentiation of the contents of the cells enables one to recognize at a glance the difference between the mucous and the nidamental regions. The actual space occupied by the mucous tubules is about one third as great as that occupied by the nidamental tubules, and the former are found mostly on the back and left sides, although a few extend into the center of the anterior genital mass and are there surrounded by the nidamental tubules. The outline of these combined glands is not regular, because some of the nidamental tubules project into the liver.

The nidamental cells are light colored after fixation in Hermann's fluid, the cell walls and nuclei being the only parts stained. In the animal thus fixed, the cells were congested, almost obliterating the lumen of the tubule, while in the one prepared in Müller's fluid and stained in iron haematoxylin the cytoplasm was faintly tinted and the cells shrunken so as to leave a large lumen. The mucous-gland cells which were fixed in Hermann's fluid were stained a deep brown, this color being due to the presence of numerous spherical bodies which fill the cell. This is the differential reaction which enables one to distinguish between these two glands. An animal that had recently discharged its mucous secretion was fixed in Müller's fluid and stained in haematoxylin followed by Bordeaux red. It showed the presence of a few small bodies in the distal ends of the flask-shaped cells. The large bodies took the haematoxylin stain in the center and the Bordeaux red around their periphery, while the small ones, just forming in the cytoplasm, took an exclusively Bordeaux red stain. It would seem, then, as if this secretion of the mucous cells was not a chemically homogeneous substance.

The prostate gland of *Polycerella zoobotryon* (Figure 8, *gl. prost.*), unlike that of *Polycera* (Pohl, :**05**, p. 434), is not folded, but consists of a large flask-like sac, the fundus of the flask being on the left side of the body, and its neck continuous with the prostate duct. The histology of this gland presents the following points of interest. The cells composing the main lining of the gland are elongated and mutually flattened; the nucleus is prominent, the cytoplasm finely and uniformly granular. For a short distance (from 15 to 20 micra) from the opening of the prostate duct, the cells (Figure 6, a) are narrow and elongated and carry long cilia, often 3 micra in length. The nucleus is much smaller than in any of the other cells, and the cytoplasm is coarsely granular.

The fundus of this flask-shaped prostate is largely occupied by the glandular area, a patch of thickened epithelium about 50 micra across. The cells in this glandular area are greatly enlarged, even at the edge of the patch, as shown in Figure 6, c. The conditions represented in Figure 6, d, show the number of layers of cells and their arrangement. At the bottom of the figure are some small basal cells which, together with a few larger ones, make up two rows similar in appearance to the cells regularly lining the gland (Figure 6, b), except that cells are frequently found in the second row which show the beginnings of the secretion so common in the distal cells of the glandular patch. The cells which cover the free surface of the glandular patch are greatly enlarged, especially in that part of each cell which is distal to the nucleus. The cytoplasm contains a number of spherical masses which, in preparations fixed in Hermann's mixture, are made up in part of 1 to 3 blackened corpuscles, the remaining portion of the mass taking no stain. The whole effect is like that of a vacuole containing differentiated bodies. After fixation in Müller's fluid, followed by haematoxylin, these masses are not apparent. That these minute bodies are secretions of the cell is abundantly shown by the fact that identical bodies nearly fill the prostate gland, and that special drops similar in form are often attached to the ends of these cells (Figure 6, d).

There are also found in the contents of the prostate gland numerous spermatozoa, and some bodies which it is difficult to explain from the present preparations. They are of about the size of the nuclei in the distal cells of Figure 6, d, but the detailed structure has degenerated to such an extent that one cannot recognize any relationship between them and other cells or parts of cells found in the organism. Pohl (:**05**, p. 434) finds abortive, undeveloped eggs in the ampulla of the sperm duct, which may be the key to the explanation in this case. The bodies appear much like pseudo cells in Hydra (Wager :**09**, Figure 14, Plate 3), which would mean that some undeveloped eggs had been set free and were being broken down in the prostate gland. A second explanation is equally probable: that the distal ends of the gland cells break off and the nucleus gradually undergoes degeneration. In only one instance, however, was there any evidence of such a breaking off of the tip end of the cell (see condition of one of the cells in Figure 6, d); but I am convinced that this is not the usual method of discharging the secretion, or it would happen frequently and there would be more than this one instance in the several animals studied. But the large number of these bodies in the immediate vicinity of the glandular patch is very suggestive, and leads one to think that these bodies are escaped nuclei. The ends of some of the other cells in the glandular patch were frayed, as if the distal part had been lost.

8. *The Genital Ducts.*

1. The hermaphroditic duct emerges from the central and dorsal region of the posterior genital mass. As it leaves the genital mass it turns, passing to the left side, and continues in this direction until it comes into contact with the body wall, where it turns forward. It then bends ventrally, and finally reaches the middle of the front surface of the anterior genital mass. Here it makes a sharp turn to the right, passing below the esophagus, and becomes partly enveloped by the nidamental gland. As the hermaphroditic duct emerges from the anterior right side of the anterior genital mass, it turns ventrally 25 micra and enlarges its diameter from 3 to 15 micra to form an ampulla. From the ampulla the duct courses dorsally over the right anterior surface of the nidamental gland and opens into the duct of the pros-

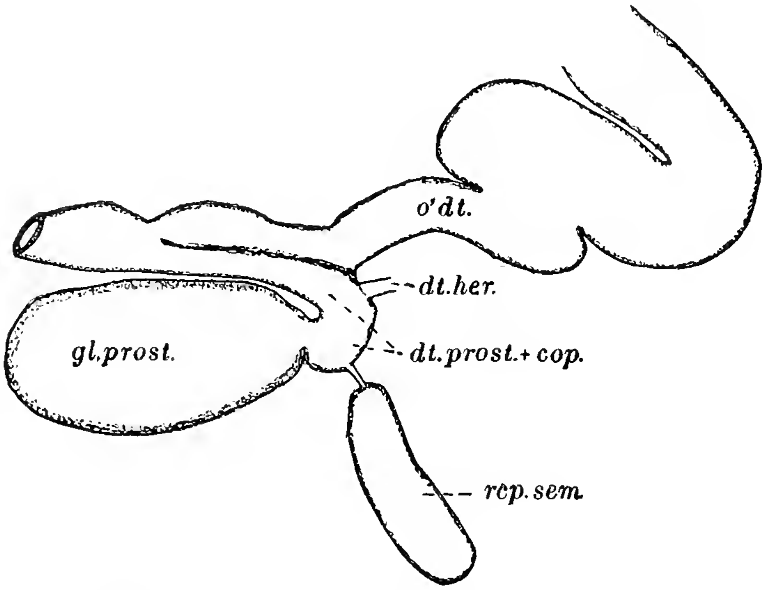

FIGURE 8. Drawing made partly from a dissection and partly from a reconstruction from sections, to show the prostate gland, its duct, the oviduct, and their relation to the hermaphroditic duct and receptaculum seminis. *dt.her.*, hermaphroditic duct; *dt. prost. + cop.*, prostate and copulation duct; *gl.prost.*, prostate gland; *o'dt.*, oviduct; *rcp.sem.*, receptaculum seminis.

tate gland. A short distance before the formation of the ampulla, the hermaphroditic duct receives the duct from the mucous gland.

2. The prostate (Figure 8) duct is relatively short, only 100 micra long, and its walls are 20 micra thick. As it emerges from the prostate gland it turns ventrally and anteriorly to open without further change of course into the genital atrium.

3. The receptaculum seminis (Figure 8, *rcp. sem.*) is an elongated sac 85 micra long, 50 micra wide, and 25 micra thick, located on the right side dorsal to the prostate gland and ventral to the kidney chamber. The duct from the receptaculum seminis is 25 micra long and 8 micra thick; it opens into the prostate duct as shown in Figure 8. In copulation, then, the penis enters the prostate duct, which makes it appropriate to designate this duct as the vagina.

4. The oviduct opens with the prostate duct into the genital atrium. From its origin it passes dorsally and to the left until the left side of the body is reached. There it turns anteriorly and then crosses to the right side, this time over the suctorial bulb, finally terminating in the genital atrium. The oviduct (Figure 8, *o'dt.*) is divided into three regions : (1) a terminal, thick-walled, muscular portion 45 micra wide, extending from the prostate duct to the middle region ; (2) this is short but much wider, being 60 micra in diameter, and thin walled ; it lies over the suctorial bulb ; finally (3), the initial part is for 50 micra of its length not more than 30 micra wide. The large cavity in the middle region of the oviduct contains a considerable amount of detritus ; the only structures that could be identified were parts of the polyzoan, upon which this species feeds. This region would seem to be, therefore, similar to a spermatheca, although placed in the oviduct. The duct from the albumen gland opens into the oviduct in the last third of its course, about 20 micra from the genital atrium.

5. Penis and vas deferens. A fleshy triangular valve separates the opening of the penis sac from the prostate duct and oviduct. The penis sac, 30 micra wide, may run crosswise in front of the anterior genital mass or back close to the body wall and lateral to the anterior genital mass (Figure 3). The penis has a general width of 10 micra, its end becomes expanded into a head 12 micra wide. The duct running throughout the center of the penis is 4 micra wide and heavily ciliated. Bergh ('**92**, p. 149) states that the penis of Polycerella is armed with hooks. Verrill ('**80**, p. 387), in describing P. emertonii, makes no mention of the reproductive organs. Balch ('**99**, p. 151) says, "No armature of the penis could be made out in sections, but this was perhaps owing to poor preservation." The enlarged end of the penis in P. zoobotryon is unquestionably ciliated and in specimens fixed in four dif-

ferent fluids no evidence of hooks on the penis appeared. Inasmuch as Bergh cites as his only authority Verrill, it is apparent that his statement "penis armata" is a mere supposition based on the fact that it is armed in Polycera. Therefore, this characterization of the genus Polycerella will have to be changed to "penis unarmed."

The vas deferens is a narrow duct of uniform diameter throughout its entire length opening into the prostate duct; it passes by several turns to the base of the penis, the latter part of its course depending upon the position of the penis in the body. The vas deferens is heavily ciliated throughout its whole length.

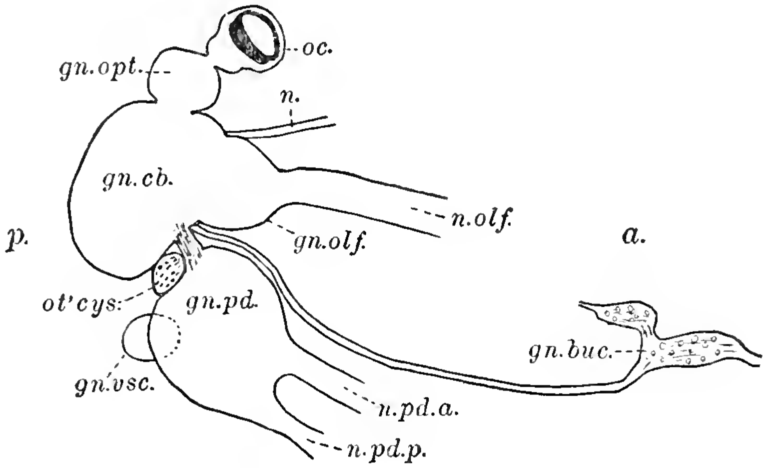

FIGURE 9. Drawing (diagrammatic) of nervous system seen from the right side. *gn.buc.*, buccal ganglion; *gn.cb.*, cerebral ganglion; *gn.olf.*, olfactory ganglion; *gn.opt.*, optic ganglion; *gn.pd.*, pedal ganglion; *gn.vsc.*, visceral ganglion; *n.*, nerve to integument; *n.olf.*, olfactory nerve; *n.pd.a.*, anterior pedal nerve; *n.pd.p.*; posterior pedal nerve; *oc.*, eye; *ot'cys.*, otocyst.

9. *The Nervous System.*

The nervous system is simpler in some respects than it is in the larger Eolidae and in some of the Doridae, although showing the same concentration of the ganglia into a nerve collar around the esophagus immediately behind the pharynx. There are three pairs of large ganglia, — cerebral, pedal, and visceral, — the usual small pair of buccal ganglia, and several minor ganglia to be described afterwards.

The cerebral ganglia (Figures 9, 10, *gn. cb.*) are nearly spherical, the antero-posterior diameter being slightly shorter than the others. They are the largest of the ganglia, each being about 30 by 20 by 20 micra, and cover the dorsal surface and a small part of each side of the esophagus. The cerebral commissure (Figure 10, *co'ms. cb.*) is three micra long and six micra wide. The cerebro-pedal connective (Figure 9) is short and narrow (5 micra long and 3 micra in diameter), while the cerebro-buccal connective, arising just anterior to the cerebro-pedal connective, is long and slender. Broadly joined to the ventral anterior face of each cerebral ganglion is an olfactory ganglion (Figures 9, 10, *gn. olf.*); a faint constriction is the only external indication of it. The olfactory ganglion is approximately spherical and gradually tapers off into the large (7 micra) nerve (*n. olf.*) that eventually penetrates the base of the rhinophore. With the lateral surface of each cerebral ganglion is connected a spheroidal optic ganglion (*gn. opt.*). As this is sessile on the cerebral ganglion, there is no conspicuous cerebro-optic connective. Joined to the optic ganglion is the simple eye.

The pedal ganglia lie ventral, and slightly posterior to the cerebral and are somewhat smaller (22 by 20 by 29 micra). The pedal commissure (Figure 9, *co'ms. pd.*) is 20 micra long and 4 micra in diameter; it lies behind and ventral to the cerebro-pedal connectives.

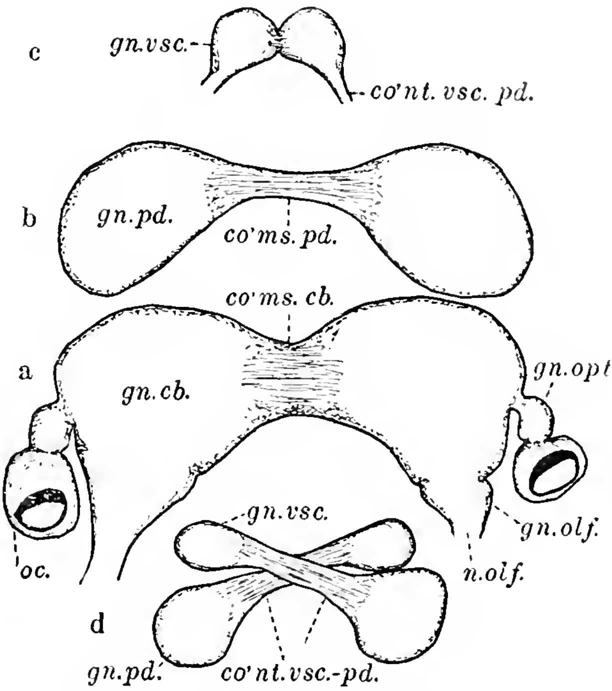

FIGURE 10. Four camera-lucida drawings (a, b, c, d) of the three pairs of ganglia in various positions to show their relative sizes and their connectives and commissures. *co'ms.cb.*, cerebral commissure; *co'ms.pd.*, pedal commissure; *co'nt.vsc.-pd.*, viscero-pedal connective; *gn.cb.*, cerebral ganglion; *gn.olf.*, olfactory ganglion; *gn.opt.*, optic ganglion; *gn.pd.*, pedal ganglion; *gn.vsc.*, visceral ganglion; *n.olf.*, olfactory nerve; *oc.*, eye.

The visceral ganglia (Figures 9, 10) are small (10 by 10 by 10 micra) in comparison with the cerebral and pedal, and lie in close contact with each other. They are situated at the side of, and posterior to, the esophagus back of the pedal commissures. In a frontal section is found an interesting form of connection between the visceral and pedal ganglia (Figure 10, *co'nt. vsc.-pd.*). These connectives are 15 micra long and 4 micra in diameter; they form a distinct chiasma with no apparent mingling of the fibres and clearly show the chiastoneuric affinities of this gasteropod.

The buccal ganglia (Figure 9) are irregular in outline, each ganglion consisting of two parts, the smaller of which lies on the lateral wall of the buccal mass, while the larger is on its ventral surface. The buccal commissure is short, lying on the ventral side of the buccal wall.

Nerves. — In addition to the several commissures and connectives already described, the ganglia have the following nerves. Each of the cerebral ganglia gives off from its posterior surface a small, short nerve which goes to the oviduct. From its dorsal posterior surface arises a large nerve which bends ventrally, passing immediately back of the optic ganglion. This nerve is enlarged on the right side of the body by ganglionic cells. From this ganglionic enlargement some branches pass to the distal portion of the oviduct and penis, others to the lateral body wall and mantle edge. On the left side no corresponding ganglion was detected, the nerve simply giving off many branches to the lateral and posterior body wall. The olfactory portion of the cerebral ganglion is the source of the largest nerve in the body. This nerve extends along the side of the pharynx, sending off to the rhinophore a branch, which spreads out into a wide, much-flattened nerve that is distributed to the integument of the rhinophore. The nerve continues anteriorly beyond the base of the rhinophore giving off several branches to the region around the mouth, while one branch enters the base of the tentacle. Just dorsal and anterior to the olfactory lobe a small nerve (Figure 9, *n.*) arises which goes directly to the integument dorsal to the mouth.

Each pedal ganglion sends to the foot two large nerves, the anterior and posterior pedal nerves. On the right side a third nerve arises from the posterior surface of the right pedal ganglion and goes to the base of the penis.

Each of the visceral ganglia gives off a single nerve which is distributed to the lateral and posterior wall of the pharynx and a small nerve to the anterior genital mass.

10. *Histological Structure of the Pedal Ganglion.*

The several ganglia are essentially like one another histologically, the conditions represented in the pedal ganglion being typical. Each ganglion is closely invested in a connective-tissue capsule. Figure 11 is a longitudinal (parasagittal) section through the right pedal ganglion, showing the cerebro-pedal connective on the left and the origin of the anterior pedal nerve ventrally. There are a few large and many small nerve cells having the base of the cell directed toward the connective-tissue capsule. The number of nerve cells is much less in the ventral region. Each cell is of the usual unipolar type, and while many send their axons directly into or through the cerebral mass, others send theirs for some distance between other cells before leaving the ganglion. The center of the ganglion is occupied by a feltwork of nerve fibres. Axons in small groups course through this feltwork and pass out into the pedal nerve. Axons in the pedal connective can readily be traced through the ganglion into the pedal nerve. The neuroglia cells (Figure 11, *n'gli.*) are few in number and found only around the periphery of the ganglia.

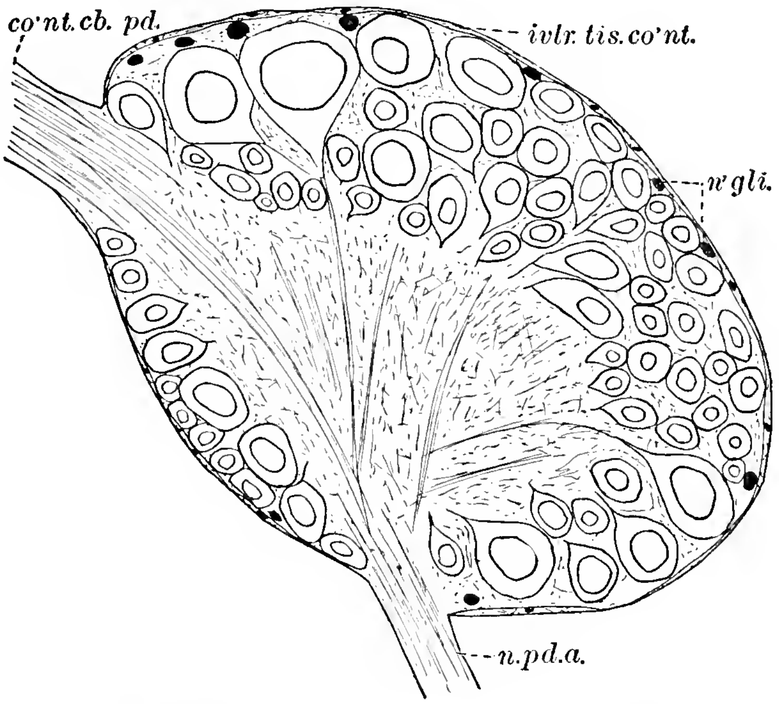

FIGURE 11. Parasagittal section of the right pedal ganglion. *co'nt.cb.-pd.*, cerebro-pedal connective; *ivlr.tis.co'nt.*, connective-tissue sheath; *n'gli.*, neuroglia; *n.pd.a.*, anterior pedal nerve.

The larger of the nerve cells give a more pronounced reaction to the various reagents than the smaller ones do, although no constant structural differences are observable. The nucleus is proportionately very large and rich in chromatin, while the cytoplasm is finely granular and contains a few vacuoles. In fixation with Hermann's fluid there are a number of blackish bodies in the cytoplasm, and bodies apparently similar are found in the ganglion outside of the nerve cells. Bodies having a similar appearance are also present in the epithelial cells of the reproductive ducts. These bodies are probably fat or related substances blackened by the osmic acid contained in the fixing fluid.

11. *Special Sense Organs.*

Otocyst. — The ear sac (Figure 9, *ot'cys.*) is of an oval outline, its longest diameter being 7.5 micra, and it lies embedded in the dorsal surface of the pedal ganglion. The otokonia are numerous, minute oval bodies not more than 0.6 micron long.

Olfactory organ. — The rhinophore possesses a large nerve that sends off numerous branches during its passage from the base to the tip of the rhinophore. It is difficult to be certain just how the axons of this nerve terminate in the epidermis. The individual branches can be made out at least half way to the surface of the epidermal epithelium, and I am inclined to believe that they simply terminate in free, unmodified fibrils between the epithelial cells. The olfactory nerve sends a branch into the tentacle and several into the region of the lips. Here, also, the individual fibrils appear to end in a similar manner to those in the rhinophore. It is probable that the general snout region, as well as the rhinophores, interprets olfactory stimuli, as both are innervated by a single nerve arising from the olfactory ganglion.

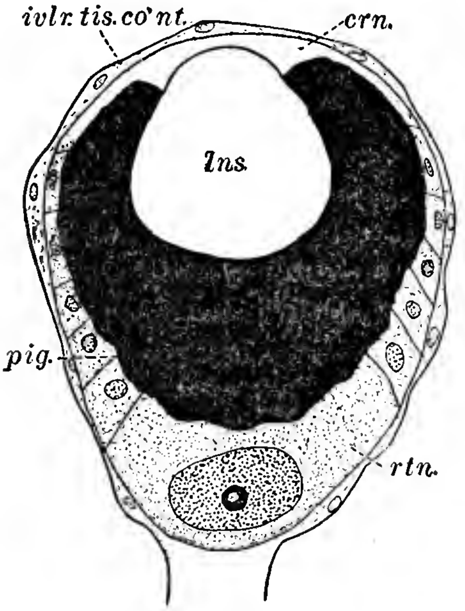

FIGURE 12. Eye. *crn.*, cornea; *ivlr. tis. co'nt.*, connective-tissue sheath; *lns.*, lens; *pig.*, pigment; *rtn.*, retina. Camera lucida, one inch ocular and one-twelfth oil-immersion objective. × 612.

Eye (Figure 12). — The eyes, as already stated in connection with the description of the cerebral ganglia, are in close contact with the optic ganglion. Each eye is completely enveloped in a connective-tissue capsule, which contains a greater amount of connective tissue, nuclei, and fibres than is found in similar tissue surrounding the ganglion. At the base of the eye the capsule is easily traced and is seen to be continuous with that surrounding the ganglion.

Each eye presents, within the cellular capsule, a single layer of cells, which is divisible into an anterior portion, the cornea, and a posterior, the retina. These together completely enclose the lens and a cup-shaped mass of pigment. The lens (Figure 12, *lns.*) is an oval or pear-shaped body completely filling the pigment cup and projecting somewhat beyond its anterior rim, where it is in contact with the cornea. The pigment (*pig.*) is very dense, consisting of numerous small granules which appear to be located in the retinal cells. At least I was not able to make out the existence of more than this one layer of cells, though it is possible that maceration preparations would have disclosed the presence of other (pigment) cells. The pigment layer is thickest at the bottom of the cup, becoming gradually thinner toward the cup's lips. The cornea and retina apparently consist of only a single layer of cells arranged radially; the cells of the cornea (*crn.*) are much flattened, and stain faintly. The layer contains but few nuclei in front of the lens. The cells become cubical in the region of the retina (*rtn.*), the center of which is occupied by a single large cell with a conspicuous nucleus. Inasmuch as the eyes were not especially fixed and stained for histological study, it was impossible to analyse further the retina or to determine the course of the fibrillae after they enter the retina. Strands of fibrillae were traced from the cerebral into the optic ganglion and thence to the proximal border of the retina.

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Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 17. — March, 1912.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

THE ANOMALOUS MAGNETIZATION OF IRON AND STEEL.

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THE ANOMALOUS MAGNETIZATION OF IRON AND STEEL.

By B. Osgood Peirce.

Presented May 10, 1911. Received January 2, 1912.

In 1863, von Waltenhofen, who had been making experiments upon the retentiveness of bars of iron and steel for magnetism, discovered the phenomena which usually bear his name. If an increasing current (I), ending in the maximum value I', be sent through a long solenoid, the final value of the magnetic moment of a solid bar of originally demagnetized soft iron or steel within the solenoid frequently depends, not only upon the final strength of the current, but also upon the manner of growth of the current in attaining this intensity. The moment will be greater if the current be suddenly applied in full strength than if it be made to grow slowly, either continuously or by short steps. If, after the current has remained steady for a short time, at the strength I', it be made to decrease to zero, the residual moment of the bar will usually be less if the current be suddenly opened than if the decrease be made slowly, by gradually introducing more and more resistance, and the demagnetizing factor of a given cylinder is considerably less when computed from observations made by the method of sudden reversals, than if it is determined by slow, step-by-step changes in the exciting current.

Von Waltenhofen also encountered some cases of apparently anomalous magnetization which he describes in the following words taken from his paper in Volume 120 of Poggendorff's Annalen :

"Es ist mir oft aufgefallen, dass die magnetischen Rückstände in weichen Eisenkernen bei wiederholter, ganz gleicher, temporärer Magnetisirung desselben Stabes, sehr ungleich ausfallen. Noch befremdender aber war mir eine Erscheinung, die ich an einem sehr dicken Eisencylinder zuerst wahrgenommen habe, und welche darin bestand, dass der nach Aufhebung des magnetisirenden Stromes zurückgebliebene Magnetismus im Vergleiche mit dem verschwundenen temporären Magnetismus manchmal sogar die entgegengesetzte Polarität hatte. . . . In der Magnetisirungsspirale wurde ein vollkommen unmagnetischer Cylinder von möglichst weichem Eisen, 103 mm. Länge und 28mm. Durchmesser, mit zunehmender Stromintensität soweit magnetisirt, dass sein temporäres Moment nahezu = 60 war. Nach plötzlicher Stromunterbrechung äusserte er das entgegengesetzte remanente Momente —0.20, und zeigte auch nach wiederholten plötzlichen Oeffnungen der wieder geschlossenen Kette entschieden negative (anomale) Rückstände. Dagegen zeigte sich nach allmählich eingeleiteter Aufhebung des magnetisirenden Stromes jedesmal ein bedeutendes, mit dem temporären Momente gleichnamiges Residuum. Wenn der Strom hierauf in derselben Richtung abermals hergestellt, sodann aber plötzlich unterbrochen wurde, zeigte sich das mit der temporären Magnetisirung gleichnamige Residuum, welches nach allmählicher Stromaufhebung immer wenigstens den Betrag 0.30 hatte, nahezu auf 0 reducirt; konnte jedoch durch Wiederholung dieses Verfahrens nicht merklich unter 0 herabgebracht werden. Wenn aber hierauf die magnetisirende Stromrichtung gewechselt wurde, so trat nach plötzlicher Unterbrechung wieder eine ganz entschiedene anomale Magnetisirung auf. So oft der Eisencylinder mehrere Tage in ostwestlicher horizontaler Lage unberührt gelassen war, zeigte er sich wieder vollkommen unmagnetisch, und ergab bei Wiederholung des zuerst beschriebenen Versuches wieder das anomale Residuum —0.20. Wenn dagegen die remanenten Magnetismen nicht durch längeres Liegenlassen, sondern durch entmagnetisirende Ströme verschwinden gemacht worden, gelang es nicht, so auffallende anomale Magnetisirungen hervorzubringen."

Seventeen years after the publication of von Waltenhofen's results,[1] Righi,[2] who was apparently unacquainted with his work, printed in the Comptes Rendus an account of some similar experiments of his own. He says: "On sait que le rapport entre le magnétisme rémanent et le magnétisme temporaire d'une barre d'acier envelopée par une bobine magnétisante devient de plus en plus petit si la barre est de plus en plus courte et grosse." "Si l'on prend des barres d'un même acier et de même diamètre mais de longueurs décroissantes, on doit arriver à une certaine longueur qui ne donne pas de magnétization, pendant qu'avec des longueurs moindres on doit obtenir une polarité rémanente opposée à celle de la bobine." "Si le courant est très fort, le phénomène de la polarité anomale ne se produit qu'après avoir magnétisé la barre quelquefois dans les deux sens."

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[1] A. v. Waltenhofen, Pogg. Ann., **120**, 1863.

[2] A. Righi, Comptes Rendus, **90**, 1880.

During the last thirty years, many persons[3] have studied the von Waltenhofen phenomena as they affect the hysteresis cycles of straight rods and of closed cores of iron, and some of these have discussed the bearing of their own measurements upon the theory of anomalous magnetization. G. Wiedemann[4] always maintained that his own researches and those of Righi showed that eddy currents in the iron, accompanying surges in the exciting circuit, accounted best for the observed facts. It seemed to von Waltenhofen, however, that the strange reversals of polarity which he had noticed could not be due to induced currents caused by sudden changes in the exciting circuit, and he explained them as consequences of the inertia of the molecular magnets turning in a viscous medium. Fromme,[5] Auerbach, Ewing, Peuckert, Zielinski, and others who have written upon the subject, seem to agree on the whole with von Waltenhofen's views.

The present paper attempts to throw some light upon the theory of the von Waltenhofen effect by a discussion of a number of experiments made for the purpose of determining the conditions under which anomalous magnetization appears. It leaves to a future article a consideration of some of the theoretical aspects of the subject.

The Demagnetizing of Stout Pieces of Iron or Steel.

It is to be said at the outset that almost every piece of iron to be obtained nowadays in the market is more or less strongly magnetized

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[3] C. Fromme, Wied. Ann., **5**, 1878; **13**, 1881; **18**, 1883; **33**, 1888; **44**, 1891. F. Auerbach, Wied. Ann., **14**, 1881; **16**, 1882; Winkelmann's Handbuch der Physik, Bd. V (214). W. Peuckert, Wied. Ann., **32**, 1887. P. Bachmetjeff, Rep. der Physik, **27**, 1891. Zielinski, Mitt. a. d. Telegraph-Ing.-Bureau d. Reichspostamtes, **2**, 1896. Ruecker, Inaugural Dissertation, Halle-Wittenberg, 1905. Peirce, These Proceedings, **43**, 1907; **46**, 1911. L. A. Babbitt, These Proceedings, **47**, 1911.

[4] "Schon bei Gelegenheit der von Righi wiederholten Versuche von v. Waltenhofen über die anomale Magnetisirung, hatte Ref. [Wiedemann] erwähnt, dass sich dieselben völlig aus dem Auftreten alternirender Inductionsströme in der Masse des Eisens beim schnellen Oeffnen des magnetisirenden Stromes u. s. f. ableiten lassen, von denen ein später auftretender weniger dichter, die Magnetisirung durch einen vorhergehenden dichteren Strom vernichten resp. umkehren kann. Die anomale Magnetisirung ist also *rein secundär*." — Beiblätter der Annalen der Physik, **5**, 1881.

[5] "Gegenüber den Bemerkungen des Herrn Ref. [Wiedemann] halte ich meine Ansicht aufrecht, dass ich durch meine Versuche mit Eisendrahtbündeln, welche ebenfalls den Unterschied der permanenten Momente in der regelmässigsten Weise zeigten, schon nachgewiesen zu haben glaube, dass Inductionsströme keinesfalls zur Erklärung ausreichen können." — Wiedemann's Annalen, **13**, 1881.

when it comes into the hands of the observer, and that it is often very difficult, if not impossible, to demagnetize a massive block thoroughly. If a slender rod be placed inside a long solenoid in circuit with the secondary coil of a suitable open-core transformer, and if this coil be slowly drawn off the core with the help of some mechanical device, it is possible to send through the solenoid a long series of currents, alternating in direction and gradually decreasing in intensity, and thus to demagnetize the rod well enough for most purposes. The Jefferson Laboratory has three large sets of apparatus of this sort.

The process just described, however, does not succeed very well with stouter rods, for several seconds may be required to establish a steady current in the solenoid under a steady electromotive force if the core be large, and the use of alternating currents of commercial frequencies is barred out. The solenoid current may be reversed in such a case, at sufficiently long intervals, by means of a mercury commutator geared to an electric motor. Such a commutator, made several years ago by Mr. George W. Thompson, the mechanician of the Jefferson Laboratory, enabled Mr. L. A. Babbitt[6] to demagnetize very completely the finely divided core of a large toroidal transformer, though a number of hours were spent each time in the process. With irregular masses of metal this process also is often ineffective, and it is not always successful with short cylinders. A piece of soft Bessemer steel 5 centimeters long, recently cut from a long rod 3 centimeters in diameter, in the Jefferson Laboratory, was found to be slightly magnetized, and Mr. Thompson and Mr. John Coulson attempted to demagnetize it in a solenoid about 38 centimeters long, consisting of about 1460 turns of large wire. They began the series of alternately directed and slowly decreasing currents with one of more than 40 amperes, corresponding to a field within the solenoid before the iron was introduced of about 1700 gausses, but the iron was still magnetized in the old direction, with nearly the same intensity, at the end of their work.

In demagnetizing a stout piece of iron by currents alternating in direction, it is well to put the metal slowly through a succession of complete hysteresis cycles with gradually decreasing ranges, but if this be inconvenient, the iron may be surrounded by a thick copper shell,[7] the eddy currents in which will prevent the magnetic changes in the iron caused by a sudden reversal of the main switch from being so violent as they otherwise might be. As will appear more clearly in the sequel, the distribution of the magnetization in a stout iron cylinder

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[6] These Proceedings, **47**, 1911.

[7] Shuddemagen, These Proceedings, **43**, 1907.

in a solenoid which carries a current of given strength is different according as the current attained its final value slowly or suddenly, and it very much facilitates the demagnetization of such a piece, if the currents be applied slowly and decreased gradually.

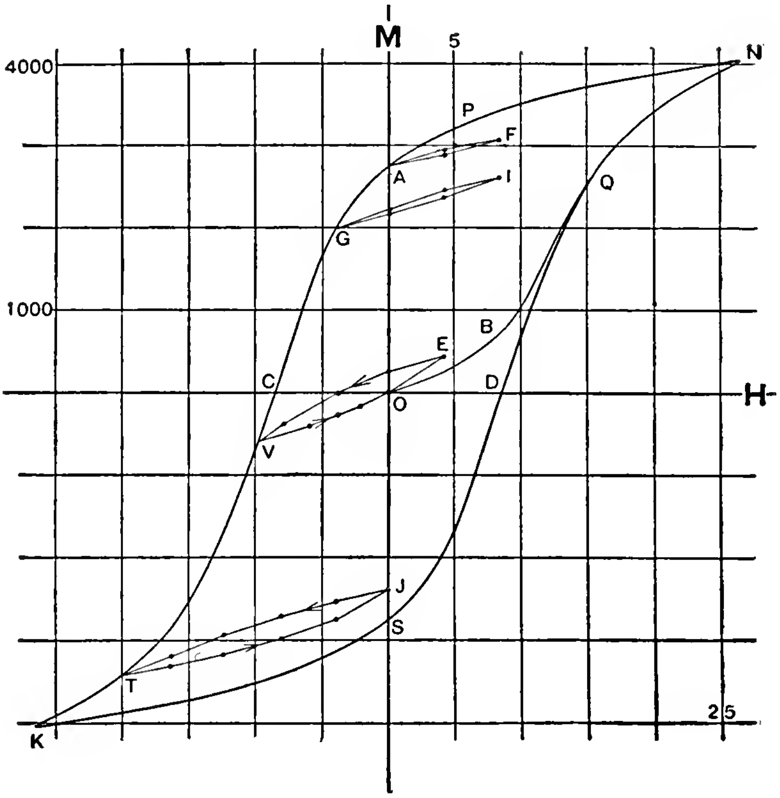

FIGURE 1.

It is often assumed that a piece of iron may always be completely demagnetized by heating it uniformly nearly to a white heat, maintaining it at this high temperature for some time, and then allowing it to cool slowly in a place where it will not be exposed to any magnetic forces; but in practice the procedure often fails, especially with material which has once been irregularly magnetized or which is not quite homogeneous. The spherical shield of a new DuBois-Rubens Panzer Galvanometer in the Jefferson Laboratory proved to be slightly magnetized and consequently useless for the purpose for which it was made. This was heated to nearly a white heat, kept hot for about half an hour, and then very slowly cooled in a protected space, without causing it to lose appreciably its original magnetization; a repetition of the process was also unsuccessful.

Most of the specimens mentioned in the experiments discussed below were packed, one or two at a time, in fine iron filings, enclosed in a piece of large iron pipe provided with screw caps at the ends, and then heated thoroughly for some time, under a power blast, in a gas furnace. The pipe was surrounded by fire bricks and after the fire had been removed it was allowed to cool for many hours with its axis perpendicular to the earth's meridian before the annealing process was regarded as complete. In this manner most of the pieces were fairly well demagnetized. Of course, the permanent magnetic moment of an iron cylinder of length only twice as great as its diameter, is never very strong, but it was usually possible to detect some evidences of magnetization in every piece tested. A stout cylinder acquires a fairly large temporary moment, even when it is held with its long axis perpendicular to the earth's field, and it is very necessary to adjust the relative positions of such a specimen and a magnetometer by which it is to be tried, so that this magnetization shall not affect the measurements. The short iron cylinders which von Waltenhofen used must have been very soft indeed if they really lost their magnetization completely when left to themselves, with their axes perpendicular to the meridian, for a number of days.

Cases of Magnetization Which are not Really Anomalous.

In many cases of so called "anomalous magnetization," it is evident that a strong magnetizing field applied in one direction has been succeeded by a weaker field in the opposite direction, and when this latter has been removed, the magnet has the polarity of the first field. This is of course not wonderful except as we may regard all hysteresis phenomena as mysterious. Figure 1 shows a hysteresis diagram for an iron rod about 80 diameters long, with a number of loops corresponding to "side trips" within the main figure. It is clear that if the rod has been magnetized by a positive current so that the magnetic condition while the current is flowing is represented by the point N, and if the current be then stopped so that the condition of the rod is denoted by A and an oppositely directed current which gives rise to a field not greater than the abscissa of the point V be applied and then removed, the resulting magnetization of the rod will be represented by some point of the line OA. If the negative field is greater than OC, the polarity of the rod while the current is on will be negative, but if it be not too strong the polarity will be positive when the field is off. This phenomenon is relatively pronounced in the case of a short, stout rod where OA is short and the slope of the lower side of an inner loop is almost parallel to the line KVAN which may be nearly straight. An example will make this statement clearer.

Table I. gives the material for a kind of hysteresis diagram for a certain round rod of hardened tool steel, 2.8 cm. in diameter, and 12 cm. long, when magnetized in a certain long solenoid. The column headed " H " gives the strengths in gausses which the fields within the solenoid would have if the rod were not there; the strengths of the exciting fields in the rod would be very hard to determine even if they did not vary from point to point in the metal. The numbers under " N " are proportional to the flux strengths through the central cross section of the rod.

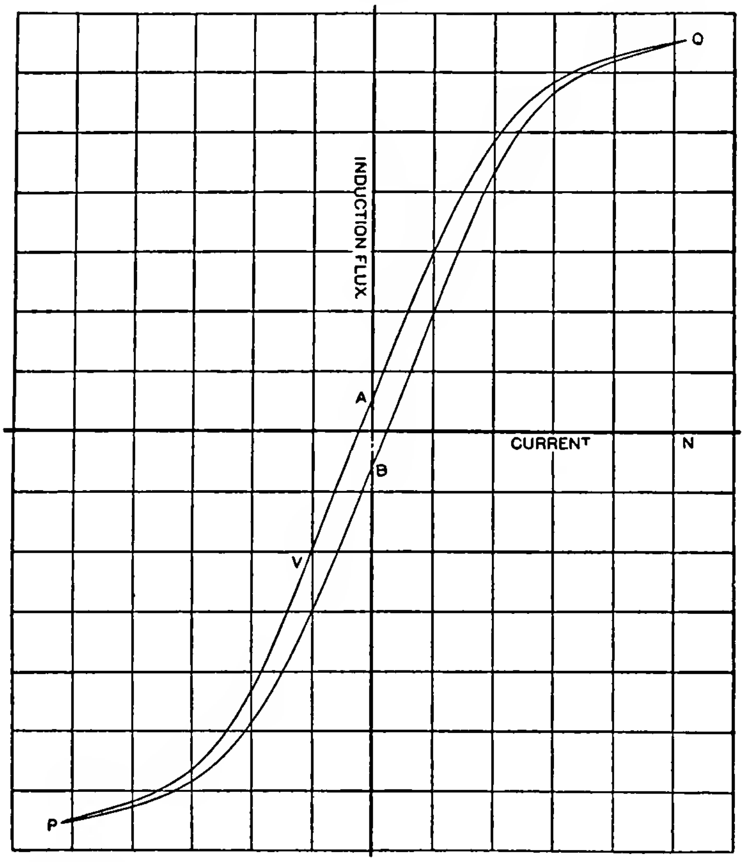

Figure 2. Magnetic cycle for a piece of Seebohm and Dickstahl's special magnet steel 12 centimeters long and 3.5 square centimeters in cross section. If the exciting current be dropped from its highest strength to 0, and then reversed and given such a strength as to carry the magnetism to the negative value represented by the point V, the residual magnetism will be slightly positive when the current is taken off.

If a positive current corresponding to $H = 976$ were sent through the solenoid and were then stopped, a negative current corresponding to $H = -35$ would make the magnetization of the rod negative while running, but a negative current corresponding to $H = -150$ could be used without making the magnetization negative when the current was taken off. A case like this may puzzle the observer if he does not happen to know that the rod he is using — which does not seem to be very strongly magnetized — has in fact been exposed to some very intense field in the process of manufacture, but this phenomenon is very different from the one which von Waltenhofen describes.

TABLE I.

H.	N.	H.	N.
960	551	0	+ 24
900	530	− 60	− 18
840	509	−120	− 61
780	489	−180	−103
720	467	−240	−137
660	443	−300	−191
600	420	−360	−231
540	392	−420	−272
480	361	−480	−316
420	321	−540	−354
360	279	−600	−391
300	237	−660	−422
240	195	−720	−451
180	144	−840	−504
120	110	−900	−528
60	66	−960	−551

The Anomalous Magnetization of Short Cylinders.

The most characteristic examples of really reversed magnetization are to be found, perhaps, among short, stout rods of soft iron and steel, as von Waltenhofen and Righi explained many years ago. If such a rod, originally annealed and demagnetized, be placed within a long solenoid and be subjected to a magnetizing field of suitable strength, and if the exciting current be then gradually reduced to zero by the introduction of more and more resistance into the circuit — by very small steps, if not continuously — the remanent magnetism will have the same sign as, but only a small fraction of the strength of, the magnetization induced in the rod when the current was running. If, however, the current be suddenly interrupted by the opening of the circuit, it frequently happens that the sign of the residual moment is opposite to that while exposed to the field. Figure 3 shows a typical case of a certain kind, that of a solid piece of carefully annealed "Cold Rolled Shafting" 8 centimeters long and 3 centimeters in diameter. The "demagnetizing effect of the ends" in a rod of these dimensions is, of course, very great, and the residual moment in this instance was for many currents less than one per cent of the moment originally induced in the metal. The long, uniformly-wound solenoid used for this experiment had a number (n) of turns per centimeter of its length such as to make $4\pi n/10$ almost exactly 25. In the figure, which represents a large number of observations, the horizontal unit corresponds to a field of 100 gausses if the iron were taken out of the solenoid. The actual field to which any portion of the rod was exposed for any value of the exciting current was of course difficult to determine. When the exciting current was suddenly broken a small spark appeared, and if the strength of the current was not greater than about 30 amperes, the remanent moment was of reversed sign.

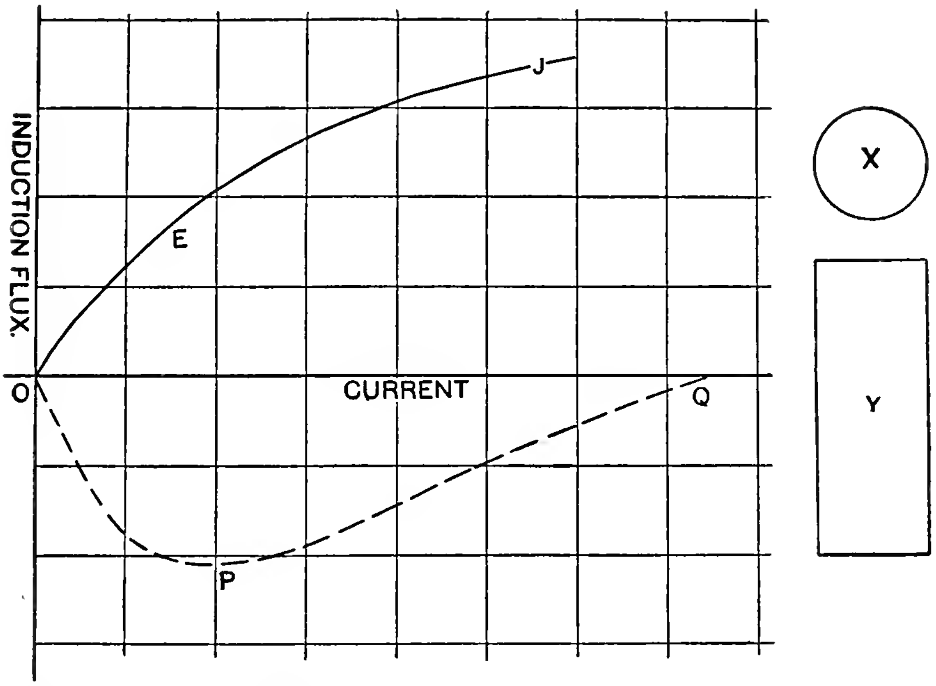

FIGURE 3. The ordinates of these curves show the magnetic condition of a soft cylinder of mild steel 8 centimeters long and 3 centimeters in diameter, when the exciting current had been taken off — gradually, in the case of the full curve — suddenly in the case of the curve OPQ in which the negative ordinates indicate anomalous magnetization.

The rod was at the outset in a nearly neutral condition. A small current (i) was at first applied to the solenoid, and then, with the help of a set of high-resistance rheostats made by the Simplex Electric Company, the rod was put many times through a hysteresis cycle with this current, positively or negatively directed, to mark the limits. After this the same current was slowly applied again and gradually removed, and the remanent induction through the central cross section of the rod was measured by means of a small test coil of very fine insulated copper wire, so mounted that it could be quickly slipped off the rod and removed from the solenoid while the rod itself remained in situ. This flux was found for both directions of the magnetizing current. Then the current was applied gradually as before and the circuit was broken by a sudden blow upon a simple switch, and the remanant flux was determined for both directions of the exciting field. The ballistic galvanometer used was a low-resistance d'Arsonval instrument made for the purpose by Mr. Coulson, who worked with me in making all the observations recorded here. The scale distance was about five meters, and the telescope was focussed upon a real image of the scale formed about two meters in front of the object glass, by a lens used as the cover glass of the galvanometer mirror.

The process just described was repeated for each of a series of currents of increasing intensities, and in this manner material for the curves shown in Figure 3 was obtained.

It is, of course, possible to use a magnetometric method in testing the residual magnetism of short rods, but although we have made a large number of determinations in this way, we have found it inconvenient for several reasons. It will appear later that the lines of magnetization in the case of an anomalously magnetized rod are so folded together that the external effect of the remanent magnetism is usually small, and if a conveniently large magnetometer deflection is to be obtained, the rod must be very near to the needle. It is not safe to remove the iron from the solenoid in order to test it outside, for a slight blow might seriously alter the moment, and if the magnetism is to be measured while the specimen is in its place within the solenoid, the magnetometer must be set up near one end of the solenoid, where it will be violently disturbed by the exciting currents and the fields incident to the process of forcing the iron so many times through the hysteresis cycles by which it is prepared for the tests. If a stout specimen of soft iron is placed with its axis horizontal and perpendicular to the meridian, a moment large compared with the residual moment to be measured is induced in it by the earth's field, and it is practically difficult to prevent this transverse magnetization from masking the effect to be measured.

In all the observations mentioned in this paper the solenoid was placed with its axis perpendicular to the meridian, and in all but a very few instances to be mentioned specially, the rod was tested while inside the solenoid.

In almost every instance, also, the exciting current was applied slowly to the magnetizing coil. That is, the circuit was closed with a very much greater resistance in it than was finally needed, and this was gradually reduced to the proper amount. If the circuit was suddenly closed with this final resistance in it, the residual moment of the rod was much smaller in absolute value, whether the current had been gradually or suddenly reduced to zero, than if the rise of the current had been slower.

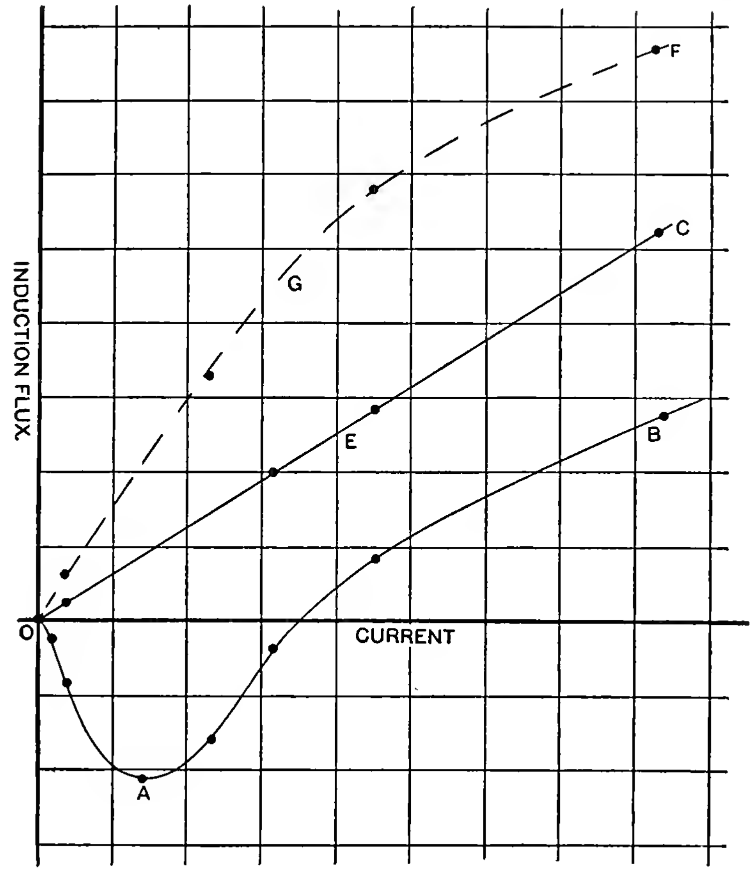

Figure 4. OGF and OAB show the flux of magnetic induction through a rod of very soft steel 2.86 cm. in diameter and 12 cm. long, after the magnetizing field had been gradually and quickly removed, respectively. OEC shows on a reduced scale the flux in the rod while it was exposed to the magnetizing field.

Figure 4 shows the results of tests similar to those described above, but made upon a phenomenally soft bar of mild steel 12 centimeters long and about 2.86 centimeters in diameter. The line OEC, which is nearly straight, represents the induction flux through the central cross section of the bar while the metal was under the action of the magnetizing field. Each ordinate has only one nine-hundredth of the length it would have if the scale of this curve were the same as for the other lines in the figure. The ordinates of OGF give the remanent flux when the slowly applied exciting current was as slowly reduced to

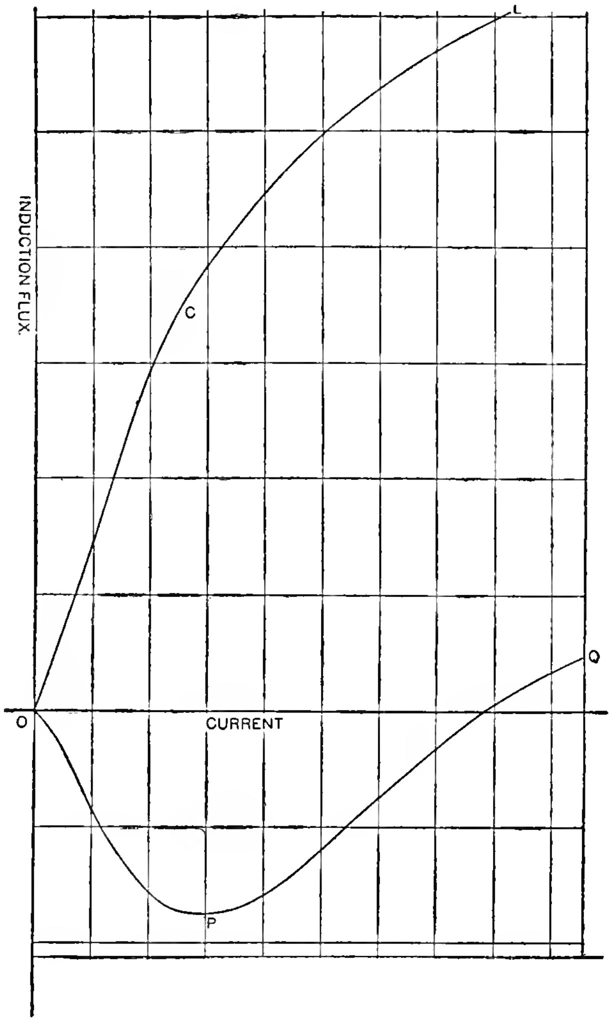

FIGURE 5. A cylindrical shell, about 12 centimeters long and 2.8 centimeters in outside diameter, was exposed in a long solenoid to exciting currents of various intensities. OCL represents the flux through the central cross section of the cylinder when the current was running, and OPQ, drawn on a somewhat exaggerated scale, the remanent flux when the circuit was suddenly broken. The horizontal unit corresponds to a field of 25 gausses in the solenoid when the iron was not there.

zero. The line OAB shows the residual flux after the current had been suddenly interrupted. The solenoid used in this work has 1460 turns in a length of 47 centimeters. The horizontal unit in the diagrams corresponds to about 80 gausses for the field ($4\pi n\, I/10$) in the solenoid due to the current in its coil. A discharge of 1 microcoulomb

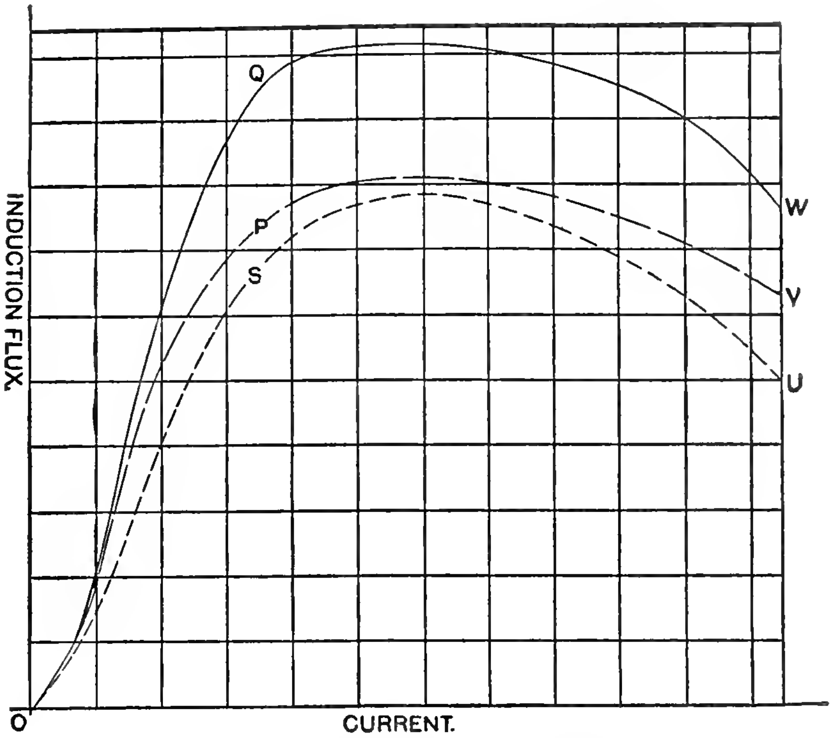

FIGURE 6. The ordinates of these curves represent the residual magnetism in a certain short, stout piece of soft steel magnetized in a solenoid, when the exciting current had been suddenly interrupted. A positive ordinate indicates reversed or anomalous magnetization. The observations recorded in each curve were taken after the specimen had been newly annealed, and the differences between the curves show that it is difficult to demagnetize a cylinder of such dimensions completely.

sent through the low-resistance galvanometer would cause a throw of 186 millimeters of the scale, and a throw of 1 millimeter corresponded to a flux of about 0.74 maxwells through the steel. The vertical unit in the diagram for the lines OGF, OAB, is 15 maxwells. It is evidence of the extraordinary magnetic softness of this specimen that whereas the flux through the rod corresponding to the point C was 70,000 maxwells, this sank to 113 maxwells when the current was slowly removed.

Figure 5 represents the results of experiments upon a soft steel shell about 12 centimeters long, 2.83 centimeters in outside diameter, and

1.9 centimeters in diameter inside. OCL represents the flux through the central cross section of the shell when the current was running, and the lower curve shows the residual flux upon a relatively larger scale. This residual flux is reversed for solenoid fields less than about 200 gausses.

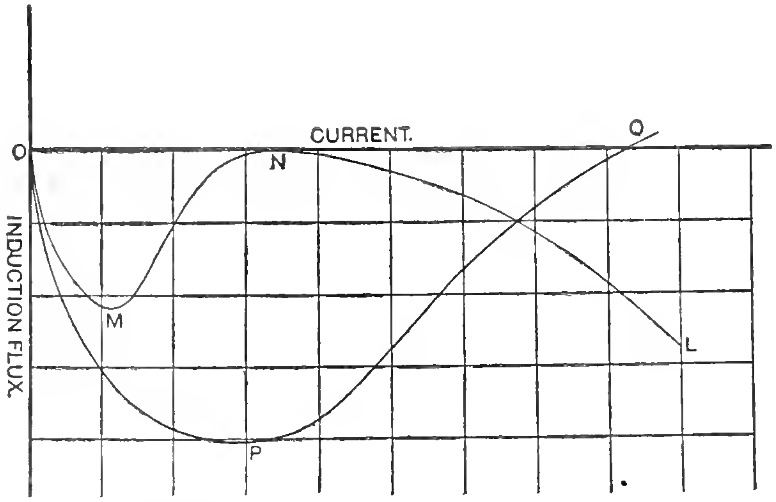

Figure 7. This diagram shows magnetic bias in a short rod of cold-drawn mild steel. This resisted the ordinary processes for demagnetizing the iron.

The three pieces of steel to which the curves of Figures 3, 4, and 5 belong were all freshly annealed just before they were magnetized, and the same precaution was taken in the case of almost every other specimen mentioned in this paper. The most careful reannealing does not generally bring a stout piece of iron which has been exposed to a strong field exactly back to its original magnetic state, though the differences are often so small as only to be discoverable when the specimen is tested for anomalous magnetization. Figure 6 shows such a test made upon a soft piece of Bessemer steel freshly annealed before the observations recorded in each curve. The residual moments were themselves very small and the differences were in absolute value very small indeed but are evidently real.

Figures 7 and 8 show the results of experiments made upon two pieces 12 and 8 centimeters long, respectively, cut from a rod of cold-rolled shafting about 3 centimeters in diameter. Each piece was exposed to a long series of magnetic fields alternating in direction and gradually decreasing in intensity, with the hope that this process would remove any magnetization that the rod might have acquired in the making, but both pieces show a decided bias which was too strong to yield to such treatment. In Figure 7, OPQ is the residual magnetism after currents which have caused positive moments have been suddenly destroyed. OMNL shows the remanent magnetism after currents which have caused negative moments. The first curve indicates that the residual magnetism was reversed in sign, but this was never the case after negative currents. In Figure 8 similar curves are shown for the shorter specimen and it appears that some of the negative currents left anomalous residuals. Annealing removed the bias from the first piece almost completely.

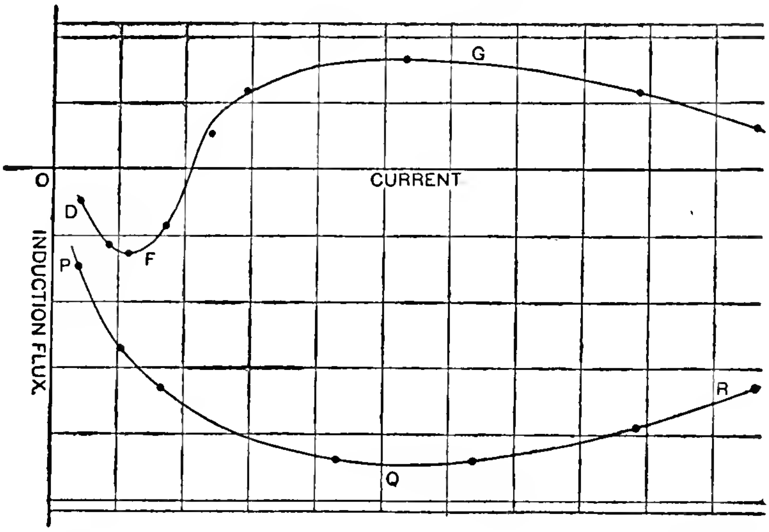

FIGURE 8. Magnetic bias in a rod of cold-rolled shafting which the demagnetizing process used could not remove.

Apart from details the observations recorded in this section are in general agreement with much that has been written upon this subject as given[8] in Wiedemann's *Elektricität*. Wiedemann denotes by T the total magnetic moment of a bar when exposed to the action of a magnetizing field and by P the residual moment after the field has disappeared. He uses the suffixes a and f to denote that the moment of which he is speaking has been reached by a gradual change in the exciting field or by a very sudden one. He says that T_f is always larger than T_a and P_a than P_f, algebraically considered, but these differences are only large in short rods. P_f is slightly increased if the rod to be magnetized is surrounded by a thick tube of nonmagnetic metal. $(P_a - P_f)/P_a$ is smaller for bundles of insulated soft iron wire than for solid rods of the same dimensions. Inversion comes with longer rods when the exciting field is weak than when it is strong. Some of these statements will need to be discussed in the light of experiments upon divided cores. The statement copied by Wiedemann

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[8] Bd. iv, §§ 338–340.

that if the iron core has been already magnetized in the normal direction by a current which has been slowly brought to zero, anomalous magnetization does not occur when a second current is applied in the same direction and then suddenly stopped, runs counter to all our experiences. Specimens which have not been really demagnetized show, of course, all sorts of abnormal behavior, but we have found it easy, with suitable cores, to get reversals after a slowly applied current has been slowly removed, by breaking suddenly a current in the same direction whether this last was applied slowly or suddenly. If a quickly applied current has been slowly cut off, we can get reversals by quickly breaking a current in the old direction, applied either quickly or slowly. If we apply either slowly or quickly a current in a fixed direction, then open it suddenly, and repeat this process a score of times, the reversal usually occurs at every break of the circuit without any reversal in direction of the exciting current. The remanent magnetism after a slow break, is greater if the current was quickly applied, but, as we have seen and as Wiedemann's statements would lead us to expect, anomalous magnetism occurs more regularly if the current has been slowly applied.

As Righi pointed out in 1880, if one cuts a number of pieces of different lengths from a stout steel rod and, beginning with the longest and taking them in order, tests the sign of the remanent magnetization of each after the exciting field has been suddenly destroyed, one often arrives at a length where anomalous reversals begin and continue for shorter pieces. Figures 9, 10, 11, are founded upon a set of such tests made upon rods cut from the very soft bar which furnished the specimen to which Figure 4 belongs. The diameter of the bar was about 2.83 centimeters, and the lengths, in centimeters, of the pieces used were 40.1, 31.8, 20.9, 18.0, 13.6, 12.0, 10.0, and 8.0. Figure 9 shows the residual fluxes through the centres of the pieces for all the specimens except the first and the fifth. These are all reversed in sign, but the amounts are extremely small because of the remarkable softness of the material. The horizontal unit corresponds to a solenoid field of 20 gausses, the vertical unit is about 7 maxwells. The first piece, 40 centimeters long, showed a slight reversed moment for excitations in the solenoid up to about 38 gausses, but the ordinates of the positive loop were not so high as the other curves of the series might lead one to expect them to be. Figure 10 shows the residual fluxes after the exciting currents had been slowly reduced to zero. The horizontal unit is here 80 gausses and the vertical unit 30 maxwells. Figure 11 shows the induction fluxes through the cross sections of the rods while they were in the magnetizing fields. The horizontal unit is in this case 80

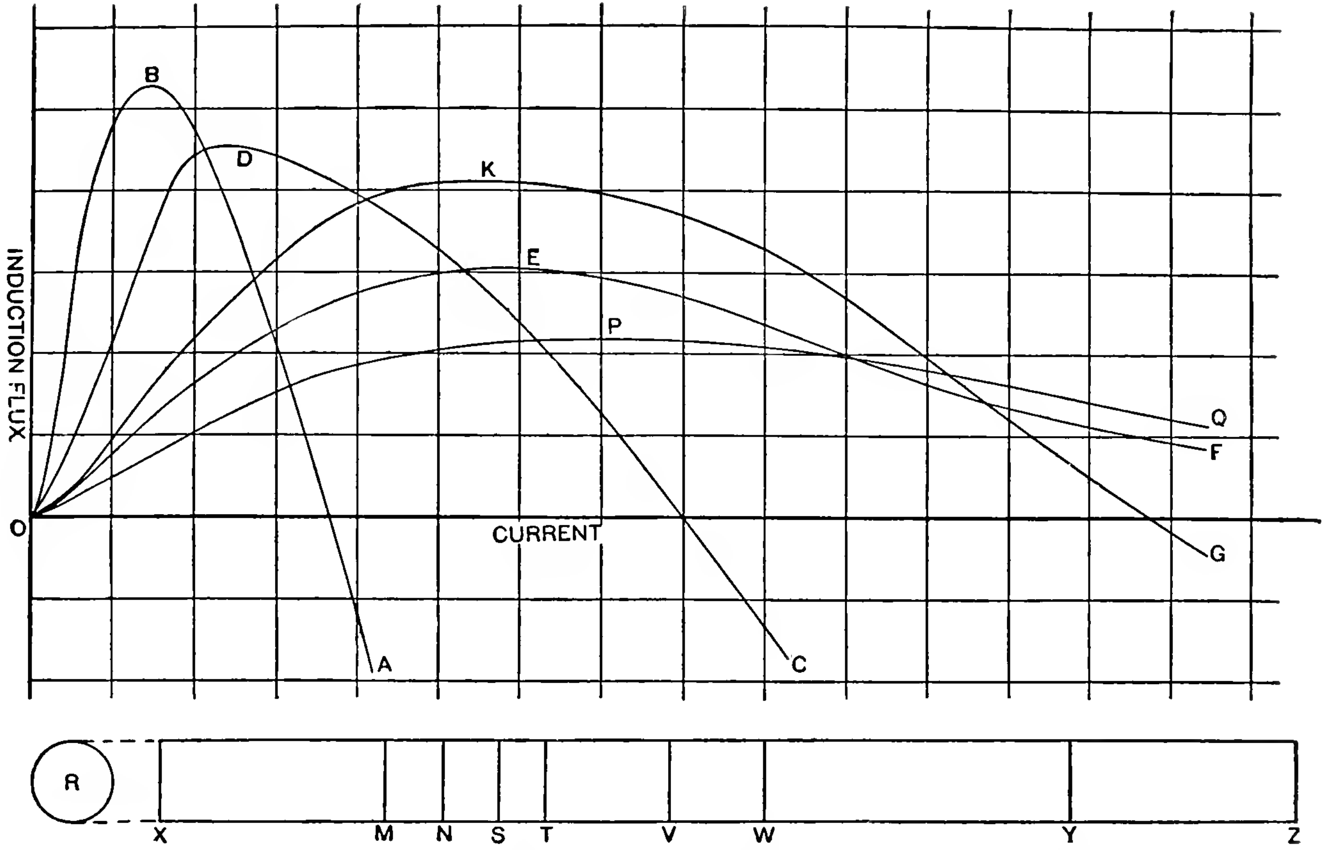

Figure 9. Abnormal residual magnetization in rods of very soft mild steel, about 3 centimeters in diameter and of different lengths.

gausses and the vertical unit very nearly 14,000 maxwells. Of 42,000 maxwells which the 8 centimeter long piece had under an exciting current of 16.4 amperes, only about 55 maxwells remained when the current had been gradually destroyed, and this for a cross section of about 7 square centimeters.

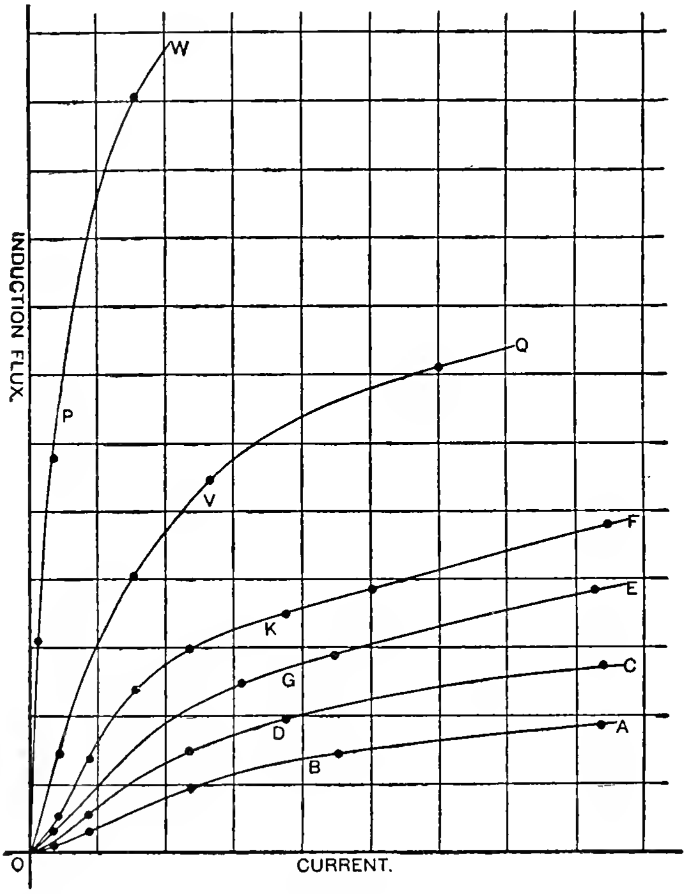

Figure 10. Residual magnetism of normal sign in rods of very soft mild steel of different lengths.

It is usually difficult to get a piece of Bessemer steel 3 centimeters in diameter and even 30 centimeters long so soft, magnetically considered, that it will show abnormal residual magnetism, and the metal just mentioned is exceptional, as has already been said.

Pieces cut from a certain round rod of soft steel, of lengths in centimeters 30, 15, 8, 6.8, and of diameter 1.6 centimeters, all refused to reverse when tested, but reversal finally appeared in a piece about 6.4 centimeters long.

It is often impossible to make a stout piece of hardened tool steel reverse unless its length be made so small that the observations become doubtful. The next table (Table II.) records the results of observations made upon a certain piece of glass-hard tool steel, 12 centimeters long and 3 centimeters in diameter. The solenoid used in this experiment, one of a large number at our disposal, was 176.2 centimeters long and had 5526 turns of insulated wire divided up into three coils of 1837, 1847, and 1847 turns respectively. The first column gives the intensity of the exciting current and the second column, on an arbitrary scale, the remanent magnetism, which always had the sign of the magnetizing field which had just been suddenly interrupted.

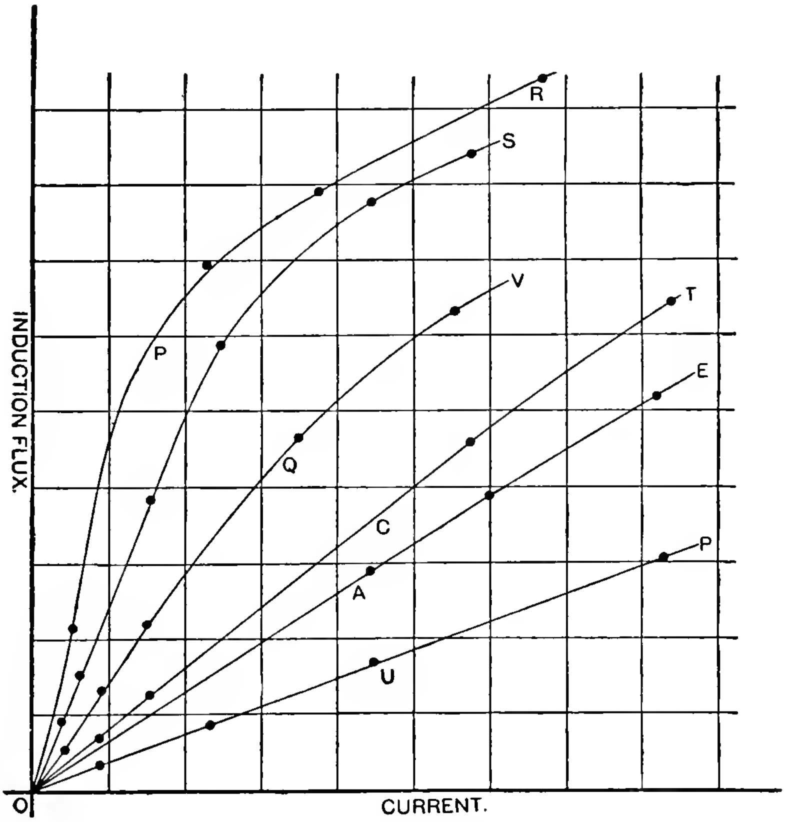

FIGURE 11. Magnetism induced by different exciting fields in a set of rods of various lengths.

TABLE II.

I.		N.	
0.2	2	2.0	98
0.4	6	2.5	148
0.6	17	3.0	196
0.8	23	4.0	302
1.0	31	5.0	415
1.5	61		

There is here no trace of anomalous magnetization.

If a strong current running through a solenoid containing a core of magnetizable metal, be suddenly broken, there will be, under favorable circumstances, an oscillatory discharge across the spark gap, and according to Wiedemann's theory, which was based upon the numerous experiments of early observers[9] upon the magnetization of steel needles by discharges from Leyden jars, the phenomena of anomalous magnetization are to be explained by the action of oscillating currents rapidly decreasing in intensity, induced in the outer portions of the core under test. Through the kindness of Mr. William Otis Sawtelle, who has a large revolving mirror driven by a powerful motor, and devices which he has himself designed and constructed for photographing electric sparks under various conditions, we were able to make sure that in the cases of the apparatus which we used in our experiments upon anomalous magnetization the discharge, when we suddenly opened the circuit, was uniformly oscillatory in character. Mr. Sawtelle and Mr. Coulson photographed a large number of these sparks; and, from their results, there cannot be any doubt, I think, that there were usually several hundred reversals in direction while the visible discharge lasted. With one of our solenoids, the period proved to be about 1/58000th of a second, and Professor G. W. Pierce, who most kindly tested one of our coils by itself, showed that such frequencies were to be expected. In each of the spark photographs, the record crossed the plate many times and the growth of the spark length with the time when the circuit was suddenly opened could be studied from them. It appeared that the manner of throwing the circuit open had very little effect upon the character of the discharge. When the current in the solenoid circuit is brought to zero by the continuous introduction of more resistance into the circuit, we do not expect that alternative currents will be induced in the core. It is difficult, however, to get any satisfactory theory upon which to base a mathematical investigation of the results of currents induced in a core of soft iron by oscillations decreasing in amplitude in a neighboring circuit. Even if the courses of such currents in a non-magnetizable core could be satisfactorily treated, and this seems difficult without a more accurate knowledge than we have about the behavior of the exciting current oscillations, we should not have any clear light

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[9] Savary, Ann. de Chim. et de Physique, **34**, 1826. Von Liphart, Pogg. Ann., **116**, 1862. Paalzow, Pogg. Ann., **117**, 1862. Reiss, Pogg. Ann., **122**, 1864. J. Henry, Scientific Writings, pp. 203 and 293. Rayleigh, Phil. Mag., **38**, **39**, 1870. Rutherford, Phil. Trans., **189**, 1897. Wilson, Electrician, **51**, 1903. Fleming, Proc. Roy. Soc., **74**, 1903.

upon what happens in a core magnetized in lines which are often closed within the metal, after the magnetizing current has been removed and the changes which come from the rapidly changing demagnetizing forces from the ends of the core itself are going on. We may content ourselves at present, therefore, by showing that, so far as we know, oscillations are always present in the circuit of the exciting current when anomalous magnetization is afterwards to be detected in the core. We must not close our eyes, however, to the fact that the demagnetizing forces due to the magnetic distribution itself complicate the problem.

Residual Magnetization in Bundles of Fine Iron Wire.

The remanent magnetism in a bundle of fine iron wire so shellacked as to prevent electric flow from one wire to the next, should be interesting because the effects of eddy currents in the core itself are nearly avoided. Fromme's work in this direction seems not to have been conclusive, and it will be instructive to consider two or three experiments.

Two similar solenoids were placed horizontal with their common axis perpendicular to the meridian, and with their nearer ends about 15 centimeters apart. These solenoids were so connected in series that a current sent through the circuit did not affect the needle of a magnetometer between them. A bundle of fine, varnished iron wire forming a cylinder 12 centimeters long and 3 centimeters in diameter was then introduced into one of the solenoids and tested to make sure that it had been properly demagnetized. A small current was next sent through the circuit and the wire put several times through the cycle corresponding to this current. Then the circuit was suddenly broken so as to bring the current from its full value to zero and the needle deflection caused by the residual magnetism was observed. This process was then repeated for a series of currents of increasing strengths. The results of the work are given in Table III. H represents the strength which the current would cause in the solenoid if the disturbing effects of the iron itself were not present. D shows the deflections of the needle on its scale caused by the residual moments. It is evident that there was nothing here similar to the abnormal magnetization of a soft iron solid cylinder of the same dimensions under similar conditions.

TABLE III.

H.	D.	H.	D.
10	19	150	182
19	45	211	208
37	81	301	233
63	112	420	253
89	138	530	263
110	156		

A bundle of the same size as the last (12 centimeters long and 3 centimeters in diameter) was then made of pieces 12 centimeters long cut from Bessemer steel wire some of it 2.4 millimeters in diameter and some of it twice as large. In this case the wires were not varnished and eddy currents were not wholly prevented. The observations were made by determining the induction flux through the central cross section of the bundle, first, when the exciting current was running and then after it had been suddenly destroyed. The first column in Table IV. gives the strength of the field in the solenoid ($4\pi nI/10$); the other columns give, on an arbitrary scale, the flux values.

TABLE IV.

H.	N.	N′.
10	293	6.8
19	592	15.0
36	1144	30.1
60	1900	52.0
84	2740	71.6
108	3490	87.2
145	4700	113
201	6900	140
290	9200	166
400	13800	188
501	17300	210

These results represent very fairly all our experiences with bundles of iron wire. Although most transformers show the von Waltenhofen phenomena unless the cores are very minutely divided, I have never been able to get even an approach to a reversal of sign of the magnetism of the short packages of fine wire that I have used. One of these, which was about 3 centimeters in diameter, was only 6.8 centimeters long.

In a stout iron cylinder made up of a small number of large pieces, anomalous magnetism is frequently to be found. Figure 12 shows the results of an interesting test upon a short cylinder of soft Bessemer steel, at first solid and then slit in a milling machine lengthwise with a very thin saw. The forms of the curves which show the magnitudes of the anomalous magnetization in these cases are similar, but the effect of the slits is very marked.

As has been already explained, we usually opened a circuit, when this had to be done suddenly, by a sharp blow upon a switch, but we experimented with other devices without finding that any of them was better. At one time we broke the current by shattering a short piece of glass-hard steel wire introduced for the purpose into the circuit, but we did not discover that this process led to different conclusions from those which we reached with the more convenient key.

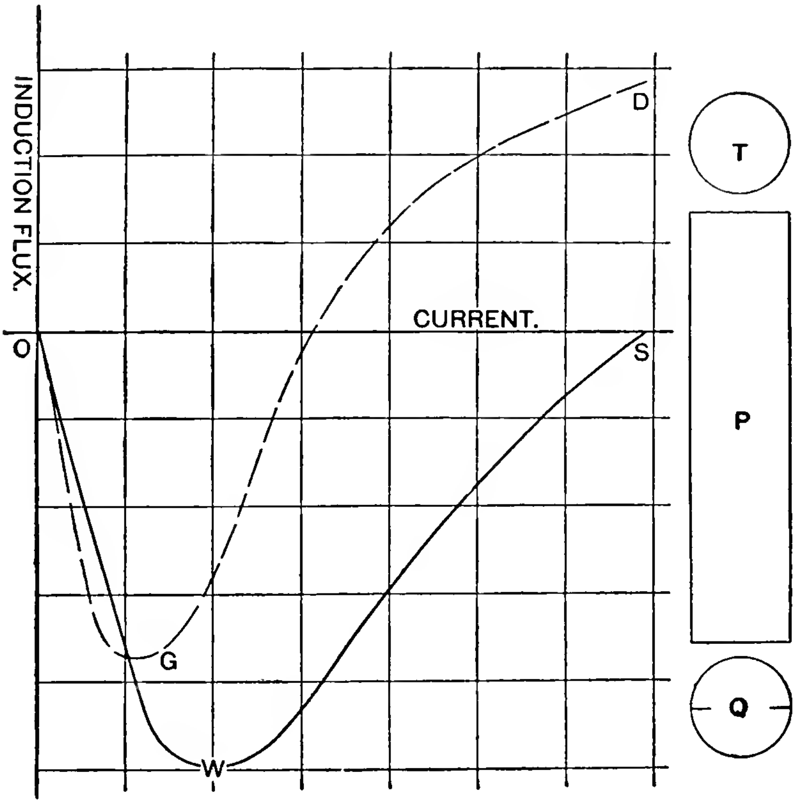

Figure 12. This diagram shows anomalous residual magnetism in the case of a piece (P) of soft Bessemer steel, 12 cm. long and 2.8 cm. in diameter. The full curve was obtained with the cylinder intact as shown at T, the dotted curve, after the specimen had been slit lengthwise in the manner shown at Q.

Anomalous Magnetization in Cylinders Formed of Shells and Cores.

As will appear more clearly in the sequel, many of the lines of polarization in a short, anomalously magnetized solid cylinder form closed curves wholly inside the metal, and a cut made in the iron in the form of a cylindrical surface coaxial with the surface of the specimen would seriously interfere with this arrangement because there would be a very sensible reluctance at the crack. We should expect, therefore, that the magnetic characteristics of an iron cylinder formed of a cylindrical core and a coaxial shell would be in some respects different from that of a solid cylinder, and this is the fact.

Figure 13 gives two curves, the first, OKED, belonging to a shell of diameters 2.83 and 1.93, with a core of diameter 1.60 centimeters; the second, OGPQ, to a shell of diameters 3.20 and 2.20, with a core of diameter 1.90. In each of these cases the residual magnetism is reversed in sign for comparatively small currents, then direct for currents somewhat stronger, and for large currents is again reversed with no apparent desire to become again positive. Curve LMNZ of Figure 14 belongs to a shell of diameters 2.83 and 1.93 with a core of diameter 1.90. The gap between core and shell is here narrower than in the cases just mentioned, and the curve which gives the magnitude of the residual magnetization in terms of the exciting current, while of the same general form as those of Figure 13, does not cross the axis of abscissas, and the residual moment is reversed for all the excitations shown in the curve.

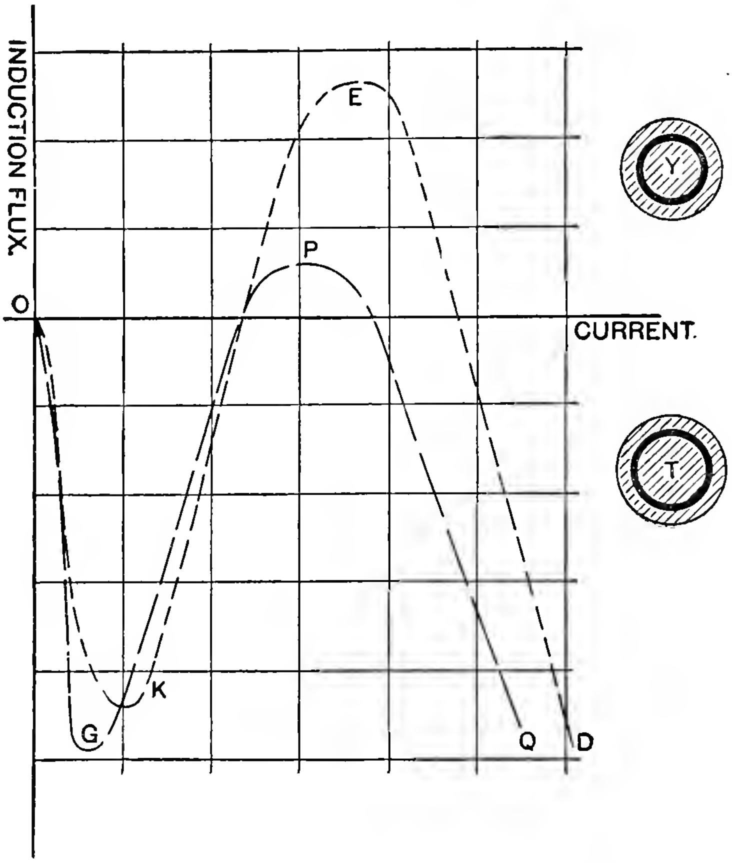

Figure 13. The ordinates of each of the curves of Figure 13 show the remanent magnetism in a combination of a soft Bessemer shell and core when the slowly applied exciting current has been suddenly broken. A negative ordinate indicates that the residual magnetism has a sign opposite to that of the field in the solenoid when the current was running.

Figure 15 shows some observations made upon a shell and core which were not very successfully demagnetized. A slight bias exists : ABC and PQZ show the residual fluxes through shell and core, the first for currents which give a negative moment while they are running, the second for positive currents.

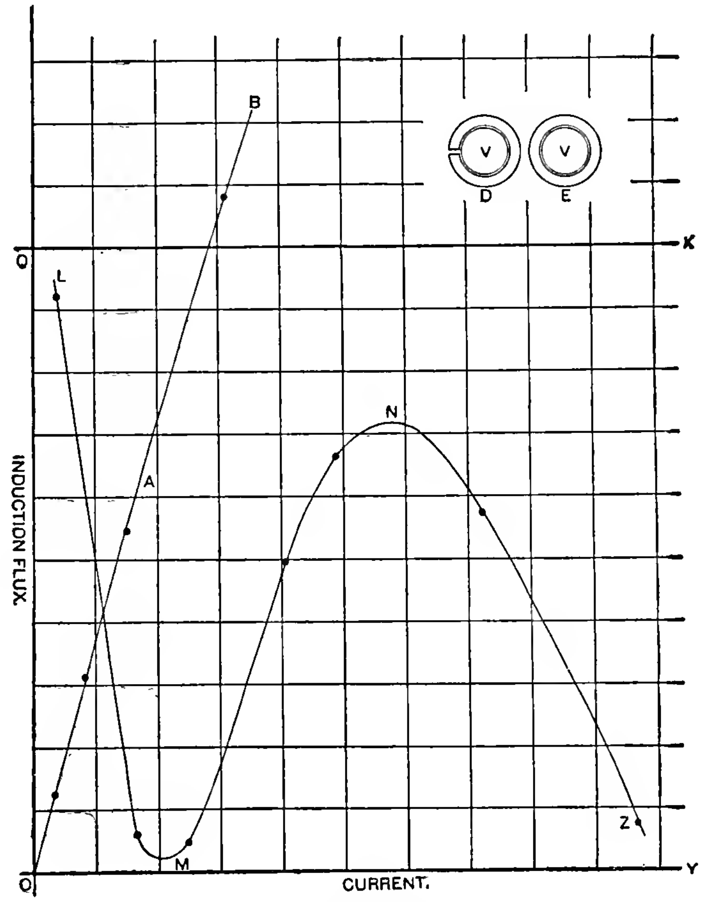

FIGURE 14. Two similar shells of soft steel, one intact, the other slit lengthwise by a thin saw cut, were used successively over the same core. LMNZ and OAB show the fluxes through the combinations in the two cases.

Figure 16 shows how greatly the manner of building up the current, which is then to be quickly broken, affects the amount of the negative or reversed magnetizations. Both of these curves show anomalous magnetization for moderate currents, but the residual flux is very much greater if the current is built up gradually than if it is built up suddenly.

The gap between core and shell in the combinations X and Y of Figure 13 and some others we have used, was purposely made wide enough to permit of the introduction of a very thin ring coil to embrace the core alone and thus make it possible to study separately the behavior of each part of the system. The results of experiments of this kind proved instructive, as will appear from an account of a typical case.

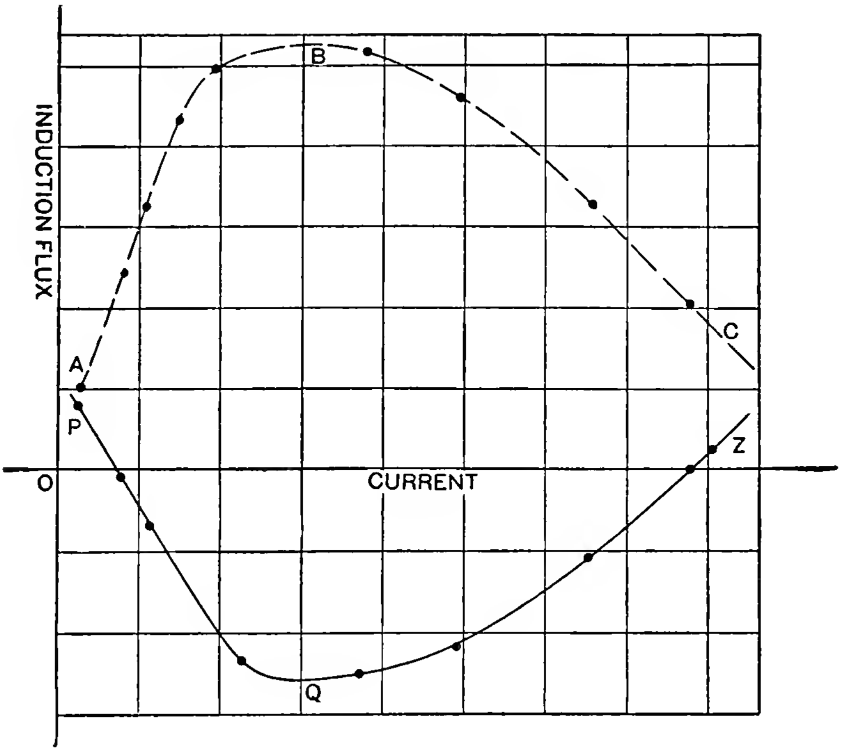

Figure 15. A combination of shell and core, made of soft Bessemer steel, was demagnetized as completely as possible and then tested in a long solenoid. The magnetizing current was built up gradually and then suddenly broken. The ordinates of ABC show the residual flux through the metal when the current gave a negative moment before it was interrupted, the ordinates of PQZ show the remanent flux for oppositely directed currents. There was a bias in the specimen which showed that the process of demagnetizing it had not been wholly successful, and the anomalous magnetization is of different magnitude on the opposite sides.

A cylindrical shell 12 centimeters long, the diameters of which were 3.00 and 2.27 centimeters, was used with a core 1.90 centimeters in diameter to form a combination (Z) which, after being thoroughly demagnetized, was placed in a long solenoid and exposed to a series of magnetizing fields, each a little stronger than the preceding. At every step, the metal was put a number of times through the hysteresis cycle corresponding to the exciting current employed, and then the fluxes through the central cross sections of core and shell were measured while the current was running. In Table V. H represents the field ($4\pi nI/10$) due to the current in the solenoid, F is the flux in maxwells through the combination of core and shell, N is the flux through the core alone, and N′ is the flux which the core would carry if the whole flux through the system were uniformly distributed. The area of the cross section of the core was about 47 per cent of that of the combination.

TABLE V.

H.	F.	N.	N′.	N/F.
10	1270	130	595	0.102
20	2500	215	1170	0.086
30	3670	295	1720	0.080
40	4830	365	2270	0.076
50	5990	430	2820	0.072
60	7150	500	3360	0.070
70	8310	565	3920	0.068
80	9470	630	4450	0.067
90	10640	700	5000	0.066
100	11820	765	5500	0.065
125	14800	930	6950	0.063

While the slowly built up current is running steadily the flux in the core, which should be nearly half that through the whole combination if the flux is to be uniformly distributed, is very much less.

When in the case of this combination (Z), the slowly built up current, so directed as to make the flux positive while it is running, is very slowly decreased to zero, the remanent flux through the system is positive, but the flux in the core becomes *negative*, in the manner indicated by the figures in Table VI. in which F, N, S, are the induction fluxes through the whole combination, the core, and the shell, respectively.

TABLE VI.

H.	F.	N.	S.
50	+ 86	−322	+408
100	+122	−410	+530
150	+132	−370	+500
200	+141	−318	+459
250	+149	−265	+415
300	+155	−213	+368

While the remanent flux through the system increases regularly with the strength of the current, the oppositely directed fluxes in the shell and the core decrease after reaching maximum values.

In all work with short bars of iron or steel, the "demagnetizing force due to the ends" becomes very important. The outer portions of a very short magnet often reverse the direction of the polarization in the inner portion so that most of the lines of polarization are closed within the metal and the effect of the magnet upon a magnetometer needle is often very slight indeed. If a cylindrical shell with a core of loose steel wires be placed inside a solenoid of stout wire and a powerful current be then suddenly sent through the coil, the wires will be thrown violently out of the shell if the latter be short and stout, in a direction which shows that the moment induced in them by the exciting current was opposite in sign to that of the shell. This experiment is sometimes very striking.

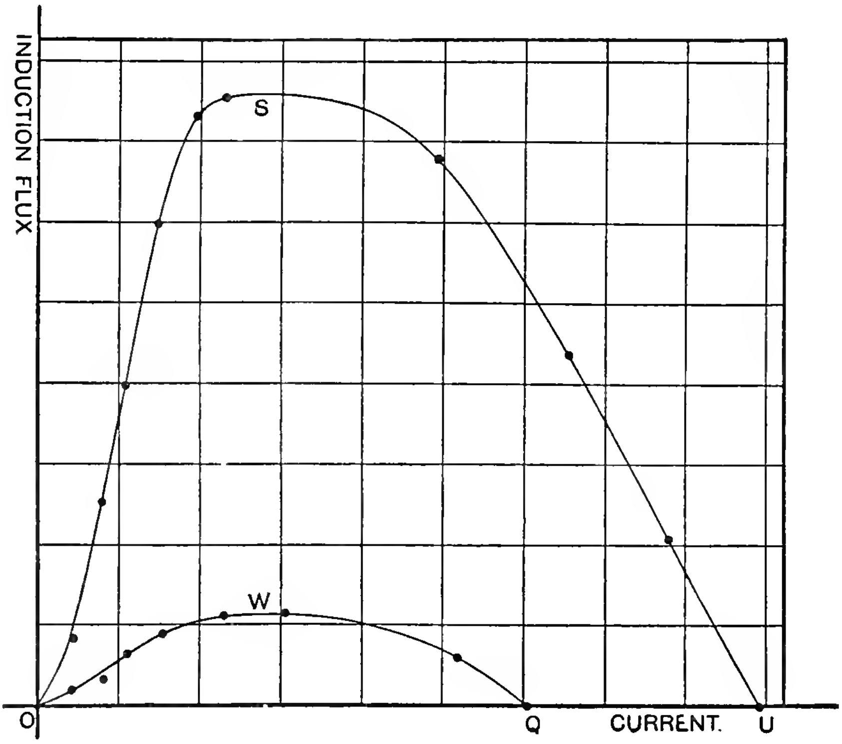

FIGURE 16. A shell and core of soft Bessemer steel about 12 cm. long were exposed to a magnetizing field of given strength in a long solenoid, and the exciting current was then suddenly broken. The ordinates of the curves OSU and OWQ represent the remanent induction flux through the central cross section of the specimen, when the solenoid current was slowly built up and suddenly applied, respectively. A positive ordinate represents a reversal of magnetism in these curves.

If, in the experiments upon the combination Z, the exciting current was suddenly destroyed, the flux in the shell became instantly *negative*, while the remanent flux in the core was *positive* just as it was when the current was running through the solenoid circuit. See Table VII.

TABLE VII.

H.	F.	N.	S.
10	— 7	+ 57	— 64
20	—18	+134	—152
40	—25	+180	—205
50	—21	+184	—205
100	— 5	+178	—183
150	+ 4	+170	—166
200	— 4	+171	—175
250	—17	+214	—231
300	—30	+320	—350

At $H = 1100$ gausses F gave a negative throw far off-scale, and N a similar positive throw. At this excitation, however, the solenoid current had to be so strong as to heat the coil rapidly and we did not attempt to make careful determinations of these fluxes. If F were plotted against H we should get a curve of the form shown in Figure 13.

All the combinations of shell and core that we have used give a set of fluxes for the F column which vary with the excitation in much the same way that the whole flux for Z does. There is always — so far as my knowledge goes — an increase in N from a low value near the outset to a rapidly increasing one at high excitations, but sometimes the increase is regular and sometimes not. As an instance of a very rapid increase in N beginning near a given excitation, I may cite the case of

TABLE VIII.

I.	F.	N.
0.22	— 1 8	+ 14
0.42	— 4.7	+ 33
0.82	—12.2	+ 78
1.44	—16.3	+118
1.77	—18.0	+138
2.25	—17.2	+148
2.73	—15.7	+162
3.43	—10.1	+177
5.00	+ 2.7	+197
7.60	+10.3	+308
12.10	—20.1	+664

a certain combination of nearly the same dimensions as Y of Figure 13, which was tested in a solenoid for which $4\pi n/10$ was very nearly equal to 25. The first column in Table VIII. gives the intensities of the exciting currents used, the second and third columns the fluxes after the currents had been suddenly interrupted.

L in Figure 17 represents a combination of two coaxial shells and a core, very accurately made and carefully annealed by Mr. Thompson. The diameters, in centimeters, of the five cylindrical surfaces were 1.12, 1.58, 2.53, 3.00, 3.96. This system was treated like all the other test pieces and the fluxes through all three members were determined after the currents which had been slowly applied had been slowly brought to zero and again after they had been suddenly destroyed. Tables IX. and X. give the remanent fluxes for the slow breaks and for the quick breaks respectively. I represents the solenoid current in amperes.

TABLE IX.

I.	Core.	Inner Shell.	Outer Shell.
0.60	− 7.8	− 38	+ 58
1.41	− 25.6	−160	+225
4.70	− 56.5	−292	+428
8.50	− 84.0	−276	+474
17.00	−156.0	− 34	+294
44.50	− 41.4	+215	+ 47

TABLE X.

I.	Core.	Inner Shell.	Outer Shell.
0.60	+ 6.2	+ 83	− 109
1.41	+ 12.1	+ 174	− 223
4.70	− 2.5	+ 299	− 318
8.50	− 0.7	+ 364	− 366
17.00	+ 1.9	+ 652	− 674
44.50	+155.0	+1445	−1922

The signs are nearly all different according as the current is slowly or quickly destroyed.

The observations already described represent fairly all our work upon combinations of solid shells and cores and it remains to mention the special case represented by the nearly straight line of Figure 14. Here the shell was of the same dimensions and of similar material as that used in the work which led to the curve LMNZ in the same figure, but this shell was slit through lengthwise by a single saw cut which prevented currents from circulating around it. Many of our specimens were made 12 centimeters long so that our observations might be more easily comparable with some which von Waltenhofen and Fromme made.

We have seen that if in a combination of a shell and a core the exciting current be gradually reduced to zero, the residual magnetization of the shell is usually normal and that of the core reversed. If, however, the current is suddenly broken, the magnetization of the shell is often reversed and that of the core is normal. These facts may be proved by removing the specimen from the solenoid and testing the two pieces which then seem to be strongly magnetized, separately with a compass or magnetometer. The separation of the members of the system alters the polarization in each, however, and the process is not to be recommended in accurate work.

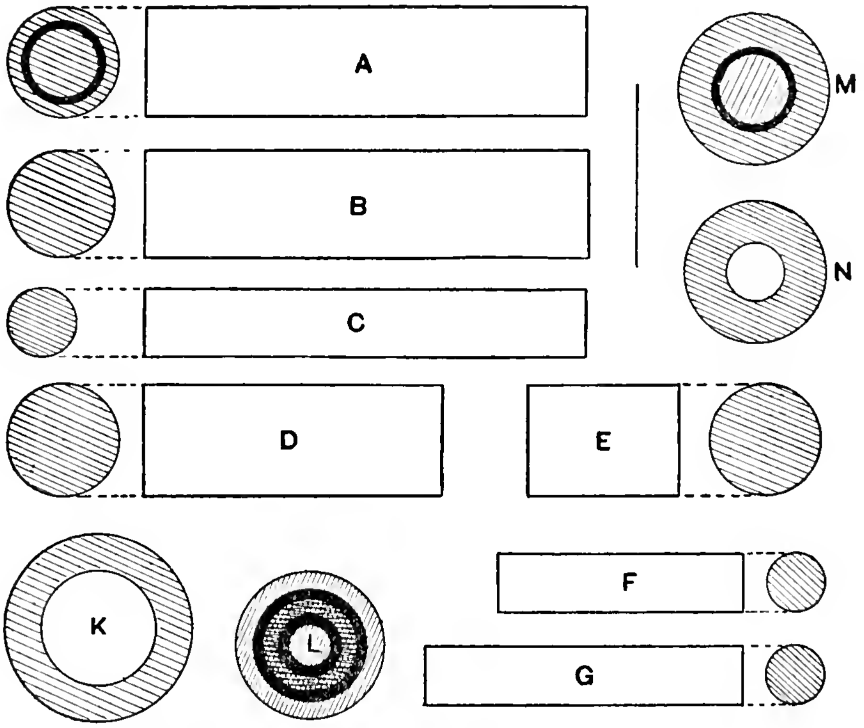

FIGURE 17. The forms of some of the test pieces.

It is very difficult to study the residual magnetism in a very short, stout soft iron cylinder, whether this be normal or anomalous, by the use of iron filings, for since so many lines of polarization are closed within the metal, the external action of the magnetization is usually small. In the case of a combination of a shell and a core, where the gap prevents the arrangements of polarization from being what they would be in a solid cylinder of the same dimensions, it is often practicable to show by the aid of very fine filings that lines emerge into the air from the outer filaments at one end of the specimen and go into the metal again at the same end at points nearer the axis.

The Influence of an Iron Shell upon the Magnetic Behavior of a Short Cylinder within It.

Some mild steel cylinders of the dimensions of the cores used in the combinations already described do not show the phenomenon of anomalous magnetization very strikingly when used by themselves, and it seemed desirable to make a series of tests upon a short piece of very soft steel about 3 centimeters in diameter, without and with shells. I have used very mild steel of various kinds for most of the observations mentioned in this paper, because it is much more homogeneous than the best procurable wrought iron, which is apt to include patches of oxide and slag which hinder the free passage of eddy currents in directions perpendicular to the grain of the material.

Tables XI., XII., and XIII., give the flux through this core when the slowly applied current *I*, which created the field $H = 4\pi n I/10$ within the solenoid, was in action, after it had been gradually reduced to zero, and after it had been suddenly destroyed. The numbers in the columns headed N, N′, N″, belong respectively to the cases where the

TABLE XI.

Current On.

H.	N′.	N″.	N‴.
40	+ 3110	+ 747	+ 681
65	+ 5450	+1120	+1012
176	+14480	+2560	+2330
370	+31200	+5360	+4740
452	. . .	+6720	+5850

TABLE XII.

Slow Break.

H.	N.	N′.	N″.
20	+ 8	— 12	— 25
50	+ 20	— 42	— 97
100	+ 35	—142	—173
150	+ 51	—191	—204
200	+ 66	—216	—223
300	+ 92	—233	—235
400	+105	—248	—242

core had no shell, where the shell of soft mild steel had the diameters 4.45 and 3.30; and where the shell made of fine, soft, varnished iron wires had diameters of 4.90 and 3.35 centimeters respectively.

TABLE XIII.

Quick Break.

H.	N.	N′.	N″.
40	−18	+ 73	+ 74
65	−23	+106	+138
176	−18	+115	+209
378	+11	+ 30	+220
576	+42	+ 14	+216

In the solid shell the alternating eddy currents which Wiedemann had in mind may encircle the core, but this would not be possible in the core made of shellacked wire. It is evident that both shells exert a strong demagnetizing effect upon the core, even while the current is running in the solenoid. All the results here tabulated agree in general with those quoted in the last section. In the case of the solid shell, the moment of core and shell taken together will usually be reversed after certain strengths of current, but this is never the case when the shell is finely divided. Figure 18 shows a typical instance. The solid core is surrounded by a wire shell, and when the exciting current is suddenly destroyed the core has a reversed magnetization for values of *H* up to about 350 gausses, as is shown in curve OQR. The whole flux through the combination of core and shell as indicated by the curve OWV is never negative, though for high excitations, when the flux through the core is strongly positive, the flux through the shell itself may be small. In one case under an exceedingly high excitation, the line corresponding to OQR bent down again something like the curves of Figure 13, but the observations were so difficult to manage that I did not attempt to follow this out in other cases. A value of *H* above 1700 or 1800 is hard to maintain without heating the metal and the solenoid employed unduly, which masks the effect to be studied.

The Influence of a Thick Copper Shell upon the Magnetic Behavior of a Short Cylinder within It.

Many years ago Fromme enclosed a stout piece of soft iron which he was testing in a thin shell or shield of copper and was able to prove that this shell did not prevent the iron from showing anomalous magnetization when the magnetizing field about it was suddenly destroyed.

Our experiences agree with his if the shell is very thin, but seem to show that a thick enough copper shell will always prevent a reversal of the magnetization in a soft iron core inside. The records of experiments on two or three specimens of soft steel with shells of different thicknesses will make clear the nature of the phenomena.

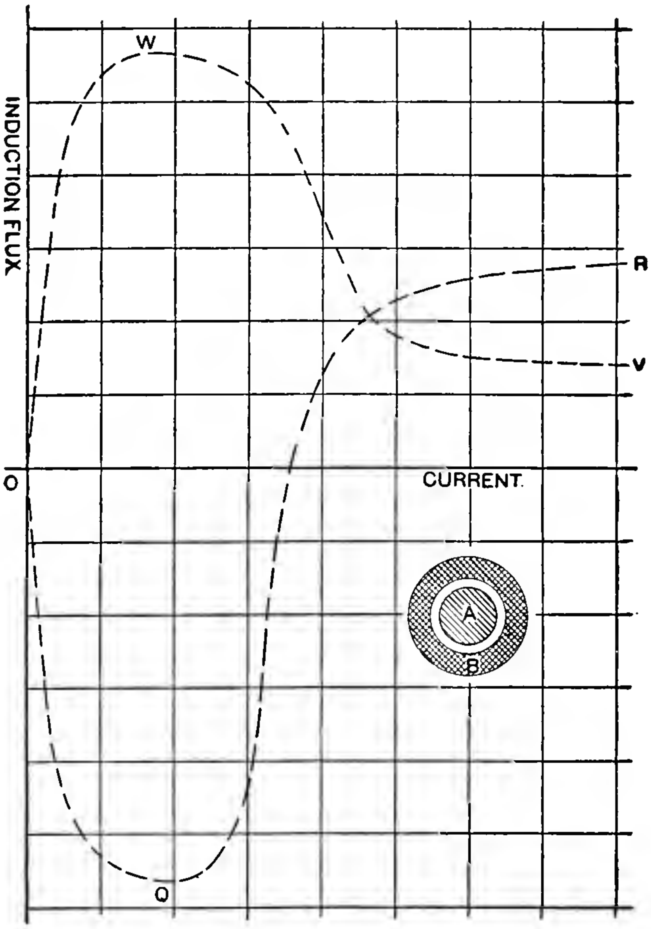

Figure 18. A represents a solid core 12 centimeters long, and B, a shell made of fine, soft, varnished iron wire. This combination was magnetized in a long solenoid by a current gradually applied, and then this current was suddenly interrupted. OWV represents the induction flux through the central section of shell and core, OQR the flux through the core alone. The vertical unit is 50 maxwells, the horizontal unit 100 gausses.

Table XIV. gives some results obtained in using a mild steel cylinder 1.9 centimeters in diameter and 12 centimeters long, with a copper shell of the same length, and with diameters of 3.80 and 2.90 centimeters. The second and third columns give the fluxes in maxwells through the central cross section of the iron when the exciting current has been slowly, and quickly, brought to zero.

TABLE XIV.

CORE INSIDE SHELL.

H.	Slow Break.	Quick Break.
22	+14.9	+ 5.5
39	+29.6	+13.3
60	+57.2	+24.3
170	+73.3	+45.0
255	+79.0	+52.7
430	+91.7	+72.5

When the shell was removed the fluxes were those given in Table XV.

TABLE XV.

CORE ALONE.

H.	Slow Break.	Quick Break.
22	+13.5	− 9.6
39	+25.3	−17.7
100	+54.0	−14.2
218	+64.0	+13.6
430	+73.8	+48.3

The eddy currents in the copper made the gradual reduction of the current by the introduction of resistance into the circuit more continuous and prevented the magnetizing field from vanishing suddenly when the circuit was broken.

A freshly annealed piece of Bessemer steel 1.6 centimeters in diameter and 12 centimeters long was tested alone, and inside each of two copper shells of its own length, with wall thicknesses of 1.20 centimeters and 0.47 centimeters respectively. Table XVI. shows the fluxes through the central cross section of the iron for slow removals of the excitation. The fluxes for the thick shell, the thinner shell, and for the core without any shell, are given in the columns headed A, B, C. Table XVII. gives the corresponding figures for the case where the exciting current was suddenly destroyed.

TABLE XVI.

SLOW BREAK.

H.	A.	B.	C.
38	+ 45.5	+ 42.4	+ 37.6
64	+ 84.2	+ 71.5	+ 67.0
168	+162.4	+126.0	+108.0
360	+207.0	+163.0	+112.5

TABLE XVII.

Quick Break.

H.	A.	B.	C.
22	+ 17.3	+ 7.0	−15.5
39	+ 33.4	+13.8	−27.4
64	+ 60.8	+20.6	−34.3
168	+127.0	+37.0	−18.9
360	+168.0	+81.5	+35.5

Only a few typical numbers are here given but these and many others are used in plotting the curves given in Figure 19. The line QW which has QR as its horizontal axis shows the reversed magnetization when the core has no shell. OS, OT, OU show the fluxes for slow breaks, QV, QZ, QW for the quick breaks.

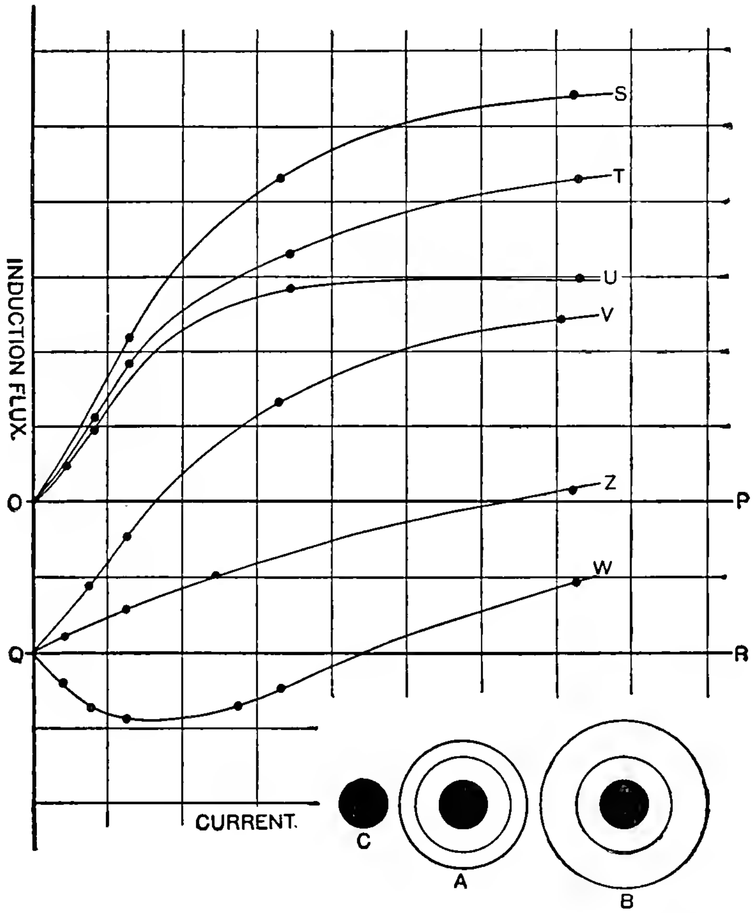

Figure 19. A soft core was used successively with a thick copper shell, with a thinner shell, and without any shell. OS, OT, OU show the remanent fluxes when the magnetizing fields were slowly removed; QV, QZ, QW the fluxes if the field had been suddenly destroyed.

As has been already explained, some of our slow breaks were made continuously with the help of a specially constructed rheostat, and others, sufficiently well for the purposes, by introducing, by relatively small steps, a series of resistances into the circuit. This last process which was not, of course, perfectly continuous, was used in the experiment recorded in Tables XVI. and XVII. and the effect of the copper in preventing any sudden change in the induction flux in the iron is evident from the figures given.

Although many complications may occur if a piece of iron or steel to be tested has a magnetic bias, or has not been uniformly tempered, the experiments described in this paper seem to lend support to the theory that the residual moment of an originally neutral bar which has been magnetized in a solenoid, is always normal unless the current on its way to extinction oscillates to and fro. When the exciting current is destroyed without oscillating in direction, even though the process be finished in a small fraction of a second, the remanent magnetization has the same sign as the magnetizing field. It appears that a bundle of very fine soft iron wire cannot be made to show anomalous magnetism and that a thick copper shell placed over a solid bar of magnetizable metal prevents reversals of magnetism under circumstances which would produce them if the shell were away.

It seems probable that in a short, stout rod of iron or steel exposed to a magnetizing field, the intensity of magnetization in the inner portions is less than in the outer filaments and that usually when the field is removed the direction of the polarization at the axis is opposite to that of the polarization at the outer surface. The direction of the lines at the outer surface may be normal or anomalous according to the manner in which the exciting current comes to its end, but in any case many of the lines of magnetization form closed curves wholly within the metal.

The placing of a thick iron shell either solid or constructed of fine insulated wire, about a core exposed to a magnetizing field, reduces the flux through the core, and, if the exciting current be reduced gradually to zero, the shell usually reverses the sign of the moment which the core would otherwise have had. If the circuit of the exciting current be suddenly broken, the residual magnetism of the core is often changed in sign by the presence of the shell. A finely divided iron shell never acquires anomalous magnetization when its exciting current is suddenly destroyed, but such a shell acts magnetically upon either a solid or a divided core and often reverses the sign which the core would have without it.

It is difficult to make even short, stout pieces of glass-hard tool steel show anomalous magnetization, and it is impossible to reverse the magnetism of very long pieces of soft iron where the end effects are not sensible.

The experiments of Mr. L. A. Babbitt, as well as previous experiments of our own, seem to show conclusively that none of the von Waltenhofen effects are to be looked for in massive transformer cores if these are made of fine varnished wire. I have never seen anomalous magnetism in a uniformly annealed closed ring.

It is evident that if the solenoid current in a test for anomalous residual magnetism be suddenly broken, the change in the electromagnetic field in the iron is much more rapid when the core is made of lengths of fine, varnished wire than when it is solid and eddy currents in it shield the inner filaments. Indeed, if the core be made of wires of a uniform size, the average rate of change of H with the time is roughly proportional to the area of one wire. If, however, the circuit be suddenly closed, the change in the field in the iron caused by the exciting current cannot be made instantaneous even if eddy currents be wholly shut out, and the effect of dividing the core is not so striking. If the magnetized particles of a piece of iron are imbedded in a quasi viscous medium, the rapidity of the changes in the forces acting upon the molecules should affect the magnetic properties of the iron.

My thanks are due to the Trustees of the Bache Fund of the National Academy of Sciences, who have lent me some of the apparatus used in making the observations mentioned in this paper.

The Jefferson Physical Laboratory,
Cambridge, Mass.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 18. — March, 1912.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

PYROSULPHURYL CHLORIDE AND CHLORSULPHONIC ACID.

By Charles Robert Sanger and Emile Raymond Riegel.

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By Charles Robert Sanger and Emile Raymond Riegel.

Presented October 13, 1909. Received January 11, 1912.

Contents.

Historical.

Results of this Investigation.

Experimental.

During certain investigations in this laboratory it became necessary to find better methods for the separation and purification of pyrosulphuryl chloride and chlorsulphonic acid than heretofore described, and to determine with greater accuracy their more important physical constants. It was very soon evident, not only that much of the literature on the subject was valueless, since most observers had worked with a mixture of the two substances or with impure material, but also that a separation of the mixture into pure components or a complete purification of either body could not be readily accomplished on the lines laid down by these observers. We have succeeded, however, by utilizing some of the facts already known and others which became evident in the course of our investigation, in preparing both of these bodies in quantity and of great purity.[1]

Historical.

Action of Metallic Chlorides on Sulphur Trioxide.

The complete history of pyrosulphuryl chloride and chlorsulphonic acid begins in 1822–1823 with the study of the reaction between sulphur trioxide and sodic chloride at high temperature by Sertürner,[2] Döbereiner,[3] and Gmelin.[4] Sertürner had erroneously considered the products to be hydrochloric acid and sodic sulphate; Döbereiner thought that a gaseous compound of chlorine and sulphur dioxide was formed, while Gmelin showed, although only qualitatively, that the gaseous product was a mixture of chlorine and sulphur dioxide. Rose [5] in 1836 investigated the reaction at low temperature, using other metallic chlorides as well. Fused sodic chloride absorbed anhydrous sulphur trioxide, forming a solid, transparent mass, which, when heated, gave chlorine and sulphur dioxide, similarly to Gmelin's observation. Undoubtedly, as R. Williamson [14] also points out, Rose had in his hands the sodium salt of chlorsulphonic acid. Rosenstiehl [6] in 1861 distils a mixture of fused

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[1] Acknowledgment is due to Mr. Laurence Haines Whitney for much assistance in the beginning of this investigation, particularly in the separation of pyrosulphuryl chloride and chlorsulphonic acid by crystallization and centrifugal filtration at low temperature, and in the study of the use of phosphorus pentoxide as a dehydrating agent, both in the preparation of the two bodies and in the conversion of chlorsulphonic acid to pyrosulphuryl chloride.

[2] Gilbert's Ann., **72**, 109 (1822).

[3] Ibid., **72**, 331 (1822).

[4] Ibid., **73**, 209 (1823).

[5] Pogg. Ann., **38**, 117 (1836).

[6] Compt. rend., **53**, 658 (1861); Jahresb., 1861, 120; Rep. chim. pur., **4**, 60 (1861).

sodic chloride and excess of sulphur trioxide until the retort contents were completely melted. On rectifying the distillate over fused sodic chloride, he obtained a liquid boiling at 145–150°; specific gravity, 1.762; vapor density, 3.76 (referred to air), which he considered from the analysis to be pyrosulphuryl chloride. These properties, however, together with the fact that it reacted violently with water, show a considerable admixture of chlorsulphonic acid. This is apparently the only source of the statement one finds in the literature that pyrosulphuryl chloride is formed by heating sodic chloride with sulphur trioxide.[7]

Action of Non-metallic Chlorides on Sulphur Trioxide.

Rose[8] in 1838 passed the vapor of anhydrous sulphur trioxide through sulphur monochloride at low temperature. On fractioning the product, an oily liquid of specific gravity 1.818 at 15° was obtained, boiling at 145°, which was slowly decomposed with water. This was the first preparation of pyrosulphuryl chloride, but it undoubtedly contained chlorsulphonic acid which is invariably formed whenever sulphur trioxide is chlorinated in the presence of even a small amount of water (*v.* Table II), and there may have been some sulphur monochloride present, since the boiling point of the latter, 138°, is so near that of the main product. By using phosphorus trichloride Rose obtained a similar liquid, boiling between 137° and 165°, containing much phosphorus. In 1839 Rose,[9] with the idea of preparing sulphuryl chloride, discovered in the same year by Regnault,[10] mixed fused sodic chloride with "pure" pyrosulphuryl chloride, probably prepared by a modification[11] of his original method, in which he distilled sulphur monochloride with ordinary fuming sulphuric acid. A solid mass was formed, resembling that which he had previously obtained[5] by the action of sodic chloride on sulphur trioxide. Distillation gave chlorine, sulphur dioxide, and a liquid boiling at 145°, which he concludes to be pure, undecomposed pyrosulphuryl chloride. From consideration of our work, the result is clear. There was much chlorsulphonic acid in the supposed "pure" pyrosulphuryl chloride, and this was converted to its sodium salt, from which the unchanged pyrosulphuryl chloride was distilled. If Rose

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[7] E. g., Roscoe and Schorlemmer, Treatise on Chemistry, I, 438 (1905); Dammer, Handbuch, I, 667 (1892).

[8] Ann. d. Phys. u. Chem., **44**, 291 (1838); Berzelius Jahresb., **19**, 201 (1840); Gmelin, Handbuch, I, 778.

[9] Pogg. Ann., **46**, 167 (1839).

[10] Compt. rend., **7**, 895 (1838).

[11] Pogg. Ann., **46**, 177 (1839).

had known that this was a process of rectification, we might have had pure pyrosulphuryl chloride at an earlier date. The further researches of Rose[12] do not throw any light on the preparation of either body.

A. Williamson[13] in 1854, by the action of phosphorus pentachloride on "sulphuric acid" (strength not stated), obtained a liquid boiling at 145°, decomposing violently with a small amount of water, quietly with an excess. No method of purification is given, nor are there any analyses of the product, but Williamson concludes that it was chlorsulphonic acid, and advances for the first time the theory of the successive substitution of the hydroxyls in sulphuric acid by chlorine. He makes a crude sodium salt, and considers the acid itself to be identical with the preparation of Rose,[8] for in his opinion that contained "the elements of water." Williamson obtains a "similar" acid by the action of hydrochloric acid on sulphur trioxide, which must be taken as the first use of this reaction in the preparation of chlorsulphonic acid. Though both of his products were impure, the first probably contained some pyrosulphuryl chloride, the second none.

R. Williamson[14] in 1857 states that chlorsulphonic acid can be made by the action of chloride of sulphur and chlorine on sulphuric acid and by the combination of chlorine and sulphur dioxide in contact with heated platinum black. The product of the first reaction is said to have the same properties as that obtained by A. Williamson, but details of purification, properties, and methods of analysis are lacking. From information supplied by A. Williamson, it is stated that continued distillation of the body leads to its decomposition into sulphuric acid and sulphuryl chloride.

Schiff[15] in 1857 shows that the supposed compound of phosphorus pentachloride and sulphur trioxide obtained by Persoz and Bloch[16] was identical with the preparation of A. Williamson, and obtained by the reaction a liquid boiling at 140–150°, which decomposed with water into sulphuric and hydrochloric acids.

Baumstark[17] in 1866, using phosphorus pentachloride with fuming sulphuric acid, obtained a liquid boiling from 145° to 156°, mainly at 150–152°, decomposing gradually with much water, violently with a small amount. The agreement of the vapor density (4.10) with the

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[12] Pogg. Ann., **52**, 57 (1841); **85**, 510 (1852).

[13] Proc. Roy. Soc., **7**, 11 (1854); Phil. Mag. (4), **7**, 365 (1854); Jour. Chem. Soc., **7**, 180 (1855); Jour. prakt. Chem., **62**, 377 (1854); Ann., **92**, 242 (1854).

[14] Jour. Chem. Soc., **10**, 97 (1858); Jour. prakt. Chem., **73**, 73 (1858).

[15] Ann., **102**, 114 (1857).

[16] Compt. rend., **28**, 86 (1849).

[17] Ann., **140**, 75 (1866).

calculated (4.03) and the analysis indicated a pure chlorsulphonic acid, but there was probably enough pyrosulphuryl chloride present to raise the low density which pure chlorsulphonic acid usually shows owing to its dissociation. Similarly, Williams[18] in 1869, repeating the Williamson reaction in the latter's laboratory, is led by density (4.56) and analyses to consider his product pure chlorsulphonic acid. The boiling point is not given.

The first recorded use of carbon tetrachloride as a chlorinating agent is by Schützenberger[19] in 1869. On warming this with sulphur trioxide until the phosgene was expelled, a product was obtained boiling at 130°, reacting "at once" with water, and giving "figures leading to the formula $S_2O_5Cl_2$." The sulphur trioxide was evidently hydrated and the product contained much chlorsulphonic acid. In the next year Armstrong[20] repeated the reaction and suggested its use as a source of phosgene. His product boiled between 141° and 145°, was difficult to purify, and did not decompose water easily. The analysis corresponded more nearly to that of pyrosulphuryl chloride. Substituting chloroform for carbon tetrachloride, Armstrong obtains what he considers from the analysis to be a mixture of the two bodies. He also investigates the action of phosphorus trichloride on sulphur trioxide, but with unsatisfactory results.

Prudhomme[21] in 1870 tried the action of hexachlorethane on sulphur trioxide in a closed tube at 150°. The product boiled at 140° and was considered to be pyrosulphuryl chloride. No analytical data are given.

The study of the question by Michaelis[22] in 1871 and succeeding years is of interest. Using sulphur trioxide "free from hydrate" with phosphorus pentachloride he obtains "pyrosulphuryl chloride" according to the reaction :

$$2SO_3 + PCl_5 = S_2O_5Cl_2 + POCl_3.$$

The product boiled at 143°, acted quietly with water, and had a specific gravity of 1.819 at 18°. With sulphuric acid, the reaction was considered to be

$$3H_2SO_4 + PCl_5 = 3SO_3HCl + HPO_3 + 2HCl$$

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[18] Jour. Chem. Soc., **22**, 304 (1869); Zeitschr. f. Chem., **12**, 665 (1869).

[19] Compt. rend., **69**, 352 (1869); Jahresb., 1869, 209; Ann., **154**, 375.

[20] J. prakt. Chem., **109**, 244 (1870); Ber., **2**, 712 (1869) and **3**, 730 (1870).

[21] Compt. rend., **70**, 1137 (1870); Ann. Chem. Pharm., **156**, 342 (1870).

[22] Jena Zeitschr., **6**, 235 (1871); Zeitschr. f. Chem. (2), **7**, 149 (1871).

and the product "pure" chlorsulphonic acid. It boiled at 158.4° and had a specific gravity of 1.776 at 18°. No sulphuryl chloride was formed by the action of phosphorus pentachloride on either sulphur trioxide or chlorsulphonic acid, as Williamson[13] and Schiff[15] had stated, nor, according to Odling[23], by treating plumbic sulphate with phosphorus oxychloride. While Michaelis did not obtain pure products, he at least brought out the association of the two bodies in the chlorination product, and his results show the influence of hydration of the sulphur trioxide. In another paper,[24] in 1871, he obtains chlorsulphonic acid from sulphuryl chloride and water and from sulphuryl chloride and sulphuric acid. The Carius[25] reaction of phosphorus pentachloride on plumbic sulphate gave neither body. In a third paper[26] in 1873 he makes chlorsulphonic acid from concentrated sulphuric acid and phosphorus trichloride in a current of chlorine. Geuther[27] had tried this without chlorine.

Müller[28] in 1873 prepares "chlorsulphonic acid" with phosphorus pentachloride and "moderately fuming" sulphuric acid. He also distils a mixture of fuming sulphuric acid and phosphorus pentoxide in a current of hydrochloric acid gas, and considers the product identical with that made by the action of hydrochloric acid on sulphur trioxide. There are no data by which the quality of these preparations may be judged, and they were probably quite impure. Clausnizer[29] in 1878 prepares chlorsulphonic acid according to Michaelis by action of phosphorus trichloride on sulphuric acid in a current of chlorine, obtaining a boiling point of 150–151° at 726 mm. Thorpe[30] in 1880 uses the Rose reaction with sulphur monochloride to prepare "pyrosulphuryl chloride," which boils at 139.59°, corr., with specific gravity 1.85846 at 0° referred to water at 4°. By action of phosphorus oxychloride on "the strongest oil of vitriol," he prepares "chlorsulphonic acid," boiling at 155.3°, corr., with specific gravity of 1.78474. He finds that chlorsulphonic acid is completely converted to sulphuryl chloride and sulphuric acid by heating for some hours at 200°.

Ogier[31] in 1882, during a thermochemical study of the oxychlorides of sulphur, prepared pyrosulphuryl chloride by the first method of Rose; the product boiling at 140.5° and reacting quietly with water. A preparation of "chlorsulphonic acid" by the Armstrong reaction of sulphur trioxide and chloroform showed violent action with water. No

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[23] Gmelin, Handbuch, **1**, 169.

[24] Jena Zeitschr., **6**, 293 (1871).

[25] Ann., **106**, 307 (1858).

[26] Ibid., **170**, 1 (1873).

[27] Ber., **5**, 924 (1872).

[28] Ibid., **6**, 227 (1873).

[29] Ibid., **11**, 2007 (1878).

[30] J. Chem. Soc., **37**, 358 (1880).

[31] Compt. rend., **94**, 82 (1882).

boiling point is given for this product, and Armstrong's opinion is overlooked, that the reaction gives a mixture of the two bodies. In a second paper[32] Ogier determines the vapor density of what was probably the same or a similar preparation of pyrosulphuryl chloride. As his analyses convinced him of the purity of his product, the deviation of the density (3.70) from the theoretical (7.49), together with his inability to synthesize pyrosulphuryl chloride from sulphur trioxide and sulphuryl chloride, causes him to find here an exception to Avogadro's Rule!

In contrast to the previous confusion, the work of Konovaloff[33] in 1882 is clear. This author prepared pyrosulphuryl chloride by the method of Schützenberger,[19] using twice distilled sulphur trioxide, in which, however, the actual amount of moisture was not determined. During the reaction and subsequent distillation, moisture was excluded and connections were of glass. The product boiled at 153° (752 mm.); another preparation at 152.5° (740 mm.). The specific gravity was 1.872 at 0°. Water acted slowly. The analyses were good, and the vapor density (in aniline, 7.31; in nitrobenzene, 7.27) showed that Avogadro's Rule was not in immediate danger of overthrow. Konovaloff notes that the boiling point of his product was much higher than that of previous observers, notably that of Ogier, and considers that previous preparations may have been contaminated with chlorsulphonic acid, which dissociates easily. On mixing equal parts of his product with chlorsulphonic acid prepared by the Williamson[13] method, a boiling point of 140–146° was obtained, with vapor density of 4.10 at 210°. From four parts of water and one hundred parts of his product, he obtained a liquid boiling at 139–140°, with vapor density of 4.07. Ogier,[34] in reply, admitted the possibility of a small amount of chlorsulphonic acid in his product, but not enough to lower the vapor density to 3.70.

Heumann and Köchlin[35] in 1883 were unable to synthesize pyrosulphuryl chloride from sulphur trioxide and sulphuryl chloride. Using the method of Rose,[8] they obtained a product which they did not think could contain chlorsulphonic acid, since it was "unchanged" by distillation with phosphorus pentoxide. Yet it boiled at 145–147°, with vapor densities from 5.84 in aniline to 2.58 in sulphur, and gave inconclusive figures on analysis. They think that dissociation of pyrosulphuryl chloride takes place into sulphur trioxide, sulphur dioxide, and chlorine, and is nearly complete at the boiling point of sulphur.

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[32] Compt. rend., **94**, 217 (1882).

[33] Ibid., **95**, 1284 (1882).

[34] Ibid., **96**, 66 (1883).

[35] Ber., **16**, 479 (1883).

Possibly the work of Konovaloff had escaped their observation. Later in another paper,[36] from the vapor density at 184°, they decide that chlorsulphonic acid (2 vols.) at that temperature is completely dissociated into sulphur trioxide, sulphur dioxide, chlorine, and water (8 vols.).

Konovaloff[37] in 1883, applying again his entirely correct theory of the necessity for anhydrous reagents, obtained through the Rose reaction with sulphur monochloride a pyrosulphuryl chloride boiling at 152–153°, with vapor density of 7.2 at 210°.

Since 1883, little more concerning the chlorination methods has been published. Erdmann[38] in 1893, as did Armstrong earlier, proposes the reaction of Schützenberger,[19] with slight modifications, as an economical method for preparing phosgene. The residue he considers a mixture of pyrosulphuryl chloride and chlorsulphonic acid. Moureau[39] in 1894, by the action of thionyl chloride on sulphuric acid of specific gravity 1.84, obtains a product boiling at 130–157°, which he concludes to be a mixture of the two bodies. Prandtl and Borinski[49] have used the method of Schützenberger in the investigation cited below, and show that both bodies are present in the reaction product.

Action of Hydrochloric Acid on Sulphur Trioxide.

As previously mentioned, A. Williamson,[13] in 1854 was apparently the first to use this reaction, of which chlorsulphonic acid and not pyrosulphuryl chloride is the product. The reaction was repeated in 1857 in A. Williamson's laboratory by R. Williamson,[14] but no details are given. Dewar and Cranston[40] in 1869, also, by the "direct action of sulphuric acid on hydrochloric acid," obtain a substance "with all the properties ascribed by Williamson."

Much more definite is the work of Beckurts and Otto[41] in 1878, who advised the use of a fuming sulphuric acid, slightly crystalline at ordinary temperature, "containing from 38 to 39 per cent of sulphur trioxide."[42] Their product boiled between 149° and 152.7°, mainly at 151.7–152.7°, and was apparently fairly pure. Beckurts and Otto consider that, if chlorsulphonic acid and sulphuric acid give pyrosul-

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[36] Ber., **16**, 602 (1883).

[37] Compt. rend., **96**, 1146 (1883).

[38] Ber., **26**, 1990 (1893).

[39] Bull. Soc. Chim. (3), **11**, 767 (1894).

[40] Chem. News, **20**, 174 (1869).

[41] Ber., **11**, 2058 (1878).

[42] This would mean about 94 per cent actual sulphur trioxide, or about 66 per cent available (*v.* Table II, p. 687).

phuric acid and hydrochloric acid, according to Williams,[18] the formation of chlorsulphonic acid by their method must be due to the concentration of the hydrochloric acid, i. e.,

$$H_2S_2O_7 + HCl \rightleftarrows H_2SO_4 + SO_3HCl.$$

Though Müller[28] in 1873 had added phosphorus pentoxide to the fuming acid, presumably to increase the yield, it is not clear that he understood the action of the hydrochloric acid to be on the free sulphur trioxide only. Beckurts and Otto could not substantiate the result of A. Williamson,[43] furthur studied by Behrend[44] and later proved by Ruff,[45] that chlorsulphonic acid, heated to 170–180°, gives sulphuric acid and sulphuryl chloride, for they considered that sulphur dioxide and chlorine were the primary products; sulphuryl chloride a secondary one.

Nothing new in regard to this method has apparently been published in the past thirty years. We find further no specific statement of its use in the preparation of material for investigation. Though it has undoubtedly been employed, yet most of the preparations of chlorsulphonic acid, so called, seem to have been made with non-metallic chlorides.[46]

The contribution of Ruff[45] in 1901 to the knowledge of chlorsulphonic acid is important, and throws light on the somewhat discordant observations of former investigators. He does not state the method of preparation, but this is of no importance to his paper. He studies the decomposition to sulphuryl chloride and sulphuric acid by means of catalysers, and bases on this study a valuable technical method for the preparation of sulphuryl chloride. In Ruff's opinion, no chlorine or sulphur dioxide is formed at the boiling point, nor between 170° and 180°, but only at higher temperatures.

The Relation of Pyrosulphuryl Chloride and Chlorsulphonic Acid to Each Other; their Separation and Purification.

The simultaneous formation of pyrosulphuryl chloride and chlorsulphonic acid by the action of chlorides on a hydrated sulphur trioxide, though noted by some observers, does not receive serious consideration until taken up by Konovaloff, who showed that the dehydration of chlorsulphonic acid by phosphorus pentoxide was only partial,[37] but

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[43] Quoted by R. Williamson (note 14, p. 676).

[44] Ber., **8**, 1004 (1875).

[45] Ibid., **34**, 3509 (1901).

[46] E. g., Besson (note 48, p. 682).

was able to convert pyrosulphuryl chloride to chlorsulphonic acid by addition of water.[33] Heumann and Köchlin [35] did not think that there was any dehydration of chlorsulphonic acid by phosphorus pentoxide.

Billitz and Heumann [47] in 1883 heated chlorsulphonic acid (method of preparation and properties not given) with nearly equal weight of phosphorus pentoxide. The product, redistilled over phosphorus pentoxide, boiled at 145–147° at 724 mm., and the analysis was close to the theory for pyrosulphuryl chloride. The vapor density was 5.89, with evidence of decomposition. Clearly the dehydration was only partial. Conversely, by adding 3 grams of water to 40 grams of pyrosulphuryl chloride, the product boiled at 154–158° at 723 mm., reacted violently with water, and gave an analysis corresponding more nearly to chlorsulphonic acid.

Besson [48] in 1897 studied the purification of the two bodies, but the method of preparation, vapor density, specific gravity, and analyses of his crude products are not given. Crude pyrosulphuryl chloride contained chlorsulphonic acid, chlorine, sulphur dioxide, and sulphur trioxide, and could not be distilled at ordinary pressure without decomposition into the last three. Mercury at low temperature removed the free chlorine ; at 60° took the chlorine from the compound, setting free sulphur dioxide and trioxide. At 100° in a closed tube, sulphur dioxide was the only gaseous product, mercuric sulphate and chloride being formed. Most of these decomposition phenomena may of course be ascribed to the chlorsulphonic acid present. By using phosphorus pentachloride, Besson thought to remove the sulphur trioxide and to dehydrate the chlorsulphonic acid in his crude pyrosulphuryl chloride, but his product boiled at 142–143° (765 mm.). Apparently, distillation at 15 mm. gave what he considered pure products ; pyrosulphuryl chloride boiling at 53°, chlorsulphonic acid at 65°. The former gave white crystals at — 39° ; the latter did not solidify at — 75°. The boiling point of chlorsulphonic acid at 765 mm. was 152°. Besson could not cause sulphuryl chloride and sulphur trioxide to unite either in sunlight or at 100°.

During the preparation of this paper, the completion of which has been unavoidably delayed, Prandtl and Borinski [49] have proposed a method for the preparation of pure pyrosulphuryl chloride which depends on the destruction of the chlorsulphonic acid in the mixture formed in the Schützenberger reaction. The method is considered by them to obviate the necessity for use of anhydrous material and ex-

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[47] Ber., **16**, 483 (1883).

[48] Compt. rend., **124**, 401 (1897).

[49] Zeitschr. anorg. Chem., **62**, 24 (1909).

clusion of moisture in carrying out the reaction, as recommended by Konovaloff. It was clear to them, from the color reactions with tellurium and selenium, as well as from analyses of the fractions, that the two bodies were both present and could not be separated by fractionation. On the assumption that chlorsulphonic acid is more readily attacked by water than pyrosulphuryl chloride, they treat the crude distillate with ice in a freezing mixture. The lower layer of pyrosulphuryl chloride is separated from the upper of sulphuric acid, and distilled, with or without phosphorus pentoxide. Seventy per cent of the crude pyrosulphuryl chloride was recovered, boiling at 150° (720 mm.). The analysis gave almost theoretical figures, and the specific gravity was 1.876 at 0° ; 1.844 at 18°. Vapor density determinations by the Meyer method gave 7.15 and 7.27 (theory, 7.49). In making these, the bulb of the apparatus was heated with phosphorus pentoxide before adding the substance. Other trials, without this desiccation, gave 5.94 and 6.32.

Prandtl and Borinski find the action of tellurium and selenium useful in distinguishing between the two bodies. Chlorsulphonic acid gives with the first a cherry red color, with the second a dark green, while pyrosulphuryl chloride gives no color with either. They consider that pyrosulphuryl chloride is not converted to chlorsulphonic acid by water, but directly to sulphuric and hydrochloric acids. Adding five grams of water to sixty grams of pyrosulphuryl chloride (equal molecules) they obtain sulphuric acid and a distillate boiling at 140–147°, which they consider to be unaltered substance, since it dissolved in water slowly and was not colored by tellurium.

Historical Summary.

The table on the following two pages shows briefly the results obtained by former investigators:

The Results of this Investigation.

It is clear, from consideration of the foregoing and from our own work, that the most reliable preparations of pyrosulphuryl chloride were those of Konovaloff and of Prandtl and Borinski, while Beckurts and Otto have described the only reasonably pure preparation of chlorsulphonic acid. It is evident, also, that while either body, with proper precautions, may be prepared without a large admixture of the other, or of the decomposition products of either, yet it is somewhat doubtful whether an absolutely pure preparation of either has been made, especially in large quantities. Further, the widely differ-

TABLE I.

RESULTS OF PREVIOUS INVESTIGATORS.

Reference Numbers.	Investigator.	Specific Gravity.	Vapor Density (air).	Boiling Point C°.	Action with Water.	State of SO_3.	Reagent used.	Probable Prepond-erating Body.
6	Rosenstiehl	1.762	3.76	145–150	Rapid	Solid	$NaCl$	C
8	Rose	1.818 (15°)	. . .	145	Slow	Vapor	S_2Cl_2	P
8	Rose	. . . .	. . .	137–165	. . .	Vapor	PCl_3	P
8	Rose	. . . .	. . .	145	. . . .	Fuming sulph. acid	S_2Cl_2	P
9	Williamson, A.	. . . .	. . .	145	Rapid	Fuming sulph. acid	PCl_5	C
13	Schiff	. . . .	. . .	140–150	. . . .	Fuming sulph. acid	PCl_5	C
15	Baumstark	. . . .	4.10	145–156 (mainly 150–152)	Rapid	Fuming sulph. acid	PCl_5	C
17								
18	Williams	. . . .	4.56	. . . .	. . . .	Fuming sulph. acid	PCl_5	C
19	Schützenberger	. . . .	. . .	130	Rapid	Solid	CCl_4	P
20	Armstrong	. . . .	. . .	141–145	Slow	Solid	CCl_4	P
21	Prudhomme	. . . .	. . .	140	. . .	Solid	C_2Cl_6	P
22 (1)	Michaelis	1.819 (18°)	. . .	143	Slow	Solid	PCl_5	P
22 (2)	Michaelis	1.776 (18°)	. . .	158.4	. . .	Fuming sulph. acid	PCl_5	C
29	Clausnizer	. . . .	. . .	150–151	. . .	Fuming sulph. acid	PCl_3+Cl_2	C
30 (1)	Thorpe	1.8585 (0°/4°)	. . .	139.6	. . .	Solid	S_2Cl_2	P
30 (2)	Thorpe	1.7847 (0°/4°)	. . .	155.3	. . .	Fuming sulph. acid	$POCl_3$	C

31	Ogier	....	3.70 (184°)	140.5	Slow	Vapor (?)	S_2Cl_2	P
33 (1)	Konovaloff	1.872 (0°)	7.31 (184°)	153	Slow	Solid	CCl_4	P
33 (2)	Konovaloff	....	4.10 (210°)	140–146	...	....	See below	Equal parts
33 (3)	Konovaloff	....	4.07	139–140	...	....	See below	C
35	Heumann and Köchlin	....	5.84(184°) 2.57(400°)	145–147	...	Vapor (?)	S_2Cl_2	P
37	Konovaloff	....	7.2 (210°)	152–153	...	Solid	S_2Cl_2	P
39	Moureau	....	...	130–157	...	Sulphuric acid	$SOCl_2$	C
41	Beckurts and Otto	....	...	151.7–152.7 (mainly)	...	Fuming sulph. acid 39% SO_3	HCl	C No P
47 (1)	Billitz and Heumann	....	5.89	145–147	Slow	....	See below	P
47 (2)	Billitz and Heumann	....	...	154–158	Rapid	....	See below	C
48 (1)	Besson	....	...	53 (15 mm.) 142–143	...	Not stated	Not stated	P
48 (2)	Besson	....	...	65 (15 mm.) 152	...	Not stated	Not stated	C
49	Prandtl and Borinski	1.876 (0°) 1.844 (18°)	7.21	150	Slow	Solid	See below	P

P = pyrosulphuryl chloride; C = chlorsulphonic acid.
In only one case, No. 41, was the actual amount of water in the sulphur trioxide or fuming sulphuric acid stated.
In No. 9 the crude product was distilled with sodic chloride, but the amount of the latter was not stated.
In No. 47 (1) chlorsulphonic acid was treated with phosphorus pentoxide.
In No. 47 (2) and No. 33 (3) pyrosulphuryl chloride was treated with water; in No. 49 with ice.
In No. 33 (2) equal parts of the two bodies were mixed.
The only properties mentioned of the product prepared with hydrochloric acid are those given in No. 41.

ing properties obtained by this long list of observers renders a revision of the constants desirable.

In deciding upon the purity of the products too much reliance has been placed by most investigators on the analysis. The difference between the two molecular weights, 233 and 215, is so small that even a very careful analysis might not detect a sufficient admixture of one body to influence the properties of the other (*v.* Table III, p. 713), nor show contamination by a slight amount of the products into which each body is easily decomposed.

In the separation and purification we have found most suggestive the early statements of Rose concerning the action of fused sodic chloride, the distillation under diminished pressure and the determination of the solidifying points as suggested by Besson. As a test of purity we have paid little attention to the analysis, but have relied upon the wide difference in melting points, the specific gravity, the action with water, the characteristic appearance of the two bodies in the solid state, and the color reactions with tellurium and selenium as given by Prandtl and Borinski.

General Methods for the Preparation of Pyrosulphuryl Chloride and Chlorsulphonic Acid.

The reaction of Schützenberger,[19] in which sulphur trioxide is acted upon by excess of carbon tetrachloride, is the one best adapted to the preparation of pyrosulphuryl chloride, since the reaction runs more nearly to completion, and excess of reagent is easily removed. While the presence of chlorsulphonic acid has been suspected or shown by other investigators in the crude product, yet it has not been definitely pointed out that the hydration of the sulphur trioxide would determine the proportion of each body in the mixture, at least roughly, and that by varying the strength of the sulphur trioxide a preponderance of either body may be secured. This we have found to be true, and we can therefore say, in general, that either pyrosulphuryl chloride or chlorsulphonic acid may be made by the Schützenberger method. The proportions of each body theoretically formed in the reaction by using different concentrations of sulphur trioxide are given in the following table, though it will be shown that these proportions do not hold good when the concentration of the sulphur trioxide is less than 89 per cent.

TABLE II.

THEORETICAL PROPORTIONS OF PYROSULPHURYL CHLORIDE AND CHLORSULPHONIC ACID FROM DIFFERENT CONCENTRATIONS OF SULPHUR TRIOXIDE.

Concentration.			Schützenberger Reaction (*a. c.*).				Per cent H_2SO_4.	Per cent excess.	Williamson Reaction (*b.*). 100 parts $xSO_3 \cdot yH_2O$ give Chlorsulphonic Acid.
Formula.	Per cent H_2O.	Per cent SO_3.	100 parts $xSO_3 \cdot yH_2O$ give		Per cent in Product.				
			Pyrosulphuryl Chloride.	Chlorsulphonic Acid.	Pyrosulphuryl Chloride.	Chlorsulphonic Acid.			
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
1. $2SO_3.3H_2O$	25.23	74.77	...	...	...	...	91.59	8.41 (H_2O)	...
2. $SO_3.H_2O$	18.37	81.63	...	59.4	...	100.0	100.00	...	...
3. $3SO_3.2H_2O$	13.04	86.96	...	105.5	...	100.0	70.99	29.01 (SO_3)	42.2
4. $2SO_3.H_2O$	10.11	89.89	...	130.8	...	100.0	55.04	44.96	65.4
5. $3SO_3.H_2O$	6.98	93.02	41.6	90.3	31.5	68.5	38.00	62.00	90.3
6. $4SO_3.H_2O$	5.33	94.67	63.5	69.0	47.9	52.1	28.95	71.05	103.4
7. $5SO_3.H_2O$	4.30	95.70	77.2	55.6	58.1	41.9	23.41	76.59	111.5
8. $10SO_3.H_2O$	2.20	97.80	105.1	28.5	78.7	21.3	11.97	88.03	128.1
9. $20SO_3.H_2O$	1.10	98.90	119.7	14.2	89.4	10.6	5.99	94.01	136.8
10. $50SO_3.H_2O$	0.45	99.55	128.3	5.8	95.7	4.3	2.45	97.55	142.0
11. SO_3	0.00	100.00	134.3	...	100.0	0.0	0.00	100.00	145.5

a. Limit for formation of chlorsulphonic acid by the Schützenberger reaction:

$$2SO_3 + 3H_2O + CCl_4 = 2H_2SO_4 + COCl_2 + 2HCl$$

b. Limit for formation of chlorsulphonic acid by the Williamson reaction:

$$SO_3 + H_2O + HCl = H_2SO_4 + HCl$$

c. Limit for formation of pyrosulphuryl chloride by the Schützenberger reaction:

$$2SO_3 + H_2O + CCl_4 = 2SO_3HCl + COCl_2$$

From the reaction

$$(1)\ 2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$$

we should have only pyrosulphuryl chloride when the sulphur trioxide is absolutely anhydrous, as Konovaloff[33] and others have shown. But from the reaction

$$(2)\ 2SO_3 + H_2O + CCl_4 = COCl_2 + 2SO_3HCl,$$

(Reaction *c* of Table II.)

the moisture conditions of which are fulfilled by ordinary fuming sulphuric acid, $H_2S_2O_7$, we should theoretically get only chlorsulphonic acid as the product. We may assume in this case that pyrosulphuryl chloride would be at first formed according to (1) and then decomposed according to

$$(3)\ S_2O_5Cl_2 + H_2O = 2SO_3HCl.$$

If now we increase the hydration of the acid, we should expect the chlorsulphonic acid to be decomposed according to

$$(4)\ 2SO_3HCl + 2H_2O = 2H_2SO_4 + 2HCl.$$

The limit of this decomposition is shown by combining equations (1), (3), and (4):

$$(5)\ 2SO_3 + 3H_2O + CCl_4 = COCl_2 + 2H_2SO_4 + 2HCl$$

(Reaction *a* of Table II.)

and we should expect no chlorsulphonic acid to be formed at a concentration equivalent to $2SO_3 \cdot 3H_2O$.

With a weaker acid, however, the greater concentration of the water causes a greater proportional decomposition of the chlorsulphonic acid and a larger amount of sulphuric acid; in other words, less sulphur trioxide is effective in attacking the carbon tetrachloride. Hence, as the proportion of water in the acid increases, there is less than the theory of chlorsulphonic acid found, more sulphuric acid left, and the limit of the formation of chlorsulphonic acid is reached sooner. The maximum effect (Preparation 8, p. 696) appears to be at a concentration of between 22 and 23 per cent of water. From 100 parts of the monohydrate, SO_3H_2O (18.37 per cent water) we should get about 22 parts of chlorsulphonic acid instead of 59.4 parts (Preparation 9) as would appear from Table II. From 100 parts of the hydration $3SO_3 \cdot 2H_2O$ (13.04 per cent water), there would be about 52 parts of chlorsulphonic acid instead of 105.5 parts (Preparation 7).

Now, as the concentration of the acid decreases to the hydration $2SO_3 \cdot H_2O$ (10.11 per cent water) there is less and less tendency to decomposition of the chlorsulphonic acid, and the latter approaches closely to its theoretical maximum at this point, as shown by Preparation 2, p. 695. This is indicated also in Preparations 1 and 2 by the small amount of sulphuric acid left in the reaction.

In view of the fact that chlorsulphonic acid has a greater avidity for water than pyrosulphuryl chloride (p. 714), reaction (3) may not be entirely completed before its product is acted upon according to reaction (4). Hence the limit of the formation of pyrosulphuryl chloride may not be exactly at the hydration $2SO_3 \cdot H_2O$ (reaction *c* of Table II), but at a somewhat greater concentration of water. This is indicated by the yield of pyrosulphuryl chloride in Preparations 1 and 2, which is higher than would be expected. Conversely, the yield of chlorsulphonic acid would be less at this concentration. The amount of sulphuric acid would be greater, which is borne out also by these preparations.

The hydration of the sulphur trioxide will similarly influence the chlorination by sulphur monochloride according to the reactions: —

$$(1)\ 5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2$$
$$(2)\ 5SO_3 + S_2Cl_2 + H_2O = 5SO_2 + 2SO_3HCl.$$

Here, while the reaction is complete, the boiling point of the sulphur monochloride is so near to that of each of the two bodies as to make purification by distillation practically impossible. With the chlorides of phosphorus, the reactions not only do not run to completion, but the purification of the product is complicated by the presence of phosphorus bodies. The use, therefore, of the chlorides of sulphur and phosphorus is of no value, especially as carbon tetrachloride is now so cheaply obtained.

We have found that the separation of the pyrosulphuryl chloride and chlorsulphonic acid formed in the Schützenberger reaction is completely accomplished by the addition of fused sodic chloride in excess and subsequent distillation under diminished pressure. The pyrosulphuryl chloride is unaffected by the sodic chloride and is distilled off. The chlorsulphonic acid is converted to its sodium salt, remains in the distillation residue, and may even be regenerated from this by distillation with fuming sulphuric acid. The recovery is not advantageous, however, owing to the difficulty of purifying the product. We have also found that pyrosulphuryl chloride may be separated in a mixture of the two bodies by crystallization. When the mixture is cooled and centrifugally filtered below the melting point of pyrosulphuryl chloride (*ca.*—37°), a very pure product is obtained, — the chlorsulphonic acid, with some pyrosulphuryl chloride, remaining entirely in the filtrate.

This method, however, is not practicable for any but small amounts, and there is danger of contamination by the moisture of the air.

In the preparation of chlorsulphonic acid the best method is the treatment of sulphur trioxide with hydrochloric acid, which must be ascribed to A. Williamson,[13] though first put in practical form by Beckurts and Otto.[41] Most convenient is a liquid oleum containing as much sulphur trioxide as possible according to the reaction:

$$H_2SO_4 + SO_3 + HCl = H_2SO_4 + SO_3HCl.$$

No pyrosulphuryl chloride can be formed, and the product is made practically pure by distillation with hydrochloric acid.

While chlorsulphonic acid may be formed under certain conditions by the addition of water to pyrosulphuryl chloride, the reaction does not serve as a method of preparation. Similarly, though dehydration of chlorsulphonic acid by phosphorus pentoxide takes place, it is only partial and hence of no advantage as a means of preparing pyrosulphuryl chloride.

The Preparation of Pyrosulphuryl Chloride.

The procedure adopted by us in treating sulphur trioxide with carbon tetrachloride according to the method of Schützenberger is as follows: — A round-bottomed flask of suitable size is sealed to the tube of an upright condenser, the upper end of the tube being carried some distance above the jacket of the condenser. A few centimeters below the top of the tube is sealed a side-tube of smaller bore, leading to a flue. An absorption bottle for the phosgene may be used here if desired. Through a rubber stopper in the top of the condenser tube and leading below the side-tube passes a separating funnel.

The oleum is prepared from an ordinary fuming acid by the addition of the requisite amount of solid sulphur trioxide, the proportion of the last in the mixture being determined by titration. For analysis, the oleum is weighed in a thin glass bulb, sealed after being filled. The bulb is broken under considerable water in a tightly stoppered bottle, the contents of which, when homogeneous, are made up to a definite volume. The carbon tetrachloride is a crude commercial product, dried over calcic chloride.

The dry apparatus is placed on a steam bath and carbon tetrachloride added through the condenser tube. The separating funnel containing the oleum is placed in position. The flask is then heated gradually and the oleum is run in slowly, the rate of addition being governed by the evolution of phosgene. After the addition of the oleum, the heating is continued for some time after the evolution stops. The proportion of carbon tetrachloride to oleum should be about two to one.

As a partly solid oleum or "anhydrous" sulphur trioxide is less easy to handle, we have preferred to use as strong a mixture as will remain liquid at ordinary temperature,[50] though the yield of pyrosulphuryl chloride is less. If one wishes to use the stronger reagent, however, the apparatus may be so modified that the top of the condenser tube is sealed and the separating funnel containing the melted trioxide is connected directly with the flask by means of a two-holed rubber stopper, through the second hole of which passes the condenser tube instead of being sealed to the flask. Without this arrangement the melted substance would solidify in passing through the condenser.[51]

The contents of the flask are transferred to a distilling flask and fractioned; the first portion, up to 120° or 130° containing a little phosgene and excess of carbon tetrachloride, being rejected. The second fraction, which may run to 160°, is best redistilled and that portion boiling above 130° submitted to the following separation: — The mixture is placed in a roomy distilling flask, cooled by ice, and treated with small portions of fused, powdered sodic chloride, dried before use by heating to *ca.* 150° and cooled in a closed bottle. The amount necessary is calculated from the amount of water in the oleum and hence the probable quantity of chlorsulphonic acid present. From ten to twenty per cent in excess of that called. for by the following equation is necessary.

$$SO_3HCl + NaCl = SO_3NaCl\,^{52} + HCl.$$

When the evolution of hydrochloric acid has ceased, and this may be promoted at the end by gentle warming, the pasty or partly dry mass is distilled under about 20 or 30 mm. pressure. For this purpose we extend the side-tube of the flask by sealing on a tube of about 50 cm., which is then surrounded by a short condenser jacket. Over the end of the lengthened side-tube is slipped a distilling flask of suitable size, fastened by a rubber stopper so that the end of the tube dips into the belly of the flask. The side-tube of the receiver is connected with the exhaust and manometer; a system of absorption tubes filled with stick

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[50] From 92.5 to 95 per cent total SO_3.

[51] See also Preparation 6, p. 696.

[52] For the preparation and analysis of sodic chlorsulphonate, see Ruff (note 45, p. 681).

sodic hydroxide being interposed as a precaution against corrosion by the acid vapors. The flask containing the reaction mixture is closed by a rubber stopper carrying a thermometer, and is about three-quarters immersed in an oil bath, the temperature of which is controlled by a second thermometer. The suction is applied until the hydrochloric acid is drawn off, and the oil bath is then gradually heated. The pyrosulphuryl chloride in the mixture distils with little or no decomposition, leaving the sodic chlorsulphonate as a dry mass. The oil bath, as distillation slackens, is kept for some time at a somewhat higher temperature than the boiling point of the pyrosulphuryl chloride, but a considerable amount of the latter adheres to the residue.

The product thus obtained melts after solidification within a few degrees of the proper point, and a single rectification over a small quantity of fused sodic chloride under diminished pressure is usually sufficient to give a perfectly pure product.

Regeneration of the Chlorsulphonic Acid. — We at first thought that it would be practicable to recover from the sodium salt residue the chlorsulphonic acid of the original reaction product, — even perhaps to use the Schützenberger method for the preparation of both bodies by employing an oleum of suitable strength. While by distillation of the residue with excess of fuming sulphuric acid according to the equation

$$SO_3NaCl + H_2S_2O_7 = SO_3HCl + NaHS_2O_7$$ [53]

the chlorsulphonic acid is indeed regenerated, it is in an impure state and its purification is not worth while, since a pure product is so easily obtained by the Williamson method.

The Properties of Pyrosulphuryl Chloride.

Pyrosulphuryl chloride is a colorless liquid, fuming slightly in moist air and becoming turbid when added to a small amount of water. It sinks in water as an oil, gradually decomposing into chlorsulphonic acid, which in turn gives sulphuric and hydrochloric acids as final products. Chlorine and probably sulphur dioxide may be formed in small amount. It boils at 152.5° to 153° at 766 mm., and is not appreciably dissociated at this temperature, if perfectly dry, but complete absence of moisture is difficult to secure, as the substance is very hygroscopic. At a pres-

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[53] We do not assume the formation of such a salt, though it is supposed to exist (e. g., Schultz-Sellac, Ber., **4**, 109 (1871)). The reaction is, however, more complete when the fuming sulphuric acid is in this proportion.

sure of 19 mm., it boils at 56–57° without decomposition. It crystallizes easily at low temperature and melts at —37.5° to —37°. The specific gravity at 20°, referred to water at 4°, is 1.837; at 0° (water at 4°), 1.872. There is no appreciable dissociation at the boiling point of aniline. It is not colored by the addition of finely divided tellurium or selenium.

For the properties of mixtures of pyrosulphuryl chloride and chlorsulphonic acid, see page 712 and Table III (page 713).

The Preparation of Chlorsulphonic Acid.

In carrying out the Williamson reaction

$$H_2SO_4 + SO_3 + HCl = H_2SO_4 + SO_3HCl,$$

the oleum should contain as much sulphur trioxide as possible. It is placed in a roomy distilling flask, closed by a three-holed rubber stopper and mounted on a tripod. Through one hole of the stopper passes a right-angle tube slightly constricted at its lower end, extending to the bottom of the flask. Through the second hole is attached a distilling tube in one piece, surrounded by a condenser jacket, and the third hole carries a thermometer.

The hydrochloric acid gas is conveniently generated by slowly adding crude, concentrated sulphuric acid from a dropping funnel to crude concentrated hydrochloric acid contained in a generating flask. The gas is carefully dried by passing at least two Emmerling towers containing glass beads saturated with concentrated sulphuric acid, and a U-tube with phosphorus pentoxide. The gas is passed through the oleum slowly, at room temperature, until there is no further evidence of absorption, the flask and condenser being inclined so that any condensed vapor may run back. At the end, the contents of the flask are distilled in a current of dry hydrochloric acid gas, the portions distilling below 145° and above 160° being rejected. A rectification of the middle portion in hydrochloric acid results in a product of sufficient purity for all purposes for which the substance may ordinarily be required, but an absolutely pure product is obtained only by crystallization at low temperature, as will be shown in the Experimental Part.

The Properties of Chlorsulphonic Acid.

Chlorsulphonic acid is a colorless liquid which fumes very strongly in moist air. If added to water, it reacts with explosive violence, and is immediately decomposed into hydrochloric and sulphuric acids. Chlorine and sulphur dioxide are also formed in small amount. It cannot be boiled without partial dissociation, but, when equilibrium sets in, the boiling point is about 151–152° at 765 mm. The slight dissociation is partly into hydrochloric acid and sulphur trioxide (which react partially to form water, sulphur dioxide, and chlorine); partly to sulphuryl chloride and sulphuric acid. The latter dissociation may be brought about at the boiling point by a catalyser. At a pressure of 19 mm. it boils at 74–75°, but the dissociation into hydrochloric acid and sulphur trioxide is increased; still more at from 2 to 4 mm., the boiling point being then approximately 60–64°. At the boiling point of aniline, the dissociation, though not complete, amounts to about two volumes. It crystallizes readily at low temperature and melts at —81° to —80°. The crude acid requires a lower temperature for solidification, changing into a vitreous body, which becomes viscous at about —130° to 125° and sometimes partly crystalline. The specific gravity at 20°, referred to water at 4°, is 1.753; at 0° (water at 4°), 1.784. With finely divided tellurium, chlorsulphonic acid gives a cherry-red color, which persists for several hours, fading gradually to purple, then pink, and becoming finally colorless. With finely divided selenium, it gives a moss green color, which gradually becomes a fainter green, then yellow, and finally colorless.

For the properties of mixtures of chlorsulphonic acid and pyrosulphuryl chloride, see page 712 and Table III (page 713).

EXPERIMENTAL.

Preparations of Pyrosulphuryl Chloride.

1. 105 g. oleum (90 per cent SO_3) were added to 110 g. CCl_4 (10 per cent over theory) in an hour. 22 g. distillate were obtained up to 130°; 83 g. from 130° to 155° (chiefly 150–152°), and the residue was less than 2 g. The main fraction melted at —128° and was chiefly chlorsulphonic acid. This was treated with 50 g. fused sodic chloride and distilled, a **U**-tube [54] in liquid air being placed after the receiver. 9 g. distillate were obtained from 53° to 60° (26 mm.); the **U**-tube contained a little hydrochloric acid. The melting point of the distillate, —39°, showed a fairly pure pyrosulphuryl chloride. The dry residue was treated with 125 g. oleum (91 per cent SO_3) and distilled, a bottle cooled by ice and salt being placed before the **U**-tube in liquid air. At 78–87° (23 mm.) 46 g. of distillate were obtained, melting at —128–125°, s. g. 1.767 at 20°. In the cooled bottle was a little sulphur trioxide, in the **U**-tube a little hydrochloric acid.

The yield of chlorsulphonic acid is low owing to insufficient carbon

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[54] Figure 1, p. 697.

tetrachloride, for much of this reagent escapes with the phosgene. The pyrosulphuryl chloride is high, but it is clear that both bodies are formed in the reaction and that chlorsulphonic acid is the chief product.

2. 116 g. oleum (90 per cent) were added to 225 g. CCl_4 (over twice the theory) in 45 minutes, and the mixture fractioned after standing over night. From 65° to 130°, 112 g. were obtained ; from 145° to 153°, 137 g., melting at −128°. There was little residue. The 137 g., treated with 81 g. salt (120 per cent theory) gave 14 g. distillate at 56–57° (23 mm.) melting at −37–36°. The residue was not examined. The yield of crude mixture, 91 per cent, has been improved by excess of carbon tetrachloride, and it is again shown that only a small amount of pyrosulphuryl chloride is formed from a low oleum.

3. 108 g. melted SO_3 (98.9 per cent) were added to 220 g. CCl_4 in 45 minutes and fractioned after 48 hours. 165 g. were obtained up to 130° ; 106 g. from 139° to 141°, and there was little residue. By redistilling the first fraction, a little more was added to the second, giving 110 g., boiling mainly at 140°, melting at −41–40°. This treated with salt and distilled gave 84 g. at 60° to 62° (25 mm.), melting at −38–35°. The residue was not examined. The yield of crude pyrosulphuryl chloride, 84 g., is about 70 per cent of the theory.

4. 175 g. oleum (93.4 per cent) were added to 347 g. CCl_4 in 90 minutes, the product standing over night. 176 g. were obtained up to 130° ; 189 g. between 130° and 152°, and the residue was slight. The main fraction melted chiefly at −90°, but there was a residual solid not melting until −45–40°. 103 g. of the main fraction, with 50 g. salt (150 per cent theory) gave 39 g. distillate at 50–55° (21 mm.), melting at −43–38°. The distillation was continued up to 80° (bath, 150°), which evidently caused decomposition, as there was much hydrochloric acid in the U-tube, a little chlorine, and, from its melting point, considerable sulphuryl chloride. The residue from the salt treatment was distilled with 130 g. oleum (89.3 per cent), slightly in excess of the theory. At 70–76° (21 mm.), most of the product, 64 g., came over, but the heating was continued to 87° (bath, 153°). The U-tube contained hydrochloric acid, chlorine, and sulphuryl chloride. On redistillation, 56 g. were obtained at 75–78° (23 mm.), melting at −133–127°. Considerable sulphuric acid was left in the flask, and in the U-tube was some sulphuryl chloride. The yield of crude mixture, 189 g., is about 75 per cent of the theory. The proportions of the two bodies, 39 g. and 56 g., are in the direction of those which should have been recovered from 103 g. of crude mixture, —36 g. and 67 g. The decomposition of the chlorsulphonic acid was in accord with the observations of other workers and with those made later by ourselves.

5. 445 g. oleum (93.2 per cent) were added to 496 g. CCl_4 (138 per cent) in two hours, and the product stood over night. 131 g. were obtained up to 135°; 497 g. from 135° to 150°, little being left in the flask. A second fractionation increased the fraction from 135° to151° to 534 g., melting at —120–115°, but redistillation gave 474 g. from 134° to 154°. This is 81 per cent of the theory. 134 g. of the product, with 65 g. salt (50 per cent excess) gave 31 g. boiling at 40–49° (19–23 mm.) and melting at —37°. The sodium salt, with fuming acid, gave 65 g. crude chlorsulphonic acid boiling at 80–85° (25 mm.). According to Table III we should expect 45 g. and 89 g. respectively.

6. 300 g. melted SO_3 (98.9 per cent) were covered with 572 g. CCl_4 in a one-liter flask provided with a long condenser and placed on a sand bath. There was but slight action in the cold; on gentle heating for two hours the reaction was complete. After distilling off the excess of CCl_4, very little came over up to 135°; nearly all distilled from 135° to 141°. Yield 345 g. or 85 per cent. On treatment with 50 g. salt, there was little evolution of hydrochloric acid, and, on distillation at atmospheric pressure, most of the product came over at 149°. Redistillation at 76° (74 mm.) with a second quantity of salt gave a very pure product, melting at —37° (corr.). This is Sample C, page 699.

7. 150 g. sulphuric acid (85.9 per cent SO_3) were added to 300 g. CCl_4 and heated for 10 hours. The product was homogeneous. On distillation, 40 g. were obtained up to 120° and 74 g. from 120° to 158°, which, from its appearance and action with selenium and tellurium, was chiefly chlorsulphonic acid. The residue, 100 g., was sulphuric acid.

8. 150 g. sulphuric acid (77.0 per cent SO_3) were added to 300 g. CCl_4 and heated for 10 hours. There was no evidence of phosgene during the heating and the product separated into two layers. 279 g. CCl_4 were recovered, with faint odor of phosgene. The fraction from 90° to 140° weighed 5 g.; that from 140° to 160°, 3 g., and neither gave any test for chlorsulphonic acid. The residue, sulphuric acid, weighed 141 g.

9. 100 g. sulphuric acid (82.0 per cent SO_3) were heated with 200 g. CCl_4 for 5 hours. Phosgene was given off and the product was homogeneous. After distilling off excess of CCl_4, a fraction of 2.5 g. was obtained from 150° to 153°; a second, of 22.5 g., from 153° to 160°. Both were evidently chlorsulphonic acid, from appearance and tests. The residue, sulphuric acid, weighed 80 g.

It is clear that the two bodies are formed practically in proportion to the hydration of the oleum used, provided the concentration of the sulphur trioxide is at least 89 per cent. Below this percentage no pyrosulphuryl chloride results, and the yield of chlorsulphonic acid is rapidly diminished by the increasing proportion of water. The economic preparation of pyrosulphuryl chloride demands an oleum containing at least 95 per cent of sulphur trioxide and a large excess of carbon tetrachloride.

The purification of the products of some of these preparations is given in the following.

Purification of Pyrosulphuryl Chloride and Determination of Constants.

Boiling Point. — 106 g. of crude substance from Preparation 5 were twice distilled over salt, and 70 g. were obtained boiling at 55–57° (18 mm.), with melting point of —38–35° (corr.). This product was then distilled into a 3-way Bredt[55] receiver, the arms of which carried (1) a small distilling flask, (2) a Y-tube in which samples could be sealed off for analysis, melting point, and vapor density, and (3) a flask adapted to the arm of the pyknometer in which the specific gravity was to be determined. The entire distillate came over at 56–57° (19 mm.) Sample A.

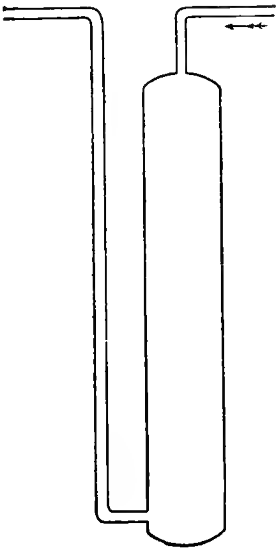

FIGURE 1.

15 g. of the above were distilled from an oil bath in the flask in which they were collected. The thread of the corrected thermometer was entirely in the vapor. A U-tube[56] in liquid air was connected with the receiver. Distillation began at 142°, the thermometer rose rapidly, and all came over mainly at 152–153° (766.6 mm., corr.). The U-tube contained some barely visible white specks, melting at room temperature with odor of sulphur dioxide. 50 g. of the original distillate, some of which had been open to the air, were also distilled. While the boiling point was again chiefly from 152° to 153°, it was not perfectly constant, and there was more

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[55] Anschütz, d. Destillation unter vermindertem Druck, 1895.

[56] These U-tubes, the construction of which is clear from Figure 1, are readily made from pieces of wide and narrow tubing to fit the Dewar liquid air container. The position of the side-tube prevents its being clogged by solids. By rapid work weighings can be made within half a gram; condensed gases are evaporated at room temperature, liquids may be poured off, and a residual solid weighed in its turn. Very satisfactory approximations may be made in this way.

evidence of decomposition in the form of unweighable white and yellow specks from which a test for chlorine was obtained.

The 84 g. from Preparation 3 were then distilled with 20 g. salt at low pressure, with special precautions against access of moisture, as provided by the apparatus shown in Figure 2. Dry air was passed through the system for 2½ hours and the glass was gently warmed. The inlet tube at A was then sealed off, the system exhausted, and the liquid distilled from F to F′. After about 60 g. had come over at 63–68° (25 mm.), with some evidence of decomposition products in the U-tube, the heating was discontinued and the tube sealed off at B. The 60 g. were then distilled at 766 mm., corr., a well-dried flask and another U-tube in liquid air being added at C. The first few drops came over at 148–150°, and all the remainder from 152.5° to 153°. There were only faint specks in the U-tube. Sample B.

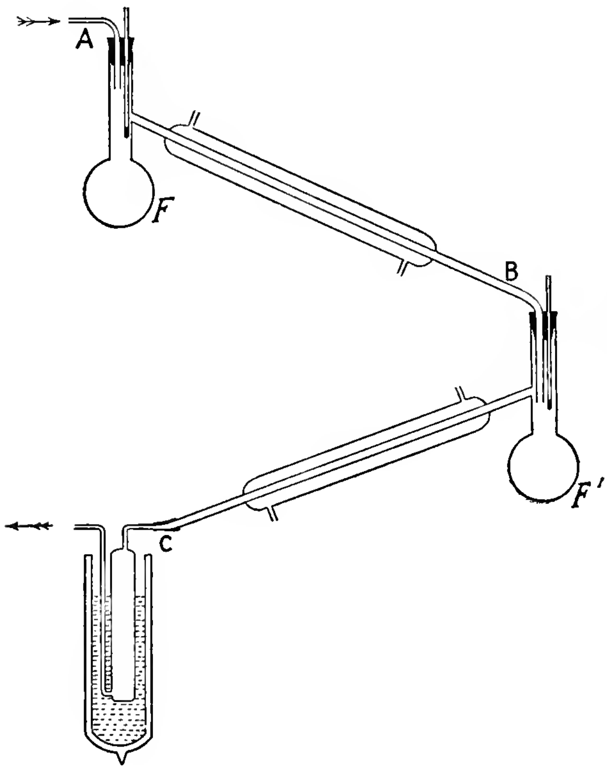

FIGURE 2.

From these two results the boiling point of pyrosulphuryl chloride may be placed at 152.5° to 153° at 766 mm. There is probably a tendency to slight decomposition at the boiling point, since the absolute exclusion of moisture from such a substance is well nigh impossible.

Specific Gravity. — The specific gravity of Sample A was taken by means of a carefully calibrated Ostwald pyknometer from a portion sealed until use.

1. At 20°, 14.0408 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8352
2. At 20°, 14.0401 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20°}{4°}$ 1.8351

From Sample B, the following figures were obtained :

3. At 20°, 14.0425 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.8354
4. At 20°, 14.0508 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.8365

The specific gravity of Sample C (Preparation 6) after taking a melting point determination, was 1.8364 at 20°, referred to water at 4°. It was again distilled with salt under diminished pressure. Of this product,

5. At 20°, 14.0538 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.8369
6. At 20°, 14.0525 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.8367
7. At 0°, 14.3292 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0^\circ}{4^\circ}$ 1.8718
8. At 0°, 14.3277 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0^\circ}{4^\circ}$ 1.8716

(The data above are corrected in order to give the figures for specific gravity: weights of water to 4°, all weights to vacuum.)

The specific gravity of pyrosulphuryl chloride at 20°, referred to 4°, is therefore 1.837 ; at 0°, referred to water at 4°, 1.872.

Melting Point. — The determination of this constant, which plays a very important part in the purification of pyrosulphuryl chloride and chlorsulphonic acid and their differentiation, was made in two ways. The first method, particularly available for small quantities of substance, is analogous to that so commonly employed in the determination of the melting point of organic substances, in which the material is placed in a thin-walled "capillary" tube, closed at one end. This we shall refer to as the "capillary method." In the second, which we shall call the "immersion method," the thermometer is placed in a test tube containing a comparatively large quantity of substance, so that the entire thread may be covered by the substance when melted.

A Rothe[57] thermometer filled with pentane was used, 35 cm. long, graduated from 30° to −200° in whole degrees. As this was grad-

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[57] Zeitschr. f. Instrumentenkunde, **24**, 5 (1904).

uated for complete immersion and in the capillary method most of the stem would be outside the bath, the reading was several degrees too high. For this method, therefore, the standardization of the instrument was based upon a definite depth of bulb immersion, the substance being always level with the bulb. As fixed points there were taken, at several room temperatures, the boiling point of oxygen (−182.8°), the sublimation point of a thin, homogeneous mixture of carbon dioxide and absolute alcohol (−78.3°), and the melting point of pure mercury (−39°).[58] The corrections thus determined were well suited for temperatures between −100° and −50°, but in the region of −28°, the uncorrected melting point of pyrosulphuryl chloride, the variation for a degree in the stem temperature (determined by a mercury thermometer alongside) was considerable. To avoid troublesome corrections at this point, the melting point of pure mercury was taken in the same manner and at the same time as that of the sample. As the melting points of mercury and pyrosulphuryl chloride differ by only two degrees, the correction could fairly be assumed to be the same for each. In the immersion method, the fixed points were the boiling point of oxygen, the sublimation point of the carbon dioxide-alcohol mixture, and the temperature of melting ice; corrections being made from a curve plotted from these.

The bath used was a naphtha, liquid and mobile at −150°, contained in a small beaker, which in turn was immersed in a beaker of liquid air. The inner beaker was covered by a stout filter paper, fastened under the rim in order to prevent the naphtha from becoming opaque through condensation of moisture and carbon dioxide. The filter paper was provided with suitable holes for the thermometer, concentric stirrer, etc.

The liquid to be tested is introduced into the capillary tube by warming and cooling the latter; sometimes the powdered frozen liquid can be added in the ordinary way. In either of the two methods, capillary or immersion, the tubes are placed in the bath and the liquid in them solidified under stirring of the bath. The liquid air beaker is then lowered and the temperature of the bath allowed to rise as slowly as possible, under careful stirring. This retardation, which may be accomplished by the approximation of the liquid air, is necessary, as otherwise the bath may rise several degrees in one minute and a fusion may take place between too great extremes. The rising thread is always read, and care is taken to see that it is unbroken, a frequent danger in these instruments.

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[58] Constants from Ostwald-Luther, Hand- und Hülfsbuch, 1910.

Two portions of Sample A, the second having remained sealed until used, gave respectively −38° to −37° and −37.5° to −37°, by the capillary method. Of Sample B a portion melted from −37° to −34.5° by the immersion method. Further precautions in using this method were taken in the examination of Sample C. The tube containing the substance was provided with a two-holed rubber stopper, through one hole of which passed the thermometer. The other hole carried a T-tube, through the vertical portion of which moved the stirrer. Into the side arm was passed a gentle current of dry air, to prevent access of moisture to the substance. The melting tube was immersed in a bath of alcohol at a temperature two to four degrees higher than that of the substance. Four determinations with Sample C gave an average of −37.3°.

The melting point of pyrosulphuryl chloride may be placed, therefore, at −37.5° to −37°.

Vapor Density. — The determinations of vapor density were made by the Victor Meyer method at the temperature of boiling aniline (184°). The weighing bulbs and the apparatus were very carefully dried and the endiometer calibrated. Readings of the volume of air replaced were not made until the meniscus had long remained constant. The following results were obtained :

Substance.		C.c. Air Replaced.	T°.	Bar. Corr.	Vapor Density.
1. Sample A	0.0480 g.	5.72	21	739.8	7.2
2. Sample A	0.2102 g.	27.53	23	742.6	6.6
3. Sample A	0.0625 g.	6.90	23.3	736.8	7.8
4. Sample C	0.1382 g.	16.95	26.5	744.6	7.1
5. Sample C	0.2501 g.	28.90	27.5	742.6	7.5
	Calculated for $S_2O_5Cl_2$				7.49

These determinations show that pyrosulphuryl chloride does not dissociate appreciably at a temperature of 184°, and it is less likely to do so at its boiling point. The presence of traces of moisture, which are not easy to guard against, would lower the vapor density slightly. In this connection, the addition of phosphorus pentoxide to the bulb of the Meyer apparatus by Prandtl and Borinski[49] is not admissible in the presence of a possible impurity of chlorsulphonic acid, which would thereby be dehydrated.

Analysis. — A volumetric analysis was made of Sample B. 1.1657 g. substance were prepared for titration as in the analysis of oleum, p. 690.

1. 100 c.c. (1/5) of the solution required 35.88 c.c. KOH (0.9078 N/5)
2. " " " 35.88 c.c. KOH (0.9078 N/5)
3. " " " 21.74 c.c. $AgNO_3$ (N/1; Volhard)
4. " " " 21.69 c.c. $AgNO_3$ (N/1; Volhard)

A gravimetric analysis of Sample C resulted as follows:

5. 0.9400 g. substance gave 2.0352 g. $BaSO_4$
6. 1.0606 " " 2.3009 g. $BaSO_4$
7. 1.1917 " " 1.5891 g. AgCl
8. 1.1813 " " 1.5751 g. AgCl

	Found.	Calculated for $S_2O_5Cl_2$
Sulphur:	(1) 29.93, (2) 29.93, (5) 29.75, (6) 29.80	29.82
Chlorine:	(3) 33.14, (4) 33.07, (7) 32.99, (8) 32.99	32.98

Preparations of Chlorsulphonic Acid.

10. Dry hydrochloric acid gas was passed into 150 g. oleum (91.1 per cent) for two hours, the flask being kept cool by ice water. After expulsion of the hydrochloric acid, distillation between 149° and 170° (chiefly 152–155°) yielded 101 g. (theory, 113 g.), and the residue, which was practically all sulphuric acid, weighed 72 g. (theory, 73 g.). On treating the 101 g. with 60 g. salt and distillation under diminished pressure, only 1.5 g. were obtained, which, from melting point and action with water, appeared to be unchanged chlorsulphonic acid.

11. 165 g. oleum (89.3 per cent) were used. The flask was not cooled. The yield of distillate between 135° and 164° was 89 g. (theory, 100 g.), and the residue was 97 g. (theory, 96 g.).

12. 147 g. oleum (89.3 per cent) were treated as in Preparation 11. The product was then distilled in a current of hydrochloric acid, and 88 g. (theory, 89 g.) were obtained from 148° to 151°, the residue weighing 82 g. (theory, 86 g.).

13. 526 g. oleum (93.9 per cent) were saturated with hydrochloric acid as in Preparation 11. Of the total increase in volume, two thirds resulted from passing the gas rapidly for two hours, one third in an additional five hours. On distilling in hydrochloric acid, 528 g. were obtained, boiling chiefly from 150° to 154° (theory, 512 g.).

14. The oleum contained 86.2 per cent SO_3. The method was as in Preparation 11, but weights were not recorded.

15. 419 g. oleum (88 per cent) were used; the method was as in Preparation 11. 261 g. product were obtained, the distillation with hydrochloric acid being very slow (theory, 212 g.).

16. 333 g. oleum (85.3 per cent) were heated on the steam bath and

hydrochloric acid passed for seven hours. The product, distilled with hydrochloric acid, gave 107 g. distillate under 162° (theory, 97 g.).

17. 550 g. oleum (89.3 per cent), treated as in Preparation 16, gave on distillation with hydrochloric acid, 375 g., boiling mainly from 149° to 151° (theory, 333 g.).

The amount of chlorsulphonic acid formed in the Williamson reaction depends upon the percentage of sulphur trioxide in the oleum not combined as sulphuric acid. The sulphuric acid is unchanged. No pyrosulphuryl chloride is formed. Attempts to increase the yield from a low oleum by addition of phosphorus pentoxide during the chlorination, according to Müller,[28] were unsatisfactory. While the total weight of product was somewhat increased, yet it was probable that some pyrosulphuryl chloride was formed by the dehydration of the chlorsulphonic acid by phosphorus pentoxide.

The reaction mixture is best distilled in a current of hydrochloric acid. As will later be shown, the chlorsulphonic acid thus obtained is fairly pure and is made no purer by distillation, owing to the partial dissociation at the boiling point. A pure product is obtained only by crystallization, as will be shown.

Purification of Chlorsulphonic Acid and Determination of Constants.

The instability of chlorsulphonic acid under heating was to be inferred from the work of other observers, but we hoped to be able to purify it by distillation at reduced pressure, and proceeded for some time under that assumption. It became evident, however, that all our efforts to get a pure product by distillation, whether at normal or reduced pressure, were nullified by the invariable presence of decomposition products, and that the decomposition was relatively complex. While the subject requires further investigation, we may state here, however, the facts concerning the dissociation which appear most probable from our work and that of others.

The Dissociation of Chlorsulphonic Acid. — Under ordinary conditions of temperature and pressure, and in absence of moisture, chlorsulphonic acid is stable. If, however, it is subjected to diminished pressure or to increased temperature, or to a combination of the two, a partial breaking down occurs, which is proportional to the change of conditions. We regard this breaking down, from our own observations and those of others, as taking place primarily in two directions, which we may represent as follows:

$$(1)\quad 2SO_2OHCl \rightleftarrows 2SO_3 + 2HCl$$

and

$$(2)\quad 2SO_2OHCl = SO_2Cl_2 + SO_2(OH)_2.$$

Following the analogy of the reduction of sulphuric acid by nascent hydriodic and hydrobromic acids, the products of reaction (1) are more or less changed according to

$$(3)\ 2SO_3 + 2HCl = SO_2 + Cl_2 + SO_2(OH)_2,$$

while the products of reaction (2) become, to a greater or less extent,

$$(4)\ SO_2Cl_2 + SO_2(OH)_2 = SO_2 + Cl_2 + SO_2(OH)_2\,;$$

hence the ultimate observed dissociation would be represented by

$$(5)\ 2SO_2OHCl = SO_2 + Cl_2 + SO_3 + H_2O,$$

the same result being reached in whichever direction the breakdown primarily started.

Under diminished pressure, at temperatures from 60° to 80°, we have found reaction (1) to take place, and in proportion to the decrease of pressure. The greater dissociation at the lower pressure is due, according to the principle of Le Chatelier, to the fact that the vapor increases in volume, and, indeed, the effect of a pressure as low as 1 to 4 mm. is to pump out the more volatile hydrochloric acid, hence that portion of the distillate which is condensed by liquid air (Figure 2) contains relatively much more hydrochloric acid than sulphur trioxide.[59] As we have found also sulphuryl chloride, sulphur dioxide, and chlorine among the products of distillation under diminished pressure, with a residue of sulphuric acid, we consider that reaction (2) occurs to a slight extent, and also reaction (3), though to a less degree than at higher temperatures.

At atmospheric pressure and at the boiling point, reaction (1) takes place, as Williams [18] and Ruff [45] have stated. But, while the primary action is less than at low pressure, the secondary action (3) is greater, and we find more sulphur dioxide and chlorine, with a larger residue of sulphuric acid, than under lower conditions of temperature and pressure. The presence of sulphuric acid, however, is partly accounted for by reaction (2), for we find sulphuryl chloride among the products of distillation at ordinary pressure, and, indeed, in greater quantity than when the pressure is low. That sulphuryl chloride is formed under these conditions was not recognized by Ruff, but he showed clearly that the presence of a catalyser brings about reaction (2) at the

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[59] The presence of sulphur trioxide in chlorsulphonic acid distilled at this pressure was indicated by the analysis and specific gravity of the product, and was confirmed qualitatively and quantitatively on careful fractionation of the product at ordinary pressure.

boiling point, and, indeed, not only to the apparent exclusion of (1) and (3), but to the completion of (2).

In addition to the phenomena of dissociation as expressed by the above reactions, we have found that the sulphur trioxide formed by the dissociation dehydrates the chlorsulphonic acid to a slight extent, giving pyrosulphuryl chloride.[60]

$$(6)\ 2SO_2OHCl + SO_3 \leftrightarrows S_2O_5Cl_2 + SO_2(OH)_2.$$

As to the character of the dissociation at temperatures above the boiling point, we can ourselves offer no direct evidence. Behrend [44] obtained a good yield of sulphuryl chloride by heating in a closed tube at 170° to 180°, and considered that reaction (2) took place. Beckurts and Otto [41] explain the reaction by the equations

$$(7)\ 2SO_2OHCl = Cl_2 + H_2S_2O_6,$$
$$(8)\ H_2S_2O_6 = SO_2 + SO_2(OH)_2,$$
$$(9)\ Cl_2 + SO_2 = SO_2Cl_2.$$

Since they found chlorine and sulphur dioxide in the closed tube at 180°, reaction (9) would not be complete. But Ruff found the equilibrium at 170° in a closed tube to be

$$\begin{array}{cccc} (2)\ 2SO_2OHCl & \leftrightarrows SO_2Cl_2 & + & SO_2(OH)_2 \\ 2.5\text{ mol.} & 1\text{ mol.} & & 1\text{ mol.} \end{array}$$

and lowered the temperature of complete decomposition to the boiling point by the catalyser. As in the presence of the catalyser Ruff found that no more sulphuryl chloride was formed by passing chlorine and sulphur dioxide into the boiling chlorsulphonic acid than without them, they were not essential to the formation of sulphuryl chloride, and reaction (9) evidently did not take place. It is also unnecessary to assume reactions (7) and (8) to explain the formation of sulphur dioxide and chlorine.

Ruff considered that at temperatures higher than 180° reactions (1) and (3) took place; Heumann and Köchlin [35] that chlorsulphonic acid was completely dissociated at 442°, according to reaction (5), but at 184° they found the dissociation incomplete.

That sulphuryl chloride, chlorine and sulphur dioxide are coëxistent products of the dissociation at temperatures short of that necessary for

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[60] For the hydration of pyrosulphuryl chloride by sulphuric acid, *v.* p. 717.

complete dissociation is undoubted. Whether we shall ascribe the formation of the last two of these bodies to reactions (1) and (3) or to reactions (2) and (4) is immaterial. But it is not unreasonable to suppose that reaction (1), which at diminished pressure and comparatively low temperature is predominant over reaction (2), becomes not only secondary to reaction (2) at atmospheric pressure and higher temperature, but also that, at the highest temperatures noted, it would merge into reaction (5).

Whatever may be the mechanism of this rather complex dissociation, it is certain that distillation of chlorsulphonic acid at any pressure will result in a product which may contain, in varying amounts, sulphuryl chloride, chlorine, sulphur dioxide, sulphur trioxide, hydrochloric acid, and sulphuric acid. The disagreeing results of previous observers on the constants of chlorsulphonic acid are therefore easily explained, for their products, though often of sufficiently good quality for practical purposes, were contaminated by more or less of these dissociation products, and hence showed varying boiling points, specific gravities, etc.

By distillation with hydrochloric acid, reaction (1) obviously runs to the left, and there should be little tendency to dissociation. Ordinary distillation, at atmospheric or low pressure, will not purify. After realization of this fact, we turned to crystallization, as will be shown.

Behavior of Chlorsulphonic Acid under Distillation. — In Preparations 10 and 11 above, in which the distillation was without hydrochloric acid, the product is contaminated by the products of dissociation, and the apparent yield is less. In the others, there is a greater or less amount of hydrochloric acid present and probably less of the dissociation products.

The crude preparations of chlorsulphonic acid showed a very characteristic behavior on cooling. At —70° to —80°, the liquid becomes thicker and gradually viscous as the temperature falls. At —130° to —140° an amorphous, vitreous mass is formed, which under rising temperature becomes gradually viscous again from —140° to —120°, averaging, say, at —130°, and is limpid at about —85°. This behavior differentiates the substance sharply from pyrosulphuryl chloride, which gave definite crystals at —40° to —35°, and at —70° to —60° even when containing 90 per cent of chlorsulphonic acid. But, while the differentiation was clear, the melting evidently indicated impure chlorsulphonic acid.

Preparation 11 became viscous at —133–127°. At 24–27 mm. it boiled chiefly at 80–82°, and the solidified product softened at —125–117°. The specific gravity was 1.786 at 20°. To avoid the presence of sulphuric acid, which was suggested by the specific gravity and boiling point of Preparation 11, the subsequent preparations were distilled with hydrochloric acid, as described above.

Preparation 12 boiled from 147° to 151°, became viscous at —138–130°, and had a specific gravity of 1.745 at 20°. Distilled at low pressure, it boiled from 77° to 81° (24–31 mm.), softened at —130–125°, with specific gravity of 1.765. Three more distillations at low pressure did not essentially change these properties, and the preparation was evidently as pure as this treatment was likely to make it. 29 grams boiled at 145–150.5° for the first half; 150.5–152° (762 mm.) for the second. The presence of white fumes of sulphur trioxide towards the end emphasized the decomposition, and about half a gram of residue was left, which was mainly sulphuric acid. A vapor density determination in aniline (184°) gave 2.6 and 2.4 (theory, 4.04). A volumetric analysis gave: chlorine, 30.00; sulphur, 28.02 (required, 30.43 and 27.52).

We did not study the decomposition in the course of these distillations by means of the liquid air tube (Figure 1) as in the subsequent trials. The product was probably more impure than would appear from the properties, for the impurities compensated each other to a certain extent. But the specific gravity and decomposition pointed to the presence of sulphur trioxide at least.

The study of the portion of Preparation 1 (46 g.), which had been recovered from its sodium salt, is now of interest. This was viscous at —128–125°, with specific gravity of 1.767 at 20°, and boiled at 78–87° (23 mm.). On distillation at atmospheric pressure, a few drops came over at 148–149°, but the greater part at 151–152°. There was some decomposition and a few drops of sulphuric acid were left. On distilling again, one fifth came over from 147° to 149°, the rest chiefly at 150–152°. A third distillation increased the amount from 146° to 150° to one half, the rest mainly from 150° to 153°. Little residue was left in the last two cases. The product now became viscous at —136–127°, but at —85° crystals appeared, which melted at —69°. The specific gravity was 1.755 at 20°. Two more distillations carried the beginning to 140°, a third to 100°, whence came a rapid rise to 144°, and two more distillations brought much under 100°. Sulphuric acid in small quantity was left in the flask each time, and there was evidence of chlorine. The melting point of the product was —126°; then crystals separated, melting at —70°. The specific gravity was 1.756. On distilling again, a few drops were collected below 100°. These gave an oil with water, dissolving quietly. The melting point was —51° (corr., —60°). This was evidently sulphuryl chloride and not pyrosulphuryl chloride,[61] as shown by the boiling and melting points and by the low specific gravity.

Preparation 10, which was viscous at —124°, was regenerated from its sodium salt and studied with more care as to exclusion of moisture. It boiled at 73–75° (21 mm.), became viscous at —128–126°, and had a specific gravity of 1.767 at 20°. 60 grams of this were then distilled at atmospheric pressure until about one third came over. Of the remainder, about 10 grams were distilled at low pressure (t°, 63°, p., 24 mm.), a U-tube with liquid air being used. In the U-tube was found a small amount of solid, with properties resembling those of sulphuryl chloride. The residue was then placed in the apparatus described on page 698 (Figure 2). After passing dry air through the system for an hour, the liquid was distilled into the second flask at 76–78°(23 mm.), when the second flask was sealed off and the distillation conducted at ordinary pressure. It began at 139°, and was chiefly from 149° to 150°. The formation of gas was evident and chlorine was found in the liquid air tube. Sulphuric acid was left in the residue. The distillate became viscous at —128°; a few crystals were visible at —80°, disappearing at —67°.

The study of the crude product of Preparation 13 was to throw more light on the question. This had boiled, in hydrochloric acid, within closer limits, 150–154°, than previous preparations. The latter, owing to presence of much hydrochloric acid or of products of dissociation, had taken the vitreous form on cooling, becoming viscous at a higher temperature without separation of crystals. In this case, however, the viscous liquid became solid with crystals at —110°, which disappeared at —70°.

330 grams of this preparation were distilled at 19 mm., after drawing off most of the excess of hydrochloric acid by exhaustion. 58 grams were collected from 67° to 76°, 177 grams from 75° to 78° and 55 grams were left, largely sulphuric acid, which had probably distilled in the hydrochloric acid current. In the U-tube was much hydrochloric acid; a little chlorine. The first fraction became viscous at —127°, crystallized at —93°, and melted at —54°. The corresponding figures for the second were —134–129°, —87°, and —74°. In both fractions cooling caused no separation of crystals. The second fraction, on redistillation at low pressure, became viscous at —130°, crystallized at —83°, and melted at —72°. There was again no separation on cooling. In the

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[61] We prepared a small quantity of sulphuryl chloride by the method of Ruff. This boiled at 69–71° and melted at —58–56°, corr. With water it formed an oil, dissolving quietly. The specific gravity of sulphuryl chloride is given as 1.661 at 21°; the boiling point 75°.

liquid air tube there was still much hydrochloric acid, some chlorine, and a few particles melting at —13°. Two subsequent distillations at low pressure resulted in a product reacting quietly and completely with water, leaving no oil. There was not much decomposition, but evidence of a little sulphuryl chloride. The crystallizing point was —80°, the melting point —70°. This product, distilled in the dry system (Figure 2) boiled at 65° to 69° (14–17 mm.), and, at 768 mm., the first half came over at 137–151°; the second at 151–152°. There was very little residue and very little in the U-tube, chiefly hydrochloric acid. On cooling, no vitreous body separated, but only the crystalline, and at —75°. That there was probably sulphuryl chloride present was shown by a redistillation, from which a portion was obtained boiling from 103° to 141° and melting at —52°. Analysis of the product showed too low chlorine and too high sulphur, as in Preparation 12, and the two preparations were probably similar.

A study of the remainder of Preparation 13, by repeated distillations at very low pressure, showed an increasing tendency to decomposition, and, indeed, more in the direction of equation (1) (page 703). The boiling point was 60° to 64° at 2 to 4 mm. The details need not be considered here, but there was clear evidence of more hydrochloric acid and sulphur trioxide, with less sulphuryl chloride. The amount of chlorine, by analysis, in the main body became less; the sulphur higher.

The deleterious effect of distillation at low pressure was strikingly shown in the treatment of Preparation 14. This crystallized readily without giving the vitreous solid, and melted at —80°, corr. After distillation at 68–70° (15–17 mm.), the product would not crystallize at all, even on inoculation with crystals from another preparation. The specific gravity was 1.782 at 20°, showing the probable presence of sulphur trioxide.

Fractional Crystallization of Chlorsulphonic Acid. — It seems therefore certain that chlorsulphonic acid cannot be purified by distillation, that it is an unstable body, and that even the purest specimens heretofore obtained, including our own, must have been contaminated by the dissociation products.

The boiling point must be always somewhat in doubt. In order to obtain identifying constants which would be less affected by temperature and pressure, e. g., the melting point and specific gravity, we had recourse to fractional crystallization.

200 g. of Preparation 17 became viscous at —132°, crystallized at —100°, and melted at —72°. The entire amount was brought to crystallization and then partly melted. 83 g. of solid were then drawn out of the melted mass by a spirally bent glass rod previously inserted. These

83 g. were then remelted and allowed to partly crystallize, and from the second, half-melted mass 42 g. were taken out. After three more similar fractional crystallizations, 8 g. were finally obtained, which became viscous at —130°, crystallized at —98°, and melted at —72° (—80°, corr.). This product reacted quickly and violently with water, and left no oil. A gravimetric analysis gave: S, 27.66; Cl, 30.32 (Calculated: 27.52 and 30.43). When cooled below —85°, crystallization was not set up by addition of crystals of either sulphuryl chloride or pyrosulphuryl chloride. On stirring or upon addition of crystals of chlorsulphonic acid, the separation was immediate.

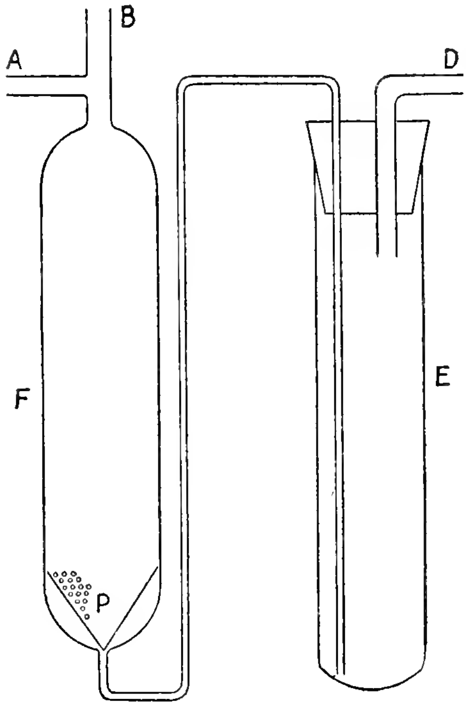

Figure 3.

Now, as we had satisfied ourselves by experiment that small amounts of both sulphuryl chloride and pyrosulphuryl chloride would alter the melting point appreciably; as both of these substances gave a residual oil with water, even when present in small quantity, and, finally, as the method of preparation precluded even traces of either substance, we could not but conclude that this preparation of chlorsulphonic acid was very pure, and that the true melting point must be in the region of —80°. It remained, therefore, to repeat the fractional crystallization in such a manner that access of moisture to the avid chlorsulphonic acid should be avoided as far as possible.

For this purpose, the apparatus shown in Figure 3 was devised, which consists of the glass separator, F, and test tube, E. The construction is clear from the figure, except that P is a perforated platinum cone fitting snugly into the lower part of F. F, in this case of 50 c. c. capacity, can be placed in a liquid air container. The outlet tubes at A and D are connected with drying tubes of phosphorus pentoxide. Through B may be passed a stirrer. By closing B and applying suction at A, the liquid is drawn from E into F. When the liquid has been partly solidified in F by immersion in the cooler, the residual melted portion is drawn back into a fresh test tube in place of E, while the crystals are held back by the platinum cone. The crystals are then melted in F and drawn into a third test tube at E.

The 261 g. of Preparation 15, which melted at —79°, corr., were introduced into the separator in several portions, and cooled until nearly solid. Crystallization was spontaneous or induced by slight stirring. The crystals were then allowed to half melt, and the residual liquid was drawn out. The remelted crystals, united, were put into the separator a second time and the crystallization repeated. The second crop of crystals was then used for determination of constants.

Melting Point. — Three determinations of melting point by the immersion method (page 699) gave —81°, —81°, and —81.5°, an average of —81.2°, which, corrected, becomes —80.2°. Taking this into consideration with the result of the fractional crystallization of Preparation 17, we may place the melting point of chlorsulphonic acid at —81° to —80°, corr. The purity of the twice crystallized product of Preparation 15 is shown by the slight change in melting point following the treatment.

Specific Gravity.

1. At 20°, 13.4138 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.7533
2. At 20°, 13.4145 g. substance occupied the same volume as 7.6333 g. water. S. g. $\frac{20^\circ}{4^\circ}$ 1.7536
3. At 0°, 13.6420 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0^\circ}{4^\circ}$ 1.7839
4. At 0°, 13.6410 g. substance occupied the same volume as 7.6423 g. water. S. g. $\frac{0^\circ}{4^\circ}$ 1.7838

(The data above are corrected in order to give the figures for specific gravity: weights of water to 4°, all weights to vacuum.)

The specific gravity of chlorsulphonic acid at 20°, referred to water at 4°, is therefore 1.753; at 0°, referred to water at 4°, 1.784.

Boiling Point. — The boiling point of this sample was compared with that of other preparations. About 60 g. were distilled at 765 mm., corr., with thread of thermometer in the vapor. Ten per cent of the distillate came over at 144–151°, with traces of hydrochloric acid and chlorine. The remainder boiled between 151° and 152°, with no evidence of decomposition in the liquid air tube, which was placed after the receiver. There was a slight residue of sulphuric acid.

Vapor Density.— The determinations of vapor density were made by the method of Victor Meyer at the temperature of boiling aniline (184°). The same precautions were taken as in the case of pyrosulphuryl chloride.

	Substance.	C.c. Air replaced.	T°.	Bar. Corr.	Vapor Density.
1.	0.0522 g.	17.93	19.5	751.1 mm.	2.4
2.	0.0516 g.	18.15	19.5	751.1 mm.	2.4
		Calculated for SO_3HCl			4.04

Analysis. — A gravimetric analysis resulted as follows:

1. 0.9145 g. substance gave 1.1272 g. AgCl
2. 1.2557 g. substance gave 1.5480 g. AgCl
3. 0.5364 g. substance gave 1.0824 g. $BaSO_4$
4. 0.7266 g. substance gave 1.4655 g. $BaSO_4$

	Found.	Calculated for SO_3HCl.
Chlorine:	(1) 30.49, (2) 30.50	30.43
Sulphur:	(3) 27.72, (4) 27.71	27.52

Properties of Mixtures of Pyrosulphuryl Chloride and Chlorsulphonic Acid.

The presence of the two bodies in the product of the Schützenberger reaction and their close relation to each other rendered of interest a comparison of certain properties of their mixtures. As differentiating properties were selected the melting point, boiling point, action with water and with finely powdered tellurium and selenium. The samples of pyrosulphuryl chloride and chlorsulphonic acid used were free from any admixture of the other. The amounts of mixture made up averaged 30 grams. The chlorsulphonic acid gave with tellurium an instantaneous cherry red, persisting for several hours but finally fading. With selenium it gave an immediate moss-green, gradually becoming fainter, then yellow in about an hour, fading in three hours. No colors were obtained with pyrosulphuryl chloride. The table on p. 713 (Table III) gives the results concisely.

From inspection of this table it will be seen that a little over five per cent of chlorsulphonic acid in a mixture of the two bodies would give a color reaction and depress the melting point. Ten per cent would not only give a color reaction, but would cause a considerable lowering of the boiling point and a more immediate action with water. Thirty per cent would give a strong color reaction, a marked action with water, and a marked lowering of the melting point. A chlorsulphonic acid containing thirty-five per cent of pyrosulphuryl chloride would hardly be distinguished from pure material by the color reactions and the action with water, nor would the boiling point suggest much impurity, but the presence of pyrosulphuryl chloride in such a mixture might be inferred from the melting point. It is noteworthy,

TABLE III.

Properties of Mixtures of the Two Bodies.

No.	Percentages.		Melting Point. Immersion Method. Corr. C°.	Boiling Point. Corr. C°.	Action with Water.	Color with Tellurium.	Color with Selenium.
	Pyrosulphuryl Chloride.	Chlorsulphonic Acid.					
1	100	0	−37.5–37	152.5–153	Quiet	None	None
2	99	1	−41–36	151–53	Quiet	None	None
3	95	5	−42–37	143–153	Quiet	Faint pink	Green; then brown to orange yellow
4	91	9	−41–38	142–147	Quiet; dissolves in 10 min.	Strong pink	Yellow brown to orange
5	82	18	−43–39	139–141	Quiet; dissolves rapidly, with heat	Purple then red	Green then orange
6	70	30	−45–39	139–140	Hissing sound; dissolves at once	Purple then red	Green then orange
7	52	48	−47–43	133–153	Loud hiss; dissolves at once	Purple then red	Green then orange
8	37	63	−50–47	135–153	Explosive	Red	Green
9	25	75	−57–53	139–153	Explosive	Red	Green
10	11	89	−66–61	137–153	Explosive	Red	Green
11	4	96	Pyrosulph. chloride did not separate	142–153	Explosive	Red	Green
12	0	100	−81–80	151–152	Explosive	Cherry red	Green

Except for the color reactions, which were obtained from the components of the mixtures, the properties of Nos. 1 and 12 are of the purest preparations.

also, that the boiling point of a mixture containing 18 to 30 per cent chlorsulphonic acid is within close limits and lower than that of either component.

The Action of Water on Pyrosulphuryl Chloride and Chlorsulphonic Acid and the Separation of the Two Bodies.

Both pyrosulphuryl chloride and chlorsulphonic acid are decomposed by water, the latter far more quickly, according to the equation:

$$(1)\ SO_2OHCl + H_2O = SO_2(OH)_2 + HCl.$$

The formation of chlorine in small quantity from this reaction is evident from the color of the product and its action with potassic iodide. This is probably due to a slight dissociation from the heat of reaction, and a consequent oxidation of the hydrochloric acid by the sulphur trioxide (reactions (1) and (3), pages 703 and 704).

The action of water upon pyrosulphuryl chloride might take place in two ways: either a direct conversion to sulphuric acid and hydrochloric acid according to

$$(2)\ S_2O_5Cl_2 + 3H_2O = 2SO_2(OH)_2 + 2HCl$$

or with intermediate formation of chlorsulphonic acid, according to

$$(3)\ S_2O_5Cl_2 + H_2O = 2SO_2(OH)Cl,$$

the chlorsulphonic acid being then decomposed according to equation (1). The observed formation of chlorine in this reaction also might be ascribed to dissociation of either body under the heat of reaction.

Konovaloff,[33] who added to 100 parts of pyrosulphuryl chloride 4 parts of water (theory for equation (2), 25.1 parts; for (3), 8.4 parts), obtained a mixture of the two bodies. Billitz and Heumann,[47] who used 7.5 parts to 100, found that chlorsulphonic acid was the chief product. Prandtl and Borinski,[49] with the proportion of 100 of substance to 8.3 of water, obtained a product which still reacted quietly with water and gave no color with tellurium, thus showing, according to our results in Table III, at most a small amount of chlorsulphonic acid. They concluded, therefore, that the reaction took place according to equation (3), but was very gradual and, in that instance, incomplete. This opinion would seem to be substantiated by their method of separation of the two bodies, which depends upon the selective attack of water in the form of ice upon the ice-cooled mixture, the chlorsulphonic acid being completely broken down and but little of the pyrosulphuryl chloride.

The question was studied by us in several ways: *a.* Pyrosulphuryl chloride was dissolved in chloroform and one molecule of water added, drop by drop. Hydrochloric acid was given off and a liquid separated which was shown to be sulphuric acid. The chloroform solution was then distilled to expel the solvent. The residue hissed with water, left some oily drops and solidified from —30° to —100°. It was then dissolved in chloroform, and a second molecule of water added as before. Hydrochloric acid was again given off, and sulphuric acid separated. The residue from the chloroform evaporation hissed more violently with water than before, and solidified at —95–100°. A similar treatment with a third molecule of water gave hydrochloric acid in clouds, more sulphuric acid separated, and the chloroform solution yielded a small residue, which still gave the reactions of chlorsulphonic acid and solidified below —80°. The reaction was followed quantitatively, though roughly, and the amount of sulphuric acid was somewhat below that demanded by equation (2).

Evidently in this experiment the reaction has taken place in two stages, represented by equations (3) and (1), the net result being according to equation (2), though the last action was not entirely complete.

b. Pyrosulphuryl chloride was dissolved in carbon tetrachloride, and water was added directly in the proportion of 8.4 to 100 (equation (3)). The mixture was allowed to stand over night. From a portion the solvent was evaporated by a rapid current of dry air; the turbid residue reacted quietly with water. The remainder was evaporated at a gentle heat, and left a residue which also gave no violent action with water. This would seem to show that reaction (3) had not taken place exclusively, but probably reaction (2) incompletely, though, of course, at least 18 per cent of chlorsulphonic acid may have been present according to Table III, 5.

c. Pyrosulphuryl chloride was exposed to the moist air of the room in a beaker covered with a watch glass for seven days, and a portion tested each day with water. There was no evidence of chlorsulphonic acid, — merely a diminishing quantity of pyrosulphuryl chloride, until, on the last day, the residue was sulphuric acid alone. The beaker walls were covered with aqueous hydrochloric acid.

d. 8.3 parts of water were added to 100 parts of pyrosulphuryl chloride, cooled to 0°, and shaken under ice cooling for an hour. The liquid became turbid at first, and a little gas containing chlorine was evolved. In twenty minutes the mixture was decidedly yellow. At the end, two layers were formed, the lower, from its action with water, being apparently unaltered pyrosulphuryl chloride and the upper sulphuric acid. The amount of unaltered substance was greater than if only one molecule of water had been added according to equation (2).

e. 8.1 parts of water were added to 100 parts of pyrosulphuryl chloride warmed to blood heat. Hydrochloric acid was given off, and the mixture separated into two layers, sulphuric acid and apparently unchanged pyrosulphuryl chloride, colored by chlorine. The amount unaltered was again greater than would have been expected if somewhat less than one molecule of water (8.1 parts) had acted according to equation (2).

From Experiments *b*, *c*, *d*, and *e* it might be concluded that pyrosulphuryl chloride was directly converted by water to hydrochloric and sulphuric acids, except for the fact that a considerable admixture of chlorsulphonic acid might show no violent action with water (Table III), and that, in Experiments *d* and *e*, the amount of unaltered pyrosulphuryl chloride is greater than it should be if only one third had been converted to hydrochloric and sulphuric acids. Experiment *a*, however, shows that there is an intermediate stage of conversion, — to chlorsulphonic acid. In general, a greater concentration of water will bring about a more complete decomposition of the pyrosulphuryl chloride, after the admixed chlorsulphonic acid has been disposed of, and, in addition, the reaction is furthered by a high temperature or long contact, or by both. If the reaction mixture is at once distilled, the first product, chlorsulphonic acid, may be isolated. This is shown by our investigation of the Prandtl and Borinski method of separation, in which distillations of moist "pyrosulphuryl chloride" obtained by this method gave invariably large amounts of chlorsulphonic acid. One instance will suffice :

f. 133 grams of moist "pyrosulphuryl chloride," which had no longer given any evolution of hydrochloric acid on adding ice, thus showing the chlorsulphonic acid in the original mixture to have been decomposed, were distilled. Up to 148°, 75 g. were obtained; from 148° to 153°, 40 g. Both fractions reacted violently with water and gave a strong red color with tellurium.

We are now in a position to explain why the results of Konovaloff and of Billitz and Heumann differed from those of Prandtl and Borinski. The first three authors apparently distilled their mixture of pyrosulphuryl chloride and water within a short time, and therefore obtained more chlorsulphonic acid, since at the *higher* temperature the pyrosulphuryl chloride was hydrated more quickly and there was not enough water left to entirely decompose the chlorsulphonic acid formed. The last two, however, distinctly state that the cooled mixture stood over night before separation and distillation, hence, at the *lower* temperature, the chlorsulphonic acid was more quickly hydrated and therefore not evident in the product of the subsequent distillation.

On this point depends much of the success of the Prandtl and Borinski method, as our study of it shows. If ice be added to a cooled mixture of the two bodies, the chlorsulphonic acid will be decomposed and a part of the pyrosulphuryl chloride. The latter must not be separated at once and distilled, but the mixture must stand for some time. The sulphuric acid does not always form the upper layer, since the specific gravities of the two are so nearly the same. Addition of concentrated sulphuric acid or a little water will bring the pyrosulphuryl chloride to the bottom. After separation, the addition of phosphorus pentoxide to the moist pyrosulphuryl chloride is not optional, as Prandtl and Borinski contend, but necessary, if the minimum amount of chlorsulphonic acid is to be formed on distillation. With proper precautions, the method can be made to give a fairly pure product, though the entire absence of chlorsulphonic acid is not assured. The yield is, however, not over 70 per cent, as Prandtl and Borinski state, and may be less.

In this connection, the behavior of pyrosulphuryl chloride toward concentrated sulphuric acid is of interest. There is no immediate action, but a partial hydration takes place on standing. The two immiscible substances were sealed in a tube and allowed to stand in the cold for a month. The product was homogeneous. On opening the tube there was no excess of pressure; on mixing a portion of the contents with water, a violent reaction took place and hydrochloric acid was given off. This indicates the formation of chlorsulphonic acid. Since we have shown that chlorsulphonic acid is partially dehydrated by sulphur trioxide (p. 673), we may express both results again by writing the reaction (6) in this place also:

$$S_2O_5Cl_2 + H_2SO_4 \leftrightarrows 2SO_3HCl + SO_3,$$

or

$$S_2O_5Cl_2 + 2H_2SO_4 \leftrightarrows 2SO_3HCl + H_2S_2O_7.$$

This condition of equilibrium explains why, in the preparation of chlorsulphonic acid by the Williamson method, the formation of pyrosulphuryl chloride is impossible, since the large amount of sulphuric acid would cause the reaction to run to the right.

SUMMARY.

The work of previous investigators on the action of sulphur trioxide upon certain chlorides is reviewed as briefly as possible and the results summarized in tabular form (Table I).

Pyrosulphuryl chloride is obtained in a perfectly pure state and its chief constants determined. A rapid method is devised for finding melting points at low temperatures.

Chlorsulphonic acid is shown to be unstable when subjected to distillation, but it is purified by crystallization and its chief constants are determined.

It is confirmed that the Schützenberger reaction of sulphur trioxide upon carbon tetrachloride, which is best adapted to the preparation of pyrosulphuryl chloride, gives also chlorsulphonic acid when the sulphur trioxide is in the form of oleum, and it is shown that the proportion of the two bodies in the product depends roughly upon the hydration of the oleum (Table II). It is also shown that, with a hydration corresponding to that of pyrosulphuric acid, $2SO_3 \cdot H_2O$, or greater, only chlorsulphonic acid is formed, and that, while the limit of the formation of chlorsulphonic acid is theoretically at the hydration corresponding to the formula $2SO_3 \cdot 3H_2O$, yet the increasing concentration of the water up to the latter point results in a more rapid decomposition of the chlorsulphonic acid than the theory demands.

A method of separation of the products of the Schützenberger reaction is described, by which the pyrosulphuryl chloride may be completely freed from chlorsulphonic acid, and the latter may also be recovered.

The conditions under which pure chlorsulphonic acid is best prepared by the Williamson method are studied, and it is confirmed that the action of the hydrochloric acid is only upon the sulphur trioxide in the oleum in excess of that corresponding to the formula $SO_3 \cdot H_2O$.

The dissociation of chlorsulphonic acid is studied and discussed.

Properties of mixtures of pyrosulphuryl chloride and chlorsulphonic acid are given (Table III).

The action of water upon pyrosulphuryl chloride is studied.

In conclusion, we desire to express our indebtedness to the C. M. Warren Fund of Harvard University for assistance in defraying the expense of the liquid air used in this investigation.

Harvard University, Cambridge, Mass.,
December, 1911.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 19. — March, 1912.

THE FALL OF A METEORITE.

By Elihu Thomson.

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Presented January 10, 1912. Received January 30, 1912.

While on a trip west last spring I took the opportunity of visiting the remarkable formation in Arizona known as Coon Butte, also called "Meteor Crater." This formation has been made the subject of several memoirs which have appeared from time to time during a number of years past. To these papers references may be made for details of exploration and measurements. In view, however, of the marked divergences of opinion concerning origin, it seemed desirable to determine, at least to one's own satisfaction, which of the explanations was in accordance with the facts. The spot had been known for many years as the locality for numerous meteorites, unique in containing diamonds; the so-called Cañon Diablo specimens. Cañon Diablo is a few miles west of the crater.

More recently these iron masses have been found to contain notable amounts of platinum and iridium, metals which have in the past few years advanced in price at an extraordinary rate.

The careful study of the class of bodies which include meteorites can doubtless assist us materially in understanding what goes on in the universe around us. They are messengers with a story. My personal interest was aroused when I was a fortunate witness to the great meteor shower in the early morning of November 14, 1867. This shower which was recurrent in thirty-three years was found to be due to meteoric masses, the path of which was identical with the orbit of Tempels' Comet, which was undergoing disintegration. Owing to some perturbation or displacement of the orbit the visitation failed to reappear in 1900.

In reaching the Meteor Crater we ride west over the Atchison, Topeka and Santa Fe railroad enjoying the wonderful scenery of the Painted Desert, its coloring and atmosphere. We may comfortably pass the night at Winslow in northern central Arizona. Taking the train next morning toward Sunshine Station, a few miles further west, if we are intent on noticing the peculiarities of the land around us we will soon see off to the southwest and rising out of the nearly level plain a peculiar hill or elevation; a butte with an apparently flat top and whose slopes have a grayish color distinguishing it completely from the red soil which covers this territory. Though it may be eight or ten miles away it is still a conspicuous object not from its height but from its form. It has an artificial look as if some great reservoir for water storage had been built. There is no other elevation near it. From Sunshine Station it is reached by a drive south of about six miles, over the plain sparsely covered with vegetation, and with here and there outcropping fantastic forms of red rock of a few feet in height.

As we approach Coon Butte, or Meteor Crater, the impression does not change except in the realization of the scale on which it exists. Distances are so deceptive in the clear air of the desert that it had seemed close at hand when we were still miles away. At last we reach the foot of the slope and climb it to a height of about 150 feet. We are now at the top looking down into a great bowl-shaped hole, the upcast rim of which we had seen from afar. This rim is a nearly circular ridge, very steep or even vertical on its inner part and sloping gradually to the plain on all sides. But the thing which rivets the attention is the deep cavity enclosed by this rim, comparatively flat at the bottom with surrounding talus slopes from the walls, in which walls are exposed various rock strata, broken, contorted, distorted, and uplifted. The bottom of the crater is about 570 feet below the rim, or more than 400 feet below the general level of the plain outside.

The sight is most impressive. The diameter of the opening is roughly three quarters of a mile; at the widest part a little over 4,200 feet.

The circular hill or rim of this huge hole is composed of material evidently uplifted, crushed and pulverized in part and cast out from the crater. Much of it is finely pulverized white silica from a white sandstone which underlies an upper stratum of limestone. Fragments of the limestone layer of all sizes are seen; some of them very large. The slope of the rim extends for about a quarter to half a mile but there is scattered material three miles or more away. Blocks of limestone and sandstone cap the ridge, ranging up to 30 feet in diameter, while one block 10 feet through, is half a mile distant. The most significant constituent of the upcast ridge, is, however, meteoric iron in pieces of varying size, and so-called shale ball iron or oxidized meteoric iron; — oxidized because in its composition there was chlorine enough to cause rapid rusting after it entered the earth's atmosphere and became subject to moisture.

The plain around the crater has yielded numerous masses of the iron, some of them several hundred pounds in weight, and one discovered during the past summer weighs about 1700 pounds.

The amount of rock blown out of the crater cavity could not have been less than two or three hundred millions of tons, not considering the large amount which fell back and which now lies at the bottom of the bowl-shaped hollow of the crater. Nowhere else on the earth's surface has meteoric iron been found so spread about.

Yet there remains an unsolved problem. What became of the enormous meteoric mass, or the cluster of them which was capable by its impact of displacing so large an amount of rock? Allowing only one ton to every 20 or 30 tons of ejected material, we still have about 10 millions of tons of meteoric iron to account for. This would constitute a solid mass of between 400 and 500 feet in diameter.

The attempts to explain this crater as the result of volcanic action, or as produced by a steam explosion from below, are certainly to be regarded as rather far fetched in view of the presence and mode of occurrence of the meteoric irons, and the many evidences presented which seem to me to lead inevitably to the conclusion that here indeed we have a huge impact crater and that only. The floor of the crater is overlain with sedimentary deposits of an aquatic nature, the washing of the walls and talus indicating the existence at some time of a small lake or pond. Below this is a vast bed of mingled materials, mostly, however, the pulverized white sandstone or "rock flour," the result of crushing of the rock layers such as now surround it.

For exploration a shaft has been sunk into this bed of a nearly pure silica, but contrary to expectations it had to be discontinued. Water was reached at about 200 feet below the crater floor and the extremely fine silica rock flour thus became a most typical and troublesome quicksand and limited the depth of the shaft. Recourse was had to drill holes, about 28 of which have been sunk to various depths not far from the central area, and some of these have reached the underlying and undisturbed red sandstone layer at about 850 feet below the crater bottom.

The material brought up has shown evidence of disseminated meteoric iron and nickel, but no large masses were found. Specimens of the silica metamorphosed by heat and steam under pressure, causing a partial aqueous fusion, have been secured.

Careful magnetic tests conducted by Prof. W. F. Magie, head of the Physics Department at Princeton, have failed of result, probably because these iron masses have too low a magnetic susceptibility under the very small values of magnetic force such as exist at low latitudes; particularly as the vertical component can alone be expected to yield indications of the presence of buried masses of iron.

If further exploration is carried on it is possible that a system of induction balance testing as proposed by me would be more fruitful, though experiment alone could determine that fact.

From many considerations which it would take too long to enumerate it seems probable that if a large mass or cluster has buried itself at this spot, it now exists under the southern and southwestern wall of the crater and not near the center. It is a significant fact that the rock layers exposed under the rim at the south show evidences of an uplift of about 100 feet while still retaining their approximately horizontal position. The depth of penetration is probably not more than 1200 feet, in which case the buried masses would lie upon or be slightly embedded in the upper part of the underlying red sandstone layer, which the bore holes put down near the center of the crater have shown to be undisturbed there.

In a recent report referring to Coon Butte, Bulletin 435 of 1910 of the United States Geological Survey, Mr. N. H. Darton says: "After an examination of the crater and consideration of all that has been written, I believe we have no evidence adequate to explain its origin. The hypothesis that it was caused by the impact of a meteor as urged by Tilghman, Barringer, Fairchild, and Merrill is in accordance with some of the features but does not accord with the all-important fact that no meteor is present, as has been demonstrated by many borings." He forgets that only 28 test holes were put down and all near the center of the crater and that such bodies rarely if ever fall vertically. If a single large mass of 500 feet in diameter fell, to be sure of finding it would demand the sinking of not less than 500 to 600 holes if the whole crater is to be explored. He says further: "It is agreed that if there was a meteor it must have been at least 500 feet in diameter. The occurrence of a few tons of meteoric iron in the vicinity and mingled with some of the debris on the rim and in the crater is an enigma." He goes on to favor a suggestion by Gilbert that it was a volcanic steam explosion that produced this crater, forgetting again that the real key to the situation is the presence of the meteoric iron in the way it is found to exist.

A considerable expenditure of time and money has been made in exploring this unique crater. This has been carried on largely by Mr. D. M. Barringer, to whom belongs the credit of pointing out the meteoric origin of the crater and collecting the proofs thereof. To him

I am indebted for the opportunity of conveniently visiting and examining the formation, and also for publications, charts, slides, and other material.[1]

The uncovering of a mass of millions of tons of iron containing about 8 per cent nickel would have great commercial value. Add to this the fact that analyses show the iron to contain an average of about 6/10 ounce of platino-iridium to the ton and the value is much enhanced. Besides, there is an undetermined amount of diamond present.

All of the iron examined and even the oxidized shale ball iron shows the characteristic Wiedmanstatten figures regarded as proof of meteoric origin. Such a structure, it may be remarked, is probably the result of slow cooling in the interior of a large body and under compression. This structure is stated to disappear when the iron is heated to about 900° C.

What happened at the Meteor Crater may be briefly outlined as follows: A large mass, or more probably a cluster resembling a small comet, passed so near to the earth as to be deflected sufficiently to cause it to strike. Its velocity, reduced by retardation in the air, may have been not more than two or three miles per second when it struck earth. As it penetrated the dry plain. some of the smaller and still more retarded and slower moving pieces following in the rear of the main cluster were diverged therefrom and so fell at various distances around the crater. As soon as the main body reached the wet rock layers superheated steam was generated at high pressure, pulverizing and metamorphosing the silicious rock, and producing an enormous lateral pressure which the disturbed and uplifted strata together with the horizontal compression as shown,in the structure of adjacent rock masses clearly indicate. As the mass advanced the pulverized material in its path and around it would be swept backward almost as a fluid and would expand outwardly at the same time, fracturing the adjacent rock layers, up-casting and folding back the strata, and discharging the enormous mass of pulverized and mixed rock material which now forms the circular rim. This blast would entangle the

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[1] Mr. D. M. Barringer, conceiving the impact theory to be the correct one, collected largely at his own expense, and through a period of years, the evidences thereof and has published his results in the following papers, to wit, "Coon Mountain and Its Crater," Proceedings of the Academy of Natural Sciences of Philadelphia, December, 1905; "Meteor Crater in Northern Central Arizona," read before the National Academy of Sciences at its meeting at Princeton, November 16, 1909. To these papers of Mr. Barringer reference may be made for an abundance of interesting detail with illustrations and maps.

smaller fragments of meteoric iron now found in the rim. Finally, as the masses of material came to rest there would settle back into the excavation a large part of the pulverized material leaving the sheer rock walls as they now are, upturned at various angles even to almost complete inversion in some places. The material which did not fall back to the crater would rest on the upcast walls and slope away upon the surface of the plain in a fairly symmetrical manner. In their flight through the air the iron was burning into oxide; the heat and debris were left behind in the wake or trail. What reached the earth was comparatively if not actually very cold, retaining in its interior, as it were, something of the cold of space.

It may be of interest here to present if possible a brief statement of what must happen during the flight of a meteoric mass through our air. In general, the earth's atmosphere acts so effectually as a protective sheath that only a few of the very numerous bodies variously known as shooting stars, aerolites, and meteors ever reach the earth's surface. If the velocity of a body entering from the outside is very high relatively to the earth, thirty or forty miles per second, for example, the crushing strains brought upon it by the air resistance in its path may be great enough to break it into fragments, while the high temperature of the compressed air opposing its movement melts or vaporizes the material composing it. Stony masses, like pieces of rock, would yield to fracture and dissemination more readily than masses of solid iron. This fact may itself account for so large a proportion of the bodies which reach the ground being composed of iron. Rock masses are occasionally found, surviving, perhaps, because of low entering velocity. The iron meteors are so strong as to resist enormous crushing strains. The metal iron is, however, so freely combustible that when exposed to a blast of hot, compressed oxygen it is burned into fused oxide very rapidly. So with the iron meteors in their flight. They are virtually blown upon by a highly heated blast of compressed air containing so much oxygen as to cause them to burn like tinder. The survival of a stony meteor, or aerolite, until it reaches the ground must therefore depend upon its entering the air at comparatively low velocities, or upon its being retarded in a long flight through the very thin higher air whereby it loses much of its initial speed before entering the denser air below, while the survival of an iron meteorite depends on its velocity being insufficient to develop crushing strains great enough to fracture it into small masses, and upon the size of the meteor itself, or of its fragments, if fractured. A small iron mass at high velocity will burn away so rapidly in the dense oxygen in front of it that the whole mass will be consumed and dissipated before any of it reaches ground. The whole energy of the flight will go into the trail or train. The fused iron oxide as soon as formed on its surface is blown off and left behind in the trail which marks the course of the body in the air. If, however, the iron mass or fragment is large, and its velocity insufficient for crushing or further breaking, it may not be entirely burned during its flight and some of it may reach the ground or the sea while still retaining a considerable velocity. It may bury itself in the earth to a depth more or less great. In the case of an iron meteorite there are two sources of heat energy and attendant luminosity, the high compression of the air in front of it and the wastage by combustion of iron in the hot compressed oxygen. The mass is in fact virtually blown upon by a blast oi oxygen in a high state of compression. As evidence of the rapidity and effectiveness of such combustion reference may be made to the work of the acetylene oxygen blowpipe now used to cut through masses of iron, as in clearing wrecks and the like. The product of the combustion in these cases is magnetic or black oxide of iron in a fused and perhaps partly vaporous state, and this is removed or blown off the surface of the iron mass as fast as it is formed. Melted pear-shaped drops have indeed been observed as falling out of the track or train left by a meteor in its course through the air. They are probably iron cinder or fused magnetic oxide. It will be understood from this that the energy given out as heat is not delivered to the body of the meteor as such, but is carried off in the air and oxide layer ripped off and left behind in the train. It has not been unusual to dig up a meteor seen to fall, and find it stone cold or only slightly warmed. Entering the air from space its temperature will naturally be very low, not much above absolute zero. Its flight in the air lasts so short a time that its conductivity for heat, even when it is of solid metal, is not adequate for the instant passage of heat to its interior. It can possess only a thin skin of hot material, a mere film in which the temperature gradient is very steep or abrupt, and this film is constantly blown off or removed as soon as its temperature of fusion is reached. This temperature is about 1500° C. The case may be illustrated by turning a vigorous blast of heated air upon a piece of ice supported in any way. The ice melts rapidly and the water formed is blown off as fast as it appears, while what remains is none the less ice to the end of the process. It is even possible that the blast be highly heated so as to boil the water formed without essentially changing the result of causing the ice to melt away rapidly but remain while so diminishing a piece of ice to the last. But the ice is not combustible. Let us therefore substitute for it a ball of wood or a mass of combustible and turn thereon a blast of hot oxygen or air. The combustible will burn on the outside and the heat be carried off in the products of combustion blown from it; while if we stop the experiment at any time we will find the interior of the mass remaining still solid and cold.

Hence in the case of a large iron meteor there is no such thing possible as an instantaneous vaporization of the whole mass. On entering the thin upper air it will condense the air immediately in front of it, increasing its temperature and raising the density of the oxygen to a point to begin the combustion of the outer layers of the moving mass. If the velocity be extremely high, the opposing pressure in front as it passes into lower air may be sufficient to crush the mass into fragments. The smaller pieces formed will now burn and the rate of waste by combustion be greatly increased. This process may go on until the whole is consumed and dissipated in the train. But if the velocity is not high enough for this, the mass either does not fracture or the breaking soon ceases and the remaining flight is marked by combustion or fusion and the continual cleansing of the surface of its fused products, as outlined above. If any of the mass has size enough to endure the rapid waste by oxidation, there may at the last remain a greater or less fraction of the original mass, which reaches the earth's surface in the solid and relatively cold condition, embedding itself in the earth or in the sea. The indications then are that a body which has so survived will neither be moving at an excessive velocity as compared with that of a projectile from a high-powered gun, nor be a hot body on striking, except as to a mere film of its outer surface. As such bodies rarely descend vertically they must pass through many miles of comparatively dense air when their course is more or less horizontal or inclined to the vertical. This and their irregular form renders possible a very great retardation; far exceeding in proportion that experienced by a well proportioned cannon shot in its flight. If crushing or fracturing took place, angular fragments would be split off, very irregular in form, making very poor projectiles, retarded rapidly. The crushing of the mass by opposing air pressure can be compared to the result of the explosion of a charge of nitroglycerine upon a mass of iron, the effect produced being that due to a high gas pressure suddenly formed. But the pressure which would be needed to fracture an approximately round and solid mass of cold nickel iron is very great, so great in fact that it is probable that only those meteors moving relatively to the earth at the very highest velocities would experience it. In fact it may be doubted that such fracturing often occurs with a solid iron meteorite of round form, on account of the somewhat gradual retardation, smaller in the upper air and increasing as the body reaches denser air, thus gradually robbing the body of its velocity. A large iron meteorite or a cluster of them has therefore a considerable chance of survival in spite of the rapid waste by burning, while the smaller ones may disappear by combustion while still in the air, especially if the initial velocity be high. But, entering air at a comparatively low velocity such as five to ten miles per second, an iron meteor of more than a few ounces in weight will probably survive in part. I have been particular to lay stress on these actions, as they entirely negative an idea which has been advanced to account for the failure to find large masses of embedded iron at the Arizona Crater. It has been claimed that the mass was vaporized on striking, a possibility which is *impossible*, as I am compelled to regard the matter.

The age of Coon Butte, the great Meteor Crater, is of course uncertain. How long a time has elapsed since the fall? In the absence of definite data for computation we can only guess. However, from the apparent absence of much erosion it must be comparatively recent. While the country is dry, it does rain at times and there are high winds. The climate may have been more moist in times past as is rendered probable by the evidences of water in the crater formerly. The age of certain cedar trees on the slope tend to place the date back perhaps of 500 to 1000 years. A mere surmise would be 2000 to 3000 years ago as the possible time of the meteoric fall.

It is stated that the Indian tribes inhabiting the region in a reservation just north of the railroad have an ancient tradition of the fall of a large body of fire from the sky which killed a number of their tribe. It is also stated that they now hold the spot in some superstitious awe from the fact that they send to the crater slopes for the white silica, which is sprinkled about during their ghost dances. I cannot, however, personally vouch for these statements without further investigation.

Such craters as this meteor crater if formed many thousands of years ago would probably be obliterated by erosive influences, and even in the desert the shifting sands would finally cover them. The water, the frost, vegetation, the atmosphere are against their indefinite preservation as features of the landscape. Let us imagine, however, a large body such as our moon, in a vacuum, with no atmosphere, no water, no winds, no frost, no vegetation, then, if any such impact took place the record must be left for all time; not quite unimpaired perhaps, for a subsequent impact may superpose its effect tending to obliteration of the first effect. Moreover, in the lapse of millions of years there may be accumulations of cosmic dust or small particles gathered up from space which will partly cloud over or cover the lower portions. But even in this case the higher ridges will remain. It is indeed no new idea that the lunar craters, instead of being the result of volcanic actions, may be in fact impact craters. This idea was put forward by Proctor in 1873 and further enforced by Gilbert some fifteen years or more ago. If they are volcanic then the comparatively diminutive moon has been the theatre of tremendous volcanic disturbances, which without water or other gases and vapors would be unlikely according to the views of some authorities on volcanic action on the earth. If the lunar craters are not volcanic, then the scarred face of our moon is a record of terrific impacts of bodies of all sizes, probably occurring during its early history millions if not billions of years ago. The earth must also have shared in this bombardment, the traces of which are entirely obliterated. Perhaps its surface was at that time molten. There are marked differences between the now existing volcanic craters on the earth and the lunar craters. On the moon they do not exist along any lines of weakness as on the earth, and they have not built up chains of cinder cones topped by craters of restricted dimensions. They occur on the moon helter skelter, alongside of each other, anywhere, everywhere over its much scarred surface. They exhibit the greatest range of sizes or diameters from the smallest dots visible by our most powerful telescopes to the huge basins such as Clavius nearly 150 miles across. Large craters are dotted with others, smaller in size, anywhere, it may be on the floor of the crater or in its walls or their slopes. These parasitic craters appear to be absent in such craters as Tycho and Copernicus, which, however, with some others, are distinguished by extensive systems of whitish streaks running for hundreds of miles in a general direction radially over all irregularities of surface. Unlike the earth's great volcanoes, the floor of the lunar craters is in nearly all cases considerably below the general level of the surrounding surface.

The Meteor Crater in Arizona has this same characteristic and in fact if looked down upon from above would appear like a lunar crater transplanted to earth. The proportional depression of the crater floor to the height of the upcast rim is much the same. The outer slope of the rim and its relative extent are likewise very similar. The agreement is, to say the least, highly suggestive of a similarity of origin. The lunar craters do not show great rivers of lava coursing down the slopes and covering the lower levels. There is indeed a notable absence on the moon of such evidences. Those whitish streaks around Tycho and Copernicus, bear far more the appearance of an instantaneous scattering of material in a vacuum (and therefore moving outwardly in a straight course) than they do of product of a prolonged volcanic eruption which in the case of such large craters must have lasted for years. Any such surrounding deposits would have been spread more generally and uniformly around the crater instead of in streaks. The appearances suggest a sudden splash. The central mountain or hill, so common a feature of the larger lunar craters, shows no volcanic vent. Its existence is then more compatible with the idea of a reaction, or "kick back," an inrush similar to that which occurs on dropping a stone into a pool of water, except that in the case of the lunar crater it is composed of solid fragments or more or less pulverized rock. This central hill is absent in the smaller craters, as in those comparable in size with the Arizona Crater. The most ancient craters on the moon have had time to become softened in outline and in a measure obliterated by cosmic dust. This may be the reason why so few show the system of radiating streaks so characteristic of Tycho and Copernicus. A thin lunar atmosphere, afterward lost, may have prevented their formation. The fact that the craters of Tycho and Copernicus are so clean cut, so sharply defined, so deep, free from parasitic craters or subsequent impacts, and still surrounded by the extensive, unobliterated system of streaks, would in this view, make them the result of the very latest or more recent large impacts which the moon has sustained.

The hypothesis of meteoric origin for the lunar craters has been combatted on the ground of the absence of tangential or grazing impacts. There may be some reason for this absence. If most of the effect was due to the fall of bodies moving in a general path similar to that of the moon, we could understand the case as one in which the gravitation of the moon itself tended to change the path from a horizontal direction and so prevent grazing impact. There are, however, some grooves or furrows on the moon's surface the most perfect example of which is the Great Valley of the Lunar Alps which looks very much as if made by a projectile at last arrested and in part deposited on the plain beyond. Near this also is the formation called the Straight Range which is remarkably suggestive of a glancing blow; as if a large body had failed to embed itself on the first impact and had tumbled along, ruffling the surface and shedding debris until its velocity was at last checked.

If it be correct to regard the moon as having been separated from the earth early in the history of our planetary system, there must have been a large amount of scattering at the time of separation. The earth would have retained the gases and water vapor almost wholly so that the moon would have gone off without an atmosphere. The moon and the earth also would gather up most of the material so scattered and the moon might then have accumulated its scars, or at least the earlier ones. The fall of any large mass would of course obliterate all smaller indentations made before its occurrence not only at the place of impact but for some distance around it. This seems to have occurred with such craters as Tycho and Copernicus. If we go farther back in time and think of the possible building up of the sun and planets of our system by gradual accretions such as are now taking place when a meteor enters our air, but which at some time, as many millions of years ago, occurred on a far grander scale, we can understand the craters on the moon as the last records of such a process, and the Meteor Crater in Arizona as the largest known record on the earth, all others belonging to the earliest geological periods having been obliterated.

In the solar system the survival of the fittest rules. The numerous comets with highly elliptical orbits must succumb and be gathered up by those bodies like the sun, and by the planets which perform their rounds in a less erratic way with orbits nearly circular. If the conclusion be correct that the comets actually belong to and form part of our system, then the thought is permissible that at an early period they were innumerable and that they have been reduced and obliterated in feeding those masses, like themselves originally, which, however, possessed more conservative orbits, to use that term.

That the meteoric masses which come to earth are solid and have a structure strongly suggests that they are fragments of a much larger body.

The solidity suggests either a high temperature or a high pressure due to gravitational forces, or both. Particles floating in free space could never themselves form such dense and solid aggregations. When as in the Arizona crater irons we find diamonds, we are fairly sure of high pressure having existed. When we find also a coarse crystalline structure and segregation we think of a long time of slow cooling. When we see that the solid mass is not only coarse but that the parts are divided by fine crevices or small cracks we infer the sudden relief from high compression, when the material was cold and solid. In short, we infer that we have before us a fragment of a large body which in the long lapse of time had consolidated and cooled, and which later has been torn to pieces, disrupted into fragments large and small. Was it a collision of two large bodies in space, such as may have given rise to a great, irregular nebula like that in Orion? Doubtless collisions can occur but they must be very rare.

The order of nature, however, may easily involve the more or less close passage of large orbs, either still hot or cooled off, past each other at a distance of a few millions of miles. In such a case the stupendous tidal and centrifugal actions attendant on the neutralization of gravity on a line joining the centers of the two bodies must inevitably result in crushing them, as if an irresistible force were exerted in all other directions than along the line joining them. This crushing would result in two streams or jets of material rushing out in diametrical directions at velocities of a great range of magnitudes, and they might in some cases, but not in all, be violent enough to produce very high temperatures and consequent vaporization. Each body so disrupted would then pursue its way no longer a spherical body but as a new-born spiral nebula, the internal forces of which would again set to work to gather up what matter remained outside of that widely dispersed in space. Thus new solar systems would be born from the wreck of those preceding. This involves a modification of the time-honored nebular hypothesis of La Place and is in line with the ideas of Chamberlin and Moulton in their planetesimal hypothesis.

We are led to suspect that this is indeed the process of nature, a process which has gone on from an infinite or indefinite past and which will continue as long as a ray of light can traverse the ether of space. To me the idea that the universe is like a clock running down is repugnant. Even though uranium, radium, thorium are disintegrating gradually, and we have no evidence of their generation by any process, there may be some source, as under the enormous pressures within a large orb, where such elements and perhaps others of still higher atomic weight and greater instability arise. Here again the law of survival holds, the electrons in the atom having unstable orbits being cast out in reducing the body to simpler and more stable forms, just as in the solar system the erratic comets must be eventually swallowed up and lost.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 20. — March, 1912.

AN ALGEBRA OF PLANE PROJECTIVE GEOMETRY.

By H. B. Phillips and C. L. E. Moore.

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Presented by H. W. Tyler, February 14, 1912. Received January 29, 1912.

Introduction.

1. The Ausdehnungslehre of Grassmann[1] has been applied to problems in geometry in two ways. In the form of vector analysis it has been used in solving problems of a metrical type. In the form of point analysis (with homogeneous coördinates as a basis) it has been used in problems of a descriptive nature. In projective geometry both of these methods have certain advantages and also certain disadvantages. The values of distances and angles occurring in vector analysis are useful as variables in terms of which to express projective relations. Yet the fact that these quantities are invariant under Euclidean motion has no place in projective geometry. The ternary form of the point algebra is of great value, but it is a decided disadvantage that λA and A (where A is a point) though distinct are not descriptively distinguishable. It is our aim in this paper to show how this coefficient λ can be interpreted as an angle invariant under a group of motions determined by the algebra itself and thus while using the homogeneous form retain the essential advantages of the metrical system.

We first develop the two systems of analysis in a purely projective way. Assuming that points and lines are represented by letters and that addition follows the usual laws, we find that there must exist exceptional elements somewhere in the plane. In fact, expressions λA, where A is a point and λ infinite, are not subject to the laws of addition. In the language of coördinate geometry such points correspond to infinite values of the coördinates and hence lie on a line. Likewise the lines λa where a is a line and λ infinite are exceptional lines passing through a point. Thus in such a system of algebra there exists a fixed point and a fixed line. We define our additions relative to these. In the vector addition the sum of two points A and B is a point C such that the harmonic of the singular line with respect to C and the fixed point is the harmonic of the same line with respect to A and B. This addition is characterized

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[1] Gesammelte Werke, Vol. I, 1896.

by the fact that λA is in general distinct from A. In the point addition the sum of two points A and B is the harmonic of the singular line with respect to those points. For this addition λA is in general coincident in position with A. The two additions are closely related. In fact, each is representable in terms of addition processes of the other kind. When the singular line is taken at infinity these additions agree essentially with those of Grassmann.

2. In the case of point addition A and λA have the same position. According to Möbius these quantities differ in weight. To give a geometric interpretation to this weight we conceive a point as a sort of double fan-shaped spread consisting of all the lines through the point and between two limiting lines. The size of the point is then measured by the angle (directed) between these limiting lines, and the weight of the point is this angle. We are thus led to define a species of angle in which the total angular magnitude about a point is infinite. The finite angle determined by two lines is that one which does not contain the singular point.

In the same way we represent a line by a segment of itself and the magnitude of the line by the length of that segment. We thus define a sort of distance in which the locus of point at a fixed distance from a given point is a straight line. This distance between two points is the dual of the angle between two lines. It has a definite algebraic sign and along each line not passing through the singular point assigns a definite positive direction.

Distance and angle are invariant under a three-parameter group of collineations (projectively equivalent to motions leaving area invariant) for which the singular point and line are fixed elements. These collineations leave invariant the correlations having the fixed point and line as coincidence loci. There are two cases depending on whether the fixed point is on the line or not. The first of these gives a distance theory similar to that in a minimum plane. The second does not occur as a special case of distance defined relative to a conic.

3. In terms of this linear distance and angle there is a very simple theory of the triangle. Most rational relations of ordinary trigonometry involving distances and sines of angles are replaced by similar relations involving distances and angles. In case the singular point is on the singular line there is a linear relation between the sides and also between the angles of a triangle making both distance and angle similar to angle in ordinary geometry. If the point is not on the line, however, any three parts determine the triangle. Every part is then rationally expressible in terms of any three, and similar triangles do not exist.

In this system there is no right angle, and distance from point to line does not properly exist. There is, however, a number associated with a point and line which has some of the properties of distance from point to line. We define an area that has the usual sum properties and in fact becomes identical (after proper choice of unit) with Euclidean area when the singular line is thrown to infinity.

In the course of the work we use the notations AB and ABC for segment and area respectively. Interpreting these as products we find that they have the properties of Grassmann's products. They are definable in terms of our distance, angle and area, in the same way that outer products are expressible in metrical concepts of Euclidean geometry.

The method used in this paper is not postulational. In fact, we are more interested in the results than in the method of obtaining them. In some cases our definitions have not been as simple as possible. In accordance with our primary aim we have interpreted quantities necessarily existing in the algebra instead of introducing notions that were not required.

4. It is our purpose to use this scheme in the solution of problems in projective geometry. Two ways of doing this are suggested. In the first place the above scheme of distance and angle gives us a great variety of coördinate systems. We may, for example, represent a point by its distance from two fixed points (singular point not on singular line) and a line by the angles it makes with two fixed lines. The equations of point and line are then of first degree and the incidence relation bilinear. The distance between two points is a bilinear function of their coördinates. Similarly for the angle between two lines. The differential of arc is of the form

$$xdy - ydx.$$

A kind of curvature is easily defined and thus we build up a differential projective geometry of plane curves.

In the second place we may start with the theory of the triangle. In terms of our distance, angle and area, we can then express descriptive relations such as perspectivity, inscribability in a conic, etc., and by processes similar to those in Euclidean geometry determine from these their projective consequences. This is especially easy since the expressions determining one part of a triangle in terms of three others are all rational. It is our intention to develop these applications in a later paper.

§ 1. Addition.

5. The addition of two points **A**, **B** naturally divides itself into two cases depending on the significance given to $\lambda\mathbf{A}$. In metric geometry these two additions have been defined in terms of metric concepts. If

$\lambda\mathbf{A}$[2] is a point different in position from **A**, the addition familiar to all is the well known vector addition. If $\lambda\mathbf{A}$ is a point coincident in position with **A**, but differing from it in magnitude, the sum of two points is commonly defined as the centroid of the two points. We shall here define these two additions in terms of projective notions.

Vector Addition.

6. To define the sum of two points **A**, **B** when λ times a point differs in position from it, we assume a line f as reference line and a point O as origin. Then the sum $\mathbf{A} + \mathbf{B}$ is the point **C** determined as follows:

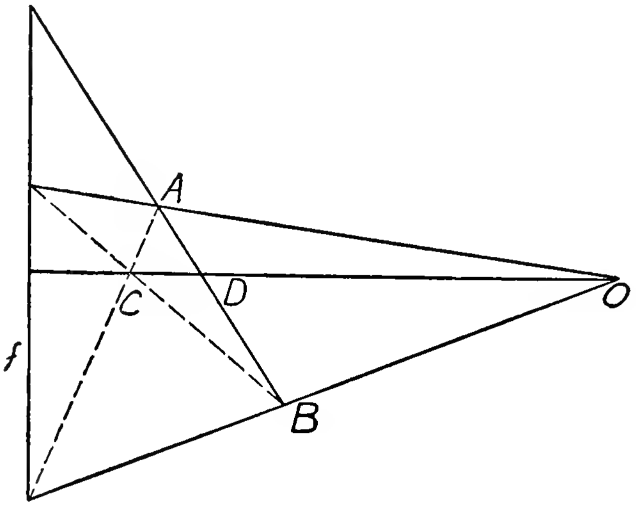

FIGURE 1.

Let D be the harmonic of f with respect to A, B. Then take a point C so that D is the harmonic of f with respect to C, O. The point C thus obtained is the point required, and we express the relation between the points by the equation

$$\mathbf{A} + \mathbf{B} = \mathbf{C}. \tag{1}$$

The geometric construction for C is shown in Figure 1, and is seen to be the ordinary vector construction where the line f has replaced the line at infinity.

From the above definition the point

$$\mathbf{A} + \mathbf{A} = 2\mathbf{A}$$

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[2] In this paper capitals will be used for points, small letters for lines. Points or lines occurring as algebraic quantities will be represented by clarendon type, their magnitudes by italics. Geometric points or lines may, however, be represented by italics when no ambiguity results. Greek letters will be used for numbers.

is the point on the line OA such that A is the harmonic of f with respect to 2A, O. The point

$$\mathbf{2A} + \mathbf{A} = \mathbf{3A}$$

from the definition is constructed as follows: Let C be the harmonic of f with respect to 2A, A and then construct the point 3A so that C is the harmonic of f with respect to 3A, O. It is at once seen from the construction of 2A that C is the point $\frac{3A}{2}$. From the theory of cross ratios it is also seen that the relation between 3A, A is expressed by the cross ratio

$$(O,f \mid 3A,\ A) = 3.$$

In like manner the points $\lambda\mathbf{A}$ for integral values of λ are constructed. If λ is the reciprocal of an integer μ, the point $\lambda\mathbf{A}$ can be constructed thus: Take a point B not on the line OA and construct the points

$$\mathbf{B},\ \mathbf{2B},\ \mathbf{3B},\ \ldots\ldots\ \mu\mathbf{B}.$$

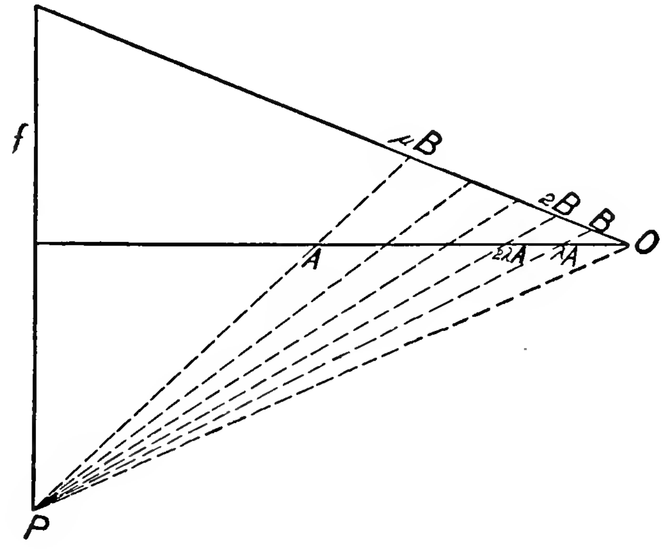

FIGURE 2.

Connect $\mu\mathbf{B}$ to $\mathbf{A}$ and let the line cut f in P. Draw a line from the point B to P. Where PB cuts OA is the point required, for the same harmonic relations hold among the A's as among the B's. The construction of the points $\lambda\mathbf{A}$ for rational values of λ is now evident. For irrational values of λ the construction is obtained by limiting processes. From the theory of cross ratios it is seen that the relation between $\mathbf{A}$ and $\lambda\mathbf{A}$ is expressed by the cross ratio

$$(\mathrm{O,f} \mid \lambda\mathrm{A},\ \mathrm{A}) = \lambda,$$

and every point on the line OA can be represented in the form $\lambda\mathbf{A}$.

7. The point

$$\lambda\mathbf{A} + \mu\mathbf{B},$$

where A and B are not collinear with O, is constructed in the same way as the point $\mathbf{A} + \mathbf{B}$, and has the following relations to the points A and B.

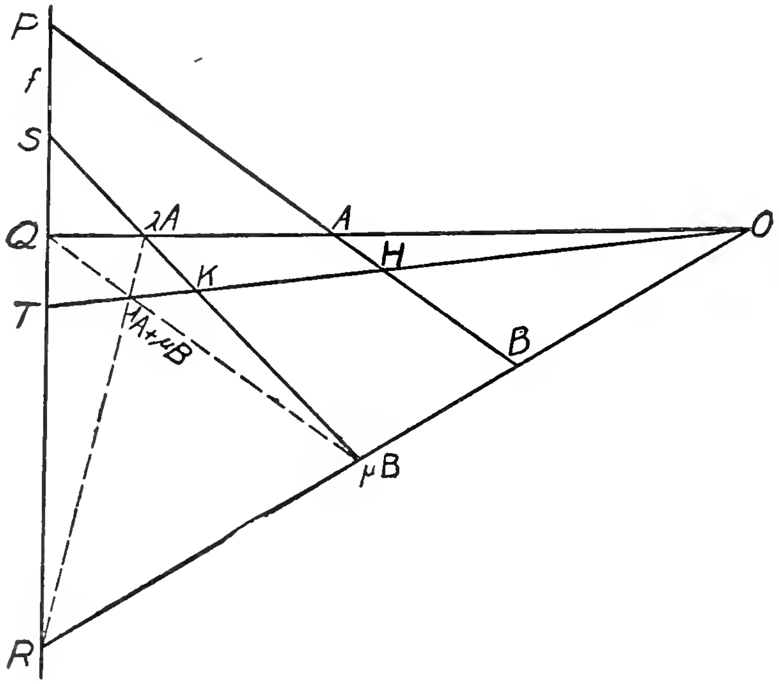

Figure 3.

(1) The point H where the line joining O to $\lambda\mathbf{A} + \mu\mathbf{B}$ cuts the line AB is such that

$$(\mathrm{Hf} \mid \mathrm{AB}) = -\frac{\mu}{\lambda}$$

$$\lambda\mathbf{A} + \mu\mathbf{B} = (\lambda + \mu)\,\mathbf{H}. \qquad (2)$$

In order to prove the above relations we shall first prove the following lemma:

If two lines intersecting in O and cutting f in Q and R are cut by two other lines (intersecting f in P, S) in A, C and B, D respectively, and if through O any arbitrary line is drawn cutting AB in H, CD in K, and f in T, then

$$\frac{(\mathrm{OQ} \mid \mathrm{AC})}{(\mathrm{OR} \mid \mathrm{BD})} = \frac{(\mathrm{HP} \mid \mathrm{AB})}{(\mathrm{KS} \mid \mathrm{CD})}.$$

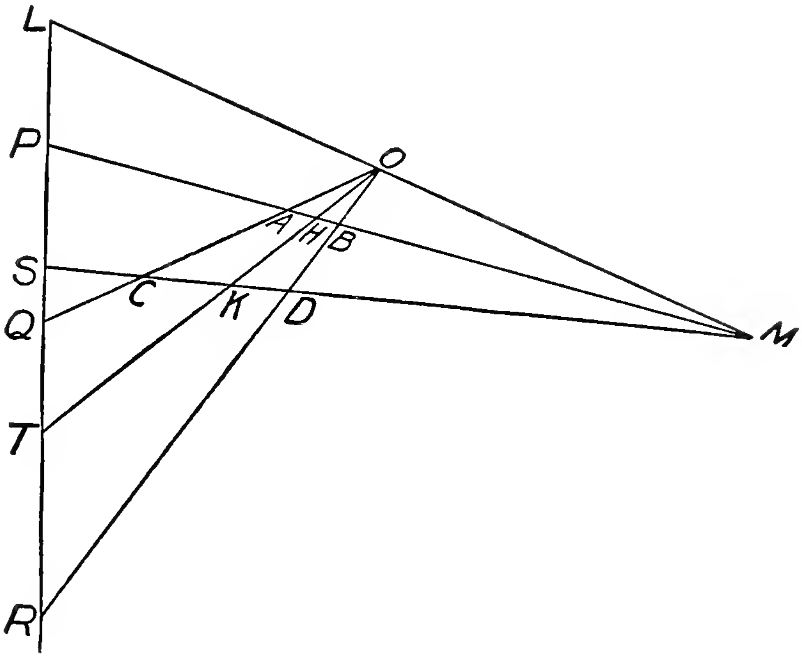

FIGURE 4.

Let M be the intersection of AB and CD, and project all points on f from O and M. The two ratios above can then be written as follows:

$$\frac{(OQ\,|\,AC)}{(OR\,|\,BD)} = \frac{(LQ\,|\,PS)}{(LR\,|\,PS)} = (RQ\,|\,PS)$$

$$\frac{(HP\,|\,AB)}{(KS\,|\,CD)} = \frac{(TP\,|\,QR)}{(TS\,|\,QR)} = (SP\,|\,QR);$$

but

$$(RQ\,|\,PS) = (SP\,|\,QR),$$

which proves the lemma.

If we apply the above lemma to Figure 3, replacing C by λA, D by μB, and K by $\frac{1}{2}(\lambda A + \mu B)$, it is at once seen that H divides AB in the cross ratio $-\frac{\mu}{\lambda}$ with respect to f. For, in this case,

$$(KS\,|\,CD) = -1,$$

$$(OQ\,|\,AC) = \frac{1}{\lambda},$$

$$(OR\,|\,BD) = \frac{1}{\mu}\cdot$$

From which it follows that

$$(HP\,|\,AB) = -\frac{\mu}{\lambda}\cdot$$

This shows that H is independent of the position of O.

To prove the second relation connecting A, B, H we have from the lemma

$$\frac{(\mathrm{OQ}\,|\,\mathrm{A}\;\lambda\mathrm{A})}{(\mathrm{OT}\,|\,\mathrm{HK})} = \frac{(\mathrm{BP}\,|\,\mathrm{AH})}{(\mu\mathrm{BS}\,|\,\lambda\mathrm{A}\;\mathrm{K})},$$

and, from the theory of cross ratios,

$$(\mathrm{OQ}\,|\,\mathrm{A}\;\lambda\mathrm{A}) = \frac{1}{\lambda},$$

$$(\mathrm{BP}\,|\,\mathrm{AH}) = \frac{\lambda+\mu}{2},$$

$$(\mu\mathrm{BS}\,|\,\lambda\mathrm{AK}) = 2.$$

Therefore

$$(\mathrm{OT}\,|\,\mathrm{HK}) = \frac{2}{\lambda+\mu} \quad \text{or} \quad (\mathrm{OT}\,|\,\mathrm{KH}) = \frac{\lambda+\mu}{2}.$$

This last relation is equivalent to the statement that

$$\mathbf{K} = \frac{\lambda+\mu}{2}\mathbf{H}.$$

But

$$\mathbf{K} = \tfrac{1}{2}(\lambda\mathbf{A} + \mu\mathbf{B}).$$

Therefore

$$\lambda\mathbf{A} + \mu\mathbf{B} = (\lambda+\mu)\,\mathbf{H}. \tag{2}$$

8. From the construction of $\mathbf{A}+\mathbf{B}$ the sum is seen at once to obey the following algebraic laws :

$$\mathbf{A}+\mathbf{B} = \mathbf{B}+\mathbf{A},$$

$$\lambda\mathbf{A} + \mu\mathbf{A} = (\lambda+\mu)\,\mathbf{A}.$$

If $\mathbf{A}+\mathbf{B} = \mathbf{A}+\mathbf{C}$ then $\mathbf{B} = \mathbf{C}$.

The associative law

$$(\mathbf{A}+\mathbf{B})+\mathbf{C} = \mathbf{A}+(\mathbf{B}+\mathbf{C}) = \mathbf{A}+\mathbf{B}+\mathbf{C}$$

evidently holds for points on a line passing through O. To prove that it holds for any three points **A**, **B**, **C**, project them on a line drawn through O from two different points P, Q on f. Let the projections be $\mathbf{A}'$, $\mathbf{B}'$, $\mathbf{C}'$ and $\mathbf{A}''$, $\mathbf{B}''$, $\mathbf{C}''$. The sum $\mathbf{A}+\mathbf{B}+\mathbf{C}$ will project into $\mathbf{A}'+\mathbf{B}'+\mathbf{C}'$ and $\mathbf{A}''+\mathbf{B}''+\mathbf{C}''$. The sum $\mathbf{A}+\mathbf{B}+\mathbf{C}$ will then be at the intersection of the line joining P to $\mathbf{A}' + \mathbf{B}' + \mathbf{C}'$ with the line joining Q to $\mathbf{A}'' + \mathbf{B}'' + \mathbf{C}''$, which is independent of the way in which **A**, **B**, **C** are combined.

9. For the dual of the above addition we assume a point O′ as reference point, and a line f′ as reference line. Then from duality we see that the lines λa all pass through the same point on f′. The sum $\mathbf{a} + \mathbf{b}$ is formed by drawing a line c harmonic of O′ with respect to a, b. Then drawing the line d so that c is the harmonic of O′ with respect to f′, D, the relation between c, d is

$$\mathbf{d} = 2\,\mathbf{c}.$$

The relations between λa, μb, a, b are the same as in the case of points. That is, the line h joining the point of intersection of f′ and $\lambda\mathbf{a} + \mu\mathbf{b}$ with the point of intersection of a, b is such that

$$(\mathrm{hO}'|\mathrm{ab}) = -\frac{\mu}{\lambda} \tag{1}$$

$$\lambda\mathbf{a} + \mu\mathbf{b} = (\lambda + \mu)\,\mathbf{h}. \tag{2}$$

The reference elements O′, f′ need not be the same as O, f. However, if the addition of points and its dual are to be used together, the line joining λA, λB should be λ times the line joining A, B. The line joining λA to λB intersects the line AB on f, for λA and λB (for variable λ) are two projective ranges with O as self-corresponding point, and consequently the ranges are perspective. The line f joins corresponding points (corresponding to the infinite value of λ) and therefore lines joining pairs of corresponding points must pass through the same point on f. Then if the line joining λA, λB is to be λ times AB the line f′ must coincide with f. The dual argument will show that O′ should coincide with O. The fundamental or reference system for this vector addition then consists of a line f and a point O.

The line f is exceptional in the addition for there is no way shown of finding the sum of two distinct points on this line.

Point Addition.

10. In this case $\lambda\mathbf{A}$[3] is coincident in position with **A** but differs from **A** in magnitude. The number λ indicates the magnitude of $\lambda\mathbf{A}$. In the case of vector addition we saw that all points on a line through O

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[3] Throughout the discussion of point addition points denoted by **A**, **B**, **C**, . . . will always be understood to be unit points.

can be represented as multiples of one of them. Then if an arbitrary line AB, not passing through O, is drawn in the plane, all points on a line through O can be expressed as multiples of the point in which this line cuts AB. Now project all points of the plane on the line AB. Each point in the plane will be uniquely represented on AB if we use the following convention for magnitude. Let K be any point and let OK intersect AB in C. If $\mathbf{K} = \lambda \mathbf{C}$ we shall say that the projection on AB of the point K is the point λC. That is, the point in which K projects is considered as having a magnitude λ and is coincident in position with C. We thus see that all points on OK will project into the same point C, but the projection of each point will be looked upon as having a different magnitude. Now to find the sum $\lambda \mathbf{A} + \mu \mathbf{B}$ we will consider $\lambda \mathbf{A}$ and $\mu \mathbf{B}$ as represented vectorially and find the vector sum, then project the three point $\lambda \mathbf{A}$, $\mu \mathbf{B}$, $\lambda \mathbf{A} + \mu \mathbf{B}$ on AB. The projections will have the magnitudes λ, μ, $\lambda + \mu$ (see equation (2)) respectively. If the point $\lambda \mathbf{A} + \mu \mathbf{B}$ projects into $(\lambda + \mu)\,\mathbf{C}$ then for points on the line AB we shall say that

$$\lambda \mathbf{A} + \mu \mathbf{B} = (\lambda + \mu)\,\mathbf{C}.$$

From equation (2) the point C is such that

$$(\mathrm{Cf} \mid \mathrm{AB}) = -\frac{\mu}{\lambda}.$$

The definition of this sum is then independent of the origin chosen for the vector addition. The reference element for this addition consists of the line f and we have : *The sum of two points* $\lambda \mathbf{A}$, $\mu \mathbf{B}$ *of magnitude* λ, μ *respectively is a point* $(\lambda + \mu)\,\mathbf{C}$ *of magnitude* $\lambda + \mu$, *dividing* A, B *in the cross ratio* $-\frac{\mu}{\lambda}$ with respect to f.

The line f is a line of exceptional points. The sum of two distinct points on this line is not defined and the sum of two coincident points on f may be any given point of the plane, and therefore violates the uniqueness of the sum ; besides, λ times a point P on f is not necessarily a point coincident in position with P.

The magnitude of the sum was seen to be the sum of the magnitudes. The difference

$$\mathbf{A} - \mathbf{B}$$

will be a point P of magnitude zero such that

$$(\mathrm{Pf} \mid \mathrm{AB}) = 1,$$

and consequently P must be on f. This point P is an exceptional point then because it is of zero magnitude and yet is not algebraically equivalent to zero. The line f plays the role of the line at infinity, and the point P of zero magnitude is analogous to zero times infinity.

11. By duality we obtain a definition for the sum of two lines $\lambda\mathbf{a}$, $\mu\mathbf{b}$ of magnitudes λ, μ respectively. For this addition we assume a fundamental point F and

$$\lambda\mathbf{a} + \mu\mathbf{b}$$

is a line $\mathbf{c}$ of magnitude $\lambda + \mu$ such that

$$(\mathrm{CF}\,|\,\mathrm{ab}) = -\frac{\mu}{\lambda}.$$

The point F is an exceptional point, i. e. all the lines passing through F are exceptional in the same sense in which the points on f were exceptional. The difference $\mathbf{a} - \mathbf{b}$ is the line of zero magnitude joining the point F to the intersection of a and b. Here also the line of zero magnitude passing through F is not algebraically equivalent to zero but indeterminate. It is analogous to zero times infinity. The complete fundamental system then consists of a line f and a point F.

12. Starting with the definition of point addition the vector addition could be derived from it. Thus take a fixed point $\mathbf{O}$ and represent any point A in the plane by the difference $\mathbf{O} - \mathbf{A}$. The addition of these quantities will lead exactly to the vector addition with which we started. The two additions are then related in such a way that either can be derived from the other.

From the definition of point addition as derived from the vector addition it follows that the point addition obeys the same algebraic laws as the vector addition.

Vectorially any point in the plane can be expressed in terms of two independent points $\mathbf{A}$, $\mathbf{B}$, where the line AB does not pass through O. Then choosing λ, μ properly any point in the plane can be represented by $\lambda\mathbf{A} + \mu\mathbf{B}$. For the point addition, however, $\lambda\mathbf{A} + \mu\mathbf{B}$ represents only the points of the line AB, where neither A nor B is on f. In this addition, however, any point $\mathbf{X}$ of the plane can be expressed as

$$(\lambda + \mu + \nu)\,\mathbf{X} = \lambda\mathbf{A} + \mu\mathbf{B} + \nu\mathbf{C}$$

where $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ are three non-collinear fixed unit points not on f. That is, the numbers λ, μ, ν can be so determined that this relation holds for any point whatever of the plane. To show this connect X to B. This line will cut AC in Q, which can be expressed in terms of $\mathbf{A}$ and $\mathbf{C}$. Then $\mathbf{X}$ can be expressed in terms of $\mathbf{Q}$ and $\mathbf{B}$. Thus

$$(\lambda + \nu)\,\mathbf{Q} = \lambda\mathbf{A} + \nu\mathbf{C}$$

$$(\lambda + \mu + \nu)\,\mathbf{X} = (\lambda + \nu)\,\mathbf{Q} + \mu\mathbf{B} = \lambda\mathbf{A} + \mu\mathbf{B} + \nu\mathbf{C}.$$

Since $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ are linearly independent, if

$$\lambda + \mu + \nu = 0$$

then X is on f.

From the above equations

$$(\lambda + \mu + \nu)\,\mathbf{X} - \mu\mathbf{B} = (\lambda + \nu)\,\mathbf{Q}.$$

Hence

$$(\mathrm{QP}\,|\,\mathrm{XB}) = \frac{\mu}{\lambda + \mu + \nu}$$

where P is the point in which BQ cuts f. Similar relations involving λ, ν can be obtained. Since λ, μ, ν are proportional to uniquely determined cross ratios the expression for X is unique.

§ 2. Distance and Angle.

13. We have considered two kinds of addition, either of which is expressible in terms of the other. The vector addition gives for the points of the plane a non-homogeneous, two-dimensional representation, the point addition, a homogeneous three-dimensional. The latter is more satisfactory for descriptive problems and will be assumed as the fundamental addition throughout the remainder of this paper. It has been remarked that expressions of the form $\mathbf{B} - \mathbf{A}$, when $\mathbf{A}$ and $\mathbf{B}$ are unit points, then combine according to the vector addition. Through a study of their expressions we shall derive a sort of distance that is intimately connected with the subject under discussion.

14. Vectors. We have seen that $\mathbf{B} - \mathbf{A}$ represents a point of zero magnitude on f. We might infer that, if

$$\mathbf{B} - \mathbf{A} = \mathbf{D} - \mathbf{C},$$

the lines AB and CD pass through a common point on f. This is proved by writing the equality in the form

$$\mathbf{A} + \mathbf{D} = \mathbf{B} + \mathbf{C}.$$

The line f thus has the same harmonic E with respect to A, D and B, C. Let AD and BC cut f in P and Q. Then from the intersection of AB and CD the points A, E, D, P and B, E, C, Q are perspective. Since f joins two corresponding points, it must pass through the intersection of AB and CD. Writing the equality in the form

$$\mathbf{A} - \mathbf{C} = \mathbf{B} - \mathbf{D}$$

we see also that AC cuts BD on f. Thus the relation of the four points is shown by the diagram (Figure 5).

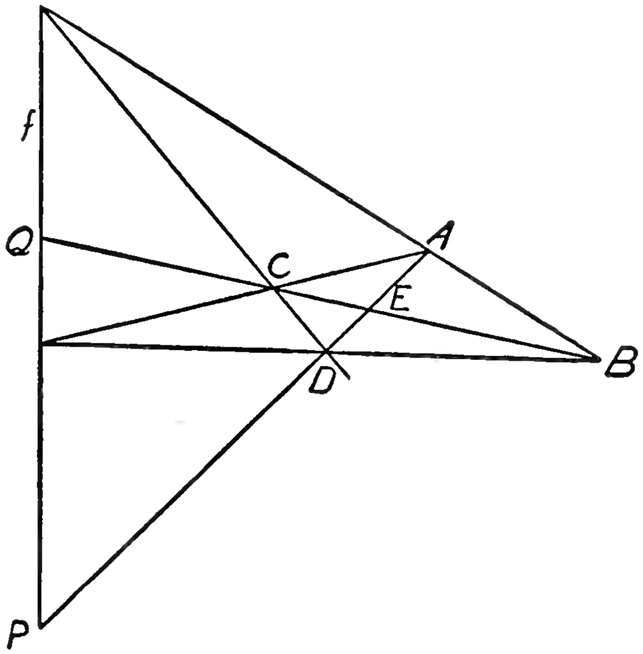

FIGURE 5.

Conversely, if the points A, B, C, D have the positions shown in the figure, f has the same harmonic with respect to A, D and B, C, or

$$\mathbf{A} + \mathbf{D} = \mathbf{B} + \mathbf{C}.$$

Consequently,

$$\mathbf{B} - \mathbf{A} = \mathbf{D} - \mathbf{C}.$$

If the four points lie on a line cutting f in P, we project, from some other point on f, the points A, B to M, N on a second line through P. Then from the intersection of MC and f we project N to D′ on AB. By construction

$$\mathbf{B} - \mathbf{A} = \mathbf{N} - \mathbf{M} = \mathbf{D}' - \mathbf{C}$$

Hence, if

$$\mathbf{B} - \mathbf{A} = \mathbf{D} - \mathbf{C},$$

the points **D** and **D′** must coincide. The relation of the four points is shown in Figure 6.

The quantity **B** — **A** has properties very similar to those of the vector AB in the ordinary vector analysis. In fact, the expressions **B** — **A** add exactly like vectors if the line f is at infinity. On account of this similarity we shall use the term vector to indicate the quantity **B** — **A**.

If

$$\mathbf{B} - \mathbf{A} = \lambda\,(\mathbf{D} - \mathbf{C}) \tag{3}$$

we might say that AB is λ times as long as CD. In what follows we shall assume this relation of lengths only when the points A, B, C, D lie on a line. In that case A, B can be expressed as linear functions of C, D, those points being assumed to be distinct and not on f. Since the sum of coefficients in any linear point identity must be zero, the expressions will be

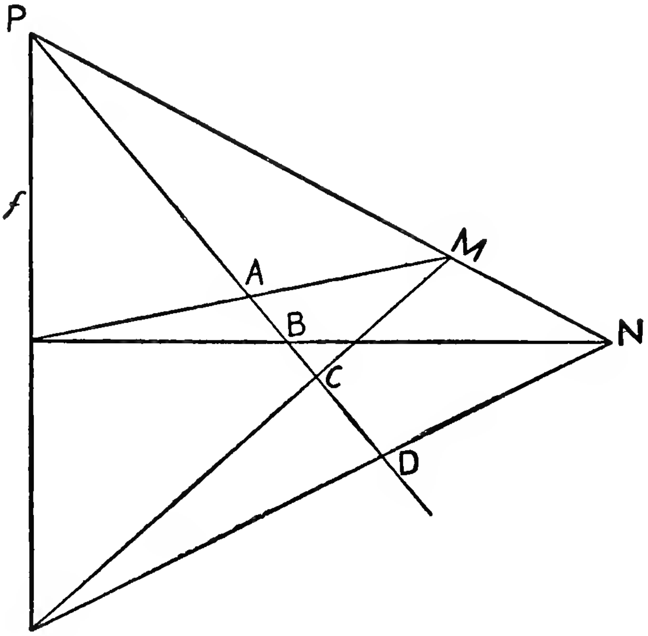

FIGURE 6.

$$\mathbf{A} = \lambda_1\,\mathbf{C} + (1 - \lambda_1)\,\mathbf{D},$$
$$\mathbf{B} = \lambda_2\,\mathbf{C} + (1 - \lambda_2)\,\mathbf{D}.$$

Then

$$\mathbf{B} - \mathbf{A} = (\lambda_1 - \lambda_2)\,(\mathbf{D} - \mathbf{C}).$$

Hence

$$\lambda = \lambda_1 - \lambda_2.$$

Now from (2) we have

$$-\frac{1 - \lambda_1}{\lambda_1} = (AP\,|\,CD)$$

where P is the intersection of CD with f. Hence from the properties of double ratios

$$\lambda_1 = (AC\,|\,DP),$$
$$\lambda_2 = (BC\,|\,DP).$$

And consequently

$$\lambda = (\mathrm{AC} \mid \mathrm{DP}) - (\mathrm{BC} \mid \mathrm{DP}). \tag{4}$$

It is to be observed that λ is finite for all positions of A and B distinct from P, but becomes infinite when one of these points coincides with P. One of the points A or B being fixed, there is an unique position of the other which gives λ a particular value.

Distance.

15. In this way we determine the relation between the magnitudes of vectors on lines intersecting on f, but arrive at no relation between vectors not so situated. To obtain a more general relation we define distance as a scalar quantity, or number, determined by two points not on f and such that distances $\overline{\mathrm{AB}}$[4] along any line are proportional to the corresponding vectors $\mathbf{B} - \mathbf{A}$. In symbols

$$\text{distance } \mathrm{AB} \equiv \overline{\mathrm{AB}} = \mathrm{K}(\mathbf{B} - \mathbf{A})$$

when K is a constant for pairs of points A, B on a given line but may (and usually does) change from line to line.

It is not obvious that there exists a distance satisfying the above definition. We shall first show (if it exists) what such a distance must be. We shall find that it is not unique and then shall make a further assumption of a function theoretic nature. Finally we prove that the distance found has the properties required.

From the definition we see that for points on a line, if

$$\mathbf{B} - \mathbf{A} = \lambda\,(\mathbf{D} - \mathbf{C}),$$
$$\overline{\mathrm{AB}} = \lambda\overline{\mathrm{CD}}.$$

From the latter equation follows the former provided $\overline{\mathrm{AB}}$ is not zero. In particular

$$\overline{\mathrm{AB}} = -\,\overline{\mathrm{BA}} \tag{5}$$

showing that distance is directed. Putting in this equation $\mathbf{B} = \mathbf{A}$, it follows that

$$\overline{\mathrm{AA}} = 0. \tag{6}$$

Furthermore, since

$$\mathbf{B} - \mathbf{A} + \mathbf{C} - \mathbf{B} = \mathbf{C} - \mathbf{A},$$

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[4] The notation $\overline{\mathrm{AB}}$ will be used to denote the distance from A to B.

for collinear points

$$\overline{AB} + \overline{BC} = \overline{AC}. \tag{7}$$

16. Distance on a line. The definition of distance can be satisfied for points *on a given line* in two ways.

(1) There may exist two points C, D on the line such that $\overline{CD}$ is finite and not zero. For every number λ and point A of CD there exists an unique point B on CD such that

$$\mathbf{A} - \mathbf{B} = \lambda\,(\mathbf{C} - \mathbf{D}).$$

Hence there exists an unique point on the line at any given distance from the point A.

(2) There may exist two distinct points C, D on the line such that $\overline{CD}$ equals zero. In this case the above equation shows that the distance between any two points on the line CD (but not on f) is zero. For the point P in which CD cuts f, λ is infinite. Hence

$$\overline{AP} = \infty \cdot 0$$

is indeterminate. We assume that this distance may have any value whatever. Here again we find an unique point at a distance not zero from A.

Along most lines our distance will be of the first type. Along certain lines, however (analogous to minimal lines in metric geometry), distance will be of the second type.

17. Distance in the plane. Along each line through a point A is a single point at a given distance from A. There is a certain locus of these points. We assume that this locus is an analytic curve. Since it cuts each line through A in a single point it is then a straight line. Thus the locus of points at a given distance from a given point is a straight line.

We assume that there exist distances $\overline{AB}$ not zero. Let

$$\overline{AB} = k$$

where k is a constant not zero and A, B points not on f. If A is held fixed B describes a line b cutting f in P. If B is held fixed A describes a line a cutting f in a point Q. Distance along any line through A except AP is of type (1). Along AP it is of type (2). Similarly distance along every line through B except BQ is of type (1). Let the intersection of AP and BQ be F. Through any point A_1 except F there passes a line A_1A or A_1B along which distance is of type (1). Therefore, for any such point A_1 there exists a line of points b, such that $\overline{A_1B_1} = k$. The only line through A_1 for which distance is of type (2) is the line joining A_1 to the intersection of b_1 and f. The intersection of two such lines must be exceptional, and since F is the only exception it follows that along any line through F the distance between two points not on f is zero and conversely if the distance between two non-coincident points is zero, their joining line passes through F.

We have just shown that if in the relation

$$\overline{AB} = k$$

A is held fixed, B describes a line b cutting f in a point P on the line AF. To determine more exactly this relation between A and b we consider the pairs of points A, B along a line CD not passing through F. On this line A and B satisfy an equation

$$\mathbf{B} - \mathbf{A} = \mathbf{D} - \mathbf{C}$$

where C, D is a particular pair. From the construction for equal vectors it is seen that A, B are corresponding points of a collineation on CD for which P is the only double point. In general to each point A corresponds a line b and for fixed B, A lies on a line. Hence to points A on a line CD correspond lines b through a point. Furthermore, these lines b pass through points B which are projective on CD with A. The correspondence between A and b is therefore a correlation. Since A and B coincide only on f, that line is the locus of points lying on their corresponding lines. To a point P on f corresponds a line through P. The distance from P to any point of this line being finite the distance between ordinary points on the line must be zero. Hence the line passes through F. This is true whether we hold A or B fixed on f. Hence F and f are corresponding elements in the correlation.

The preceding results may be summed up in the statement that if $\overline{AB}$ and $\overline{CD}$ are equal, B and D lie on the correspondents of A and C with respect to a correlation in which F and f are corresponding elements and f the coincidence locus. The construction of these correlations depends on whether F is or is not on f.

18. Point F on line f. We first consider the case in which the point F is on the line f. We have seen that the locus of points at a given distance from a point A is a line through the intersection of FA with f. In the present case all such lines pass through F. The correlation that determines equal distance is degenerate with F as singular point. The distance from this point to any point whatever is indeterminate.

Take two lines AC and BD passing through F. Since all points of BD are at the same distance from A and all points of AC at the same distance from D, and $\overline{AB} = -\overline{BA}$,

$$\overline{AB} = \overline{AD} = \overline{CD}.$$

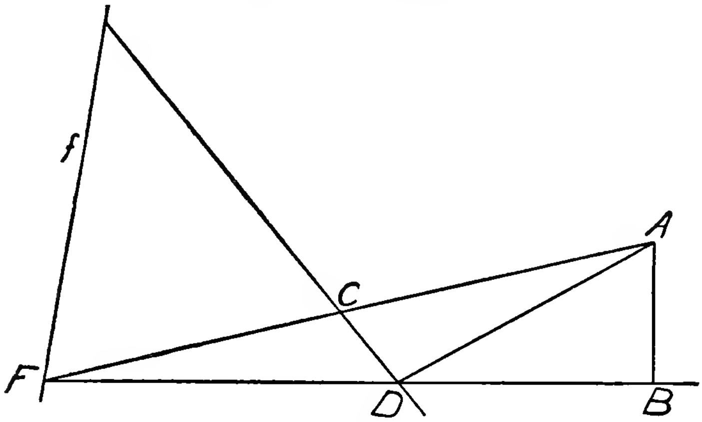

FIGURE 7.

Therefore the distance from any point of a line through F to any point of another line through F is constant. The distance between two points depends only on the lines joining them to F.

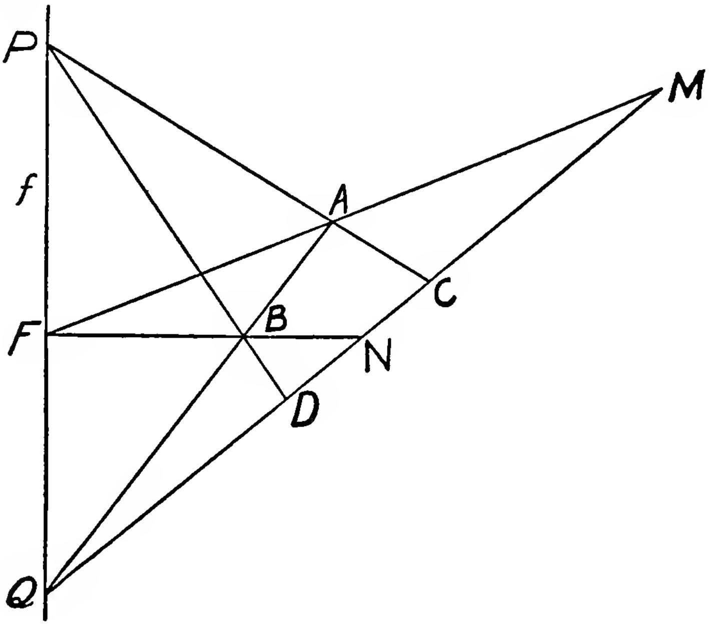

FIGURE 8.

Take any line CD, not passing through F, as a scale. Let distances along this line be proportional to the corresponding vectors. Then any distance AB is equal to the distance CD into which it projects from F. The ratio of two vectors on a line is a difference of double ratios involving the end points of the vectors and the point of intersection of their line with f. That ratio is then unchanged when we project from F upon another line. Therefore distances as here constructed are proportional along any line to the corresponding vectors and consequently satisfy our definition.

In this case equal vectors are always of equal length, i. e. the opposite sides of a parallelogram are equal (parallel lines intersecting on f). This is shown in Figure 8. Let ABCD be a parallelogram. Draw FA and FB to cut CD in M and N. Then since the vectors MN and CD are equal,

$$\overline{\mathrm{AB}} = \overline{\mathrm{MN}} = \overline{\mathrm{CD}}.$$

We shall see later that if F is not on f, equal vectors on different lines are not in general of equal length.

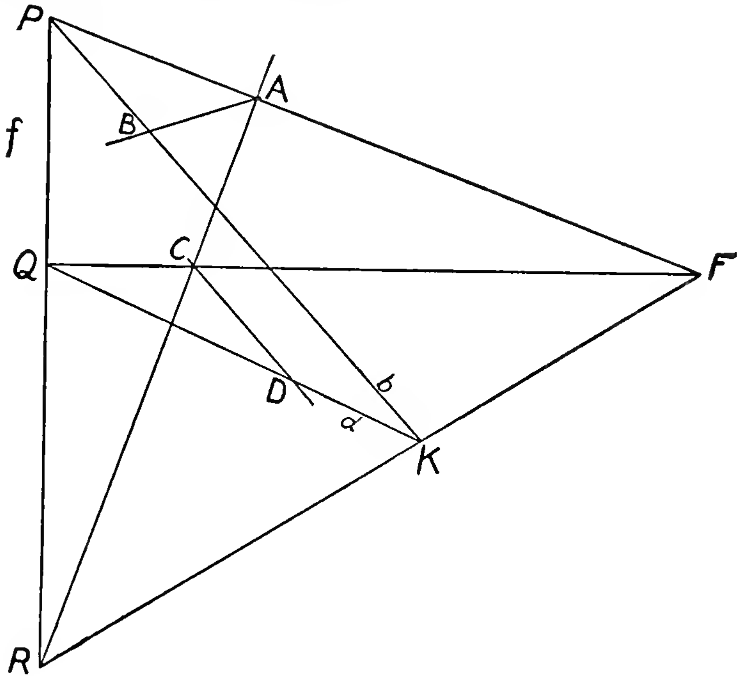

FIGURE 9.

19. Point F not on line f. If F is not on f, the locus of points at a given distance from a point A is a line through the point P in which FA cuts f. The locus of points at a constant distance from P is the line FP. The equation

$$\overline{\mathrm{AB}} = k$$

gives for fixed A a line b, the locus of points B, and b is the correspondent of A in a certain correlation. If a certain point C and its corresponding line d are given, we construct b the correspondent of A as follows. Draw AF and CF cutting f in P and Q and let CA cut f in R. To R corresponds the line FR. Then since three points A, C, R on a line must have corresponding to them three lines through a point, b, d, and FR pass through a point. Let d cut FR in K. Then PK is the line b required. The construction is shown in Figure 9.

To construct on any line through A a distance $\overline{AB}$ equal to a distance $\overline{CD}$, we construct the line b and where it cuts the line through A is the point B required. If on a fixed line CD we determine a scale making distances along that line proportional to the corresponding vectors D — C, our construction enables us to transfer the scale to any other line except f and so to assign to every pair of points, not on f, a distance. We must still show that this construction is consistent (if two distances so constructed are equal to a third, they are equal to each other) and that the resulting distance has the properties assumed in the definition.

We first show that if C and D (Figure 9) are held fixed, A and b are correspondents in a correlation. The figure gives for each point A an unique line b. If A moves along a line, since F and C are fixed, P and R describe, on f, ranges projective with A. Also K describes on d a range projective with R. Therefore P and K describe on f and d projective ranges. Also when A is on CF, P and R, and consequently K, are at Q. Since the ranges on f and d have a self-corresponding point Q, the line PK passes through a fixed point. Thus as A moves along a line, b turns about a point. Furthermore, b describes a pencil projective with the range described by A. The correspondence between A and b is therefore a correlation.

In particular if A is on f, A and R coincide. To R therefore corresponds the line RF. Also if A is at C, b coincides with d. The fact that Ab, Cd, and R, FR are pairs of corresponding elements in a correlation shows that the three lines intersect in K and thus determines the relation between A, B and C, D. If $\overline{A_1B_1}$ and $\overline{A_2B_2}$ are both equal to $\overline{CD}$, we have just shown that A_1, b_1 and A_2, b_2 are corresponding pairs in a correlation which gives for a point R on f the line RF. Therefore A_1, B_1 and A_2, B_2 are related by the same kind of diagram as A, B and C, D. Consequently, if two distances are by this construction equal to a third, they are equal to each other.

We now show that distances as constructed along any line AB are proportional to the corresponding vectors **B** — **A**. We have already remarked that vectors along a line preserve their ratios when projected upon another line from a point on f. If we hold A and C fixed (Figure 9) we may consider AB as resulting from CD by first projecting from Q upon RF and then from P upon AB. Vectors on AB have therefore the same ratios as vectors on CD. Since distance has been defined as proportional to the vector along CD, it is proportional to the vector along any other line AB.

20. It has been mentioned that two vectors on different lines may be equal though their lengths are not equal. This is shown in Figure 10. Let AC and BD intersect on f at P and let AB, CD cut PF in M, N. The vectors AB and CD are equal. Suppose now

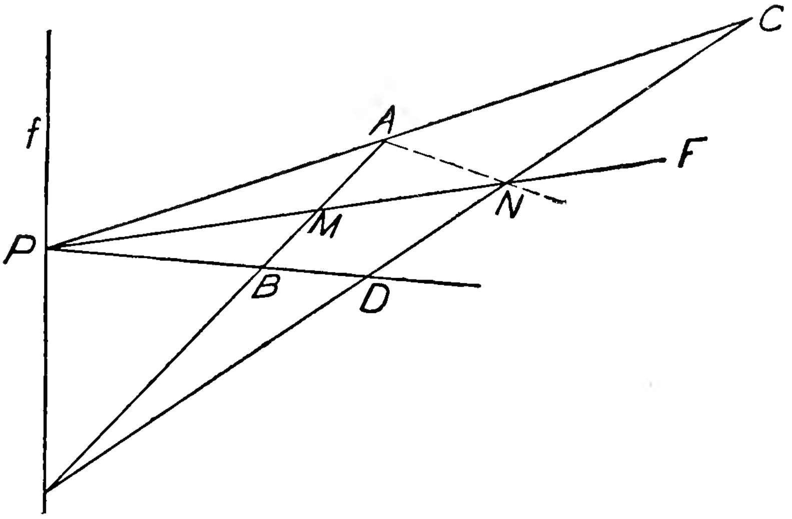

FIGURE 10.

$$\overline{AB} = \overline{CD}.$$

Then, by proportionality

$$\overline{AM} = \overline{CN},$$

and

$$\overline{BM} = \overline{DN}.$$

Also since $\overline{NA} = \overline{NC}$,

$$\overline{AM} = \overline{AN}.$$

Consequently P must be on the line AF. For the same reason B lies on the line FP. The vectors AB and CD are then zero. Non-vanishing equal vectors on different lines can not have the same length unless the point F lies on the line f.

21. Summary. In this section we have found a species of linear distance defined by a point F and line f. The distance between any two points on a line through F (but not on f) is zero. The distance between a point on a line through F and the point in which that line cuts f is indeterminate. The distance between two distinct points of a line not passing through F is finite and not zero but becomes infinite when one of the points is on f. The locus of points at a constant distance from a point A is a line b through the intersection of FA with f. For fixed distance A and b are correspondents with respect to a definite correlation in which F and f are corresponding elements and f, the locus of points whose lines pass through them. On any line distances AB are proportional to the vectors $\mathbf{B} - \mathbf{A}$. Equal vectors on different lines have equal length if F is on f, but not otherwise.

Angle.

22. Point vectors. Just as $\mathbf{A} - \mathbf{B}$ may be considered as a point of zero magnitude on f, or as a vector associated with the segment AB not crossing f, so $\mathbf{a} - \mathbf{b}$ may be considered as a line of zero magnitude passing through F or as a point vector associated with the angular segment (or vector) not containing F.

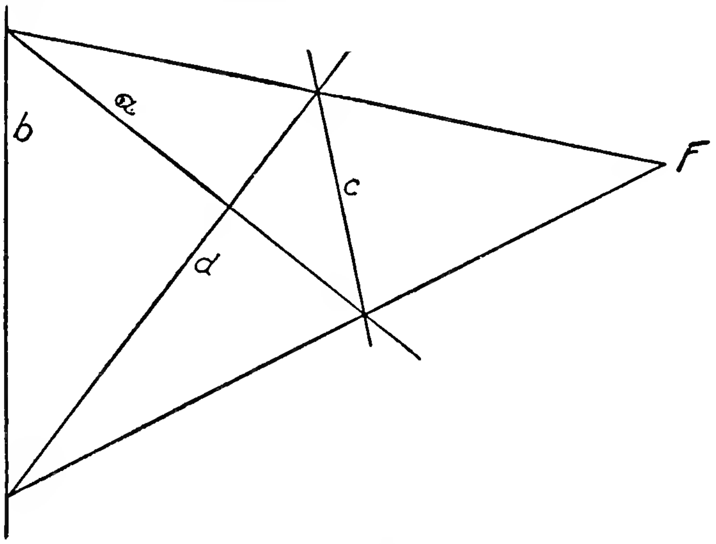

FIGURE 11.

Point vectors have properties dual to those of line vectors. Thus, if

$$\mathbf{a} - \mathbf{b} = \mathbf{c} - \mathbf{d}$$

ac and bd are points of a line through F. The relation of the lines a, b, c, d is shown in the diagram (Figure 11).

If $$\mathbf{a} - \mathbf{b} = \lambda(\mathbf{c} - \mathbf{d})$$

where c, *d* are distinct and a, b, c, d pass through a point, we shall say the angle $\overline{ab}$ is λ times the angle $\overline{cd}$. In this case, if p is the line joining F to the common point,

$$\lambda = (ac \mid dp) - (bc \mid dp) \qquad (8)$$

and λ is finite for all positions of a and b distinct from p but becomes infinite when one of these lines coincides with p.

23. Definition and properties of angle. We now define angle as a scalar quantity determined by two lines not passing through F and such that pairs of lines through a point give angles proportional to the corresponding point vectors. We further assume that one of the lines being fixed and the angle kept constant, the locus of the other line is an analytic curve. That locus is then a straight line.

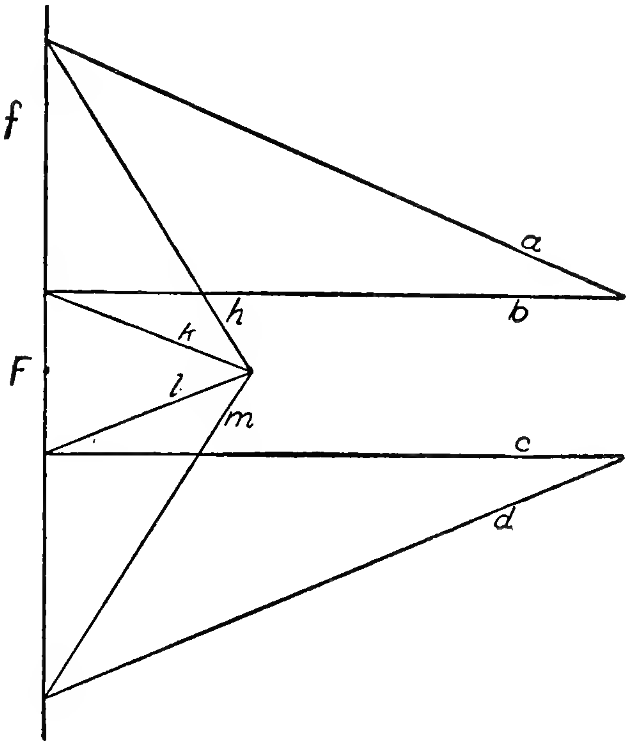

FIGURE 12.

Angle is thus the dual of distance. We find accordingly that there exists a line f such that if two lines (not passing through F) intersect on f, their angle is zero. If one of the lines passes through F, the angle is indeterminate. Two lines not intersecting on f determine an angle that is not zero. This angle is finite if neither of the lines passes through F, but infinite if one of them passes through that point. If

$$\overline{\mathrm{ab}} = k,$$

the locus of b for fixed a is a point B on the line joining fa to F. The correspondence between a and B is a correlation in which f and F are corresponding elements and F is the locus of lines passing through their corresponding points. There are two cases depending on whether F is on f, or not. The constructions for equal angles are shown in Figures 12 and 13.

The equal angles are $\overline{ab}$ and $\overline{cd}$. In Figure 12,

$$\mathbf{h} - \mathbf{k} = \mathbf{l} - \mathbf{m}.$$

24. In the discussion of distance we found besides the fixed line f (locus of exceptional points in our algebra) a fixed point F′, that need not be the fixed point of our algebra. Again in the discussion of angle we have a fixed point F (locus of exceptional lines) and a fixed line f′, which need not be the fixed line occurring in the algebra. If we transform the plane by a collineation leaving F′, and f fixed, the ratios of distances will not be changed. If then there are to exist fixed relations between distances and angles in a figure (between sides and angles of a triangle, for example) the ratios of angles must be at the same time unchanged. We therefore choose the same fixed elements for distance and angle. These must then be the exceptional elements F and f in our algebra.

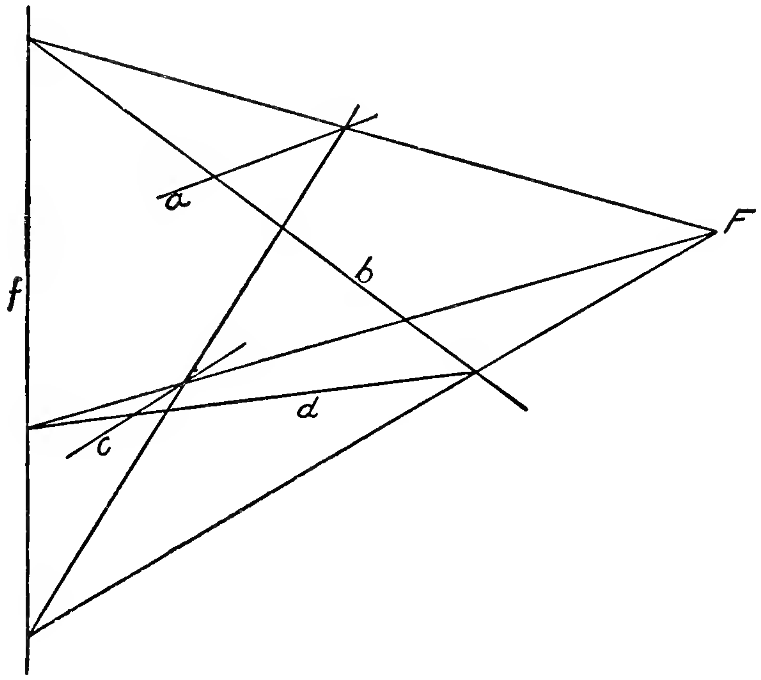

Figure 13.

Distance as here discussed has a definite algebraic sign and hence along every line is assigned a definite positive direction. In Euclidean geometry there is no definite direction along a line because by a rotation preserving distance one direction can be turned into the other. That it is not possible, by our construction for equal distances, to rotate one direction along the line into the other is shown in Figure 14. Rotation of AB around A causes B to describe the line BP. We have defined AB to be the segment not crossing f. Hence, as B passes P, the segment AB changes into the segment AB′ not crossing f (i. e. connecting A to B′ by way of infinity). Thus all segments into which AB can be rotated lie on the same side of AF and consequently one end of the line AB cannot be rotated into the other.

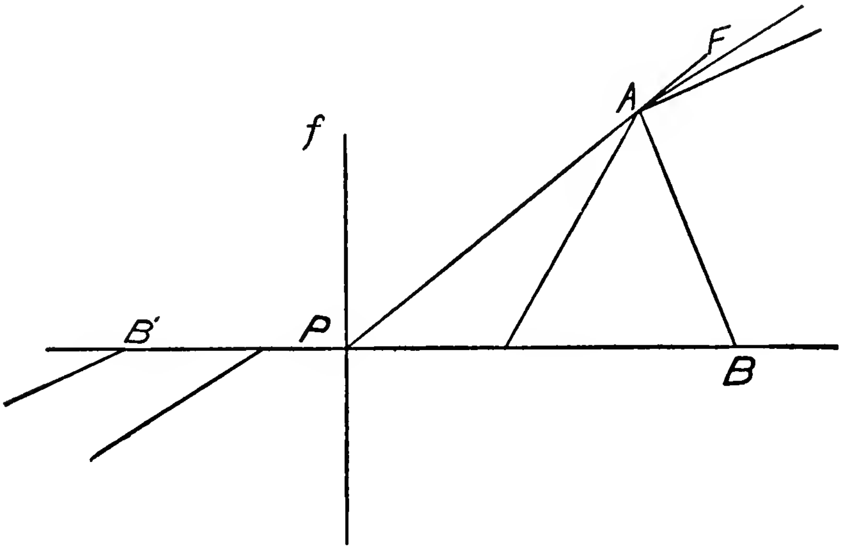

FIGURE 14.

A point describing (from A to B) any one of the segments AB (Figure 14) determines the same direction of rotation about F. Distances are then positive or negative according as their description gives rotation in one direction or the other around F.

Similarly the angle ABP is the angle which does not include F. If A is held fixed and B moves along BP, the angle is not changed. As B passes P the angle changes into AB′P. If around B we rotate the side AB into the side BP, the direction of translation (of the point of intersection of AB with f) along f is always the same. Hence an angle is positive or negative according as this translation along f is in one direction or the other.

In Euclidean geometry we have an unique direction of angle about any point since the equation

$$\text{angle} = \text{const.},$$

one side being fixed, factors into two linear conditions and so gives a separation of classes, but no definite direction along a line since

$$\text{distance} = \text{const.},$$

one point being fixed, is an irreducible quadratic form. Our distance and angle are more like Euclidean angle than Euclidean distance.

Metric representation of points and lines.

25. We wish to obtain a representation of point and line which distinguishes A and λA in the case of point addition. Then λA is coincident in position with A but differs from it in something that we have called magnitude. Grassman replaced a line by a segment joining two of its points. Then **a** and λ**a** give segments differing in length. We wish in this section to determine, if possible, a representation in which a line is replaced by a segment beginning at an arbitrary point of the line, and a point by a sector beginning at an arbitrary line through the point and to determine an addition of these segments or sectors such that their addition relations shall be the same as those of the corresponding lines or points.

Consider the lines through a point A not on f. We assume that to a line through A, corresponds a segment **AB**, to a segment **AB** a point B, and conversely. Since there is a [1,1] correspondence between the lines and the points B, it follows that to an addition of lines corresponds an addition of points, and that the two additions have the same formal laws. Since **a** and λ**a** are represented by different segments, B and λB are different points. The addition of points thus suggests the vector addition of § 1. The segments corresponding to lines through a point should then add like vectors from that point as origin. Distances along a line being proportional to the corresponding vectors, **a** and λ**a** should be represented at A by segments whose lengths have the ratio λ.

We thus represent a line of magnitude λ by a segment of length λ joining two points A, B of the line. Unit lines are represented by segments of unit length. These segments are like localized vectors in physics. Segments on the same line are proportional to their lengths. Segments on different lines may be added by moving them to the point of intersection of the two lines and there adding them like vectors.

To add two lines λ**c**, μ**d**, of magnitudes λ and μ, we construct, at their point of intersection A, segments of lengths λ, μ ending in the points C, D. We then draw through A and the harmonic of f with respect to C, D the line h required. Our earlier method of constructing the sum λ**c** + μ**d** was to draw a line h through A such that

$$(\mathrm{hd} \mid \mathrm{cF}) = -\frac{\mu}{\lambda}.$$

That the two constructions are consistent follows since F and P (Figure 15) determine the same cross ratios with triads of lines through A. In fact, let

$$\overline{AB_1} = \overline{AB_2} = 1.$$

It was shown in § 1 that

$$\lambda\,(AB_1) + \mu\,(AB_2)$$

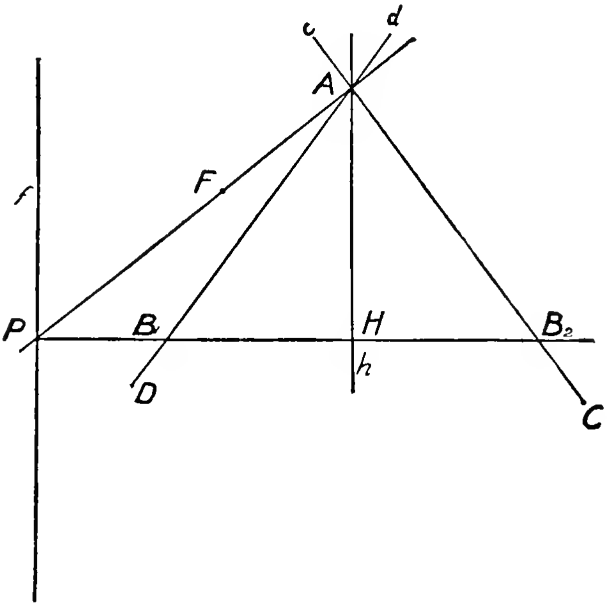

Figure 15.

intersects B_1B_2 in a point H such that

$$(HB_1 \mid B_2P) = -\frac{\mu}{\lambda}.$$

26. To add two segments we have moved them to the point of intersection of their lines. If the two lines intersect on f, this is not possible. We shall now derive a construction for the sum of two segments not at the same point. We have seen that equal vectors along a line (also equal segments on a line) project from a point on f into equal vectors on any other line. Since the sum of segments at a point is determined by harmonic constructions involving only those segments and f, it follows that addition relations connecting segments through a point are projective from a point on f. Any sum of segments may be found by a succession of processes consisting of moving two of the segments to the point of intersection of their lines and then adding them vectorially. Hence any linear relation connecting segments holds for the projections of those segments upon any line from a point on f.

This gives us a means of constructing the sum of two segments **AB** and **CD**. Let DA and BC cut f in P and Q. The sum **AB** + **CD** lies on some line LM through the intersection of AB and CD. From P (Figure 16) **AB** + **CD** is projected upon any line into a segment limited by the lines PC, PB. Likewise from Q it projects into a segment limited by QA, QD. Let PC intersect QA in L, and PB intersect QD in M. Then

$$\mathbf{AB} + \mathbf{CD} = \mathbf{LM}.$$

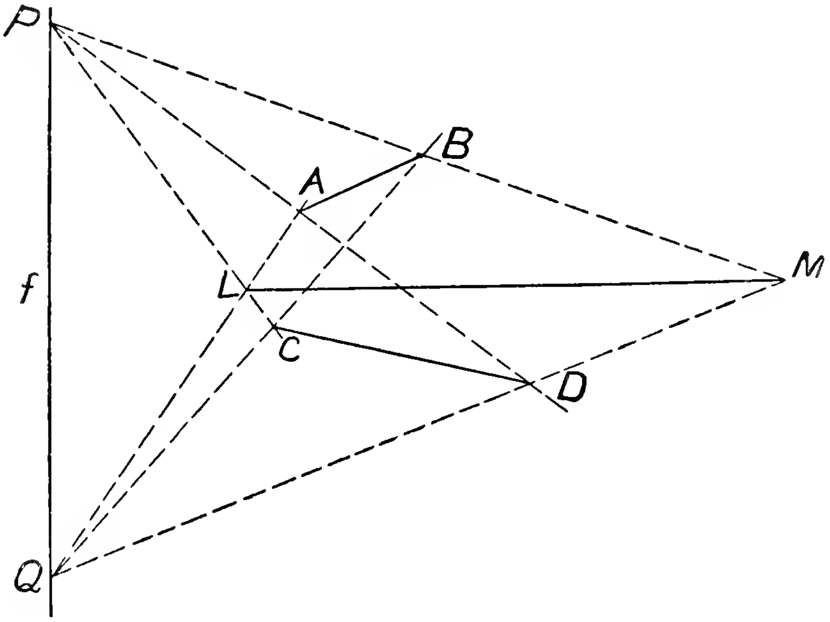

Figure 16.

27. Just as we represent a line by a segment (sequence of points between two given points) so we represent a point by a sector (sequence of lines between two given lines). The sector used is the one no line of which passes through F. A point of magnitude λ is represented by a sector of angle λ.

We conceive that the points in a discussion are thus replaced by fan-shaped spreads (the lines extending on both sides of the point). This spread, or sector, may be rotated about its vertex without changing its value by merely keeping the angle constant. Two of these sectors may be added vectorially after turning them around until the initial lines are the same. Let the sectors then be **ab** and **ac** and let the harmonic of F with respect to b and c be d. Then

$$\mathbf{ab} + \mathbf{ac} = 2\mathbf{ad}.$$

The sum of any two sectors may be found at once by a construction dual to that for adding segments (Figure 17).

We thus have two means of finding the sum

$$\lambda\mathbf{A} + \mu\mathbf{B}.$$

The one is an anharmonic construction involving the points A,B and the line f. The other is a harmonic or vector construction involving the sectors λA, μB and the point F. These constructions are both used in ordinary geometry, but the one only for adding points, the other only for adding lines. We have used both constructions in dual forms for both purposes.

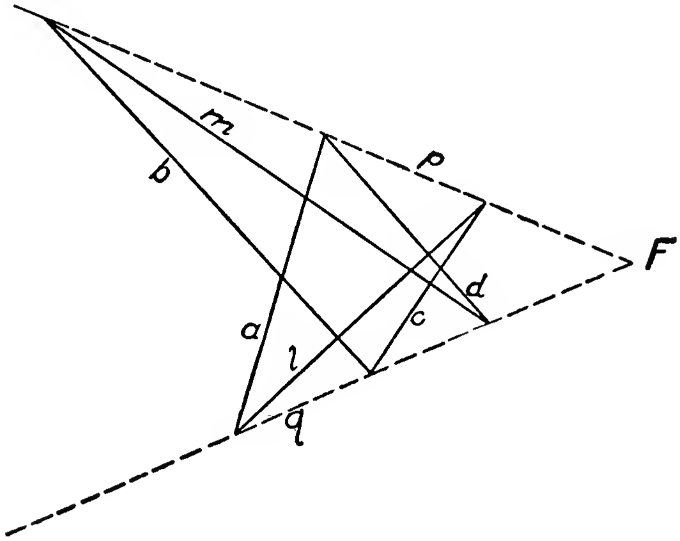

FIGURE 17.

§ 3. THE TRIANGLE.

28. In this section we shall apply the notions of distance and angle, as given in the previous section, to the study of plane figures, in particular to triangles. We have already seen that many properties are quite different according as the point F is on the line f or not. We shall therefore consider these two cases separately, taking first the case in which F is not on f and then the other as a special case.

Case I. *Point F not on line f.*

29. Relation between distance and angle. A comparison of the construction for equal distances with that for equal angles shows that the two are given by the same diagram. The group of collineations that leaves distance unaltered will then leave angle unaltered and conversely. We should therefore expect these quantities to be related.

When A is fixed and

$$\overline{\mathrm{AB}} = \text{const.}$$

B lies on a line b. The same figure gives

$$\overline{\mathrm{ab}} = \text{const.}$$

where b is a fixed line and a is a line making a constant angle with b (Figure 18).

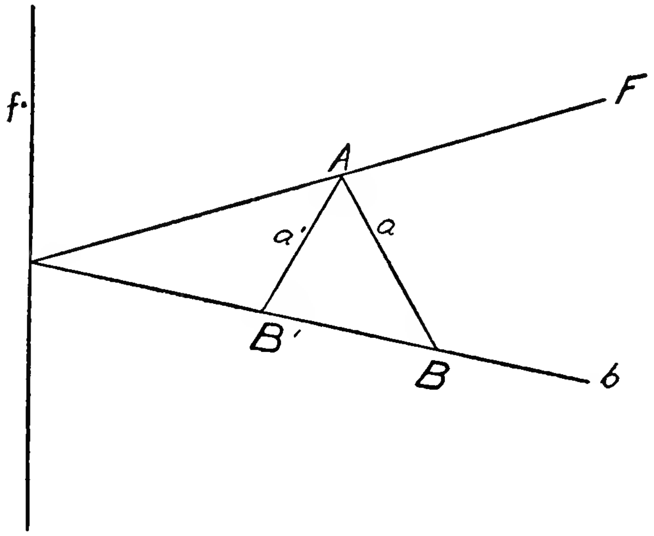

FIGURE 18.

This amounts to saying that if two sides of a triangle are equal the opposite angles are equal and have values independent of the third side or angle. Thus with every distance $\overline{\mathrm{AB}}$ is associated an angle $\overline{\mathrm{ab}}$. With any equal distance is associated the same or equal angle, since as previously mentioned the construction for equal distances at the same time makes the angles equal.

We shall determine the relation between these corresponding distances and angles. For this purpose take two distances $\overline{\mathrm{AB}}$ and $\overline{\mathrm{AC}}$ along the same line and with them the corresponding angles $\overline{\mathrm{ab}}$ and $\overline{\mathrm{ac}}$ (Figure 19). Let FA and AB cut f in P and Q. Draw FQ cutting PB and PC in D and E.

In the isosceles triangles ABD and ACE

$\angle$ ABD[5] $= \angle$ BAD,

---

[5] The angle ABD is the angle whose first side is AB and second side BD and which does not contain F. Thus in the figure the angle ABD is the angle ABP. The triangle ABD is isosceles in the sense that

$$\overline{\mathrm{PA}} = \overline{\mathrm{DB}}.$$

We shall later call triangles isosceles or equilateral when the sides described in a definite order around the triangle are equal, i. e. when

$$\overline{\mathrm{BD}} = \overline{\mathrm{DA}}.$$

$$\angle \mathrm{ACE} = \angle \mathrm{BAE}.$$

Hence
$$\frac{\overline{\mathrm{ab}}}{\overline{\mathrm{ac}}} = \frac{\angle \mathrm{ABD}}{\angle \mathrm{ACE}} = \frac{\angle \mathrm{BAD}}{\angle \mathrm{CAE}}.$$

From the definition of angle this last expression is the double ratio of the lines AD, AE, AB, AF, i. e. equal to

$$(\mathrm{DE} \mid \mathrm{QF}) = (\mathrm{BC} \mid \mathrm{AQ}) = (\mathrm{CB} \mid \mathrm{AQ}).$$

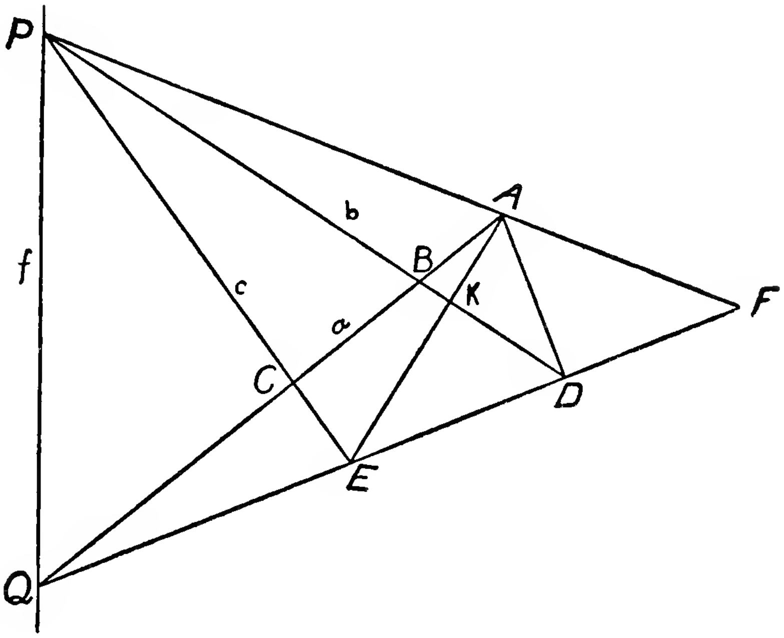

Figure 19.

From the definition of distance the last ratio is $\frac{\overline{\mathrm{AC}}}{\overline{\mathrm{AB}}}$. Hence

$$\frac{\overline{\mathrm{ab}}}{\overline{\mathrm{ac}}} = \frac{\overline{\mathrm{AC}}}{\overline{\mathrm{AB}}},$$

or
$$\overline{\mathrm{ab}} \cdot \overline{\mathrm{AB}} = \overline{\mathrm{ac}} \cdot \overline{\mathrm{AC}}.$$

We have already remarked that $\overline{\mathrm{ac}}$ is uniquely determined by $\overline{\mathrm{AC}}$. If then we keep $\overline{\mathrm{AC}}$ constant

$$\overline{\mathrm{ab}} \cdot \overline{\mathrm{AB}} = \mathrm{k}.$$

The product of side and angle in an isosceles triangle is an absolute constant. We shall choose the units so that the constant is unity.

Then
$$\overline{\mathrm{ab}} = \frac{1}{\overline{\mathrm{AB}}}. \qquad (9)$$

Angle is therefore of dimension minus one in distance. In fact, since angle and distance are dual if there is to be a dimensional relation between them the first should be of the same dimensions in the second that the second is in the first. The dimensions could then be only 1 or —1 in distance.

We have $$\frac{\angle \mathrm{BAK}}{\angle \mathrm{BAD}} = (\mathrm{KD} \mid \mathrm{BP}) = \frac{\overline{\mathrm{BK}}}{\overline{\mathrm{BD}}}.$$

Now $$\angle \mathrm{BAD} = \frac{1}{\overline{\mathrm{AB}}}$$

and $$\overline{\mathrm{BD}} = \overline{\mathrm{AD}} = \overline{\mathrm{AB}}.$$

Hence $$\angle \mathrm{BAK} = \frac{\overline{\mathrm{BK}}}{\overline{\mathrm{AB}}^2}.$$

We may consider the line BD as a circle of radius $\overline{\mathrm{AB}}$ and center A. (The same line may be considered as a circle in an infinite number of ways but to each center corresponds a unique length of radius. Any point on AF may be taken as center of the same circle BD.) Then the angle at the center is given by

$$\text{angle} = \frac{\text{arc}}{(\text{radius})^2}. \tag{10}$$

30. Triangle relations. Analogy with Euclidean geometry leads us to expect relations between the sides and angles of a triangle. We shall now determine these relations.

Let ABC be the given triangle. Draw the lines as indicated in figure 20. Denote the length of the sides BC, CA, AB by a, b, c respectively and the angles CAB, ABC, BCA by A, B, C respectively.

Then $$a + b + c = \overline{\mathrm{BC}} + \overline{\mathrm{CA}} + \overline{\mathrm{AB}} = \overline{\mathrm{BE}} + \overline{\mathrm{DA}} + \overline{\mathrm{AB}} = \overline{\mathrm{DE}}.$$

Also $$\frac{\overline{\mathrm{DE}}}{\overline{\mathrm{DA}}} = (\mathrm{EA} \mid \mathrm{DR}) = (\mathrm{QS} \mid \mathrm{PR}) = (\mathrm{BH} \mid \mathrm{AR}) = \frac{\overline{\mathrm{AB}}}{\overline{\mathrm{AH}}}$$

Therefore $$A = \frac{1}{\overline{\mathrm{AH}}} = \frac{\overline{\mathrm{DE}}}{\overline{\mathrm{AB}} \cdot \overline{\mathrm{DA}}} = \frac{a + b + c}{bc}. \tag{11}$$

Similarly $$B = \frac{a + b + c}{ac}. \tag{12}$$

$$C = \frac{a + b + c}{ab}. \tag{13}$$

These relations solved for a, b, c give

$$a = \frac{A + B + C}{BC}, \tag{14}$$

$$b = \frac{A + B + C}{AC}, \tag{15}$$

$$c = \frac{A + B + C}{AB}, \tag{16}$$

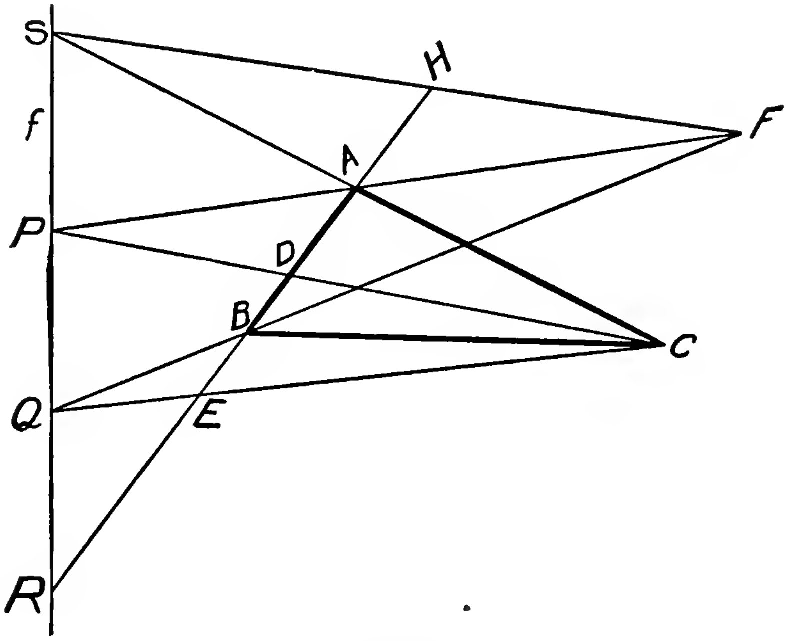

FIGURE 20.

which have the same form as before as they should have by duality. These equations can be solved for any three of the quantities A, B, C, a, b, c in terms of the other three. Thus any three of these parts determine the triangle uniquely. In particular the three angles determine the triangle and therefore similar triangles do not exist.

We can construct a triangle having any three given lengths for sides. In fact, take any segment BC of length a. Construct lines at distances c, b from B and C respectively. These lines intersect in a point A such that the triangle ABC has the sides required. There is no relation between the three sides of a triangle. Since any three parts determine the triangle there is no relation between any three parts. Since we have already found three independent equations connecting the six quantities it follows that any other must be a consequence of these.

It is to be noted in particular that the three angles of a triangle are not functionally related. The reason that the angles of a triangle in Euclidean geometry are so related is because angle is there of zero dimension in distance. The three angles of a triangle being homogeneous functions of zero dimensions in the sides are functions of two ratios $\frac{a}{c}$, $\frac{b}{c}$, and hence must be functionally related.

From (11) by division we get

$$\frac{A}{a} = \frac{a+b+c}{abc}.$$

Hence
$$\frac{A}{a} = \frac{B}{b} = \frac{C}{c}, \tag{17}$$

a set of relations similar to the sine proportions in trigonometry. In this system angle often replaces sine of the angle in ordinary trigonometry

31. Area. To determine the sides and angles of a triangle a direction around the triangle must be given. In speaking of the triangle ABC we shall assume this direction to be A, B, C. The lengths of the sides are there $\overline{AB}$, $\overline{BC}$, $\overline{CA}$ and the angles $\overline{ab}$, $\overline{bc}$, $\overline{ca}$ where a is opposite A, b opposite B, etc. Quantities such as area connected with a triangle may depend on this direction of description.

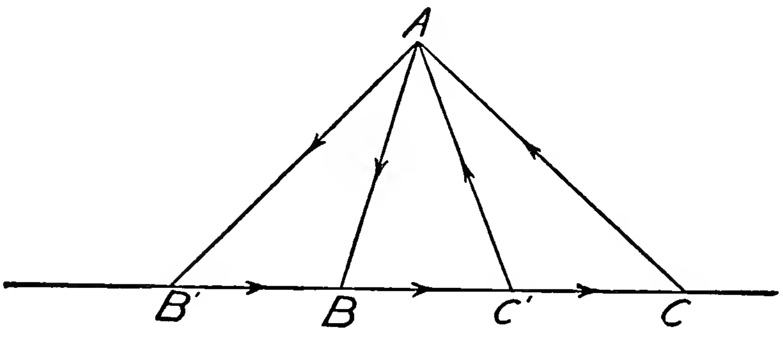

FIGURE 21.

We define the *line area* of a triangle as a scalar quantity, determined by three points taken in a definite order, such that triangles having a vertex in common and their bases on the same line have areas proportional to the lengths of their bases.

Take two triangles ABC and AB′C′ having the same vertex A and bases $\overline{BC}$, $\overline{B'C'}$ on the same line (Figure 21).

Consider the triangle AC′C. $\overline{\mathrm{AC}'} = -c'$, and angle AC′C $= -C'$, where C is the angle of the triangle AB′C′. Then from relation (17) we have

$$\frac{C'}{b} = \frac{C}{b'} \text{ or } b'C' = bC.$$

Then if we have the relation

$$\frac{\text{Area ABC}}{\text{Area A}'\text{B}'\text{C}'} = \frac{a}{a'},$$

multiplying both numerator and denominator by the above equality we have

$$\frac{\text{Area ABC}}{\text{Area A}'\text{B}'\text{C}'} = \frac{abC}{a'b'C'}.$$

The two terms of the right member are equal to the sum of the sides of the respective triangles. Hence

$$\frac{\text{Area A}'\text{B}'\text{C}'}{\text{Area ABC}} = \frac{a'}{a} = \frac{a' + b' + c'}{a + b + c}.$$

Triangles having the same vertex and bases on the same line have line areas proportional to their perimeters.

Starting with the triangle ABC by a succession of operations consisting of moving a side along its line and changing its length, we arrive finally at any triangle A′B′C′. Since under each of these operations the area is changed in the same ratio as the sum of the sides, it follows that the areas of any two triangles are proportional to their perimeters. We choose the unit of area such that

$$\text{Area ABC} = a + b + c. \tag{18}$$

That this expression for area has the properties required is evident since it is determined by an ordered sequence of three points, and since as already shown two triangles having the same vertex have perimeters proportional to their bases.

Perhaps the most fundamental property of area is the sum property, i. e. that the area of a region is the sum of the areas of its parts. This is a property of the sum $a + b + c$. For if we divide a triangle into two triangles by a line through one of the vertices the sum of the perimeters of the two is equal to that of the original triangle since the dividing line is counted twice in opposite directions. If then we define the area of any closed polygon as the sum of the areas of the triangles into which it can be divided the area of any polygon will be its perimeter.

32. Similarly we define the *angle area* of a triangle as a scalar quantity determined by three lines taken in a definite order and such that triangles having the same vertex and bases on the same line have areas proportional to the angles at the vertex. By a proper choice of units the angle area takes the form

$$\text{Area } abc = A + B + C. \tag{19}$$

Defining the angle area in general as having the sum property we see that any closed polygon has an angle area equal to the sum of the angles between consecutive sides.

33. The formulae for the two areas may be written in other forms that show more clearly the analogy with the ordinary trigonometric formulae for area. Thus from the equation

$$A = \frac{a + b + c}{bc}$$

we have

$$\text{Area ABC} = a + b + c = bcA$$

analogous to the formula

$$2 \text{ Area ABC} = \text{bc} \sin \text{A}$$

in trigonometry. Our formula thus corresponds to the formula for twice the ordinary area.[6]

Again from the equation

$$a = \frac{A + B + C}{BC}$$

we have

$$\text{Area } abc = A + B + C = aBC$$

which is to be compared with the ordinary formula

$$2 \text{ Area } abc = a \sin \text{B} \sin \text{C}.$$

In both of these pairs of formulae for area angle replaces the sine of an angle of trigonometry.

---

[6] As the present scheme of distance and angle is entirely distinct from the ordinary distance and angle, the one being linear, the other quadratic, it does not seem advisable to complicate our formulae by the introduction of the multiplier ½ necessary to make the analogy complete. The only case common to the two systems is that in which the circular points at infinity coincide, which corresponds to our scheme when F is on f.

Another analogy is obtained by comparing the ordinary area of a sector of a circle with our corresponding area of an isosceles triangle. The area of sector of angle A and radius b is

$$\tfrac{1}{2}b^2\mathrm{A}.$$

The area of our isosceles triangle having a vertical angle A and the sides $\overline{\mathrm{AB}} = \overline{\mathrm{AC}} = b$ is

$$-\,b^2\mathrm{A}$$

which can be obtained from the formula Area $= bc\mathrm{A}$, remembering that in the isosceles triangle $\overline{\mathrm{AB}} = b$, $\overline{\mathrm{CA}} = c = -\,b$. Thus in this case angle replaces angle.

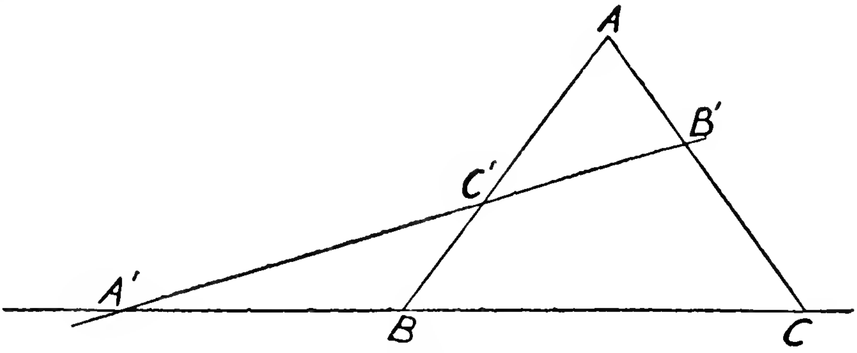

Figure 22.

34. In connection with the similarity between the trigonometric formulae in this geometry and in the ordinary geometry, it is interesting also to note some of the similarities and differences of the geometric relations of triangles in the two cases. The following theorems are good illustrations.

If the sides BC, CA, AB *of a triangle are cut by a transversal in the points A', B', C' respectively, then*

$$\frac{\overline{\mathrm{C'A}}}{\overline{\mathrm{C'B}}}\cdot\frac{\overline{\mathrm{A'B}}}{\overline{\mathrm{A'C}}}\cdot\frac{\overline{\mathrm{B'C}}}{\overline{\mathrm{B'A}}} = 1.$$

For writing the three vertices in order to denote the line area of the triangle we have (Figure 22)

$$\frac{\mathrm{A'B'C}}{\mathrm{C'B'A}}\cdot\frac{\mathrm{C'B'A}}{\mathrm{B'C'C}}\cdot\frac{\mathrm{B'C'C}}{\mathrm{C'A'C}}\cdot\frac{\mathrm{C'A'C}}{\mathrm{C'A'B}}\cdot\frac{\mathrm{C'A'B}}{\mathrm{A'C'A}} = 1.$$

Since triangles having the same vertex and bases on the same line have line areas proportional to the lengths of their bases, this relation can be written

$$\frac{\overline{A'C'}}{\overline{C'B'}}\cdot\frac{\overline{B'A}}{\overline{CB'}}\cdot\frac{\overline{B'C'}}{\overline{C'A'}}\cdot\frac{\overline{A'C}}{\overline{A'B}}\cdot\frac{\overline{BC'}}{\overline{C'A}} = 1,$$

which is equivalent to

$$\frac{\overline{C'A}}{\overline{C'B}}\cdot\frac{\overline{A'B}}{\overline{A'C}}\cdot\frac{\overline{BC}}{\overline{B'A}} = 1.$$

The converse of this theorem is immediately seen to be true.

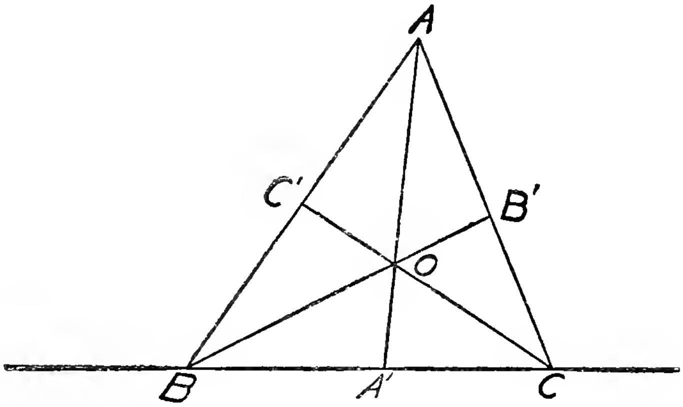

Figure 23.

If through any point O *in the plane of a triangle ABC lines are drawn to the vertices cutting the sides opposite* A, B, C *in* A′, B′, C′ *respectively, then*

$$\frac{\overline{A'C}}{\overline{A'B}}\cdot\frac{\overline{C'B}}{\overline{C'A}}\cdot\frac{\overline{B'A}}{\overline{B'C}} = -1.$$

For we have the identity (Figures 23 and 24),

$$\frac{\overline{OA'}}{\overline{OC}}\cdot\frac{\overline{OC}}{\overline{OB'}}\cdot\frac{\overline{OB'}}{\overline{OA}}\cdot\frac{\overline{OA}}{\overline{OC'}}\cdot\frac{\overline{OC'}}{\overline{OB}}\cdot\frac{\overline{OB}}{\overline{OA'}} = 1,$$

which becomes, on rearranging the terms,

$$\frac{\overline{OA'}\cdot\overline{OC}}{\overline{OA}\cdot\overline{OC'}}\cdot\frac{\overline{OB'}\cdot\overline{OA}}{\overline{OA'}\cdot\overline{OB}}\cdot\frac{\overline{OC'}\cdot\overline{OB}}{\overline{OC}\cdot\overline{OB'}} = 1,$$

or since triangles with the same vertical angle have areas proportional to the product of the including sides.

$$\frac{\mathrm{OA'C}}{\mathrm{OAC'}} \cdot \frac{\mathrm{OB'A}}{\mathrm{OBA'}} \cdot \frac{\mathrm{OC'B}}{\mathrm{OCB'}} = 1.$$

Rearranging

$$\frac{\mathrm{OA'C}}{\mathrm{OBA'}} \cdot \frac{\mathrm{OB'A}}{\mathrm{OCB'}} \cdot \frac{\mathrm{OC'B}}{\mathrm{OAC'}} = 1.$$

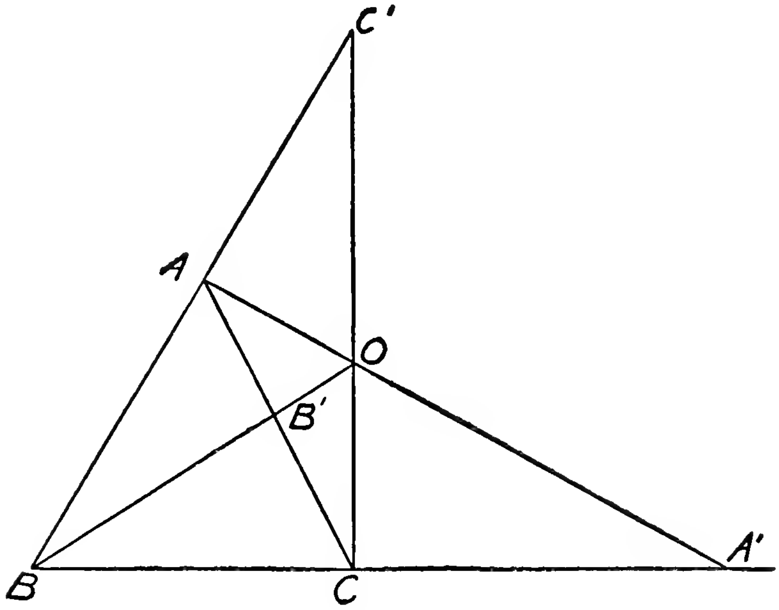

FIGURE 24.

But triangles having the same vertex and bases on the same line have line areas proportional to their bases. Hence

$$\frac{\mathrm{A'C}}{\mathrm{BA'}} \cdot \frac{\mathrm{B'A}}{\mathrm{CB'}} \cdot \frac{\mathrm{C'B}}{\mathrm{AC'}} = 1,$$

which on changing the sign of the denominators becomes

$$\frac{\overline{\mathrm{A'C}}}{\overline{\mathrm{AB'}}} \cdot \frac{\overline{\mathrm{B'A}}}{\overline{\mathrm{B'C}}} \cdot \frac{\overline{\mathrm{C'B}}}{\overline{\mathrm{C'A}}} = -1.$$

The converse of this theorem is also easily proved. These two theorems are the same for ordinary geometry as they are here, and in fact the demonstrations here given are applicable to either geometry.

In this geometry we have duals of the two preceding theorems, which is not the case in ordinary geometry.

If from a point in the plane of a triangle lines a', b', c' *are drawn to the vertices* A, B, C *respectively, then*

$$\frac{\overline{c'a}}{\overline{c'b}} \cdot \frac{\overline{a'b}}{\overline{a'c}} \cdot \frac{\overline{b'c}}{\overline{b'a}} = 1,$$

and conversely, *if the above relation holds, the three lines* a', b', c' *pass through the same point.*

If any line b *in the plane of the triangle* abc *cuts the three sides in* A', B', C', *respectively, and the lines* a', b', c' *are drawn from these points to the opposite vertices, then*

$$\frac{\overline{a'c}}{\overline{a'b}} \cdot \frac{\overline{c'b}}{\overline{c'a}} \cdot \frac{\overline{b'a}}{\overline{b'c}} = -1,$$

and conversely, *if this relation holds, the three points* A', B', $C,'$ *lie on a line.*

From these theorems result many propositions analogous to those of ordinary geometry:

Lines intersecting the base of a triangle on f *divide the other two sides into proportional parts.* (It should not be expected that the bases of the triangles thus formed have the same ratio, for this would be equivalent to symmetry which does not exist in this geometry.)

If one of the vertices of a triangle is joined to F *and lines are drawn from any point on this line to the other vertices these lines divide the angles into proportional parts.*

Lines drawn from the vertices to the mid points of the opposite sides of a triangle meet in a point which is a point of trisection for the medians, the longer part being toward the vertex.

The bisectors of the angles of a triangle meet the opposite sides in three points on a straight line. It should be observed that the three bisectors in this geometry cannot all cut the opposite sides between the vertices. This is because the angle was defined to be that one which does not contain F.

If through any point O *in the plane of a triangle* ABC, *lines* OA, OB, OC *are drawn, intersecting the opposite sides in* A', B', C'; *and if* $A'B'$, AB *meet in* G, $B'C'$, BC *in* H *and* $A'C'$, AC *in* K, *the points* G, H, K *lie on a straight line.*

35. Point-line Invariant. In this system we have nothing analogous to perpendicularity, and there is no minimum distance from point to line. If then we are to find a quantity analogous to the distance from a point to a line in Euclidean geometry the analogy must have as its basis some other property. Now the distance from the vertex to the base of a triangle is ordinarily determined by the formula

$$h = b \sin C.$$

Hence in our system we try the value

$$\delta = bC.$$

It is evident from the definition that δ depends only on the positions of A and BC, for we have

$$\frac{b}{B} = \frac{c}{C},$$

and hence

$$\delta = bC = cB = \frac{a + b + c}{a}. \tag{20}$$

The first value of δ shows that it is independent of the position of B along the line, the second, that it is independent of the position of C along the line.

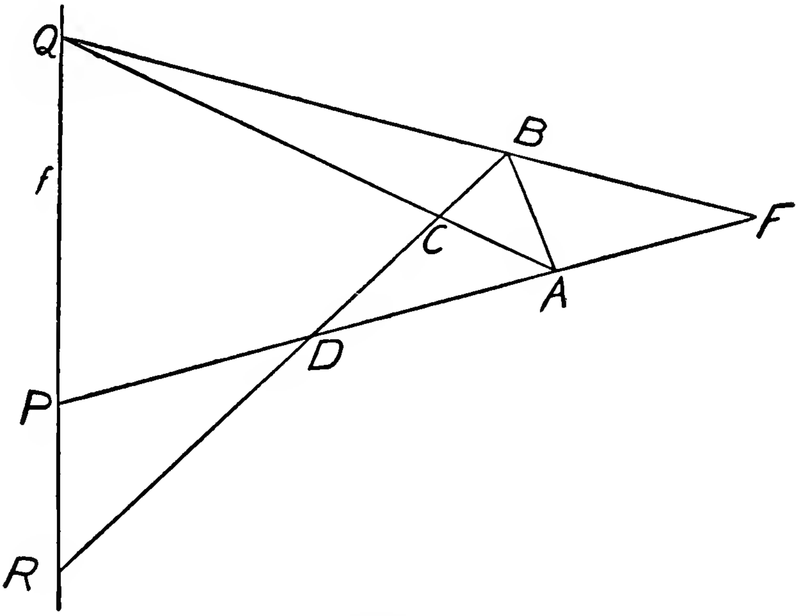

FIGURE 25

To determine more exactly the meaning of this quantity δ, we draw lines FA and FB meeting f in P and Q. Let BC cut AQ in C, FP in D, f in R.

From the triangle ABD we get

$$\delta = \frac{\overline{\mathrm{BD}} + \overline{\mathrm{DA}} + \overline{\mathrm{AB}}}{\overline{\mathrm{BD}}}.$$

Since in the isosceles triangle ABC, $\overline{\mathrm{AB}} = \overline{\mathrm{CB}} = c = -a$, and since $\overline{\mathrm{DA}} = 0$, being measured on a line passing through F, the above relation can be written

$$\delta = \frac{\overline{\mathrm{BD}} + c}{\overline{\mathrm{BD}}} = \frac{\overline{\mathrm{BD}} - a}{\overline{\mathrm{BD}}} = \frac{\overline{\mathrm{CD}}}{\overline{\mathrm{BD}}} = (\mathrm{CB}\,|\,\mathrm{DR}) = (\mathrm{AF}\,|\,\mathrm{DP}).$$

Thus the invariant δ is the cross ratio determined by the point A, the point F and the points in which FA cuts the given line BC and the line f.

From the fundamental relations of the triangle we have

$$\frac{a + b + c}{a} = \frac{A + B + C}{A}.$$

Therefore

$$\delta = \frac{A + B + C}{A}, \tag{21}$$

which is the same function of the angles that the former is of the distances. It is to be noted also that if A describes a line passing through R, δ will be unchanged.

The group of collineations which leaves F, f fixed leave δ invariant although distance and angle are not invariant.

36. Metrical Illustration. When we throw the line f to infinity the system takes an interesting metrical form. The equation

$$\overline{\mathrm{AB}} = \text{const.}$$

gives for fixed A a line b parallel to FA (Figure 26).

For points B on this line the distance $\overline{\mathrm{AB}}$ is then a constant times the Euclidean area of the parallelogram ABF. Further, our distances along the line AB are proportional to the Euclidean distances and therefore to the area of the parallelogram. Hence distance from a point A is proportional to the area of the parallelogram ABF, or

$$\overline{\mathrm{AB}} = k \,\square\, \mathrm{ABF}$$

where k is a function of A.

Similarly from B we have

$$\overline{\mathrm{BA}} = \mathrm{k}_1 ▱\ \mathrm{BAF}.$$

Now

$$\overline{\mathrm{BA}} = - \overline{\mathrm{AB}}$$

and

$$▱\ \mathrm{ABF} = - ▱\ \mathrm{BAF},$$

hence

$$\mathrm{k}_1 = \mathrm{k},$$

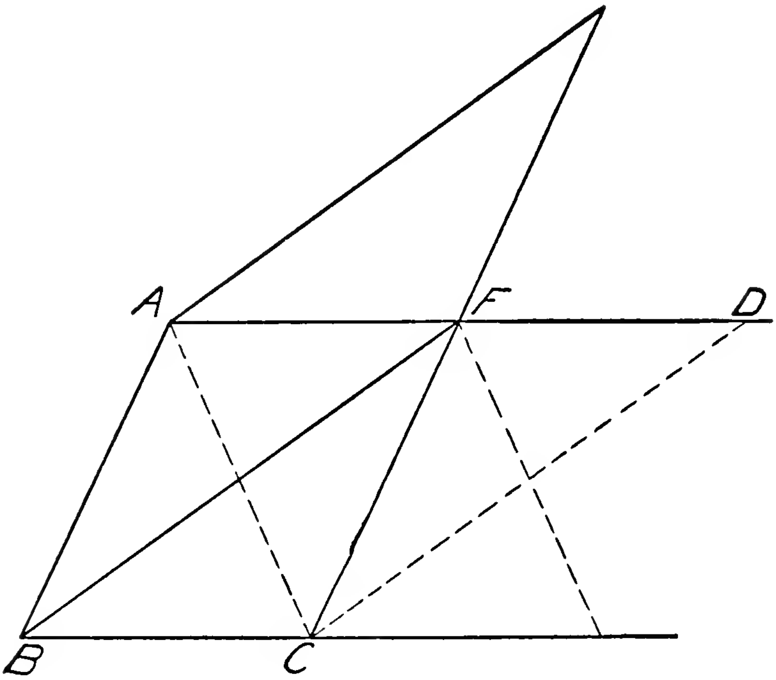

FIGURE 26.

and

$$\overline{\mathrm{AB}} = \mathrm{k}\ ▱\ \mathrm{ABF}$$

where k is constant for all values of A and B. We may choose the units so that k equals unity. Then

$$\overline{\mathrm{AB}} = ▱\ \mathrm{ABF}. \tag{22}$$

We know that

$$\overline{\mathrm{a}}\mathrm{b} = \frac{\overline{\mathrm{BC}}}{\mathrm{AB}^2},$$

consequently

$$\overline{\mathrm{a}}\mathrm{b} = \frac{▱\ \mathrm{BD}}{(▱\ \mathrm{AC})^2} = \frac{1}{▱\ \mathrm{AC}}. \tag{23}$$

Thus distance is the moment of Euclidean distance with respect to F and angle is the reciprocal of a moment.

It is to be observed that the sum of the three sides of a triangle is twice the Euclidean area. In fact,

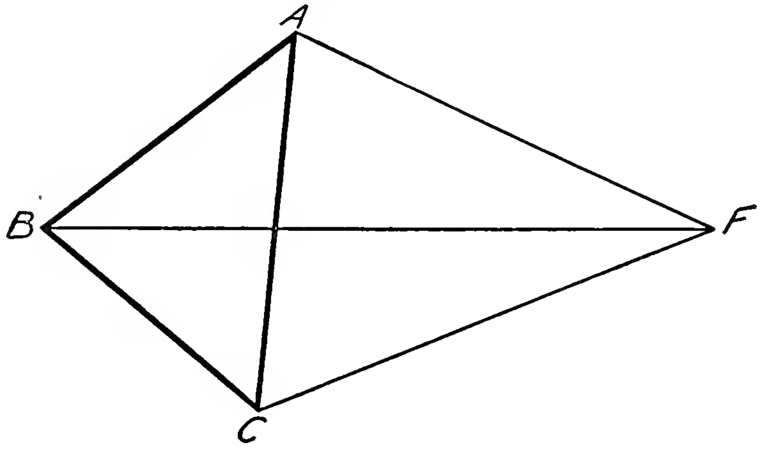

FIGURE 27.

$$\overline{AB} + \overline{BC} + \overline{CA} = 2\ (ABF + BCF + CAF) = 2\ ABC.$$

This is another justification for calling the sum of the sides of a triangle the area of the triangle.

CASE II. *The Point F on the Line f.*

37. In this case distances are equal if they project from F into equal vectors on a line. All triangles having vertices A, B, C respectively on fixed lines passing through F have equal sides, but may have different angles. Hence in this case it is not possible to express an angle in terms of the sides as was done in Case I.

Furthermore (Figure 28).

$$\overline{AB} + \overline{BC} = \overline{AD} + \overline{DC} = \overline{AC}.$$

Similar relations hold for angles. We thus have two equations connecting the parts of a triangle.

$$\begin{aligned} a + b + c &= 0, \\ A + B + C &= 0. \end{aligned} \tag{24}$$

We should expect one other relation. This may be found as follows: Let AB, BC, and CA cut f in P, Q, R. Then

$$\frac{a}{b} = \frac{\overline{DC}}{\overline{CA}} = -\ (DA|CR) = -\ (FP|QR).$$

Since angles are proportional to the point vectors determined at a fixed point by their intersections with the line f, we may consider them as represented by vectors on f measured relative to F as infinite point. Thus

$$\frac{A}{B} = \frac{\mathrm{RP}}{\mathrm{PQ}} = -\ (\mathrm{RQ}|\mathrm{PF}) = -\ (\mathrm{FP}|\mathrm{QR}).$$

Consequently $$\frac{a}{b} = \frac{A}{B},$$

and $$\frac{a}{A} = \frac{b}{B} = \frac{c}{C}. \tag{25}$$

These equations, together with the two already found, form a set of three independent relations connecting the six parts of a triangle. A triangle can be constructed having a given side and two given angles. There cannot then be more than three relations connecting the six parts, and therefore any other is a consequence of these.

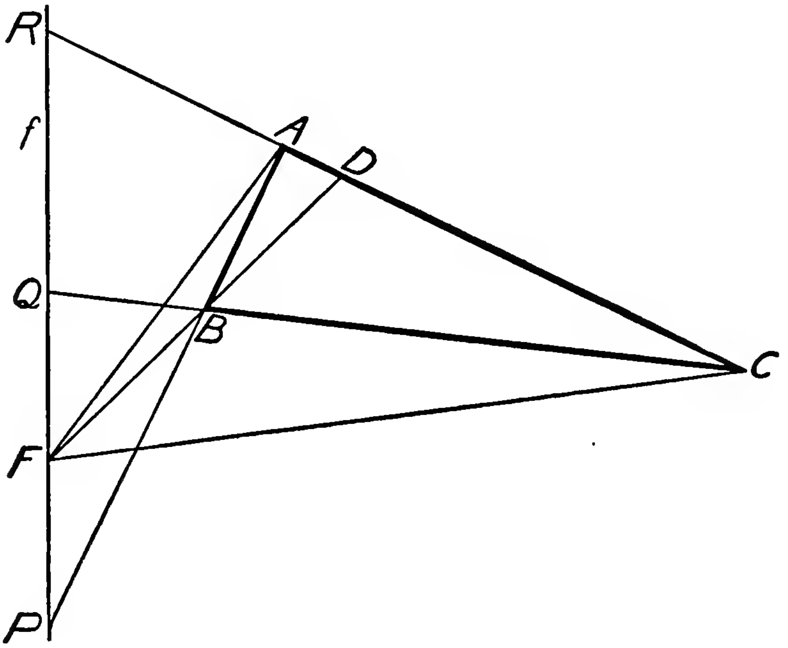

FIGURE 28.

38. Point-line Invariant. If we have a fixed point A and a fixed line LM and take a triangle with vertex A and base BC on the line LM, we have from the above relation

$$\delta = bC = cB, \tag{26}$$

which shows that the quantity δ is an invariant here just as in Case 1.

There is one difference, however, for in Case I this invariant was expressible as a ratio of distances, and consequently was independent of the unit of length assumed. In this case δ is not so expressible. It is not, therefore, an absolute invariant, but depends upon the units.

39. Area. The line area again will be defined by the property that triangles having the same vertex and bases on the same line have areas proportional to their bases. By the same argument as used in Case I it is seen that

$$\frac{\text{Area ABC}}{\text{Area A}'\text{B}'\text{C}'} = \frac{abC}{a'b'C'},$$

and the same argument will show that the factor of proportionality is the same for the whole plane and hence can be assumed to be unity, and we write

$$\text{Area ABC} = abC. \tag{27}$$

It is to be kept in mind that here the area is not equal to the perimeter, for the perimeter is zero.

By duality the angle area of the triangle ABC is

$$\text{Angle area ABC} = aBC. \tag{28}$$

§ 4. Products.

40. We have represented a line by a segment joining two of its points A and B and have used the notation

AB

to represent this segment. We shall now consider this expression as the product of two unit points and seek to determine its laws of combination. When the points are not unit points we shall take the product to be the segment[7] **AB** multiplied by the product of the magnitudes of the points.

The operation of multiplication will be denoted by writing the quantities together as is done in ordinary algebra. A dot between quantities will indicate how the quantities are to be associated, e. g. AB · CD will be used to indicate that the two products AB and CD are to be multiplied together.

---

[7] It should here be kept in mind that segment is not to be confused with its length, which measures only the magnitude of the segment. The length of a segment can be zero without the segment being zero, which is the case of a segment of a line passing through F.

From the fact that segments are directed we see that the product of two points obeys the alternative law

$$\mathbf{AB} = -\mathbf{BA}. \tag{29}$$

Also when the two points coincide the segment is zero, that is,

$$\mathbf{AA} = 0 \tag{30}$$

On the other hand, if

$$\mathbf{AB} = 0,$$

either the magnitude of one of the points is zero or the segment is zero. Then if neither point is a zero point and the product vanishes, the two points will coincide. Here again it is well to note that the product of two points on a line through F does not necessarily vanish although the segment is of zero length or magnitude.

41. We have used the notation

$$\mathbf{ABC}$$

to represent the triangle determined by the three points. We shall consider this also as the product of the three unit points and take it to mean the line area of the triangle determined by the three points. If the points are not unit points, the product will mean the area multiplied by the product of the magnitudes of the points. From this definition we see that the product vanishes if the three points are on a line, neither point being on f. Conversely, if the points are not zero points and the product vanishes, they are on a line. Therefore

$$\mathbf{ABC} = 0$$

is a necessary and sufficient condition that the three points be linearly related, i. e. collinear.

From the fact that area is directed we see at once that

$$\mathbf{ABC} = \mathbf{BCA} = \mathbf{CAB} = -\mathbf{ACB} = -\mathbf{CBA} = \ldots\ldots \tag{31}$$

42. From duality we now define the product of two lines as the sector determined by the two lines multiplied by the product of the magnitudes of the lines. When the two lines coincide the sector vanishes and we have as for points

$$\mathbf{ab} = 0.$$

Conversely, if the lines are not zero lines, $\mathbf{ab} = 0$ is the condition that the two lines should coincide. In the case of two lines as in the case of two points it should be kept in mind that the magnitude of the sector may be zero without the product necessarily being zero, e. g. if the lines intersect on f. In this case the magnitude of the sector is zero, but the product is not zero. If we now take the two lines $\mathbf{a}$ and $\mathbf{b}$ as represented by segments starting at the point of intersection, thus

$$\mathbf{a} = \mathbf{BC} \qquad \mathbf{b} = \mathbf{AC}$$

where $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ are unit points, then

$$\mathbf{AB} \cdot \mathbf{AC} = (\mathbf{ABC})\, \mathbf{A}. \tag{32}$$

Since the magnitudes of the lines $\mathbf{a}$, $\mathbf{b}$ are represented by the lengths of the segments, from the definition the product would be $\overline{BC} \cdot \overline{AC} \cdot \mathbf{A}_1$ where $\mathbf{A}_1$ represents the sector determined by the two lines. But $\mathbf{A}_1$ can be written as $A \cdot \mathbf{A}$ where $\mathbf{A}$ means a unit sector and the product takes the above form.

The product of three unit lines is defined to be the angle area of the triangle determined by the three lines, and the product of any three lines is this product multiplied by the product of the magnitudes of the lines. When the three lines pass through a point the angle area of the triangle is zero and conversely. Hence, *The necessary and sufficient condition that three lines* $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ (not zero lines) *should pass through the same point is*

$$\mathbf{abc} = 0.$$

Since the angle area is also a directed quantity

$$\mathbf{abc} = \mathbf{bca} = \mathbf{cab} = -\ \mathbf{bac} = \ldots\ldots \tag{33}$$

43. The product of a line $\mathbf{a}$ and a point $\mathbf{A}$ will be defined as the invariant δ of the point and line multiplied by the product of the magnitudes of the point and line. The invariant vanishes when and only when $\mathbf{A}$ lies on $\mathbf{a}$. Therefore if neither $\mathbf{a}$ nor $\mathbf{A}$ are zero elements, *the necessary and sufficient condition that* $\mathbf{A}$ *lies on* $\mathbf{a}$ *is*

$$\mathbf{Aa} = 0.$$

If the line $\mathbf{a}$ is represented by a segment of length a determined by two unit points $\mathbf{B}$ and $\mathbf{C}$, then from the above definition

$$\begin{aligned} \mathbf{Aa} &= aA\delta = aABc \\ &= a\ (ABc) \\ &= A\ (acB). \end{aligned} \tag{34}$$

That is, the product of a point and a line (represented by one of its segments) is equal to the line area of the triangle having the point for vertex and the segment for base multiplied by the magnitude of the point. Or dually, the product is equal to the angle area of the triangle having the sector **A** for vertex and **a** for base line, multiplied by the magnitude of **a**. If the line a passes through F, the above product becomes indeterminate since $a = 0$ and $B = \infty$; this can be evaluated by

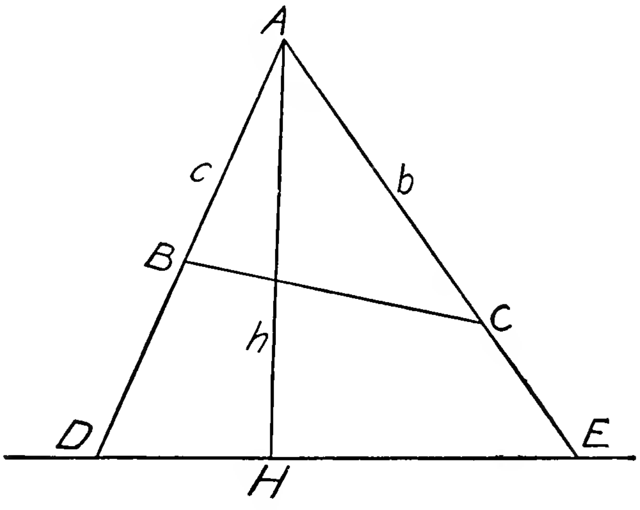

FIGURE 29.

remembering the relation $bA = aB$. Both b and A are finite and the product becomes determinate as before. From the above expression for the product we see that

$$\mathbf{Aa} = \mathbf{aA}. \tag{35}$$

44. The product of two unit points was defined as the segment joining the two points. This segment we may now consider as represented by the line joining the two points taken with a magnitude equal to the length of the segment. Then making use of the definition of the product of a point and a line we see at once

$$\mathbf{ABC} = \mathbf{AB} \cdot \mathbf{C} = \mathbf{A} \cdot \mathbf{BC}. \tag{36}$$

That is, the product is associative. Likewise the product of three lines is associative.

45. **The distributive law.** The distributive law for points

$$(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC} \tag{37}$$

follows from the definition of addition. Let the magnitudes of the three points be λ, μ, ν respectively. Then (Figure 29)

$$\mathbf{AB} = \lambda\mu\mathbf{C}, \quad \mathbf{AC} = \lambda\nu\mathbf{b}.$$

Let $\overline{AD} = \lambda\mu c, \quad \overline{AE} = \lambda\nu b.$

Then by definition **AB** + **AC** = 2**h**, where H is the harmonic of f with respect to D, E and h joins A to H. It was shown that the line AH divides the segment BC in the ratio $-\frac{\nu}{\mu}$ and therefore the line must pass through **B** + **C**. It is evident that the magnitude of **A** (**B** + **C**)

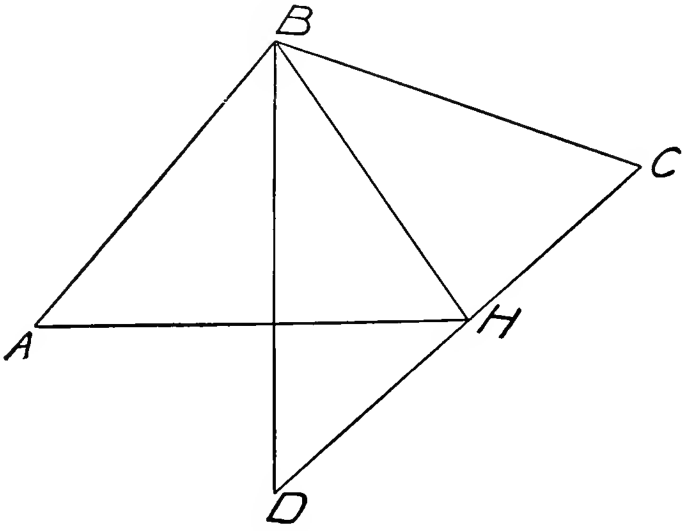

Figure 30.

is equal to the magnitude of **AB** + **AC**, each being equal to $\lambda\ (\mu + \nu)$, and since these lines have two points in common they are then equal.

The distributive law for points and lines

$$\mathbf{a}\ (\mathbf{C} + \mathbf{D}) = \mathbf{aC} + \mathbf{aD} \qquad (38)$$

can be proved as follows : Let **a** = **AB** where **A** and **B** are unit points. Then the left member can be written

$$\mathbf{AB}\ (\mathbf{C} + \mathbf{D}),$$

or, since the products are associative,

$$\mathbf{A}\ (\mathbf{BC} + \mathbf{BD}).$$

Let (Figure 30) $\mathbf{H} = \frac{1}{2}(\mathbf{C} + \mathbf{D}).$

Then $\mathbf{BH} = \frac{1}{2}\mathbf{B}\ (\mathbf{C} + \mathbf{D}) = \frac{1}{2}(\mathbf{BC} + \mathbf{BD})$

and
$$\begin{aligned}\mathbf{A}\,(\mathbf{BC}+\mathbf{BD}) &= 2\mathbf{ABH}\\ &= 2(\overline{AB}+\overline{BH}+\overline{HA})\\ &= 2\overline{AB}+(\overline{BC}+\overline{BD})+\overline{DA}+\overline{CA}\\ &= (\overline{AB}+\overline{BC}+\overline{CA})+(\overline{AB}+\overline{BD}+\overline{DA})\\ &= \mathbf{ABC}+\mathbf{ABD}\\ &= \mathbf{aC}+\mathbf{aD}.\end{aligned}$$

By duality the distributive law

$$\mathbf{A}\,(\mathbf{b}+\mathbf{c}) = \mathbf{Ab}+\mathbf{Ac} \tag{39}$$

is also true.

46. We have defined the product of two lines and have expressed it in terms of three unit points when the segments representing the two lines have an end point in common. This product can also be expressed in terms of unit points when the segments representing the lines do not have an end point in common. That is, we know that the product **AB · CD** is the sector determined by the two lines and we seek to express this sector in terms of the four points **A**, **B**, **C**, **D**. Grassmann has called such a product a regressive product. Let the two lines be represented by segments thus

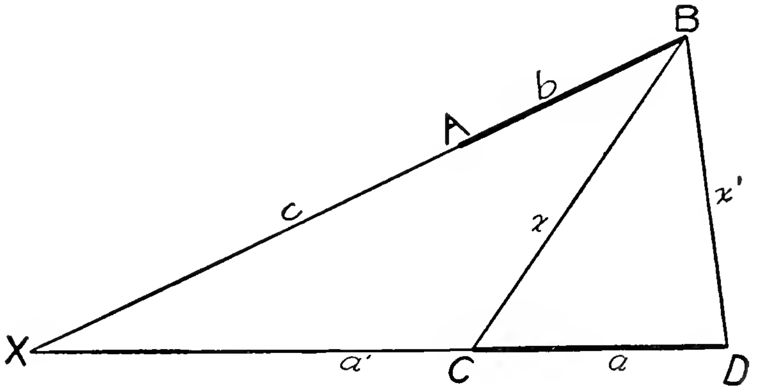

FIGURE 31.

$$\mathbf{a} = \mathbf{CD},\quad \mathbf{b} = \mathbf{AB}$$

and let **X** be the unit point at the intersection of **a**, **b**.

Then we can express **A** in terms of **B** and **X**.

$$(\lambda+1)\,\mathbf{A} = \mathbf{X}+\lambda\mathbf{B}. \tag{40}$$

Multiplying by **B**

$$(\lambda + 1)\,\mathbf{AB} = \mathbf{XB}.$$

Multiplying by **CD**

$$\begin{aligned}(\lambda + 1)\,\mathbf{AB}\cdot\mathbf{CD} &= \mathbf{XB}\cdot\mathbf{CD}\\ &= \mathbf{XB}\,(\mathbf{CX} + \mathbf{XD})\\ &= (\mathbf{XBD} - \mathbf{XBC})\,\mathbf{X}\\ &= (\mathbf{BCD})\,\mathbf{X}.\end{aligned}$$

Again multiplying (40) by **CD**

$$(\lambda + 1)\,\mathbf{ACD} = \lambda\,(\mathbf{BCD}).$$

Using the last two relations with (40)

$$(\lambda + 1)\,\mathbf{A} = \frac{(\lambda + 1)\,(\mathbf{ACD})}{(\mathbf{BCD})}\,\mathbf{B} + (\lambda + 1)\frac{\mathbf{AB}\cdot\mathbf{CD}}{(\mathbf{CBD})}.$$

From which we get

$$\mathbf{AB}\cdot\mathbf{CD} = (\mathbf{CDA})\,\mathbf{B} - (\mathbf{CDB})\,\mathbf{A}. \qquad (41)$$

Starting with the relation

$$(\lambda + 1)\,\mathbf{C} = \mathbf{X} + \lambda\mathbf{D}$$

the following relation is obtained :

$$\mathbf{AB}\cdot\mathbf{CD} = (\mathbf{ABD})\,\mathbf{C} - (\mathbf{ABC})\,\mathbf{D}. \qquad (42)$$

These last two relations are the general formulae for Grassmann's regressive product. Similar formulae can be obtained for the regressive product

$$\mathbf{ab}\cdot\mathbf{cd}.$$

Subtracting (41) from (42) we get

$$(\mathbf{ABC})\,\mathbf{D} - (\mathbf{ABD})\,\mathbf{C} + (\mathbf{ACD})\,\mathbf{B} - (\mathbf{BCD})\,\mathbf{A} = 0 \qquad (43)$$

for the identical relation connecting four points of the plane.

Scalar Products.

47. The point F was exceptional only in the addition of lines. It is lines through this point that are exceptional and not the point itself. The preceding product theory then holds when F is one of the quantities involved. If **A**, **B** and **F** are unit points not on f

$$(\mathbf{ABF}) = \overline{\mathrm{AB}} + \overline{\mathrm{BF}} + \overline{\mathrm{FA}}.$$

Hence

$$(\mathbf{ABF}) = \overline{\mathrm{AB}} \tag{44}$$

since the distances from F to A and B are zero. As F is fixed throughout the discussion we may consider (ABF) or $\overline{\mathrm{AB}}$ as a product of **A** and **B**. Since it is a number we call it the *scalar product.* If **A** and **B** are not unit points we shall use the notation $\overline{\mathrm{AB}}$ for the product (**ABF**). It is then the distance from A to B multiplied by the product of the magnitudes of **A** and **B**.

From the definition, if

$$\mathbf{B} + \mathbf{C} = \mathbf{D},$$

we have

$$\begin{aligned} \overline{\mathrm{AB}} + \overline{\mathrm{AC}} &= (\mathbf{ABF}) + (\mathbf{ACF}) \\ &= (\mathbf{ADF}) \\ &= \overline{\mathrm{AD}}. \end{aligned}$$

The scalar product of two points has then the following properties :

$$\overline{\mathrm{AB}} = -\overline{\mathrm{BA}}$$

$$\overline{\mathrm{A}\,(\mathrm{B}+\mathrm{C})} = \overline{\mathrm{AB}} + \overline{\mathrm{AC}}. \tag{45}$$

These laws hold for both **AB** and $\overline{\mathrm{AB}}$. The two differ in the fact that **AB** is a multiple quantity, $\overline{\mathrm{AB}}$ a number. The first forms an associative product

$$\mathbf{AB} \cdot \mathbf{C} = \mathbf{A} \cdot \mathbf{BC},$$

while the second does not.

If **a**, **b** and **f** are unit lines not passing through F,

$$(\mathbf{abf}) = \overline{\mathrm{ab}} + \overline{\mathrm{bf}} + \overline{\mathrm{fa}}.$$

Since the angles $\overline{\mathrm{bf}}$ and $\overline{\mathrm{fa}}$ are zero

$$(\mathbf{abf}) = \overline{\mathrm{ab}}. \tag{46}$$

The angle between two lines may then be considered as a *scalar product* of those lines. If **a** and **b** are not of unit magnitude, we define $\overline{\mathrm{ab}}$ by equation (45). This product dual to $\overline{\mathrm{AB}}$ has the following properties:

$$\overline{\mathrm{ab}} = -\overline{\mathrm{ba}} \tag{47}$$

$$\overline{\mathrm{a}\,(\mathrm{b}+\mathrm{c})} = \overline{\mathrm{ab}} + \overline{\mathrm{ac}}.$$

Equations (45) together with the fact that $\overline{\mathrm{AB}}$ is a number suggests geometry in one dimension. In fact, if a point A is represented as a linear function of three points, one of which is F, the multiple of F is lost in the product

$$\overline{AB} = (\mathbf{ABF}).$$

Thus, so far as concerns their values in products of the form $\overline{AB}$, points of the plane are linear functions of two points. In respect to this multiplication the plane is then one dimensional. Thus any homogeneous identical relation between products **AB** along a line will hold for distances $\overline{AB}$ in the plane. For example, along a line

$$\mathbf{AB} \cdot \mathbf{CD} = \mathbf{AC} \cdot \mathbf{BD} - \mathbf{AD} \cdot \mathbf{BC}.$$

Therefore

$$\overline{AB} \cdot \overline{CD} = \overline{AC} \cdot \overline{BD} - \overline{AD} \cdot \overline{BC} \qquad (48)$$

where **A**, **B**, **C**, **D** are any four points in the plane. This can be proved directly by using the equation

$$(\mathbf{ABF})\ \mathbf{C} - (\mathbf{ABC})\ \mathbf{F} + (\mathbf{AFC})\ \mathbf{B} - (\mathbf{BFC})\ \mathbf{A} = 0$$

which is obtained from (43) by changing the notation. Multiplying by **DF** and transposing we get

$$(\mathbf{ABF})\ (\mathbf{CDF}) = (\mathbf{ACF})\ (\mathbf{BDF}) - (\mathbf{ADF})\ (\mathbf{BCF})$$

which is equivalent to (48).

Massachusetts Institute of Technology.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 21.—March, 1912.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

ON ELECTRICAL PROPERTIES OF CRYSTALS.

I.—*STRATIFICATION AND CAPACITY OF CARBORUNDUM.*

By G. W. Pierce and Rhys D. Evans.

With a Plate.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON ELECTRICAL PROPERTIES OF CRYSTALS.

I. STRATIFICATION AND CAPACITY OF CARBORUNDUM.

By George W. Pierce and Rhys D. Evans.

Presented by G. W. Pierce, February 14, 1912. Received February 1, 1912.

This work is a continuation of some investigations by one of us on Crystal Rectifiers for Alternating Currents.[1]

Capacity of Carborundum. — In the experiments that are described in the present paper it has been found that a fragment of carborundum, with certain attachments of the electrodes, shows a large electrostatic capacity. Measurements are given of this capacity in two typical cases.

Character of the Phenomenon. — The discussion of the measurements is followed by an account of a microscopic and electrical investigation of the carborundum, which shows that the carborundum crystal is made up of an insulating mass permeated by fine layers of conducting material. These conducting layers are nearly parallel, and, separated as they are in the crystal by non-conducting sheets, form a *natural electrical condenser*, provided electrical contacts are made to two conducting layers or sets of layers that do not happen to short-circuit within the crystal.

Method of Measuring the Capacity of the Crystals.

Method of Charge and Discharge. — The capacity of the carborundum crystals was measured directly by a method of charge and discharge. A simplified diagram of the circuits employed is shown in Figure 1. By means of a motor-driven commutator C the crystal Cr was con-

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[1] G. W. Pierce: "Crystal Rectifiers for Electric Currents," Part I, Physical Review, **25**, pp. 31–60, 1907; Part II, ibid., **28**, pp. 153–187, 1909, and These Proceedings, **44**, pp. 317–349, 1909; Part III, Physical Review, **29**, pp. 478–484, 1909. See also "A Simple Method of Measuring the Intensity of Sound," These Proceedings, **43**, 1908, and "Principles of Wireless Telegraphy," McGraw-Hill, New York, 1910.

nected alternately first with the charge circuit VG′Cr and then with the discharge circuit CrG. A galvanometer, used for measuring the current out of or into the crystal, could be placed either in the discharge circuit at G or in the charge circuit at G′.

When the galvanometer was placed at G and allowed to come to a steady reading, while the commutator C was in operation, the reading of the galvanometer gave the discharge current made up of a series of discharge impulses from the crystal. Placed at G′, the steady deflection of the galvanometer, with the commutator in operation, gave the charge current made up of charge impulses going into the crystal.

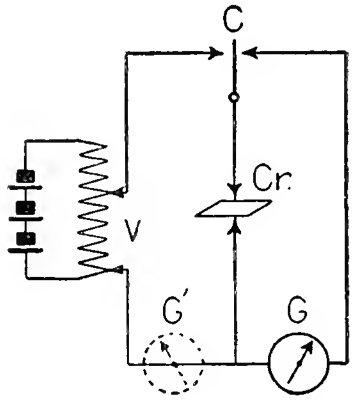

Figure 1. Circuit employed in capacity measurements.

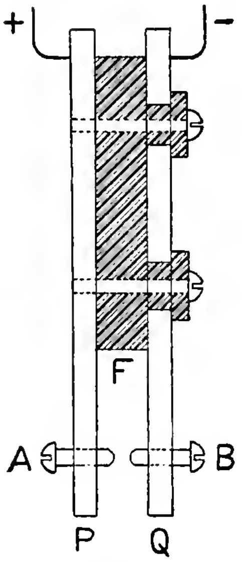

Figure 2. Clamp for holding specimen between screws A and B.

The Commutator. — The commutator was made of cold-rolled copper and was used with brushes of the same material so as to avoid thermoelectric currents in this part of the apparatus.

In order to minimize the leak current, the segments of the commutator and the brushes pressing against them were so arranged as to make the time of open circuit between charge and discharge as small as possible.

In order to simplify the interpretation of results, the time of contact for charge was made approximately equal to the time of contact for discharge.

Measurement of Frequency of Commutation. — Various speeds of the commutator were obtained by the use of a series of pulleys of different sizes on the axle of the motor and a corresponding series of different-sized pulleys on the axle of the commutator, which was driven by a belt from the motor. The speed of the commutator was measured by putting a standard mica condenser in the place of the crystal Cr of Figure 1, and reading the galvanometer at G with a known impressed voltage. In practice, in order to eliminate any errors arising from lack of proportionality of the galvanometer deflections, the impressed voltage was varied so that the readings of the galvanometer in the speed determinations were brought always to the same deflection (20 cm.), under which condition the number of charges or discharges per second was inversely proportional to the voltage required to give the standard deflection.

While the galvanometer deflection and voltage were under observation, one of these speeds was found absolutely by means of a revolution-counter attached to the shaft of the commutator, and the other speeds were then known in terms of the speed given by the revolution counter.

The capacity method of measuring the frequency of charges or discharges had the advantage of permitting instantaneous observations of the constancy of the commutator speed before and after measurements with the crystal as condenser.

Measurements Capable of Repetition. — Although the adjustment of the electrodes upon the crystal so as to get the capacity effects afforded some difficulty, yet when the adjustments were once made, the galvanometer readings, under given conditions, were about as constant with the crystal as capacity as with the standard mica condenser as capacity, and all the observations, with ordinary precautions, were capable of repetition with an error of about 1 per cent, which represented the irregularities of the speed of the commutator.

Galvanometer. — A D'Arsonval Galvanometer of 2000 ohms resistance was used. This galvanometer was provided with a heavy closed-coil electromagnetic damper, so as to obtain steady deflections even with comparatively slow speeds of the commutator. High resistance or high inductance in the galvanometer used with this method of determining capacity, if the capacity is large, is objectionable, because of the danger of having incomplete charge or discharge. In the present experiments attention was given to the matter of the completeness or incompleteness of the charge or discharge. In one of the experiments described below (Experiment II.) the charges and discharges were probably incomplete, but this was due not to the resistance or inductance of the galvanometer, but to the high resistance of the conducting sheets which served, in the crystal, as armatures of the condenser or else to the high resistance of the contacts of the electrodes with these sheets.

Experiment I.

Crystal held in a Clamp. — In this experiment a flat piece of carborundum, about 1 mm. thick, was clamped between two screws A and B of Figure 2. These screws passed through brass supports P and Q insulated from each other by a fibre block F. The screws had copper-plated ends, and were screwed down upon the specimen with sufficient pressure to cause the brass supporting strips (1 cm. wide and 1.5 mm. thick) to spring apart perceptibly. Later experiments showed that the amount of this pressure probably has no influence on the capacity, so long as the increase or decrease of pressure does not change the position of the contacts with respect to the conducting laminae.

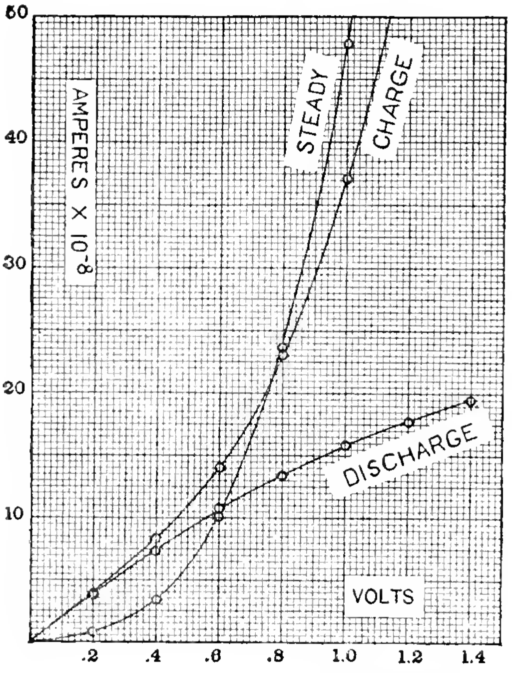

Figure 3. Current *vs.* voltage. A positive. $n = 24.2$.

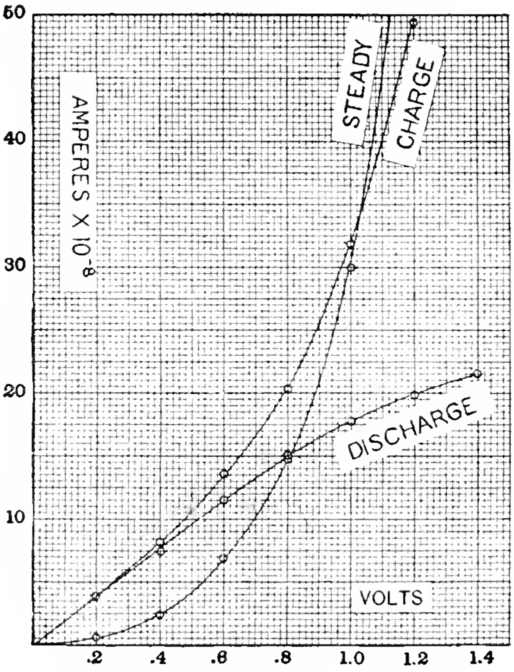

Figure 4. Current *vs.* voltage. B positive. $n = 24.2$.

Choice of Specimen. — The particular specimen used in this experiment and the particular setting of the crystal between the supports was obtained only by groping. It had been found accidentally that a specimen of carborundum used in temperature measurements of conductivity showed a slight capacity effect. Incited by this observation, we selected a large number of pieces of carborundum and put them one after the other in the clamp and tested for capacity. Most of them showed no capacity. Finally the piece used in this experiment was tried with the adjustment that happened to give the capacity effect in a marked degree.[2] Then without changing the adjustment a complete set of data with different speeds and different applied voltages was taken. After the experiment was completed, the specimen was examined with a microscope and was explored electrically while under the microscope, and the existence of the conducting laminae separated by insulating sheets was discovered. After the discovery of these laminae, other specimens could be selected and, with a somewhat difficult adjustment of the electrodes against the conducting laminae, could be shown to act as condensers with larger capacity in some cases than that of the specimens with which the present data were obtained.

Data with Specimen I. — Table I. following contains values of the charge and discharge current obtained with Specimen I, in a circuit of the form of Figure 1, under various impressed voltages and for various numbers of charges and discharges per second. The crystal was connected into the circuit so that one side should be positively charged (see column headed "A positive") and then, without changing the adjustment of the specimen in the clamp, the leads to the crystal were reversed so that it should be charged with the other side positive (see column headed "B positive").

Charge and Discharge Current not a Linear Function of the Voltage. — From these data, sample curves of charge and discharge current plotted as a function of the impressed voltage, with $n = 24.2$, are given, in Figure 3, with the charge applied so that the side A was positive, and in Figure 4 with the charge applied in the opposite direction. Along with the "charge" and "discharge" curves there is plotted, in each figure, a curve of steady current through the crystal obtained when the various voltages were applied directly in circuit with the crystal and galvanometer without the intermediation of the commutator. These curves, which are marked "steady," are the *current-voltage characteristics* of the crystal in the two opposite directions.

The curves of Figures 3 and 4 show that the charge and discharge

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[2] In his testimony, on May 22, 1911, in the case of the National Electric Signaling Company *vs.* The United Wireless Telegraph Company, Equity No. 643, District of Maine, Dr. Louis Cohen stated that a certain carborundum detector had a capacity of about .004 microfarads. This result he obtained by measurements with a high frequency generator of 72,500 cycles. So far as we know, his result has not been published except in the Court Record. Dr. Cohen gave no explanation of the phenomenon.

Our own discovery of the capacity was made before the date of Dr. Cohen's experiments, and our delay in publication has been occasioned by a long and tedious search for the explanation of the phenomenon, which we believe we have now found.

TABLE I.

Observations in Measurement of the Capacity of Specimen I.

No. of Charges or Discharges per Second, n.	Impressed Voltage E in Volts.	Current in Amperes × 10^{-8}.			
		A Positive.		B Positive.	
		Charge.	Discharge.	Charge.	Discharge.
11.43 for A positive and 11.85 for B positive	.2	2.46	2.14	2.35	2.11
	.4	5.49	4.01	5.20	4.22
	.6	10.00	5.80	8.87	6.36
	.8	17.90	7.17	15.00	7.85
	1.0		8.23		8.75
	1.2		9.26		9.50
	1.4		10.22		10.27
16.60 for A positive and 16.90 for B positive	.2	3.17	2.80	3.30	2.71
	.4	6.80	5.54	6.85	5.60
	.6	11.70	8.05	11.33	8.72
	.8	20.00	10.02	18.04	11.04
	1.0		11.65		12.79
	1.2		13.20		14.20
	1.4		14.25		15.55
20.0 for A positive and 20.4 for B positive	.2	3.43	3.20	3.43	3.16
	.4	7.25	6.34	7.40	6.62
	.6	12.40	9.00	12.13	10.00
	.8	20.4	11.17	19.30	12.75
	1.0		12.70		14.80
	1.2		13.98		16.35
	1.4		14.80		17.84
24.3 for A positive and 24.2 for B positive	.2	3.94	3.62	3.94	3.64
	.4	8.36	7.34	8.21	7.47
	.6	14.00	10.73	13.35	11.50
	.8	23.05	13.50	20.30	15.04
	1.0		15.83		17.75
	1.2		17.70		19.80
	1.4		19.50		21.60
29.1 for A positive and 29.5 for B positive	.2	4.41	4.17	4.43	4.25
	.4	9.21	8.23	9.22	8.71
	.6	15.10	12.10	14.80	13.30
	.8	23.75	15.32	22.40	17.40
	1.0		17.83		20.32
	1.2		20.05		22.90
	1.4		21.90		24.40
32.7 for A positive and 33.1 for B positive	.2	5.02	4.43	5.01	4.75
	.4	10.30	9.25	10.56	9.75
	.6	16.85	13.70	16.77	15.25
	.8	25.90	17.30	25.02	20.20
	1.0		20.60		23.80
	1.2		23.20		26.85
	1.4		25.65		29.60
39.80 for A positive and 39.83 for B positive	.2	5.67	5.36	5.78	5.28
	.4	11.80	10.77	11.96	11.12
	.6	19.10	15.91	19.33	17.16
	.8	30.35	20.54	28.40	23.03
	1.0		24.75		27.95
	1.2		28.20		31.95
	1.4		31.45		35.10

current obtained with this specimen is not a linear function of the applied e. m. f. This might have been anticipated from the fact that the leak current through the crystal which increases the charge current and diminishes the discharge current is not a linear function of the voltage.

TABLE II.

Equations of Current as Function of n.

Impressed Voltage E.	Charge Equation.	Discharge Equation.
	With A Positive.	
.2	$I_1 \times 10^8 = 1.3 + 1.12\,n$	$I_2 \times 10^8 = .9 + 1.10\,n$
.4	$3.0 + 2.25\,n$	$1.8 + 2.24\,n$
.6	$6.3 + 3.33\,n$	$1.8 + 3.46\,n$
.8	$13.3 + 4.02\,n$	$1.5 + 4.80\,n$
1.0		$1.5 + 5.85\,n$
1.2		$1.6 + 6.72\,n$
1.4		$1.9 + 7.28\,n$
	With B Positive.	
.2	$I_1 \times 10^8 = 1.0 + 1.20\,n$	$I_2 \times 10^8 = .7 + 1.20\,n$
.4	$2.3 + 2.45\,n$	$1.4 + 2.46\,n$
.6	$4.4 + 3.74\,n$	$2.3 + 3.74\,n$
.8	$9.3 + 4.82\,n$	$1.7 + 5.44\,n$
1.0		$1.4 + 6.66\,n$
1.2		$.6 + 7.87\,n$
1.4		$-.1 + 8.35\,n$

Charge and Discharge Currents are Linear Functions of n. — If, instead of being plotted against voltage, the charge and discharge current-readings be plotted against the number of charges and discharges per second, the curves of Figures 5, 6, 7, and 8 are obtained. These curves show that with either orientation of the crystal ("A positive" or "B positive") the current-reading of the galvanometer on charge or on discharge is a linear function of the number of charges or discharges per second.

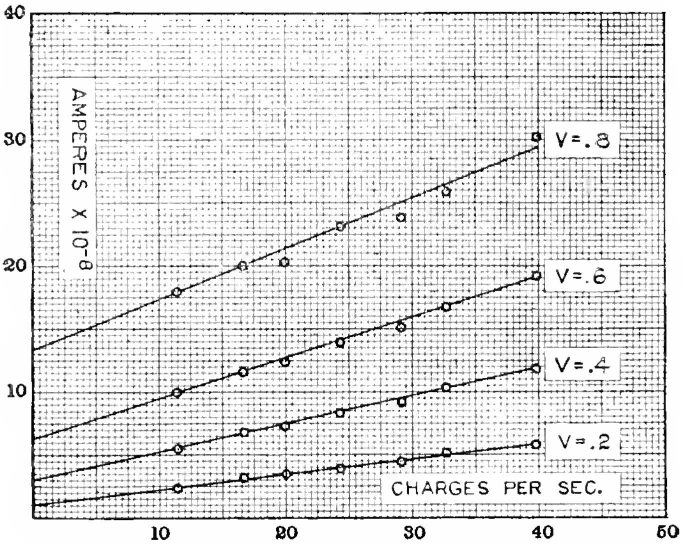

FIGURE 5. A positive. Charge current *vs.* no. charges per second, for various applied voltages *v.*

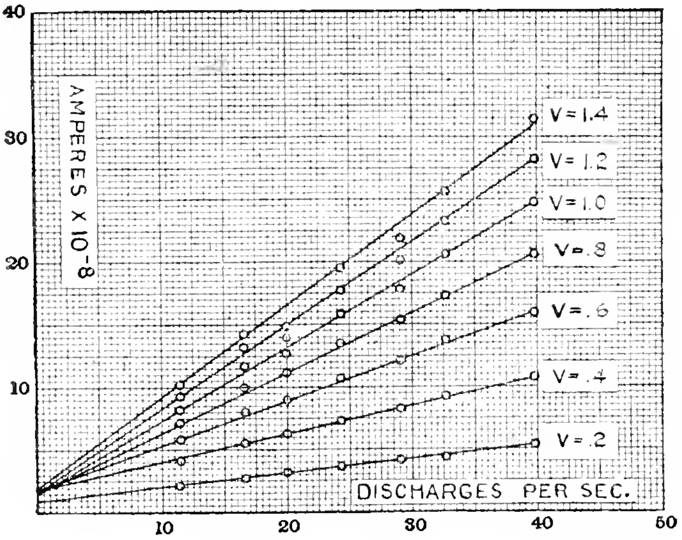

FIGURE 6. A positive. Discharge current *vs.* no. discharges per second, for various applied voltages *v.*

The empirical equations of the curves of Figures 5 to 8, as taken from the curves, are given in Table II. above.

The equations of Table II. agree closely with the data of Table I. The simplicity of these equations indicates that we are dealing with an orderly phenomenon. The linear relation between charge or discharge current and number of charges or discharges per second, we have taken to indicate that the charge and discharge were practically complete at each commutation; for it is apparent that if this charge or discharge were not complete the incompleteness would be greater at the higher frequencies of commutation and we should not have the linear relation.

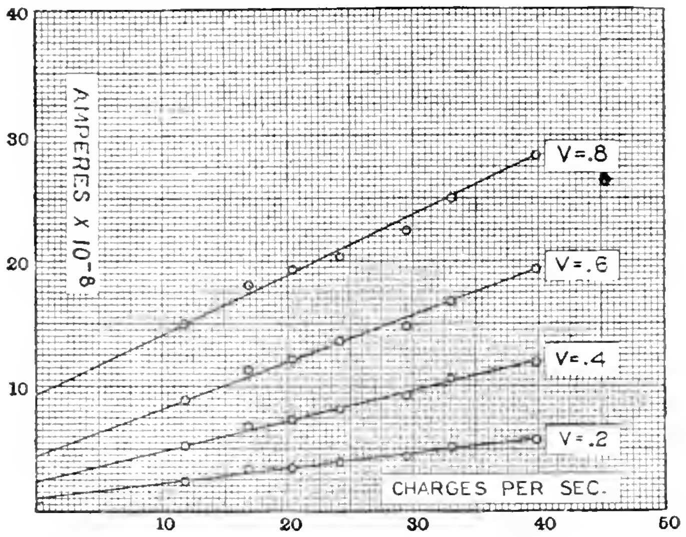

FIGURE 7. B positive. Charge current *vs.* no. charges per second.

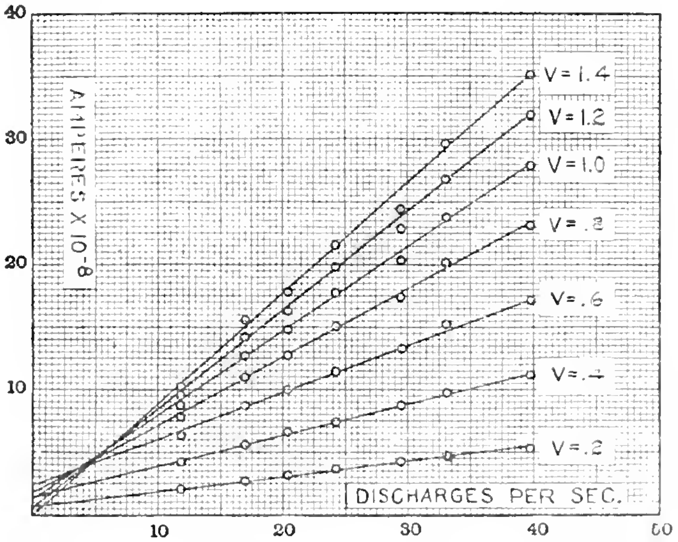

FIGURE 8. B positive. Discharge current *vs.* no. discharges per second.

There follows a mathematical investigation of the phenomenon with the assumption of a complete charge and discharge at each cycle of the commutator. The problem is an interesting one on account of the fact that the leak current through the crystal is not proportional to the voltage.

THEORY OF ACTION OF CRYSTAL AS A LEAKY CONDENSER ON THE ASSUMPTION THAT CHARGE AND DISCHARGE ARE COMPLETE.

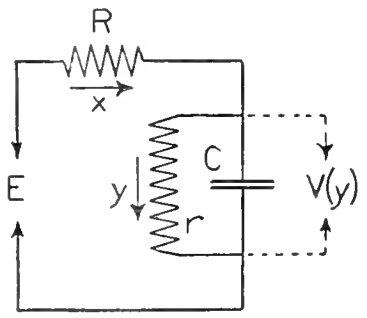

FIGURE 9.

Let us suppose an e. m. f. E (Figure 9) to be applied to a condenser C through a resistance R, and suppose that the condenser is shunted by a resistance r, through which the leak occurs — the resistance r being of such a character that the current through it is not proportional to the voltage.

Let x = the feed current in the main lead R,
y = the leak current through r,
v = difference of potential between the ends of the resistance r; this is a function of y, and is also the p. d. between the plates of the condenser.

These quantities, x, y, and v are functions of the time t.

Kirchhoff's laws give the following equations:

$$E = Rx + v, \tag{1}$$

obtained by taking the e. m. f. around the circuit $ERCr.$; and

$$\int (x - y)dt = Cv, \tag{2}$$

since $(x - y)$ is the current charging the crystal capacity.

By integration of equation (2) from $t = 0$ to $t = T$, we have

$$q_1 = \int_0^T x dt = C(v_T - v_0) + \int_0^T y dt, \tag{3}$$

in which q_1 is the quantity of electricity flowing through the charge leads during the time T of one complete connection of the condenser to the charging e. m. f.

If we suppose the previous discharge of the condenser to have been complete

$$v_0 = 0. \tag{4}$$

If also we suppose the charge of the condenser is complete in the time T, the current x flowing through the leads at time T is Y, where Y is the steady current through the crystal under the impressed e. m. f. E; therefore, by equation (1), we have

$$v_T = E - RY. \tag{5}$$

Whence equation (3) becomes

$$q_1 = (E - RY)C + \int_0^T y\,dt. \tag{6}$$

With n charges of the condenser per second, we have for the galvanometer current-reading I_1 in the charge circuit $I_1 = nq_1$; whence

$$I_1 = nC(E - RY) + n\int_0^T y\,dt. \tag{7}$$

In this equation R is the resistance of the charge circuit from the source of e. m. f. up to the point at which the charge is deposited on the condenser. This includes the resistance of the galvanometer, the resistance of the contacts of the electrodes with the conducting laminae, and the resistance of these laminae up to the point of leak.

Equation (7) is an exact expression for the current-reading of the galvanometer in the charge circuit when the commutator is driven so as not to exceed the speed at which the charge of the condenser at each impulse is complete.

Equation (7), therefore, holds for

$$T \geqq \tau$$

in which T is the time during which the condenser is in charge relation to the circuit during one cycle of the commutator, and τ is the interval required for practically complete charging of the condenser. Let us now break up the last term of equation (7) into two integrals, one from zero to τ and the other from τ to T. During the first of these intervals the leak current $y = y_1$ (say) is variable, and during the second interval the leak current $y = Y$ (say) is constant. Then we have

$$I_1 = nC(E - RY) + n\int_0^\tau y_1 dt + n\int_\tau^T Y dt,$$

in which y_1 is the variable leak current during the short interval for the potential of the condenser to attain substantially its final value, and Y is the steady current through the crystal and the leads under the steady e. m. f. E during the remainder of its connection with the charge circuit. The steady-leak term may be integrated, and we have after integration

$$I_1 = nC(E - RY) + nY(T - \tau) + n\int_0^\tau y_1 dt. \qquad (8)$$

Now it should be noted that the quantity nT is independent of the speed, since the geometrical dimensions of the commutator, which is of the rotating type, are fixed. The value of nT is $1/p$, — this quantity $1/p$ being the part of the whole circumference of the commutator occupied by the charge segment. Replacing nT by its value $1/p$, we have

$$I_1 = \frac{Y}{p} + n\{CE - RYC - Y\tau + \int_0^\tau y_1 dt\}. \qquad (9)$$

In equation (9) τ is arbitrarily defined as the time for a practically complete charge. Let us be a little more specific and suppose that τ is of such value that when substituted for t in the exponential expression $e^{-\frac{t}{RC}}$ it reduces this exponential to .006. This would make the charge complete so far as measurements of the accuracy of the present experiment would show. If

$$e^{-\frac{\tau}{RC}} = .006,$$

$$\tau = 5RC \text{ (by tables of exponentials).} \qquad (10)$$

With this definition of τ equation (9) becomes

$$I_1 = \frac{Y}{p} + n\{CE - 6RYC + \int_0^{5RC} y_1 dt\}. \qquad (11)$$

This is the equation of current-reading of the galvanometer in the leads to the crystal during *charge*.

Let us next examine briefly the theoretical problem of the *discharge* of the crystal condenser.

A mathematical treatment similar to that of the charge shows that the current-reading of the galvanometer in the discharge circuit, if there are n discharges per second, is

$$I_2 = nCE_0 - n\int_0^{5RC} y_2 dt, \qquad (12)$$

in which y_2 is the leak current during discharge and E_0 is the potential of the condenser at the beginning of the discharge. The potential of the condenser at the beginning of the discharge is less than E the applied e. m. f. for two reasons; first, because on account of the leak, the crystal was not charged to the applied e. m. f.; and second, because there has been a small loss of charge during the insulation time while the commutator was changing from charge to discharge.

As may be seen by reference to equation (5) the deficiency of potential due to the first of these causes is RY. The fall of potential due to the second of these causes is $\frac{1}{C}\int_0^{T_2} y_3 dt$, in which y_3 is the leak current during insulation, and T_2 is the length of time of the insulation period during each cycle. Therefore the current reading of the galvanometer in the discharge circuit is

$$I_2 = n\left\{CE - RYC - \int_0^{T_2} y_3 dt - \int_0^{5RC} y_2 dt\right\}. \tag{13}$$

This is the exact equation on *discharge.*

As an approximation let us suppose that the leak current during insulation was constant and equal to its value at the end of the preceding charge. This is approximately true, because the insulation time was short. With the approximation we have

$$n\int_0^{T_2} y_3 dt = nYT_2 \tag{14}$$

$$= \frac{Y}{m},$$ in which $\frac{1}{m}$ is the part of the commutator circumference occupied by the insulation segment. With this approximation equation (13) becomes

$$I_2 = -\frac{Y}{m} + n\left\{CE - RYC - \int_0^{5RC} y_2 dt\right\}, \quad \text{(approx.)} \tag{15}$$

in which the first term Y/m is a little too large.

EXAMINATION OF THE DATA OF EXPERIMENT I.

In order to compare the data of Experiment I. with the theoretical equations for charge and discharge current derived above, let us write the charge equation (11) in the form

$$I_1 = \frac{Y}{p} + nEC'_1, \tag{16}$$

in which C'_1 is related to the capacity C by the equation

$$C = \frac{C'_1}{1 - \frac{6RY}{E} + \frac{1}{CE}\int_0^{{\cdot}5RC} y_1 dt}. \tag{17}$$

Likewise writing the discharge equation (15) in the form

$$I_2 = -\frac{Y}{m} + nEC'_2, \tag{18}$$

in which C'_2 is related to the capacity C by the equation

$$C = \frac{C'_2}{1 - \frac{RY}{E} - \frac{1}{CE}\int_0^{{\cdot}5RC} y_2 dt}. \tag{19}$$

Let us now tabulate the values of C'_1 and C'_2 obtained from the experimental data. These quantities which we shall call approximate values of capacity are obtained by dividing the coefficients of n of the equations of Table II. by the corresponding values of E, and are collected in Table III.

In the attempt to get a nearer approximation to the capacity in terms of these coefficients C'_1 and C'_2, it should be noted that the integral terms of equations (17) and (19) are greater than would be obtained by putting y_1 and y_2 respectively equal to zero, and are less than would be obtained by setting y_1 and y_2 equal to their greatest value Y; whence it may be seen from equation (17) and equation (19) respectively that

$$\frac{C'_1}{1 - \frac{6RY}{E}} > C > \frac{C'_1}{1 - \frac{RY}{E}}, \tag{20}$$

and

$$\frac{C'_2}{1 - \frac{6RY}{E}} > C > \frac{C'_2}{1 - \frac{RY}{E}}, \tag{21}$$

in which C is the capacity.

It is, therefore, evident that C, the capacity of the crystal, is greater than the coefficients C'_1 or C'_2 of Table III.

In the attempt to ascertain whether or not the resistance terms could influence the coefficients sufficiently to account for the large excess of these coefficients with B positive over the corresponding values of A positive, or whether on the other hand it is necessary to assume different capacities in the two opposite directions, we have computed approximate values of the integrals in the denominators of equations (17) and (19). These computations were made by omitting second-order effects and assuming that the electromotive force on charge is $v_1 = E(1 - e^{-\frac{t}{RC}})$, and on discharge $v_2 = Ee^{-\frac{t}{RC}}$. With these values of the e. m. f. as functions of t/RC and with the steady current-voltage curves of Figures 3 and 4, y_1 and y_2 were plotted as functions of t/RC and integrated by measuring areas, with the result, which is only an approximation, that on charge [3]

TABLE III.

Applied Voltage E, Volts.	Approximate Value of Capacity of Specimen I.			
	With A Positive.		With B Positive.	
	C'_1 Farads Charge.	C'_2 Farads Discharge.	C'_1 Farads Charge.	C'_2 Farads Discharge.
.2	$.560 \times 10^{-8}$	$.550 \times 10^{-8}$	$.600 \times 10^{-8}$	$.600 \times 10^{-8}$
.4	.562	.560	.612	.615
.6	.555	.580	.623	.623
.8	.503	.600	.603	.681
1.0		.585		.666
1.2		.560		.656
1.4		.520		.632
average	.545	.565	.619	.639

$$C'_1 = C\left(1 - \frac{2.6R}{\rho}\right), \tag{22}$$

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[3] An independent investigation of the problem imposing the condition that the leak resistance obey *Ohm's law* (i. e. is independent of voltage) leads also exactly to equation (16) for charge and to equation (18) for discharge, with, however, $C'_1 = C'_2 = \frac{C}{\left(1 + \frac{R}{\rho}\right)^2} = C\left(1 - \frac{2R}{\rho}\right)$, approximately.

and on discharge

$$C'_2 = C\left(1 - 1.5\frac{R}{\rho}\right), \tag{23}$$

in which R is the resistance from the impressed e. m. f. into the condenser, and ρ is equal to V/E and is the resistance to steady e. m. f. of the circuit from the source of e. m. f. through the leads and through the plates and dielectric of the condenser. The resistance ρ is a function of E and is smaller the greater E is.

These equations are consistent with the fact that the coefficient C'_2 on discharge is greater than the coefficient C'_1 on charge. This is seen from Table III. to be true both for A positive and for B positive. Now the current-voltage curves of Figures 3 and 4 show that ρ is smaller for A positive than for B positive. This would make the coefficients for B positive smaller than those for A positive, whereas the converse is the case. In order to explain this discrepancy it is necessary to suppose either

(1) that the capacity of the crystal condenser is actually greater in direction B positive than in the opposite direction, or

(2) that the resistance R is also a function of E and decreases with increasing E more rapidly than ρ does.

The second of these propositions is entirely consistent with previous experiments with carborundum crystals, which showed that if the electrodes were plated to the specimen a large part of the dependence of resistance on current disappeared.

We cannot, however, be sure that the apparent inequality of capacity in the two opposite directions is entirely an effect of leak current; for we give next data obtained with another specimen with which the leakage through the crystal is almost entirely absent, and yet the capacity given by the measurements is different in the two opposite directions.

Experiment II. Specimen with very Small Leakage.

Mounting in Wood's Metal. — This specimen of carborundum was mounted in a metallic cup in a matrix of Wood's metal. The Wood's metal which served as a solder was placed in the cup and was melted. The specimen was pushed into the molten solder and held with all but its upper face submerged until the solder solidified, forming a close-fitting mold about the specimen. The cup served as one electrode. The other electrode was a pointed brass rod brought down upon the crystal and held by a spring. The cup containing the specimen was

TABLE IV.

DATA IN MEASUREMENT OF THE CAPACITY OF SPECIMEN II.

No. of Charges or Discharges per Second, n.	Impressed e. m. f. E. in Volts.	Current in Amperes × 10^{-7}.			
		Point Positive.		Point Negative.	
		Charge.	Discharge.	Charge.	Discharge.
11.0	.3			.787	.787
	.6	1.43	1.43	1.66	1.64
	.9	2.07	2.06	2.71	2.54
	1.2	2.68	2.66	4.48	3.52
16.7	.3			1.16	1.16
	.6	2.14	2.14	2.46	2.43
	.9	3.18	3.17	3.98	3.81
	1.2	4.05	4.03	6.20	5.34
22.5	.3			1.59	1.59
	.6	2.92	2.92	3.30	3.27
	.9	4.30	4.29	5.41	5.22
	1.2	5.61	5.59	8.04	7.26
30.9	.3			2.16	2.16
	.6	3.97	3.97	4.42	4.39
	.9	5.92	5.89	7.17	7.02
	1.2	7.64	7.60	10.7	10.0
38.3	.3			2.60	2.60
	.6	4.81	4.78	5.40	5.37
	.9	7.15	7.15	8.72	8.54
	1.2	9.18	9.10	12.75	12.08
46.2	.3				
	.6	5.67	5.67	6.37	6.33
	.9	8.30	8.34	10.17	10.00
	1.2	10.67	10.67	14.76	14.40
54.6	.3			3.48	3.38
	.6	6.41	6.40	7.35	7.34
	.9	9.50	9.50	11.41	11.27
	1.2	12.50	12.30	16.45	15.85

carried by a mechanical microscope stage, so that the specimen could be moved around under the point terminal until a point of contact that gave the capacity effect was located by the capacity measurements. The pressure of the point electrode was then increased so as to avoid accidental disturbance of the connections during the measurements of capacity.

Data. — Current-readings on charge and discharge were taken with the crystal charged so that the point electrode was positive and then with the point electrode negative. Table IV. contains the record.

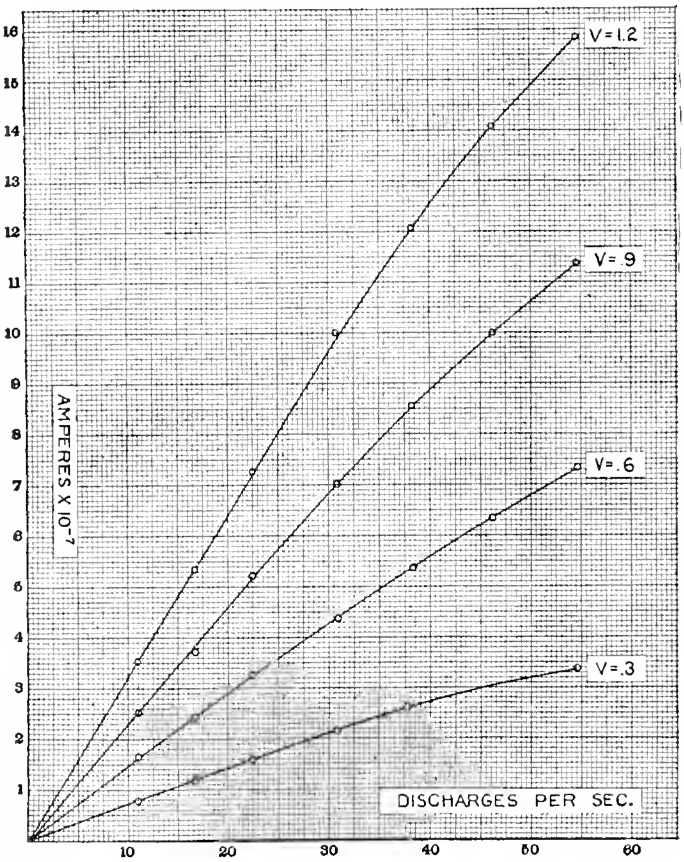

FIGURE 10. Point negative. Discharge current *vs. n*, for various applied voltages *v*.

By a reference to Table IV. it will be seen that with the crystal charged so that the point was positive this specimen gives the same current on discharge as on charge. With this direction of charging *the crystal condenser shows practically no leak.* Table V., which contains the steady current-voltage data for this specimen, shows also that with this direction of application of the e. m. f. the crystal lets through only $.09 \times 10^{-7}$ amperes at 1.2 volts. With the e. m. f. applied in the opposite direction (point negative) the charge and discharge currents (Table IV.) differ by about 5 per cent, at the highest voltage, 1.2 volts. At .9 volts, and lower, this difference is one per cent or less. With the point negative the steady current at 1.2 volts amounts to 1.79×10^{-7} amperes as is seen in Table V. Therefore the crystal with the point charged negative is not non-leaky as with the opposite direction of charging, but the leak is so small as to make the analysis of the problem much more satisfactory than with Specimen I.

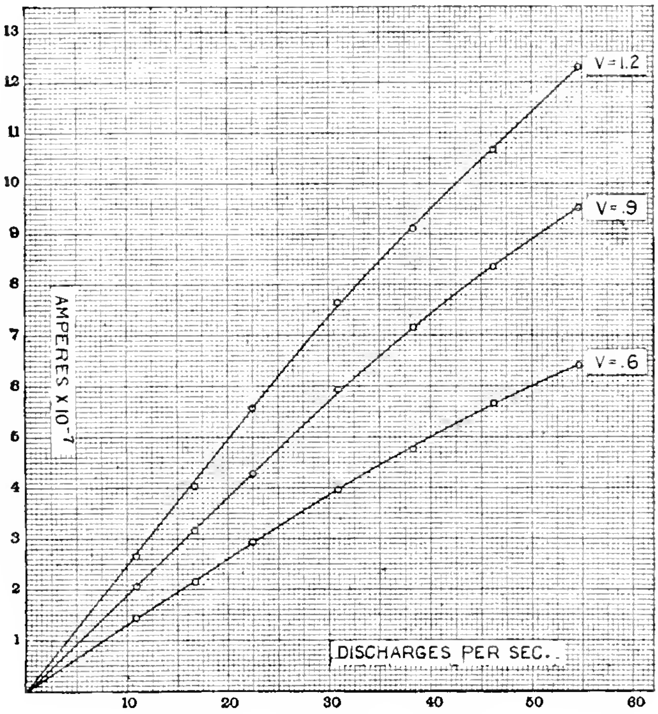

Figure 11. Point positive. Discharge current *vs.* n, for various applied voltages v.

Figures 11 and 10 show the discharge current plotted against n, the number of discharges per second, obtained with point positive and point negative respectively. The corresponding charge curves depart so slightly from the discharge curves that they are not here reproduced.

All of the charge and discharge curves for this specimen pass through the origin. This is a result such as one obtains with an ordinary condenser possessing no leakage.

The curves all droop at higher values of n, but are nearly straight for small values of n. Now this fact is in agreement with results obtained with good condensers provided they possess such high resistance in the charge or discharge circuit that the charge and discharge are incomplete. It is interesting that the treatment of the experimental curves of Figures 10 and 11 as due to a condenser with incomplete charge and discharge leads to the result that the capacity is independent of n but is dependent, as in Experiment I., upon the magnitude and *direction* of the impressed e. m. f. We shall give a brief derivation of the formula for multiple incomplete charge and discharge.

SKETCH OF THEORY OF MULTIPLE INCOMPLETE CONDENSER DISCHARGE.

Let a condenser of capacity C be alternately charged and discharged through a resistance R which is so great as to permit only a partial charge or discharge in the time T of one connection of the condenser into the charge or discharge circuit.

Let the applied e. m. f. on charge be E, and suppose that the charge and discharge have been repeated until a final state is reached.

Let q_1 = quantity of electricity in the condenser at the end of a charge,
q_0 = the quantity in the condenser at the end of a discharge.

If we write down the differential equation for the quantity in the condenser on charge and integrate it subject to the conditions of the problem, we obtain

$$q_1 = q_0 e^{-\frac{T}{RC}} + CE\left(1 - e^{-\frac{T}{RC}}\right). \tag{24}$$

Similarly from the differential equation for discharge we get

$$q_0 = q_1 e^{-\frac{T}{RC}}. \tag{25}$$

Eliminating between equations (24) and (25) we have

$$q_1 = \frac{CE}{1 + e^{-\frac{T}{RC}}}.$$

$$q_0 = \frac{CEe^{-\frac{T}{RC}}}{1 + e^{-\frac{T}{RC}}}.$$

The quantity of electricity flowing into the condenser during one charge, or out of the condenser during one discharge, is

$$q = q_1 - q_0 = CE\frac{1 - e^{-\frac{T}{RC}}}{1 + e^{-\frac{T}{RC}}}. \tag{26}$$

This equation by expansion becomes

$$q = CE\,(1 - 2e^{-\frac{T}{RC}} + 2\,(e^{-\frac{T}{RC}})^2 - 2\,(e^{-\frac{T}{RC}})^3 + \ldots\ldots). \qquad (27)$$

If we may neglect $2\,(e^{-\frac{T}{RC}})^2$ in comparison with unity, equation (27) becomes

$$q = CE\,(1 - 2e^{-\frac{T}{RC}}) \qquad \text{approximation.} \quad (28)$$

If there are n charges per second, the current-reading of a galvanometer in the charge or discharge circuit is

$$I = nq,$$

and the time of charge or discharge is

$$T = \frac{1}{pn},$$

where $1/p$ is the fraction of the circumference of the commutator occupied by the charge segment or discharge segment, the two being equal.

With these substitutions equation (28) becomes

$$I = nCE\,(1 - 2e^{-\frac{1}{pnRC}}). \qquad (29)$$

With the commutator used in these experiments $1/p$ was .48, whence

$$I = nCE\,(1 - 2e^{-\frac{0.48}{nRC}}). \qquad (30)$$

Examination of the Data of Experiment II.

The curves of discharge current of Figures 10 and 11 with current plotted against number of discharges per second are accurately described by equation (30), as may be seen by reference to Tables VI. and VII., which contain a comparison of observed and calculated values.

The equations of Table VIII. were obtained as follows: Consistent with the theoretical equation (30), the slope of each of the curves of Figures 10 and 11 was taken at the origin. This slope is the coefficient of n in equation (30), and the corresponding coefficient in Table

VIII. Having obtained the slope term, the exponential was next obtained by assuming the upper end point of one of the experimental curves to satisfy equation (30). This gave the exponent $-165/n$, and by trial the same exponent was found to apply approximately to all of the other curves. That is, all the equations of Table VIII. were obtained by employing the slope at the origin of each of the experimental curves, and in addition assuming the exponential equation to be correct for one other point of one of the curves. All of the points of all the curves were then found to be closely given by the equations so derived.

TABLE V.

STEADY CURRENT-VOLTAGE CHARACTERISTIC OF SPECIMEN II.

E. m. f. Volts.	Current in 10^{-7} Amperes.	
	Point Positive.	Point Negative.
.3	.004	.012
.6	.02	.083
.9	.04	.45
1.2	.09	1.79
1.5	.165	6.13

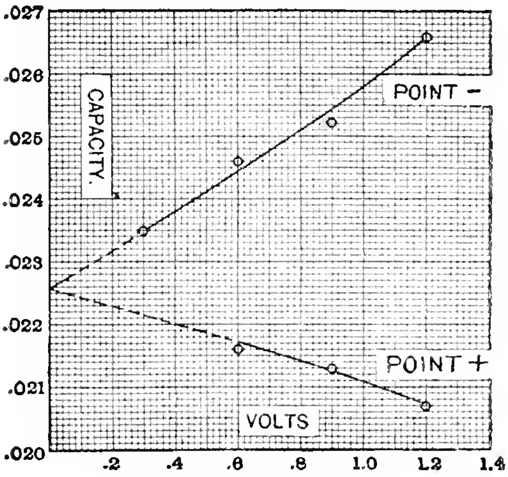

FIGURE 12. Capacity in microfarads of Specimen II. for different values of applied e. m. f.

The conclusion is that the droop of the several curves of Figures 10 and 11 may be reasonably explained as due to incompleteness of charge and discharge. On this assumption it will be seen that the capacity of the crystal, obtained by dividing the coefficients of the equations of Table VIII. by the corresponding values of E, are functions of the applied e. m. f. and of the direction of charge, while the product of R by C, as given by the exponent, is constant. These quantities are collected in Table IX., and plotted in the curves of Figure 12.

TABLE VI.

Data of Experiment II. Compared with Equation (30).

No. of Discharges per Second, n.	Point Positive. Discharge Current in 10^{-7} Amperes.					
	E = .6.		E = .9.		E = 1.2.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
11.0	1.43	1.43	2.06	2.11	2.66	2.73
16.7	2.14	2.15	3.17	3.17	4.03	4.09
22.5	2.94	2.94	4.29	4.32	5.59	5.58
30.9	3.97	3.99	5.89	5.90	7.60	7.62
38.3	4.78	4.85	7.15	7.18	9.10	9.26
46.2	6.40	6.42	9.50	9.50	12.30	12.30

The curves of Figure 12 show that the capacity, as given by equation (30), is changed by a mere reversal of the direction of charge. The capacity is the greater when the point electrode is negative, and with this orientation the capacity increases with increase of applied e. m. f. With the opposite direction of application of e. m. f. the capacity is less and decreases with increasing applied e. m. f.

Whether this result is evidence of a unilateral dielectric constant of the carborundum — which seems improbable — or whether the result is due to an imperfect comprehension of the various factors that may enter into the phenomenon and appear in the final coefficient as capacity, we are at present unable to say.

Among the various factors neglected in the mathematical discussion of the data there is the possibility that heat effects may be important. It looks at first glance as if a thermoelectromotive force at the junction of the electrode with one of the laminae of the crystal might aid the charge in one direction of charge and hinder it with the opposite direction of charge, and might, hence, cause differences in the capacity coefficients in the two directions, and might also account for the form of the curves of Figure 12. We have submitted the thermoelectric hypothesis to a mathematical treatment, assuming that both Joulean heat and Peltier heat act at the junction of one of the electrodes with the crystal, and have arrived at the result

TABLE VII.

Data of Experiment II. Compared with Equation (30).

No. of Disch. per Sec., n.	Point Negative. Discharge Current in 10^{-7} Amperes.							
	E = .3.		E = .6.		E = .9.		E = 1.2.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
11.0	.78	.77	1.64	1.59	2.54	2.52	3.52	3.52
16.7	1.16	1.17	2.43	2.42	3.81	3.80	5.34	5.35
22.5	1.59	1.58	3.27	3.26	5.22	5.11	7.26	7.20
30.9	2.16	2.22	4.39	4.58	7.02	7.17	10.00	10.10
38.3	2.60	2.61	5.37	5.38	8.54	8.45	12.08	11.92
46.2			6.33	6.32	10.00	9.95	14.10	14.30
54.6	3.38	3.48	7.34	7.18	11.27	11.25	15.85	15.85

(1) That the assumption of Joulean heat alone in combination with capacity gives a capacity coefficient that is *the same in the two opposite directions, and for both directions the effect of the heat term is to make the capacity coefficient diminish with increasing applied e. m. f.*

(2) Peltier heat and Joulean heat, if both present in combination with the capacity, would give different capacity coefficients in the two opposite directions, but the effect of the heat would still manifest itself as *an apparent decrease of capacity with increase of applied e. m. f. for both directions of application of the e. m. f.*

Neither of these results is in complete accord with the experimental facts.

Various other possible explanations of the apparent unilateral capacity of the crystal condenser have suggested themselves, but we have decided to make further measurements before entering into an attempt to consider more of the factors of the problem.

Specimen with Soldered Attachment under Test. — We have succeeded in soldering on the electrodes to one specimen now under test, and are able to preserve the condenser for a more extensive study of its characteristics. Up to the present this study has not added anything to the results given above. The new condenser leaks badly in one direction but very little in the opposite direction of charge. We are putting it through an ageing process before submitting it to final measurement.

TABLE VIII.

Equations Used in Calculating Values in Tables VI. and VII.

E.	Point Positive. Equation.	Point Negative. Equation.
.3	....	$I = .0703 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
.6	$I = .13 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .144 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
.9	$I = .192 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .227 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
1.2	$I = .248 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .320 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$

Microscopic and Electrical Exploration of the Specimens.

Illumination and Magnification. — Plate I. contains some micrographs of fragments of the crystals. These pictures — which are reproduced with a magnification of 20 diameters — were obtained by reflected light, with the aid of an illuminating objective. The light, which entered the side of the objective, was reflected downward by a prism so that it fell nearly perpendicularly upon the face of the crystal. This vertical illumination from above is most favorable for showing the stratifications in the crystals. Viewed by transmitted light the characteristics are hardly discernible.

Micrograph *a*, Plate I, shows two of the crystallographic angles of the carborundum crystal. The distance between these two vertices is 1.6 mm., and will serve as a convenient standard of reference for the dimensions of the other pictures, which were magnified to the same scale.

Conducting and Insulating Strata. — Micrograph *c* shows very clearly the characteristic stratification, which we have found to be the foundation of the electrostatic capacity of the carborundum. The black lines running in a general horizontal direction across the surface of the specimen are outcroppings of conducting dykes of the crystal; while the white spaces separating the black lines are outcroppings of the insulating matrix in which these dykes are imbedded. The lines which are black and white in the pictures are really merely *differently colored* in the crystal. The white regions are generally a transparent blue in the crystals, and the regions reproduced as black are usually seen as brown or red in the specimen.

TABLE IX.

VALUES OF C, RC, AND R FOR SPECIMEN II.

Applied e. m. f. E.	Capacity C, in Micro-farads.	RC in Ohm-farads.	R in Ohms.
FOR POINT POSITIVE			
.6	.0216	.0029	1.34×10^5
.9	.0213	.0029	1.36
1.2	.0207	.0029	1.40
FOR POINT NEGATIVE			
.3	.0234	.0029	1.24×10^5
.6	.0246	.0029	1.18
.9	.0252	.0029	1.14
1.2	.0267	.0029	1.08

The difference in electrical conductivity of the dark and light strata was discovered by mounting the specimen in the field of the microscope, and exploring it with two pin-points serving as electrodes. The pin-point electrodes were connected with a battery and galvanometer, or telephone, and were moved about over the surface of the specimen by means of two independent mechanical microscope stages insulated from each other. By means of the slow motion of the mechanical stages, the two pin-points could be put down upon the same dyke or on two different dykes, or one pin could be placed on a dyke while the other was placed on one of the lighter colored strata separating the dykes.

It was found that the insulation resistance of a very thin layer of the lighter colored material was so great that the current through it under an impressed e. m. f. of 7 volts did not give a perceptible deflection on the galvanometer, that is, the resistance was more than 7000 million ohms, whereas the resistance of the circuit when both pins were upon the same dark-colored dyke was only a few thousand ohms at this voltage.

It was not possible with some of the specimens to get into electrical contact with all of the dark-colored outcroppings, because in some cases it was evident that the outcroppings were in depressions or were coated over so that the electrodes could not be brought against them. With other specimens and with the aid of a telephone receiver in the exploring circuit, we could make attachment of one electrode to a solder-bed in which the crystal was mounted and could draw the other electrode across an exposed face of the crystal in the field of the microscope and hear a click in the telephone as the moving electrode passed over each of the dark-colored outcroppings.

Outcrop of Conducting Points. — In addition to the linear outcroppings of the conducting dykes, there are also with some of the specimens minute points of outcrop of conducting material. Some of these points are visible in Micrograph *d.* They are the globular markings near the left-hand side of the picture. Each globular marking is a minute darker speck surrounded by a whitish circle. In some cases we found an outcrop in the form of a minute speck, which evidently communicated with one or more conducting layers within the crystal, and which showed measurable capacity when one electrode was brought into contact with the speck while the other electrode was in contact with a distant corner of the crystal. In fact, with the specimen of *d* many of the apparently linear outcroppings are made up of discrete points of conducting material.

A Visible Condenser in Micrograph b. — As an illustration of a condenser completely visible, reference is made to Micrograph *b.* The left half of the picture shows two nearly parallel lines running up through the center and down along the left-hand side of the specimen. These lines, which run out of the field at the bottom and top of the picture, were seen, by moving the specimen in the original examination of this specimen, to be really two closed curves, one inside of the other. They are the outcroppings of two practically flat parallel strata nearly perpendicular to the direction of vision. By exploration with the pin-point electrodes these strata were found to be conducting, whereas the whitish band between the dark lines is the outcrop of an insulating layer separating the two conducting strata. Thus we have a visible condenser in the specimen. The capacity of this condenser was too small to be measured by the method we were employing, and this specimen is kept for future investigation.

Micrograph of Specimen I. — The pictures *e* and *f* of Plate I. show micrographs of the two opposite sides, respectively, of Specimen I. The electrical connection of the specimen into the test circuit was by means of screws set up against the two sides of the crystal. The ends of the screws were so large that the exact point of contact of the screws against the crystal could not be accurately determined, but one of the screw contacts was apparently against the ridge near the center of *e*; the other screw contact was near the center of *f*, which is opposite to *e*. Judging from the large value of the capacity obtained, we are of the opinion that more than one conducting dyke was in contact with each electrode, and that we were dealing with a multiple-plate condenser. Of this, however, we cannot at present be certain, as we have not as yet been able to measure the dielectric constant of the insulating strata, and have not yet been able to determine accurately the geometrical dimensions of the crystal condensers.

NOTE ON RELATION OF STRATIFICATION TO ACTION OF CARBORUNDUM CRYSTALS AS DETECTORS FOR ELECTRIC WAVES.

Not all points of a carborundum crystal are equally good detectors for the electric waves of wireless telegraphy. After our discovery of the existence of alternate conducting and insulating strata in the carborundum crystal, we arranged circuits, with the crystal connected to a multiple-pole switch so that it could be thrown into a wireless telegraph circuit and tested for its sensitiveness to electric waves produced by a test buzzer; then into a circuit of the form of Figure 1, and tested for conductivity and capacity.

The crystal was mounted in the field of a microscope and was carried by a mechanical stage with micrometer adjustment so that different parts of the crystal, while under observation with the microscope, could be brought into contact with the pin-point electrode.

It was found that

1. The crystal and its contact (i. e. the detector) did not respond to electric waves, and did not conduct, and did not have capacity when the point electrode was on one of the light-colored strata;

2. The crystal detector did respond whenever the contact was against one of the darker strata. In general, however, no capacity was dis-

cernible with one of these random adjustments sensitive to electric waves;

3. In rare cases, obtainable only after numerous trials, the adjustment of the contact upon the crystal would give a capacity; in these cases the system would also act as a detector for electric waves.

These observations show that the detection of electric waves occurs for practically any conductive high-resistance contact of the electrode with the crystal, whereas only a rarely attainable adjustment of the contact against a conducting stratum that happens to be pretty well insulated from the other electrode gives the capacity effect measurable by the method of charge and discharge. It is however apparent that if the capacity measurements could be made with the high frequency oscillations of wireless telegraphy, the capacity effect would appear much more commonly.

SUMMARY.

1. An electrostatic capacity is found in carborundum.
2. The capacity-measurements with two specimens are given for different voltage and different frequencies of charge and discharge. The capacity of one of the specimens was about .006 microfarads; that of the other about .022 microfarads.
3. With Specimen I. a leak, different in different directions of charge and not obeying Ohm's law, made the measurements uncertain of accurate interpretation.
4. Specimen II. was practically non-leaky but showed incompleteness of charge and discharge such as would be obtained with a high resistance (120,000 ohms) in the circuit. A reduction of the observation on the assumption of incomplete charge and discharge gives a capacity, which for voltages not zero, is different in the two opposite directions of charge. In one direction of charge the capacity increases with increase of applied voltage; while in the opposite direction of charge the capacity decreases with increase of voltage.
5. The existence of capacity in the crystal was found to be due to the existence of numerous alternate conducting and insulating strata within the crystal. These strata are visible with vertical illumination and moderate magnification.
6. Micrographs showing the stratification are given.
7. So far as the present experiments show, the action of the carborundum as a detector for electric waves and as a rectifier for electric currents is independent of its action as a capacity. But it will detect electric waves or rectify only provided contact is made to one or more of

the conducting strata. It may detect electric waves with an adjustment that shows no capacity by the present method of measuring capacity. On the other hand, with every adjustment at which we found capacity, we found also rectification and detection of electric waves.

Acknowledgment. — The authors gratefully acknowledge their indebtedness to the National Academy for an appropriation from the Bache Fund, which was employed in defraying a part of the expenses of this investigation.

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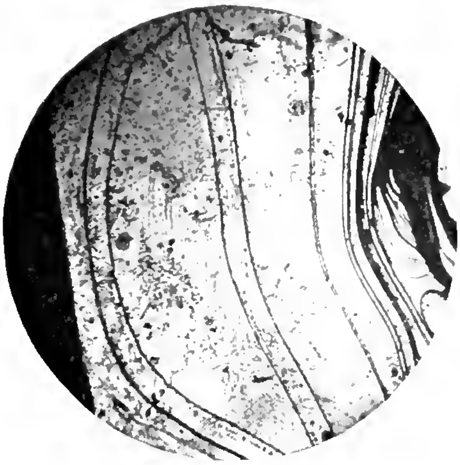

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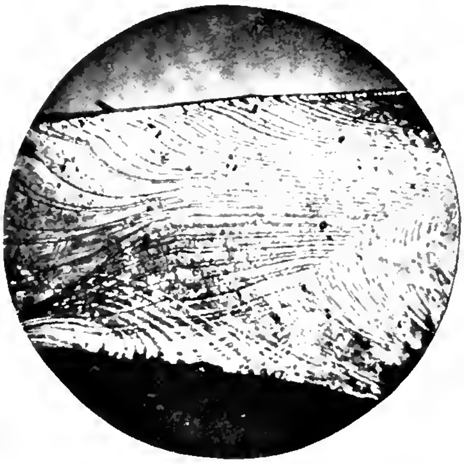

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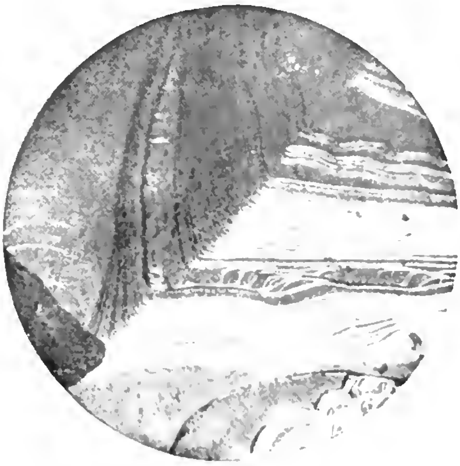

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 22. — November, 1912.

RECORDS OF MEETINGS, 1911-1912.

OFFICERS AND COMMITTEES FOR 1912-1913.

LIST OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

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Frederick Irving Knight. By Francis H. Williams.

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RECORDS OF MEETINGS.

One thousand and seventh Meeting.

OCTOBER 11, 1911. — STATED MEETING.

The Academy met in Ellis Hall, in the Massachusetts Historical Society's Building.

The PRESIDENT in the chair.

There were thirty-seven Fellows present.

The Corresponding Secretary presented the following letters and circulars: — from the University of Minnesota, inviting the Academy to be represented at the inauguration of George Edgar Vincent as its President; the preliminary announcement of the eighth International Congress of Applied Chemistry; a notice of contest for the Elia de Cyon prize; a request for subscriptions for the purchase of the birthplace of Pasteur; from the Naturforschende Gesellschaft zu Görlitz, inviting the Academy to be represented at the celebration of its centenary; a notice from the Surrogates' Court of New York regarding the property of Catherine R. B. Griffith; a notice regarding the probating of the will of Mary H. Cooke.

The following deaths were announced by the Chair: —

Samuel Hubbard Scudder, Resident Fellow in Class II., Section 3, Corresponding Secretary and Chairman of the Publication Committee from 1896 to 1900, Librarian from 1877 to 1885; Cyrus Gurnsey Pringle, Associate Fellow in Class II., Section 2.

At the request of the C. M. Warren Committee it was

Voted, That the sum of two hundred dollars ($200) be appropriated from the income of the C. M. Warren Fund for the use of the Committee.

The following gentlemen were elected Fellows of the Academy: —

In Class I., Section 1 (Mathematics and Astronomy): —

Joel Hastings Metcalf, of Winchester; Edwin Bidwell Wilson, of Cambridge; Lewis Boss, of Albany.

In Class I., Section 2 (Physics): —

Harvey Nathaniel Davis, of Cambridge; Harry Wheeler Morse, of Cambridge; Joseph Sweetman Ames, of Baltimore.

In Class I., Section 3 (Chemistry): —

William Crowell Bray, of Boston; Forris Jewett Moore, of Boston; Willis Rodney Whitney, of Schenectady.

In Class I., Section 4 (Technology and Engineering): —

Dugald Caleb Jackson, of Boston; Frederic Pike Stearns, of Boston; Charles Proteus Steinmetz, of Schenectady.

In Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe): —

Herdman Fitzgerald Cleland, of Williamstown; Hervey Woodburn Shimer, of Boston; Charles Richard Van Hise, of Madison.

In Class II., Section 2 (Botany): —

Oakes Ames, of North Easton; Edward Murray East, of Jamaica Plain; Robert Almer Harper, of Madison.

In Class II., Section 3 (Zoölogy and Physiology): —

Henry Bryant Bigelow, of Concord; Otto Knut Olof Folin, of Brookline.

In Class II., Section 4 (Medicine and Surgery): —

Milton Joseph Rosenau, of Boston; Elmer Ernest Southard, of Boston; Simon Flexner, of New York.

In Class III., Section 1 (Philosophy and Jurisprudence): —

Melville Madison Bigelow, of Cambridge; Marcus Perrin Knowlton, of Springfield; George Vasmer Leverett, of Boston; Roscoe Pound, of Belmont; Woodrow Wilson, of Princeton.

In Class III., Section 2 (Philology and Archaeology): —

Fred Norris Robinson, of Cambridge; Charles Cutler Torrey, of New Haven.

In Class III., Section 3 (Political Economy and History): —

Edward Channing, of Cambridge; Frederick Jackson Turner, of Cambridge; John Franklin Jameson, of Washington.

In Class III., Section 4 (Literature and the Fine Arts): —

William Sturgis Bigelow, of Boston.

The following report of the Committee on the Revision of the Statutes was read by the Chairman, Mr. Henry H. Edes: —

At the Stated Meeting of the Academy in March, several amendments to the Statutes were adopted upon the favorable report of the Committee to which they had been duly referred. At the same meeting, further important amendments were proposed, chiefly for the purpose of defining some of the newly-created functions and powers of the Council, of enlarging the functions of the Class Committees, and of prescribing the procedure of both bodies with respect to the nomination and election of Fellows and Foreign Honorary Members. These new amendments also proposed an increase in the number of Councillors from nine to twelve and of their terms of service from three years to four years, thereby insuring always to each Section of each Class at least one representative in the Council, which, with the eight *ex-officio* members, elected annually for terms of one year, would then be composed of twenty persons.

These amendments having been duly referred to a Committee for consideration and report, it was suggested from the floor, that as the recent adoption by the Academy of the several far-reaching recommendations of the Committee on Policy necessitated so many alterations in the Statutes, other changes, doubtless, would, in consequence, suggest themselves to the Committee; and the hope was expressed that it would feel warranted in incorporating in its report upon the amendments then referred to it such further changes as it might deem expedient. Whereupon, it was unanimously voted by the Academy that the Committee be authorized and requested to act accordingly.

The present Code of Statutes was adopted on the thirtieth of May, 1854. When the last printed edition appeared, in June, 1910, it had been then amended twenty-one times. Among the inevitable results of so many changes are tautology, repetition, and the distribution under two or more heads of subjects which should be treated in a single chapter. There are also strange omissions. For instance, there are no Articles describing the Corporate Seal of the Academy or providing for the attestation and delivery of the Academy's Diploma; indeed, the fact that the Society has a Common Seal is not even recognized, save by a casual allusion to it in the Chapter defining the duties of the President, while there is no mention whatever of a Diploma.

The new powers given to the Council by the amendments adopted in March last necessitated the draughting of an entirely new Chapter; while a proper recognition of the Seal required another. On the other hand, it was desirable that certain chapters should be consolidated, and repetitions eliminated, especially in the Chapter on Standing Committees, where three lines of print are five times repeated, and three other lines are four time repeated.

From what has been already said, it will be readily seen that the only way in which the problem before us could be satisfactorily dealt with was by recasting and re-arranging the whole Code. This has been done and the result submitted to the Academy in print during the past few days.

The principal changes, beside those already referred to, are (i) the fixing of the limit of the number of Fellows at Six hundred, — those residing in Massachusetts not to exceed Four hundred, as provided in the amended Charter; (ii) raising the limit of the Annual Dues, to be annually voted and determined by the Academy, from Ten dollars to Fifteen dollars; (iii) providing for a Commutation of the Annual Dues by the payment at one time of Two hundred dollars; (iv) restricting elections to the Stated Meetings in January and May; (v) providing that the Annual Report of the Treasurer shall be submitted in print; (vi) establishing the date when the financial year of the Academy shall begin; (vii) reducing the time in which delinquents may pay their Annual Dues from two years to six months; and (viii) the incorporation of some Standing Votes with those Chapters of the Statutes to which they pertain and in which they appear to your Committee to be more appropriately placed.

The new machinery for the nomination and election of Fellows and Foreign Honorary Members, if adopted by the Academy, cannot fail to result in a closer scrutiny by the Class Committees of the names proposed, and a more careful and discriminating selection by the Council of those presented to the Academy for its consideration.

Conciseness, concentration, comprehensiveness, and conformity were the principal objects aimed at by your Committee in redraughting the Code. Except in one or two unavoidable instances, no provision of the Statutes affecting more than one officer, committee, or subject has been repeated, such provisions being clearly indicated under their appropriate secondary headings by cross-references to the Chapter and Article where the text of the provision is printed.

Your Committee has given careful consideration to proposals for rotation in office applying to the eight Officers and the Standing Committees annually elected by the Academy, and for an increase in the number of members of some of the other Committees; but it is unanimously of opinion that the adoption of these propositions would not be wise. Experience gained by long, continuous service on such a committee, for instance, as that which administers the Rumford Fund, is valuable to the Academy; while for such service as is expected from those committees which it was proposed to enlarge, small bodies are generally more efficient than large ones.

In conclusion, your Committee begs leave to present for consideration the accompanying votes, intended to give effect to the new Code if it shall prove acceptable to the Academy.

Respectfully submitted,

HENRY H. EDES,
ELIHU THOMSON,
HENRY LEFAVOUR,
Committee.

BOSTON, October 11, 1911.

I. That the Report of the Committee on the Revision of the Statutes and Standing Votes is hereby accepted and the Code submitted therewith adopted.

II. That all previously adopted Statutes and Standing Votes are hereby repealed.

III. That the places of those Councillors whose terms will expire in May, 1913, and May, 1914, are hereby declared vacated at the Annual Meeting in May, 1912; and that the Councillors affected by this vote shall be eligible for renomination and reelection at that time.

This was followed by discussion. As the time was too limited to consider the whole subject, it was

Voted, To meet on adjournment, November 8th, when the discussion would be continued.

The following papers were presented by title: —

"Water, in the Liquid and Five Solid Forms, under Pressure." By P. W. Bridgman. Presented by G. W. Pierce.

"Mercury, Liquid and Solid, under Pressure." By P. W. Bridgman. Presented by G. W. Pierce.

"A New Method of Impact Excitation of Undamped Oscillations and Analysis by Means of Braun Tube Oscillographs." By E. L. Chaffee. Presented by G. W. Pierce.

"The Measurement of Hydrostatic Pressures up to 20,000 Kilograms per Square Centimeter." By P. W. Bridgman. Presented by G. W. Pierce.

"Polycerella Zoobotryon (Smallwood). By W. M. Smallwood. Presented by E. L. Mark.

Because of the lateness of the hour the communication announced was not presented.

One thousand and eighth Meeting.

NOVEMBER 8, 1911. — ADJOURNED STATED MEETING.

The Academy met at Ellis Hall.

The PRESIDENT in the chair.

There were forty-four Fellows and one guest present.

The Corresponding Secretary read letters from the following gentlemen, accepting Fellowship: — Joel H. Metcalf, Lewis Boss, Harvey N. Davis, Harry W. Morse, Joseph S. Ames, William C. Bray, Willis R. Whitney, Dugald C. Jackson, Frederic P. Stearns, Herdman F. Cleland, Hervey W. Shimer, Charles R. Van Hise, Oakes Ames, Edward M. East, Robert A. Harper, Milton J. Rosenau, Melville M. Bigelow, Marcus P. Knowlton, George V. Leverett, Woodrow Wilson, Fred N. Robinson, Charles C. Torrey, Edward Channing, Frederick J. Turner, William S. Bigelow; from John F. Jameson, declining Fellowship; from the Executive Committee of the Eighth International Congress of Applied Chemistry, inviting the Academy to join the Congress and to take part in its proceedings in Washington, September 4, 1912, and New York, September 5–13, 1912; from Wssewolod Tscheschichin, Riga, regarding a new international language.

Mr. Charles P. Bowditch presented a subscription paper, dated March, 1849, and signed by prominent members of the Academy. This interesting paper, which gave the amounts subscribed to a publication fund, was found among his father's papers.

The President announced that the Boston Athenaeum had consented to return to the Academy the bust of Franklin which was given it by the American Philosophical Society in 1802, and read the following letters: —

10 APPLETON STREET, CAMBRIDGE, October 23, 1911.

Mr. JOHN TROWBRIDGE, President.

Dear Sir: — I am authorized by the Trustees of the Boston Athenaeum to announce to you that the Athenaeum presents to the Academy, the bust of Franklin which has for many years stood in the vestibule of the Athenaeum building. The circumstances under which I have become an intermediary in this transaction are these —

In 1800, the American Philosophical Society received by gift a plaster cast of a bust of Franklin. In 1802, the same society received another and probably a different bust. At any rate, the Philosophical Society presented a bust of Franklin to the Academy, presumably one of these, and to-day the Academy has no such bust.

On the other hand, the Athenaeum has no conclusive record as to the source from which possession was derived by that society of the bust in the vestibule.

It appears by our records that the gift by the Philosophical Society was made in 1802, the same year that the second bust was given to that society. The Athenaeum bust is said to be a replica of a bust by Houdon. It is not a replica of the bust in possession of the Philosophical Society, but represents Franklin at the same period of life, and in many respects there is a close resemblance between the two busts.

Believing that the Athenaeum bust was probably ours, yet feeling that there was no method available for proving this, I requested permission to have a replica made of that bust, either for us, or to replace the Athenaeum bust, as the Trustees might prefer.

The application brought me a reply, a copy of which I enclose, in which it will be seen that the Athenaeum presents the bust to the Academy. I have the honor to be,

Yours very truly,

A. McF. Davis.

The following is a copy of the letter enclosed: —

Library of the Boston Athenaeum,
Charles Knowles Bolton, Librarian.

Boston, Mass., October 17, 1911.

Andrew McFarland Davis, Esq.,
10 Appleton Street, Cambridge, Mass.

Dear Sir: — Your letter addressed to me and dated October 14th was brought before the Trustees of the Athenaeum at their meeting yesterday. The Trustees wish me to say that, on account of the long and friendly relation which has existed between the American Academy of Arts and Sciences and the Proprietors of the Boston Athenaeum, they welcome your letter as an opportunity to continue these evidences of good will. They therefore instruct me to present through you to the American Academy the plaster replica of the bust of Franklin mentioned in your letter.

If at some time in the future the Athenaeum should desire a replica of this bust, we have no doubt that the Academy would look with favor upon our request; but that may be left to the future.

Very truly yours,

CHARLES K. BOLTON.

It was

Voted, That the thanks of the Academy be extended to the Boston Athenaeum for restoring to the Academy the replica of the bust of Benjamin Franklin, and their courteous expression of interest in the Academy. Also that the thanks of the Academy be extended to Mr. Davis for his efforts in securing this bust for the Academy.

The consideration of the Report of the Committee on the Revision of the Statutes continued from the October meeting was resumed and the Code discussed at length, after which the following votes were passed: —

1. *Voted*, That the Report of the Committee on the Revision of the Statutes and Standing Votes is hereby accepted and the Code submitted therewith, as amended, adopted.

2. *Voted*, That all previously adopted Statutes and Standing Votes are hereby repealed.

3. *Voted*, That the places of those Councillors whose terms will expire in May, 1913, and May, 1914, are hereby declared vacated at the Annual Meeting in May, 1912; and that the Councillors affected by this vote shall be eligible for renomination and re-election at that time.

On motion of Dr. G. F. Moore, it was also

Voted, That the Committee on the Revision of the Statutes is hereby authorized to make such verbal changes in the code just adopted as may be necessary or desirable to bring all its provisions into harmony with the Academy's action at this meeting, or to improve the style.

The final wording of the Statutes, here adopted, is as follows:

STATUTES AND STANDING VOTES

STATUTES

ADOPTED NOVEMBER 8, 1911

CHAPTER I

THE CORPORATE SEAL

ARTICLE 1. The Corporate Seal of the Academy shall be as here depicted:

ARTICLE 2. The Recording Secretary shall have the custody of the Corporate Seal.

See Chap. v. art. 3; chap. vi. art. 2.

CHAPTER II

Fellows and Foreign Honorary Members and Dues

Article 1. The Academy consists of Fellows, who are either citizens or residents of the United States of America, and Foreign Honorary Members. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, and each Class is divided into four Sections, namely:

Class I. *The Mathematical and Physical Sciences*
  Section 1. Mathematics and Astronomy
  Section 2. Physics
  Section 3. Chemistry
  Section 4. Technology and Engineering

Class II. *The Natural and Physiological Sciences*
  Section 1. Geology, Mineralogy, and Physics of the Globe
  Section 2. Botany
  Section 3. Zoölogy and Physiology
  Section 4. Medicine and Surgery

Class III. *The Moral and Political Sciences*
  Section 1. Theology, Philosophy, and Jurisprudence
  Section 2. Philology and Archaeology
  Section 3. Political Economy and History
  Section 4. Literature and the Fine Arts

Article 2. The number of Fellows shall not exceed Six hundred, of whom not more than Four hundred shall be residents of Massachusetts, nor shall there be more than Two hundred in any one Class.

Article 3. The number of Foreign Honorary Members shall not exceed Seventy-five. They shall be chosen from among citizens of foreign countries most eminent for their discoveries and attainments in any of the Classes above enumerated. There shall not be more than Twenty-five in any one Class.

Article 4. If any person, after being notified of his election as Fellow, shall neglect for two months to accept in writing and to pay his Admission Fee (unless he be at that time absent from the Commonwealth) his election shall be void; and if any Fellow resident within fifty miles of Boston shall neglect to pay his Annual Dues for twelve months after they are due, provided his attention shall have been called to this Article of the Statutes in the meantime, he shall cease to be a Fellow; but the Council may suspend the provisions of this Article for a reasonable time.

With the previous consent of the Council, the Treasurer may dispense (*sub silentio*) with the payment of the Admission Fee or of the Annual Dues or both whenever he shall deem it advisable. In the case of officers of the Army or Navy who are out of the Commonwealth on duty, payment of the Annual Dues may be waived during such absence if continued during the whole financial year and if notification of such expected absence be sent to the Treasurer. Upon similar notification to the Treasurer, similar exemption may be accorded to Fellows subject to Annual Dues, who may temporarily remove their residence for at least two years to a place more than fifty miles from Boston.

If any person elected a Foreign Honorary Member shall neglect for six months after being notified of his election to accept in writing, his election shall be void.

See Chap. vii. art. 2.

Article 5. Every Fellow hereafter elected shall pay an Admission Fee of Ten dollars.

Every Fellow resident within fifty miles of Boston shall, and others may, pay such Annual Dues, not exceeding Fifteen dollars, as shall be voted by the Academy at each Annual Meeting, when they shall become due; but any Fellow shall be exempt from the annual payment if, at any time after his admission, he shall pay into the treasury Two hundred dollars in addition to his previous payments.

All Commutations of the Annual Dues shall be and remain permanently funded, the interest only to be used for current expenses.

Any Fellow not previously subject to Annual Dues who takes up his residence within fifty miles of Boston, shall pay to the Treasurer within three months thereafter Annual Dues for the current year, failing which his Fellowship shall cease; but the Council may suspend the provisions of this Article for a reasonable time.

Only Fellows who pay Annual Dues or have commuted them may hold office in the Academy or serve on the Standing Committees or vote at meetings.

Article 6. Fellows who pay or have commuted the Annual Dues and Foreign Honorary Members shall be entitled to receive gratis one copy of all Publications of the Academy issued after their election.

See Chap. x. art. 2.

Article 7. Diplomas signed by the President and the Vice-President of the Class to which the member belongs, and countersigned by the Secretaries, shall be given to all the Fellows and Foreign Honorary Members.

Article 8. If, in the opinion of a majority of the entire Council, any Fellow or Foreign Honorary Member shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his membership; and if three fourths of the Fellows present, out of a total attendance of not less than fifty, at a Stated Meeting, or at a Special Meeting called for the purpose, shall adopt this recommendation, his name shall be stricken from the Roll.

See Chap. iii.; chap. vi. art. 1; chap. ix. art. 1, 7; chap. x. art. 2.

CHAPTER III

Election of Fellows and Foreign Honorary Members

Article 1. Elections of Fellows and Foreign Honorary Members shall be by ballot, and only at the Stated Meetings in January and May. Three fourths of the ballots cast, and not less than twenty, must be affirmative to effect an election.

Article 2. Candidates must be proposed in writing by two Fellows of the Section for which the proposal is made. These signed nominations shall be sent to the Corresponding Secretary and shall be retained by him until the fifteenth of the following October or February, as the case may be, when all nominations then in his hands shall be immediately sent in printed form to every Fellow having the right to vote, with the names of the proposers in each case, and with a request to send to the Corresponding Secretary written comments on these names not later than the fifth of November or the fifth of March respectively.

All the signed nominations, with the comments thereon, received up to the fifth of November or the fifth of March shall be sent at once to the appropriate Class Committees, which shall report their decisions to the Council at a special meeting to be called to consider nominations, not later than two days before the meeting of the Academy in December and April respectively.

Article 3. All nominations approved by the Council shall be read to the Academy at a meeting in December or in April, or be sent to the

Fellows in print with the official notice of the meeting, and shall then be posted in the Hall of the Academy until the balloting.

Not later than two weeks after any nomination is reported to the Academy, the Corresponding Secretary shall send to every Fellow having the right to vote a brief printed account of the nominee.

See Chap. ii. ; chap. vi. art. 1 ; chap. ix. art. 1.

CHAPTER IV

OFFICERS

ARTICLE 1. The Officers of the Academy shall be a President (who shall be Chairman of the Council), three Vice-Presidents (one from each Class), a Corresponding Secretary (who shall be Secretary of the Council), a Recording Secretary, a Treasurer, and a Librarian, all of whom shall be elected by ballot at the Annual Meeting, and shall hold their respective offices for one year, and until others are duly chosen and installed.

There shall be also twelve Councillors, one from each Section of each Class. At the Annual Meeting in 1912 three Councillors, one from each Class, shall be elected by ballot to serve for one year, three for two years, three for three years, and three for four years. At each subsequent Annual Meeting three Councillors, one from each Class, shall be elected by ballot to serve for the full term of four years and until others are duly chosen and installed. The same Fellow shall not be eligible for two successive terms.

The Councillors, with the other officers previously named, shall constitute the Council.

See Chap. x. art. 1.

ARTICLE 2. If any office shall become vacant during the year, the vacancy may be filled by the Council in its discretion for the unexpired term.

ARTICLE 3. At the Stated Meeting in March, the President shall appoint a Nominating Committee of three Fellows having the right to vote, one from each Class. This Committee shall prepare a list of nominees for the several offices to be filled, and for the Standing Committees, and cause it to be sent to the Recording Secretary not later than four weeks before the Annual Meeting.

Article 4. Independent nominations for any office, if signed by at least twenty Fellows having the right to vote, and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted, together with the list of nominees prepared by the Nominating Committee, in the call therefor, and shall be mailed to all the Fellows.

See Chap. vi. art. 2.

Article 5. The Recording Secretary shall prepare for use in voting at the Annual Meeting a ballot containing the names of all persons duly nominated for office.

CHAPTER V

The President

Article 1. The President, or in his absence the senior Vice-President present (seniority to be determined by length of continuous fellowship in the Academy), shall preside at all meetings of the Academy. In the absence of all these officers, a Chairman of the meeting shall be chosen by ballot.

Article 2. Unless otherwise ordered, all Committees which are not elected by ballot shall be appointed by the presiding officer.

Article 3. Any deed or writing to which the Corporate Seal is to be affixed, except leases of real estate, shall be executed in the name of the Academy by the President or, in the event of his death, absence, or inability, by one of the Vice-Presidents, when thereto duly authorized.

See Chap. ii. art. 7; chap. iv. art. 1, 3; chap. vi. art. 2; chap. vii. art. 1; chap. ix. art. 6; chap. x. art. 1, 2; chap. xi. art. 1.

CHAPTER VI

The Secretaries

Article 1. The Corresponding Secretary shall conduct the correspondence of the Academy and of the Council, recording or making an entry of all letters written in its name, and preserving for the files all official papers which may be received. At each meeting of the Council he shall present the communications addressed to the Academy which have been received since the previous meeting, and at the next meeting of the Academy he shall present such as the Council may determine.

He shall notify all persons who may be elected Fellows or Foreign Honorary Members, send to each a copy of the Statutes, and on their acceptance issue the proper Diploma. He shall also notify all meetings of the Council; and in case of the death, absence, or inability of the Recording Secretary he shall notify all meetings of the Academy.

Under the direction of the Council, he shall keep a List of the Fellows and Foreign Honorary Members, arranged in their several Classes and Sections. It shall be printed annually and issued as of the first day of July.

See Chap. ii. art. 7; chap. iii. art. 2, 3; chap. iv. art. 1; chap. ix. art. 6; chap. x. art. 1; chap. xi. art. 1.

ARTICLE 2. The Recording Secretary shall have the custody of the Charter, Corporate Seal, Archives, Statute-Book, Journals, and all literary papers belonging to the Academy.

Fellows borrowing such papers or documents shall receipt for them to their custodian.

The Recording Secretary shall attend the meetings of the Academy and keep a faithful record of the proceedings with the names of the Fellows present; and after each meeting is duly opened, he shall read the record of the preceding meeting.

He shall notify the meetings of the Academy to each Fellow by mail at least seven days beforehand, and in his discretion may also cause the meetings to be advertised; he shall apprise Officers and Committees of their election or appointment, and inform the Treasurer of appropriations of money voted by the Academy.

He shall post in the Hall a list of the persons nominated for election into the Academy; and after all elections, he shall insert in the Records the names of the Fellows by whom the successful candidates were nominated.

In the absence of the President and of the Vice-Presidents he shall, if present, call the meeting to order, and preside until a Chairman is chosen.

See Chap. i.; chap. ii. art. 7; chap. iv. art. 3, 4, 5; chap. ix. art. 6; chap. x. art. 1, 2; chap. xi. art. 1, 3.

ARTICLE 3. The Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the records of the meetings of the Academy as may seem to them likely to promote its interests.

CHAPTER VII

The Treasurer and the Treasury

Article 1. The Treasurer shall collect all money due or payable to the Academy, and all gifts and bequests made to it. He shall pay all bills due by the Academy, when approved by the proper officers, except those of the Treasurer's office, which may be paid without such approval; in the name of the Academy he shall sign all leases of real estate; and, with the written consent of a member of the Committee on Finance, he shall make all transfers of stocks, bonds, and other securities belonging to the Academy, all of which shall be in his official custody.

He shall keep a faithful account of all receipts and expenditures, submit his accounts annually to the Auditing Committee, and render them at the expiration of his term of office, or whenever required to do so by the Academy or the Council.

He shall keep separate accounts of the income of the Rumford Fund, and of all other special Funds, and of the appropriation thereof, and render them annually.

His accounts shall always be open to the inspection of the Council.

Article 2. He shall report annually to the Council at its March meeting on the expected income of the various Funds and from all other sources during the ensuing financial year. He shall also report the names of all Fellows who may be then delinquent in the payment of their Annual Dues.

Article 3. He shall give such security for the trust reposed in him as the Academy may require.

Article 4. With the approval of a majority of the Committee on Finance, he may appoint an Assistant Treasurer to perform his duties, for whose acts, as such assistant, he shall be responsible; or, with like approval and responsibility, he may employ any Trust Company doing business in Boston as his agent for the same purpose, the compensation of such Assistant Treasurer or agent to be fixed by the Committee on Finance and paid from the funds of the Academy.

Article 5. At the Annual Meeting he shall report in print all his official doings for the preceding year, stating the amount and condition of all the property of the Academy entrusted to him, and the character of the investments.

Article 6. The Financial Year of the Academy shall begin with the first day of April.

Article 7. No person or committee shall incur any debt or liability in the name of the Academy, unless in accordance with a previous vote and appropriation therefor by the Academy or the Council, or sell or otherwise dispose of any property of the Academy, except cash or invested funds, without the previous consent and approval of the Council.

See Chap. ii. art. 4, 5; chap. vi. art. 2; chap. ix. art. 6; chap. x. art. 1, 2, 3; chap. xi. art. 1.

CHAPTER VIII

The Librarian and the Library

Article 1. The Librarian shall have charge of the printed books, keep a correct catalogue thereof, and provide for their delivery from the Library.

At the Annual Meeting, as Chairman of the Committee on the Library, he shall make a Report on its condition.

Article 2. In conjunction with the Committee on the Library he shall have authority to expend such sums as may be appropriated by the Academy for the purchase of books, periodicals, etc., and for defraying other necessary expenses connected with the Library.

Article 3. All books procured from the income of the Rumford Fund or of other special Funds shall contain a book-plate expressing the fact.

Article 4. Books taken from the Library shall be receipted for to he Librarian or his assistant.

Article 5. Books shall be returned in good order, regard being had to necessary wear with good usage. If any book shall be lost or injured, the Fellow to whom it stands charged shall replace it by a new volume or by a new set, if it belongs to a set, or pay the current price thereof to the Librarian, whereupon the remainder of the set, if any, shall be delivered to the Fellow so paying, unless such remainder be valuable by reason of association.

Article 6. All books shall be returned to the Library for examination at least one week before the Annual Meeting.

Article 7. The Librarian shall have the custody of the Publications of the Academy. With the advice and consent of the President, he may effect exchanges with other associations.

See Chap. ii. art. 6; chap. x. art. 1, 2.

CHAPTER IX

The Council

Article 1. The Council shall exercise a discreet supervision over all nominations and elections to membership, and in general supervise all the affairs of the Academy not explicitly reserved to the Academy as a whole or entrusted by it or by the Statutes to standing or special committees.

It shall consider all nominations duly sent to it by any Class Committee, and present to the Academy for action such of these nominations as it may approve by a majority vote of the members present at a meeting, of whom not less than seven shall have voted in the affirmative.

With the consent of the Fellow interested, it shall have power to make transfers between the several Sections of the same Class, reporting its action to the Academy.

See Chap. iii. art. 2, 3; chap. x. art. 1.

Article 2. Seven members shall constitute a quorum.

Article 3. It shall establish rules and regulations for the transaction of its business, and provide all printed and engraved blanks and books of record.

Article 4. It shall act upon all resignations of officers, and all resignations and forfeitures of fellowship; and cause the Statutes to be faithfully executed.

It shall appoint all agents and subordinates not otherwise provided for by the Statutes, prescribe their duties, and fix their compensation.

They shall hold their respective positions during the pleasure of the Council.

ARTICLE 5. It may appoint, for terms not exceeding one year, and prescribe the functions of, such committees of its number, or of the Fellows of the Academy, as it may deem expedient, to facilitate the administration of the affairs of the Academy or to promote its interests.

ARTICLE 6. At its March meeting it shall receive reports from the President, the Secretaries, the Treasurer, and the Standing Committees, on the appropriations severally needed for the ensuing financial year. At the same meeting the Treasurer shall report on the expected income of the various Funds and from all other sources during the same year.

At the Annual Meeting it shall submit to the Academy, for its action, a report recommending the appropriations which in the opinion of the Council should be made.

On the recommendation of the Council, special appropriations may be made at any Stated Meeting of the Academy, or at a Special Meeting called for the purpose.

See Chap. x. art. 3.

ARTICLE 7. After the death of a Fellow or Foreign Honorary Member, it shall appoint a member of the Academy to prepare a Memoir for publication in the Proceedings.

ARTICLE 8. It shall report at every meeting of the Academy such business as it may deem advisable to present.

See Chap. ii. art. 4, 5, 8; chap. iv. art. 1, 2; chap. vi. art. 1; chap. vii. art. 1; chap. xi. art. 1, 4.

CHAPTER X

STANDING COMMITTEES

ARTICLE 1. The Class Committee of each Class shall consist of the Vice-President, who shall be chairman, and the four Councillors of the Class, together with such other officer or officers annually elected as may belong to the Class. It shall consider nominations to Fellowship in its own Class, and report in writing to the Council such as may receive at a Class Committee Meeting a majority of the votes cast, provided at least three shall have been in the affirmative.

See Chap. iii. art. 2.

Article 2. At the Annual Meeting the following Standing Committees shall be elected by ballot to serve for the ensuing year:

(i) *The Committee on Finance*, to consist of three Fellows, who, through the Treasurer, shall have full control and management of the funds and trusts of the Academy, with the power of investing the funds and of changing the investments thereof in their discretion.

See Chap. iv. art. 3; chap. vii. art. 1, 4; chap. ix. art. 6.

(ii) *The Rumford Committee*, to consist of seven Fellows, who shall report to the Academy on all applications and claims for the Rumford Premium. It alone shall authorize the purchase of books, publications and apparatus at the charge of the income from the Rumford Fund, and generally shall see to the proper execution of the trust.

See Chap. iv. art. 3; chap. ix. art. 6.

(iii) *The Cyrus Moors Warren Committee*, to consist of seven Fellows, who shall consider all applications for appropriations from the income of the Cyrus Moors Warren Fund, and generally shall see to the proper execution of the trust.

See Chap. iv. art. 3; chap. ix. art. 6.

(iv) *The Committee of Publication*, to consist of three Fellows, one from each Class, to whom all communications submitted to the Academy for publication shall be referred, and to whom the printing of the Proceedings and the Memoirs shall be entrusted.

It shall fix the price at which the Publications shall be sold; but Fellows may be supplied at half price with volumes which may be needed to complete their sets, but which they are not entitled to receive gratis.

Two hundred extra copies of each paper accepted for publication in the Proceedings or the Memoirs shall be placed at the disposal of the author without charge.

See Chap. iv. art. 3; chap. vi. art. 1, 3; chap. ix. art. 6.

(v) *The Committee on the Library*, to consist of the Librarian, *ex officio*, as Chairman, and three other Fellows, one from each Class, who shall examine the Library and make an annual report on its condition and management.

See Chap. iv. art. 3; chap. viii. art. 1, 2; chap. ix. art. 6.

(vi) *The House Committee*, to consist of three Fellows, who shall have charge of all expenses connected with the House, including the general expenses of the Academy not specifically assigned to the care of other Committees or Officers.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(vii) *The Committee on Meetings*, to consist of the President, the Recording Secretary, and three other Fellows, who shall have charge of plans for meetings of the Academy.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(viii) *The Auditing Committee*, to consist of two Fellows, who shall audit the accounts of the Treasurer, with power to employ an expert and to approve his bill.

See Chap. iv. art. 3 ; chap. vii. art. 1 ; chap. ix. art. 6.

Article 3. The Standing Committees shall report annually to the Council in March on the appropriations severally needed for the ensuing financial year ; and all bills incurred on account of these Committees, within the limits of the several appropriations made by the Academy, shall be approved by their respective Chairmen.

In the absence of the Chairman of any Committee, bills may be approved by any member of the Committee whom he shall designate for the purpose.

See Chap. vii. art. 1, 7 ; chap ix. art. 6.

CHAPTER XI

Meetings, Communications, and Amendments

Article 1. There shall be annually four Stated Meetings of the Academy, namely, on the second Wednesday of January, March, May, and October. Only at these meetings, or at adjournments thereof regularly notified, or at Special Meetings called for the purpose, shall appropriations of money be made, or amendments of the Statutes or Standing Votes be effected.

The Stated Meeting in May shall be the Annual Meeting of the Corporation.

Special Meetings shall be called by either of the Secretaries at the request of the President, of a Vice-President, of the Council, or of ten

Fellows having the right to vote; and notifications thereof shall state the purpose for which the meeting is called.

A meeting for receiving and discussing literary or scientific communications may be held on the second or the fourth Wednesday, or both, of each month not appointed for Stated Meetings, excepting July, August, and September; but no business shall be transacted at any meeting which may be held on the fourth Wednesday.

ARTICLE 2. Twenty Fellows having the right to vote shall constitute a quorum for the transaction of business at Stated or Special Meetings. Fifteen Fellows shall be sufficient to constitute a meeting for literary or scientific communications and discussions.

ARTICLE 3. Upon the request of the presiding officer or the Recording Secretary, any motion or resolution offered at any meeting shall be submitted in writing.

ARTICLE 4. No report of any paper presented at a meeting of the Academy shall be published by any Fellow without the consent of the author; and no report shall in any case be published by any Fellow in a newspaper as an account of the proceedings of the Academy without the previous consent and approval of the Council.

ARTICLE 5. No Fellow shall introduce a guest at any meeting of the Academy until after the business has been transacted, and especially until after nominations to Fellowship have been read and the result of the balloting for candidates has been declared.

ARTICLE 6. The Academy shall not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its Publications.

ARTICLE 7. All proposed Amendments of the Statutes shall be referred to a committee, and on its report, at a subsequent Stated Meeting or at a Special Meeting called for the purpose, two thirds of the ballots cast, and not less than twenty, must be affirmative to effect enactment.

ARTICLE 8. Standing Votes may be passed, amended, or rescinded at a Stated Meeting, or at a Special Meeting called for the purpose, by a vote of two thirds of the members present. They may be suspended by a unanimous vote.

See Chap. ii. art. 5, 8; chap. iii.; chap. iv. art. 3, 4, 5; chap. v. art. 1; chap. vi. art. 1, 2; chap. ix. art. 8.

The following communication was given: —

"A biographical notice of Dr. Henry Pickering Bowditch," by Professor W. B. Cannon.

The following paper was presented by title: —

"An Electromagnetic Theory of Gravitation," by D. L. Webster. Presented by B. O. Peirce.

One thousand and ninth Meeting.

DECEMBER 13, 1911.

The Academy met at the Museum of Fine Arts, Huntington Avenue.

The PRESIDENT in the chair.

There were eighteen Fellows and three guests present.

The Corresponding Secretary read the following letters: — from Henry B. Bigelow and Elmer E. Southard, accepting Fellowship; from the New Hampshire Historical Society, inviting the Academy to be represented at the dedication of its Library building.

The PRESIDENT read the following letter from Mrs. George R. Agassiz.

76 MOUNT VERNON STREET, December 11, 1911.

To Professor JOHN TROWBRIDGE,
President of the American Academy of Sciences:

My dear Mr. TROWBRIDGE,

May I offer the American Academy, through you, a bas-relief of Mr. Alexander Agassiz by Bela Pratt? It is life size, and most satisfactory to us all, and I hope you will find it so.

If it is accepted by the Academy, I should consider it as a favor to me, if Mr. Pratt may be allowed to confer with Mr. Page as to the placing of this bas-relief.

Yours very sincerely,
MABEL S. AGASSIZ.

It was

Voted, To accept the gift from Mrs. Agassiz, and the Secretary was instructed to acknowledge it.

The following communication was given by Dr. Fairbanks: —

"Some Aspects of the Fine Arts."

One thousand and tenth Meeting.

JANUARY 10, 1912. — STATED MEETING.

The Academy met in Ellis Hall.

The PRESIDENT in the chair.

There were twenty-eight Fellows present.

The following letters were presented by the Corresponding Secretary: — from Edwin B. Wilson, accepting Fellowship; notices of the deaths of Sir J. D. Hooker and J. B. E. Bornet; a preliminary notice of the International Congress of Anthropology and Prehistoric Archaeology, to be held at Genoa, in September, 1912.

The President announced the following deaths: — Dr. Algernon Coolidge, Fellow in Class II., Section 1; Sir Joseph D. Hooker, and J. B. E. Bornet, Foreign Honorary Members in Class II., Section 2.

The following report of the Building Committee was read by the chairman: —

At the Annual Meeting of the Academy, it was voted that the President appoint a building committee composed of the chairman of the house committee, the librarian, and such other persons as they should add to their number to have oversight of the carrying on of the building, and to decide such matters of detail in connection therewith, as might come up. The President accordingly appointed Dr. Louis Bell, in addition to the two officials above named, to whom was subsequently added Dr. H. M. Goodwin, who with the President constituted the committee. The committee held several meetings during the summer, and considered a number of matters of detail. Several conferences were held by representatives of the committee with the architect, who seemed very averse to treating with the committee or taking any of their suggestions. The Agassiz heirs were also consulted and finally agreed to change the elevator which had been ordered to a self-acting one. The committee feel bound to state that this is the chief tangible result that their labors have accomplished. They have been unable until very recently to secure access to the stack so that it has has been impossible to consult books or records, and many of their recommendations have not been carried out. It was the opinion of the committee that the reading room should have low book shelves entirely around it, which would permit placing in the reading room the recent volumes of all the transactions of the learned societies now in our book stack. It was also our opinion that convenience required a door opening directly from the librarian's room into the reading room. This, however, the Messrs. Agassiz refused to allow. We do not think that the shelving should have glass doors nor that five sofas are desirable, believing that the room should have the requisites of a reading room rather than of a club room. The committee hope that the members of the Academy may express their opinion on this point, and that either the functions of the committee may be determined more definitely or that the committee may be discharged.

Respectfully submitted,

A. G. Webster.

After discussion, on the motion of A. C. Lane, it was

Voted, 1. That the President notify the architects of the names of the Building Committee, and that they are expected to carry out the wishes of the same, so far as is compatible with the wishes of the Agassiz heirs.

2. That the Building Committee be requested to continue.

It was also

Voted, That the Report of the Building Committee be accepted.

The following communication was given: —

"The Fall of a Meteorite." By Dr. Elihu Thomson.

The following paper was presented by title: —

"A Revision of the Atomic Weight of Phosphorus. Second Paper. — The Analysis of Phosphorus Tribromide." By G. P. Baxter, C. J. Moore, and A. C. Boylston.

One thousand and eleventh Meeting.

January 17, 1912. — Special Meeting.

The Academy met at Ellis Hall, called by the President to consider the furnishing of the new building.

The President in the chair.

There were twenty-three Fellows present.

In the absence of the Recording Secretary, the Corresponding Secretary acted in his place.

The President stated the object of the meeting and gave his views of the matter in question.

A representative of the firm of Page and Frothingham, the architects of the new building, was present, and after discussion the Academy took a recess of five minutes to examine the plan of the Reading-room which he presented.

After business was resumed, on motion of the Treasurer, it was

Voted, That in the opinion of the Academy it is desirable that the plan of furnishing the Academy building as suggested by the Agassiz heirs through the architects be carried out. This was passed by a vote of 13 to 6.

At 9.45 the meeting adjourned.

One thousand and twelfth Meeting.

FEBRUARY 14, 1912.

The Academy met in Ellis Hall.

The PRESIDENT in the chair.

There were thirty-three Fellows and one guest present.

The Corresponding Secretary presented the following communications: — letters from Forris Jewett Moore, accepting Fellowship; and from Heinrich Oscar Hofman, resigning Fellowship; an invitation from the Royal Society of London, to send a delegate to the celebration of its 250th anniversary, in July, 1912; an invitation from the American Philosophical Society, to send a delegate to its Annual General Meeting, April 18–20, 1912; an invitation from the Academy of Natural Sciences of Philadelphia, to send a representative to the celebration of its centenary anniversary, March 19–21, 1912; a notice of the eighth International Congress of Applied Chemistry, to be held in Washington and New York, in September, 1912, enclosing blanks for application for Membership.

The President announced the death of Dr. O. F. Wadsworth, Fellow in Class II., Section 4, and of Joseph Lister, Foreign Honorary Member in Class II., Section 4.

The President was authorized to appoint a delegate to the celebration of the 250th anniversary of the Royal Society, London; to the celebration of the centenary anniversary of the

Academy of Natural Science of Philadelphia, and also to the Annual General Meeting of the American Philosophical Society.

On motion of Mr. C. P. Bowditch, the following resolution was passed, and the Corresponding Secretary requested to send copies to the Carnegie Institution, the Smithsonian Institution, and the Library of Congress: —

Whereas, In 1908, the Carnegie Institution published the "Handbook of Learned Societies and Institutions in America" which had been compiled by Mr. J. D. Thompson, of the Library of Congress,

Whereas, This book is of inestimable value to Librarians and to all interested in a knowledge of the history, or publications of Societies, and

Whereas, Material has been collected for a Handbook relating to Societies of the Old World, which is now kept on file in the Library of Congress, it is therefore

Voted, That the American Academy of Arts and Sciences request that this unpublished material may be published with as little delay as possible, if not by the Carnegie Institution, then by the Library of Congress or the Smithsonian Institution.

On motion of Professor Lanman, it was

Voted, That the Chairman of the Committee of Publication be requested to see that the bound volumes of the Proceedings be lettered on the back with the date as well as the volume number.

The Secretary of the Council announced that at his own request, Dr. Harold C. Ernst had been transferred from Class II., Section 3, to Class II., Section 4.

The following communications were given: —

Dr. F. H. Williams. "A Biographical Notice of Dr. Frederick I. Knight."

Mr. Charles P. Bowditch. "The Results of the American Occupation of the Philippines."

The following papers were presented by titles: —

"Electrical Properties of Crystals. Capacity in Carborundum." By G. W. Pierce and R. D. Evans.

"Pali Writing-machines — a Study for a Rational Keyboard." By C. R. Lanman.

"An Algebra of Plane Projective Geometry." By H. B. Phillips and C. L. E. Moore. Presented by H. W. Tyler.

One thousand and thirteenth Meeting.

MARCH 13, 1912. — STATED MEETING.

The Academy met at the X-ray department of the Boston City Hospital, Harrison Avenue and Massachusetts Avenue.

The PRESIDENT in the chair.

There were present twenty-six Fellows and two guests.

The Corresponding Secretary presented the following communications: from Otto Folin, Roscoe Pound, Charles P. Steinmetz accepting Fellowship; from R. S. Woodward, of the Carnegie Institution, Charles D. Walcott, of the Smithsonian Institution, in reply to Resolution of the Academy sent to them.

The following deaths were announced by the Chair: —

Charles Robert Sanger, Class I., Section 3; Edward Henry Hall, Class III., Section 4; Henry Williamson Haynes, Class III., Section 2, Librarian from 1886 to 1899.

The Corresponding Secretary reported that the Council had voted to invite Doctor H. P. Walcott to deliver the dedicatory address at the opening of the new Academy Building, and had requested the President, with two other members to be selected by himself, to serve as a Committee of Arrangements for the opening of the new building.

On the recommendation of the Council it was

Voted, To appropriate five hundred ($500) dollars from the income of the Publication Fund for use of the Publication Committee.

On the recommendation of the Council it was

Voted, To appropriate two hundred ($200) dollars from the income of the General Fund for the use of the House Committee.

The Council proposed the following amendment to the Statutes: —

Omit paragraph 2, of Article 6, of Chapter IX., and insert in its place the following:

"A report from the Council shall be submitted to the Academy, for action at the March meeting, recommending the appropriations which in the opinion of the Council should be made."

The above proposed amendment to the Statutes was referred to a Committee consisting of Messrs. Bowditch and Edes, with a request to report at the Annual meeting in May.

On the recommendation of the Council it was

Voted, That in the opinion of the Academy it is desirable that twenty-five new Fellows, living within fifty miles of Boston, should be elected in May, in addition to such a number as is needed to fill vacancies occasioned by deaths or resignations since January 1, 1912.

The President appointed the following gentlemen to serve as Nominating Committee: —

Henry Lefavour, of Class I.
William T. Sedgwick, of Class II. (Chairman).
George L. Kittredge, of Class III.

Professor Kittredge having declined service on the Committee, Mr. Worthington C. Ford was appointed by the President in his stead.

The following communication was given: —

Dr. Francis H. Williams. "X-rays and Radium," with demonstrations.

The following paper was presented by title: —

"On the Ultra Violet Radiation of Practical Illuminants." By Louis Bell.

One thousand and fourteenth Meeting.

APRIL 10, 1912.

The Academy met at Ellis Hall.

The PRESIDENT in the chair.

There were twenty-two Fellows present.

The Corresponding Secretary presented the following correspondence: — an invitation from the Trustees and Faculty of Princeton University requesting a delegate from the Academy at the inauguration of John Grier Hibben, as President of the University; from the Secretary of the third International Congress of Archaeology, to be held in Rome, October 9–16, 1912, requesting delegates; from the Organizing Committee of the fourth International Congress of Religions, to be held September 9–13, 1912, at Leiden.

The President was authorized to appoint delegates to represent the Academy at the inauguration of the new President at Princeton, and at the Congresses to be held at Rome and Leiden.

The President announced the death of A. Lawrence Rotch, Class I., Section 1, Librarian of the Academy since 1899.

At the suggestion of the President, it was

Voted, To thank the Massachusetts Historical Society for their very generous hospitality in allowing the Academy the use of Ellis Hall during the year.

The following paper was presented by title: —

"New or Critical Laboulbeniales from the Argentine." By Roland Thaxter.

The following communication was given: —

"Recent Applications of the Gyroscope," with lantern illustrations. By Arthur G. Webster.

One thousand and fifteenth Meeting.

MAY 8, 1912. — ANNUAL MEETING.

The Academy met for the first time in its new building, erected on the site of its former house and the adjoining lot. Numbers 28 and 26 Newbury Street.

The PRESIDENT in the chair.

There were forty-four Fellows present.

The Corresponding Secretary presented the following correspondence: — from the Regents and Secretary of the Smithsonian Institution, an invitation to view the art objects of the Freer Collection; from the chairman of the Organizing Committee of the Eighteenth International Congress of Americanists, requesting a representative of the Academy to attend the session in London, May 27–June 1; from the President of the Association des Ingenieurs Electriciens, giving the conditions of the competition for the George Montefiore prize.

The Chair announced the deaths of the following Fellows: — George Davidson, Class I., Section 1; George Jarvis Brush, Class II., Section 1.

The following report of the Council was read: —

Since the last report of the Council, there have been reported the deaths of ten Fellows: — Algernon Coolidge, O. F. Wadsworth, S. H. Scudder, H. W. Haynes, C. R. Sanger, Edward H. Hall, A. Lawrence Rotch, C. G. Pringle, G. J. Brush, and George Davidson; and of three Foreign Honorary Members: — Sir Joseph Hooker, Lord Lister, and J. B. E. Bornet.

One Fellow has resigned: — H. O. Hofman.

Thirty-four Fellows have been elected, of which number one declined Fellowship, and one has not yet accepted, as he is out of the country.

The roll now includes (counting the one who has not yet accepted) 272 Fellows and 52 Foreign Honorary Members.

The annual report of the Treasurer was read, of which the following is an abstract: —

General Fund.

Receipts.

Balance, May 1, 1911	$438.14	
Investments	3,459.96	
Assessments	2,110.00	
Admission fees	230.00	
Use of water	19.77	$6,257.87

Expenditures.

Expense of House	$815.14	
Expense of Library	2,388.12	
Expense of Meetings	171.69	
Treasurer	143.57	
General expenses of Society	473.96	
Interest on bonds	2.91	
Income transferred to principal	227.10	$4,222.49
Balance, April 1, 1912		2,035.38
		$6,257.87

Rumford Fund.

Receipts.

Balance, May 1, 1911	$1,498.10	
Investments	2,850.93	
Sale of Publications	5.00	$4,354.03

Expenditures.

Research	$1,400.00	
Books, periodicals, and binding	221.70	
Publication	756.53	
Medals	400.00	
Sundries	40.85	
Income transferred to principal	147.03	$2,966.11
Balance, April 1, 1912		1,307.92
		$4,354.03

C. M. Warren Fund.

Receipts.

Balance, May 1, 1911	$897.72	
Investments	620.60	$1,518.32

Expenditures.

Research	$750.00	
Vault rent, part	4.00	
Interest on bonds	70.14	
Income transferred to principal	16.84	
Charged to cancel premium on bonds	300.00	$1,140.98
Balance, April 1, 1912		377.34
		$1,518.32

Publication Fund.

Receipts.

Balance, May 1, 1911	$1,066.18	
Appleton Fund investments	665.56	
Centennial Fund investments	2,076.41	
Sale of Publications	49.04	$3,857.19

Expenditures.

Publication	$2,981.08	
Vault rent, part	12.50	
Income transferred to principal	148.26	$3,141.84
Balance, April 1, 1912		715.35
		$3,857.19

The following reports were also presented: —

Report of the Library Committee.

Owing to the death of Mr. A. Lawrence Rotch, the usual report of the Librarian devolves upon the Library Committee; and the Committee has also lost by death Mr. Henry W. Haynes. Mr. Rotch served as Librarian from May 10, 1899, until his death, April 7, 1912. Mr. Haynes died February 16, 1912; he had been a member of the Library Committee since May, 1899, and had previously been the Librarian of the Academy for thirteen years.

During the year the Library has been conducted at the rooms temporarily occupied by the Academy at 711 Boylston Street. The Newbury Street book stack was accessible only from November, 1911, and during this time 62 books were borrowed by 10 persons.

Upon the completion of the new building in April, 1912, the current numbers of serials and of the publications of institutions were removed to the Librarian's room and the pamphlets to the gallery of the same room; the duplicate books have been placed in the stack room on the fourth floor, and the stock of the publications of the Academy in the stack room in the basement.

725 volumes have been placed on the shelves since the last report; this includes 626 volumes received by gift and exchange, 81 volumes purchased from the income of the General Fund, and 18 volumes purchased from the income of the Rumford Fund.

The number of volumes now in the library is 32,068.

578 volumes have been bound, 147 have been stamped and plated at a cost of $656.25.

The expenses charged to the Library are: — Miscellaneous (including $20.13 for cataloguing), $382.29; Binding, $597.80 General, and $58.45 Rumford, Funds; Purchase of periodicals and books, $491.37 General, and $163.25 Rumford, Funds.

H. M. Goodwin of Class I.,
Samuel Henshaw of Class II.,
Committee.

May 8, 1912.

Report of the Rumford Committee.

During the present year appropriations in aid of research have been made by the Committee as follows: —

May 10, 1911 (evening meeting), to Professor Daniel F. Comstock, in aid of his research on the effect of motion of the source on the velocity of light	$150
Nov. 8, 1911, to Mr. Frank W. Very, in aid of his research on the intensity of spectrum lines (additional)	150
To Professor John Trowbridge, in aid of the researches of Mr. Harvey C. Hayes in thermo-electricity	300

To Professsor Robert W. Wood, in aid of his researches on the optical properties of vapors and long heat waves (additional) .	150
Dec. 13, 1911, to Professor Arthur L. Clark, in aid of his research on the physical properties of vapors in the neighborhood of the critical point (additional)	250
Feb. 14, 1912, to Professor Gilbert N. Lewis, in furtherance of his researches on the free-energy changes in chemical reactions (additional)	250

Since the last annual meeting of the Academy, papers have been published in the Proceedings at the expense of the Rumford Fund, wholly or in part, as follows: —

Hayes, Harvey C. — An Investigation of the Errors in Cooling Curves and Methods for Avoiding these Errors; also, a new Form of Crucible.

Richards, Theodore W., and Kelley, George L. — The Transition Temperatures of Sodium Chromate as Convenient Fixed Points in Thermometry.

Bridgman, Percy W. — Mercury, Liquid and Solid, under Pressure.

Bridgman, Percy W. — Water, in the Liquid and Five Solid Forms, under Pressure.

At the meeting of March 13, 1912, it was voted to authorize the Chairman to proceed to the printing of the Supplement to the "Rumford Fund" pamphlet, the copy for which is now complete.

The Committee has succeeded in locating all the Rumford medals which have been awarded, and has procured casts or photographs from which replicas can be made at any time.

At the meeting of Nov. 8, 1911, the Committee made a change in the requirements as to the publication of papers embodying the results of researches aided from the Rumford Fund. The rule as modified now reads, "Persons carrying on researches with the aid of the Rumford Fund should submit to the Academy an account of their researches not less complete than that published elsewhere. These researches may be published in any place or form, with the proviso that due recognition be made of the grant."

At the meeting of the Committee held on February 14, 1912, it was unanimously voted for the first time, and at the meeting held on March 13 it was unanimously voted for the second time, to recommend to the Academy the award of the Rumford Premium to Frederic Eugene Ives for his Optical Inventions, particularly in Color Photography and Photo-engraving.

Charles R. Cross, *Chairman.*

May 8, 1912.

REPORT OF THE C. M. WARREN COMMITTEE.

The C. M. Warren Committee beg to report that during the past year grants have been made as follows: —

To Dr. S. F. Acree, Johns Hopkins University, for the study of the physical and chemical properties of pure ethyl alcohol	$200
To Professor H. G. Byers, University of Washington, for work upon passivity of metals	250
To Professor W. D. Harkins, University of Montana, for work upon the energy relations in a surface between two liquid phases	300
To Dr. Latham Clark, Harvard University, for work on the paraffin hydrocarbons	150

Reports have been received from the various recipients of the grants from the Warren Fund, indicating the progress which is being made upon the researches not yet completed.

The Committee has suffered a serious loss in the death of Professor Charles R. Sanger, who has for many years taken a marked interest in this work. The members of the Committee desire to record their sense of personal loss which Professor Sanger's death occasions.

H. P. TALBOT, *Chairman.*

May 8, 1912.

REPORT OF THE PUBLICATION COMMITTEE.

Between May 1, 1911, and April 1, 1912, there were published seven numbers of Volume XLVI. (Nos. 19–25) and twenty-one numbers of Volume XLVII. of the Proceedings. The total publication amounted to 1001 pages. The expense of publishing five numbers and a part of a sixth has been assumed by the Rumford Committee.

There was available for the use of the Publication Committee an unexpended balance from last year of $375.72, an appropriation of $2500 and an additional appropriation of $500, and an amount of $33.99 from the sale of publications up to March 4th — in all $3409.71 from the Publication Fund and Sales. Bills against this appropriation to the amount of $2981.08 have been approved by the Chairman of the Publication Committee, and have been submitted to the Treasurer. This leaves an unexpended balance of $428.63.

Bills aggregating $756.53, incurred in publishing papers on light and heat, have been referred to the Rumford Committee for payment in accordance with their authorization.

G. W. PIERCE, *Chairman.*

May 8, 1912.

Report of the House Committee.

The rooms at 711 Boylston Street were occupied from March 25, 1911, to April 11, 1912. Out of an appropriation of $1004.93, the sum of $858.89 has been spent, leaving a balance of $146.04.

A. G. Webster, *Chairman.*

May 8, 1912.

Financial Report of the Council.

Estimated Income — May 1, 1912, to April 1, 1913.

General Fund			$3,846.84
Publication Fund	Appleton Fund	$688.06	
	Centennial Fund	2,087.66	2,775.72
Rumford Fund			2,754.18
Warren Fund			620.60

Available for Appropriation.

General Fund	Unappropriated balance.	$992.76	
	Cash for current expenses	2,000.00	
	Income, less 5% added to capital	3,645.00	$6,637.76
Publication Fund	" " "		2,636.93
Rumford Fund	" " "		2,616.47
Warren Fund	" " "		589.58

Appropriations recommended.

General Fund	House expenses	$1,540.00	
	Library expenses	1,466.67	
	Books, periodicals, and binding	1,100.00	
	Expenses of Meetings	183.33	
	Treasurer's Office	191.67	
	" " Insurance	450.00	
	General expenses	366.67	$5,398.34
Publication Fund.			
	Publication		$2,500
Rumford Fund.			
	Research	$1,000	
	Periodicals, books, and binding	200	
	Publication	600	
	To be used at discretion of Committee	800	$2,600
Warren Fund.			
	Research		$500

In accordance with the recommendation in the foregoing report it was

Voted, To appropriate for the purposes named the following sums: —

From the General Fund, $5,398.34.
From the income of the Publication Fund, $2,500.
From the income of the Rumford Fund, $2,600.
From the income of the Warren Fund, $500.

On the recommendation of the Rumford Committee, it was

Voted, To award the Rumford Premium to Frederic Eugene Ives for his Optical Inventions, particularly in Color Photography and Photo-engraving.

The following report was read: —

Your Committee, appointed to consider and report on the Amendment to the Statutes offered at the March meeting, respectfully report, —

They advise the adoption of the Amendment, as follows: —

Omit Paragraph 2 of Article 6 of Chapter IX and insert the following: —

"A Report from the Council shall be submitted to the Academy, for action, at the March meeting, recommending the appropriations which in the opinion of the Council should be made."

Charles P. Bowditch,
Henry H. Edes,
Committee.

On the motion of Mr. Bowditch, it was

Voted, To adopt the amendment as reported.

Upon motion of Mr. Lanman, it was

Voted, 1. That among the volumes kept upon the shelves of the Reading Room there be included one set of the publications of this Academy, complete from the beginning; and also any other such volumes as throw light upon the history and activities of the Academy.

2. That the Librarian be requested to give effect to this vote as soon as that may conveniently be done.

The annual election resulted in the choice of the following officers and committees: —

John Trowbridge, *President.*
Elihu Thomson, *Vice-President for Class I.*
Henry P. Walcott, *Vice-President for Class II.*
A. Lawrence Lowell, *Vice-President for Class III.*

EDWIN H. HALL, *Corresponding Secretary.*
WILLIAM WATSON, *Recording Secretary.*
CHARLES P. BOWDITCH, *Treasurer.*
HARRY W. TYLER, *Librarian.*

Councillors for One Year.

GEORGE F. SWAIN, of Class I.
REGINALD H. FITZ, of Class II.
HENRY H. EDES, of Class III.

Councillors for Two Years.

ROBERT W. WILLSON, of Class I.
THOMAS A. JAGGAR, JR., of Class II.
JOSEPH H. BEALE, of Class III.

Councillors for Three Years.

ARTHUR G. WEBSTER, of Class I.
MERRITT L. FERNALD, of Class II.
GEORGE F. MOORE, of Class III.

Councillors for Four Years.

JAMES F. NORRIS, of Class I.
GEORGE H. PARKER, of Class II.
FRANK W. TAUSSIG, of Class III.

Finance Committee.

JOHN TROWBRIDGE,
GARDINER M. LANE,
JOHN COLLINS WARREN.

Rumford Committee.

CHARLES R. CROSS,
EDWARD C. PICKERING,
ARTHUR G. WEBSTER,
ERASMUS D. LEAVITT,
ELIHU THOMSON,
LOUIS BELL,
ARTHUR A. NOYES.

C. M. Warren Committee.

HENRY P. TALBOT,
CHARLES L. JACKSON,
ARTHUR A. NOYES,
WALTER L. JENNINGS,
GREGORY P. BAXTER,
JAMES F. NORRIS,
WILLIAM H. WALKER.

Publication Committee.

George W. Pierce, of Class I.
Walter B. Cannon, of Class II.
Albert A. Howard, of Class III.

Library Committee.

Harry W. Tyler,
Harry M. Goodwin, of Class I.
Samuel Henshaw, of Class II.
William C. Lane, of Class III.

House Committee.

Henry P. Talbot, Louis Derr,
Hammond V. Hayes.

Committee on Meetings.

The President, The Recording Secretary,
William M. Davis, Wallace C. Sabine,
Arthur Fairbanks.

Auditing Committee.

Elliot C. Clarke, Worthington C. Ford.

The following gentlemen were elected Fellows of the Academy: —

In Class I., Section 1 (Mathematics and Astronomy): —

George Russell Agassiz, of Boston; Ernest William Brown, of New Haven; Frederick Shenstone Woods, of Newton.

In Class I., Section 2 (Physics): —

Louis Agricola Bauer, of Washington; Percy Williams Bridgman, of Cambridge; Daniel Frost Comstock, of Boston; Arthur Louis Day, of Washington; Charles Sheldon Hastings, of New Haven; Maurice deKay Thompson, of Boston.

In Class I., Section 3 (Chemistry): —

Russell Henry Chittenden, of New Haven; Lawrence Joseph Henderson, of Cambridge; Samuel Parsons Mulliken, of Boston.

In Class I., Section 4 (Technology and Engineering): —

William Herbert Bixby, of Washington; Desmond FitzGerald, of Brookline; George Washington Goethals, of Culebra; Canal Zone; Lionel Simeon Marks, of Cambridge.

In Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe): —

Waldemar Lindgren, of Washington; William Berryman Scott, of Princeton.

In Class II., Section 2 (Botany): —

Ezra Brainerd, of Middlebury; Vt.; Alexander William Evans, of New Haven.

In Class II., Section 3 (Zoölogy and Physiology): —

William Healey Dall, of Washington; John Eliot Thayer, of Lancaster, Mass.

In Class II., Section 4 (Medicine and Surgery): —

Elliott Proctor Joslin, of Boston; Charles Pickering Putnam, of Boston; Simeon Burt Wolbach, of Boston; James Homer Wright, of Boston.

In Class III., Section 1 (Philosophy and Jurisprudence): —

John Adams Aiken, of Greenfield, Mass.; Simeon Eben Baldwin, of New Haven; Frederic Dodge, of Belmont; Richard Olney, of Boston; Elihu Root, of New York; Arthur Prentice Rugg, of Worcester.

In Class III., Section 2 (Philology and Archaeology): —

Franz Boas, of New York; George Henry Chase, of Cambridge; Alfred Louis Kroeber, of Berkeley, Cal.; Hanns Oertel, of New Haven.

In Class III., Section 3 (Political Economy and History): —

Irving Fisher, of New Haven.

In Class III., Section 4 (Literature and the Fine Arts): —

Henry Leland Chapman, of Brunswick, Maine; Wilberforce Eames, of New York; Henry Lee Higginson, of Boston; Mark Antony DeWolfe Howe, of Boston; George Herbert Palmer, of Cambridge; Robert Swain Peabody of Boston; William Jewett Tucker, of Hanover, N. H.; Williston Walker, of New Haven.

The following gentlemen were elected Foreign Honorary Members: —

In Class I., Section 2 (Physics): —

Svante August Arrhenius, of Stockholm; Hendrik Antoon Lorentz, of Leyden; Augusto Righi, of Bologna.

In Class III., Section 4 (Literature and the Fine Arts): —

Jean Adrien Aubin Jules Jusserand, of Paris.

Dr. C. S. Minot presented the following paper by Professor Hugo Kronecker: —

"Unexpected Effects of Electrical Stimuli on the Human Biceps."

The following paper was presented by title: —

"A Theory of Linear Distance and Angle." By Dr. H. B. Phillips and Dr. C. L. E. Moore. Presented by H. W. Tyler.

BIOGRAPHICAL NOTICES.

FREDERICK IRVING KNIGHT.

Dr. Frederick Irving Knight was born in Newburyport, Massachusetts, on May 18, 1841, was graduated at Yale College in 1862, from which later he received the degree of A.M., and at the Harvard Medical School in 1866. While studying in Europe he was made Instructor in Percussion, Auscultation, and Laryngology in this school, and in 1886 Clinical Professor of the last subject. He inaugurated a clinic for diseases of the chest and throat at the Massachusetts General Hospital, was consulting physician there, as well as at the Free Home for Consumptives, and the Sharon Sanatorium. A pioneer in the movement against tuberculosis, he gave time and thought to its furtherance, and it was largely through the advice given by him to Governor Greenhalge that the Massachusetts Sanatorium at Rutland was established. One of the founders of the Boston Medical Library, he was a student, as well as a practitioner, of medicine, a frequent contributor to the medical press, and a member of well-known medical societies.

His knowledge of laryngology and diseases of the chest, founded upon a broad knowledge of medicine as a whole, made him one of the foremost authorities on these subjects in the country. Possessed of every quality for which we respect the older physician, he was also conspicuously cordial to what was new in medicine, spared no pains to inform himself, and weighed the evidence critically before accepting or rejecting the new remedy or method. No one in the profession reached sounder conclusions or more quietly and courageously held his secure ground.

In the care of his patients he took exceptional pains to have everything done that might contribute to their welfare and recovery.

He was just, considerate, and generous, to the younger as well as to the older medical men, and it was a privilege to be counted among his friends.

He was elected a Fellow of the Academy March 13, 1889. He died February 20, 1909.

Francis H. Williams.

THOMAS WENTWORTH HIGGINSON.

Thomas Wentworth Higginson, preacher, soldier, author, was born in Cambridge, Massachusetts, December 22, 1823. His preliminary education was obtained in a private school at Cambridge, and he was graduated from Harvard College in 1841. After graduation he taught for six months in a boarding-school at Jamaica Plain, and then became private tutor to the sons of a cousin, who at that time resided in Brookline. Here, domesticated in an affectionate and interesting family, and having access to a library the shelves of which were loaded with the works of French and German writers with which for the first time he then came in contact, he led a happy life. The beautiful country about Brookline fascinated him, and he spent hours in rambling over the hills, watching the birds and animals and gathering wild flowers. "We often had school," he says, "in the woods adjoining the house, perhaps sitting in large trees, and interrupting work occasionally to watch a weasel gliding over a rock or a squirrel in the boughs."

The Brook Farm experiment was then in full career and Higginson came in contact, while living in Brookline, with several of the young men who were at that time giving practical proof of their faith in communistic theories. Obviously these theories did not reach him, although, so far as money matters were concerned, he at this time deliberately renounced all thoughts of the accumulations that might be had from the law as a profession, and under the influence of the books that he was then reading, concluded that a life of extreme economy was without terror for him. So minded, he became engaged to be married, and returned to Cambridge in September, 1843, where he entered college as a "resident graduate," having no clearly defined purpose or intention as to the future, but attracted by the thought of a purely literary life carried on in an unworldly spirit with the possible chance of an appointment as professor as a reward. The influences that surrounded him while in Cambridge are best told by himself: "There were always public meetings in Boston to be attended, there were social reform gatherings where I heard the robust Orestes Brownson and my eloquent cousin, William Henry Channing;

there were anti-slavery conventions, with Garrison and Phillips; then on Sunday there were Theodore Parker and James Freeman Clarke, to show that one might accomplish something and lead a manly life even in the pulpit." Then, as ever after, manliness was with him an essential feature of life, and it was with the thought that "even in the pulpit" a man might lead a "manly life," that he gravitated towards the "liberal ministry," and in preparation therefor entered the Harvard Divinity School. He completed the regular course of study there and graduated in 1847.

On the 30th of September of that year he married, in Boston, his cousin, Mary Elizabeth, daughter of Dr. Walter Channing. Mrs. Higginson, not long after her marriage, became a confirmed invalid, but she survived until September 2, 1877, when she died at Newport, Rhode Island. In the preface of "Malbone," Higginson makes the statement that "Aunt Jane," a character in that novel, was studied as closely as possible from real life, and the bright sayings of the lady were the fruit of a long habit of jotting down her actual conversation. We shall probably not be far out of the way if we conclude that this statement points out where a clue to the character of Mrs. Higginson may be found.

In 1847, the year that he graduated at the Divinity School, and the year also in which he was married to his cousin, he received a call from the First Religious Society at Newburyport, then ostensibly Unitarian, which call he accepted. He was ordained, at his own suggestion, by the Society itself without the intervention of an ordaining council. In Newburyport he was drawn into the temperance agitation, the peace movement, the woman's rights movement, and the anti-slavery movement. He did, indeed, accept in 1848 — though hopeless of election — the nomination for Congress from the Free Soil party, a party defined by him as "political abolitionists," and, while still a settled clergyman at Newburyport, he actually entered upon an active campaign in that congressional district. His nomination was due, partly at any rate, to Whittier. At Cambridge he had been a friend and associate of Lowell. His life at Newburyport brought him in contact with Whittier. The anti-slavery sentiments of both these poets drew him into close and sympathetic touch with them, and though he was strong enough to stand alone, he welcomed the support of their influence.

His career as an anti-slavery candidate for Congress, stumping the district in search of votes, or perhaps it would be better to say in an effort to create public opinion and to identify himself with a cause, naturally aroused hostility in his congregation. He himself says that he preached himself out of the pulpit. His sermons doubtless had to do with his separation from this congregation, but his political speeches must also be reckoned in the general accounting. For two years and a half he retained connection with this parish, and during all that time he had the cordial support of the younger members of his congregation. Then, for two years after the severance of this connection, he continued to live in Newburyport, teaching private classes, serving on the school committee, organizing public evening schools, and enlisting the young ladies of the town in the instruction of factory girls, thus making himself a living force in local affairs. As if all this were not enough for one man, he was at the same time busily engaged in writing editorials and communications for three or four newspapers.

In February, 1851, a fugitive slave, known as Shadrach, was rescued by Boston negroes from the hands of the officers having him in custody, while actually within the precincts of the Suffolk Court House. This evasion of the enforcement of the fugitive-slave law caused a commotion even in Washington, and it was not long before a second test was made of the power of the federal government to enforce in Massachusetts an obnoxious law in a community thoroughly loyal and obedient to law, but hostile to the principles on which this particular law was based.

Following the rescue of the negro Shadrach in February, 1851, Higginson joined the Vigilance Committee in Boston, an organization the purpose of which was apparently to be on the alert and ready to aid in such cases, but without definite plans as to how assistance might be given. The committee was divided in opinion on the question of forcible resistance to the authorities. His official connection with this organization soon caused him to be summoned to Boston, where in April of the same year the arrest of Thomas Simms, another fugitive, brought the Vigilants face to face with the question of what they should do. At the meeting of the committee Higginson urged action in opposition to the enforcement of the law, and at a crowded public meeting held subsequently in Tremont Temple he spoke vehemently, his counsels on this occasion being characterized as of a nature to bring the community to the verge of a revolution. More moderate speeches at the same meeting had the effect of counteracting the influence of his speech, and Higginson was left to organize secretly, as best he could, a plan for the rescue of Simms. Precautions taken by the officers having the fugitive in charge prevented the success of the plan for the rescue.

It happened that the United States Marshal having charge of the fugitive was Charles Devens, a schoolmate and a friend of Higginson. The relations of these two men to each other and to the subject under discussion thoroughly illustrate the complexity of the political situation in Massachusetts caused by the attempts at that time to enforce the fugitive-slave law. Here were two men, both hostile to slavery, both animated by a keen sense of honor, both striving to do their duty. The one if he should perform the duties of the office which he had accepted would be compelled to restore to slavery an individual, entitled under local laws to his personal freedom. The other, should the decision of the case have the effect of returning the fugitive to his master, and should opportunity offer to attempt the rescue of the fugitive, would be prompted by a sense of duty to violate the laws of his country and in such event would himself become, in all probability, either a fugitive from justice or a prisoner.

Higginson wrote to Devens imploring him to resign rather than to be the instrument of sending a man into bondage. The answer was courteous, but Devens considered that, however repugnant the performance of this service might be, the service was nevertheless inherent upon his having accepted the office of marshal. Simms was returned to servitude. The vigilance of the police prevented any attempt to release him. Devens showed how deeply he felt the burden of rendering official service which would perhaps cost a man his freedom, by making two efforts at a later date to secure through purchase the liberty of the negro, the first offer being refused by the master and the second attempt being frustrated by the outbreak of the war. In the course of military events Simms recovered his freedom, and Devens at a later period was able to help him pecuniarily and otherwise.

In 1852 Higginson was invited to take charge of the Worcester Free Church, an organization which sprang up under the influence of Theodore Parker's society in Boston, in which there was no church membership, which did not call itself specifically Christian, and which held no communion service. This call he accepted and his evening lectures or sermons soon became very popular. He retained connection with this church for six years and in 1858 resigned in order to devote his life to literary pursuits.

It will be seen at a glance that his relations with his followers here were widely different from those which existed between himself and his congregation at Newburyport. Fresh from the Divinity School, without political record, he had assumed charge at Newburyport of a congregation having a history of two hundred years behind it and having as a body no pronounced political opinions. There was, however, a certain amount of denominational adherence and of pride in the old church. On the other hand, he came to Worcester, a preacher without a congregation and an open advocate of resistance to the government in all attempts to enforce the fugitive-slave law. This move was made at the call of a body of active reformers, all abolitionists, having no strong element of cohesion; a mere aggregation of extremely independent individuals; leaders in public movements, whose popular influence was restrained by the fact that they were combating local prejudices and attacking opinions sustained by conservatism and social power. Higginson says of Wendell Phillips that to abolitionism he "sacrificed his social position, his early friendships, his professional career," and of himself he says that he found himself in fashion in Worcester, "at least with the unfashionable." The portals of society could not have remained closed in that place to a Higginson married to a Channing if he had cared to cause them to open, but the illness of his wife and the gratification that he derived from social intercourse with those who sympathized with his views prevented him from penetrating abodes where an abolitionist, a woman's rights man, and a Parkerite would not have been altogether *persona grata*. He says in one place, "I cannot dispense with the society which we call uncultivated." If he found any such in Worcester he did not rely upon it altogether, for he discovered cultivated, genial friends, unknown to society, with whom he had delightful intercourse. The home of a tailor, for instance — of whom Higginson wrote that he had the freshest and most original mind in Worcester — who stood at his cutting board all day, and who at night read Browning with his charming wife, and this too at a time when to be able to read Browning meant even more than it does to-day, furnished one place of resort. In such families as this, where the free interchange of opinions on all topics was permissible, he found the sort of social intercourse that he wanted. His time was taken up with outdoor exercise, writing for the papers, and at times in giving a helping hand to some escaped slave. Naturally, fugitives from servitude claimed assistance from such a body as his church, and it follows of course that actual aid was freely given to help them on their way to freedom.

He quotes in his "Cheerful Yesterdays" from a contemporary journal, apparently his own, in illustration of that curious period, a paragraph describing the impression of the writer on thus participating in revolutionary work, in which the journalist states that it is strange "to see law and order, police and military, on the wrong side and find good citizenship a sin, and bad citizenship a duty. . . ."

On the 25th of May, 1854, there came to him a summons to Boston to attend a public meeting to be held in Faneuil Hall in consequence of the arrest of Anthony Burns, another fugitive. Higginson found the Vigilance Committee inadequate for the situation through the non-resistance element and through division of opinion. Those who were willing to act personally in forcible resistance were, however, left in charge of the situation, and of these Higginson was selected as the leader. The fugitive was confined in the United States Court room in the Suffolk Court House, the jails of the state not being at the behest of Federal officers for the confinement of persons who had not violated any state law. A plan was devised to take advantage of the Faneuil Hall meeting. An announcement was to be made, while the meeting was in progress, that an attack on the Court House was being made. This would break up the meeting and bring a mob up to Court Square, under cover of which such an attack might be successful. The various parts of this disjointed scheme did not fit very well together, and the attack resulted in a mere fiasco. The killing of one of the deputies at an early stage of the affair seems to have paralyzed the combatants, and out of it all the only visible result was that T. W. Higginson, alone of all the clamorous abolitionists, had shown conspicuous courage, the only real contestant for supremacy in that time being an unknown colored man. Then followed the consequences of the assault; an inquest by the grand jury and the indictment of Theodore Parker, Wendell Phillips, Thomas Wentworth Higginson, and others. The fact that a man had been killed at the Court House gave to the proceedings a solemnity and an importance which they might otherwise have lacked. The distinguished men thus brought to the bar made no effort to escape their trial, but the issue was never fairly met by the submission of the case to the jury. The indictment was quashed on a technicality. This episode cost Higginson the good will of many persons whose approval he would have enjoyed, but this fact did not cause him to swerve a jot from his position. Neither then nor thereafter did he offer excuse or apology for what he had done. He was actuated by principle, firm, unyielding, and unchangeable.

Serious as was the position of these men while under indictment, it is evident that Higginson's family were not much disturbed by it, nor had they much fear of the result. His mother, writing concerning it, picked out a curious phrase in the indictment and referring to it facetiously informed her correspondent that she was not troubled at having a son "riotously and riotously disposed," while on the occasion of a suggestion made by his wife that her letters to him while he was in prison might be read by the jailer, another member of the family remarked, "Not if he writes them in his usual handwriting."

In October, 1854, a deputy supposed to have come to Worcester in search of evidence against the participants in the Burns riot was recognized and was attacked by a mob of negroes. A number of abolitionists, among whom was Higginson, interposed, protected the deputy, and with much difficulty saved him from serious harm and succeeded in getting him out of the city. Higginson rode with him in the vehicle in which he was transported to safety, and, although his feelings of hostility towards the man were not vile enough to permit his sacrifice by the mob, he humorously tells us that while he thus had him at his mercy he took an inhuman advantage of him and gave him a discourse on the baseness of his career.

After the Burns affair all attempts to enforce the fugitive-slave law in Massachusetts ceased, but the abolitionists made preparation for active interference in case opportunity offered, and kept in commission a yacht which was nominally for hire, but which was ready at all times for several years to receive a fugitive or, as the case might be, his master, and take him on a cruise while the excitement should last. Higginson was a stockholder in this yacht.

As was the case when in Newburyport, he did not allow his crusade against slavery to prevent his taking an active part in Worcester in affairs of more immediate and local importance. He interested himself in the new question of a prohibitory law, was for a time secretary of the state committee, and took a hand in the local enforcement of the law. He was deeply concerned with the problem of discharged convicts, and at a later period he served as a delegate to a meeting of prison reformers in Europe. He was firm in the conviction that the lives of many of these convicts could be rescued.

The peculiar nature of his religious society led to a certain amount of ostracism. Edward Everett Hale was for a time, at any rate, the only clergyman in Worcester who would exchange with him. Later he was brought into amicable relations with others. As was to be expected, he was put on the school committee, from which, however, he was subsequently dropped for defending the right of a Roman Catholic father to decide which version of the Scriptures his child should read in school. Later he was reinstated. He had a hand in organizing the Worcester Public Library. He, with others, organized a local Natural History Society. His fondness for out-of-door exercise took shape in tramps over the hills about Worcester and in boating on Lake Quinsigamond and in the organization of a gymnastic club, a skating club, and a cricket club, of each of which he was president.

He dates the beginning of his literary life from the publication of "Saints and their Bodies" in the "Atlantic Monthly" in 1858. It is true that the "North American Review," the "Christian Examiner," and "Putnam's Magazine" had already published articles from his pen, and that numerous communications and short poems had found a ready welcome in the columns of certain newspapers, but for such recognition as this he cared but little. The acceptance of an article by the Atlantic was for him a baptism as a litterateur.

From November, 1855, to May, 1856, he was in Fayal. What he found there worth observing is set forth in a paper entitled "Fayal and the Portuguese," originally published in the "Atlantic Monthly" in November, 1860, and reprinted in "Outdoor Papers."

The Kansas Nebraska Act was passed in 1854, and the struggle for possession of the territory of Kansas between the free states and the slave states began at once. In Massachusetts organized emigration from that state to Kansas was effected through the agency of the Emigrant Aid Society. This movement was at first of a peaceful nature, but later such emigrants as went forth were better prepared for emergencies. Higginson arrived in Boston from Fayal in May, 1856. A public meeting which was held in Worcester in honor of his return was converted into a call for volunteer emigrants to Kansas. A committee was appointed, of which he was secretary, under whose auspices three parties of emigrants were sent forward armed with rifles and pistols and prepared for camping out. He himself was first sent to St. Louis to look out for a stray party of emigrants whose progress had been hindered, and later, as agent of the National Kansas Committee, having its headquarters at Chicago, he was sent to Kansas with a convoy of rifles to oversee a party of emigrants. On this expedition he met the famous "Jim Lane" at the head of a party of mounted followers, and was honored by an appointment on Lane's staff with the rank of brigadier-general. He passed safely through Kansas, though the trip was not without the fascination of actual peril. He speaks of the "tonic life" of these weeks, and says that when they were over and he arrived where he could call for help upon a policeman, he felt as if "a despicable effeminacy had set in."

In January, 1857, he joined with a few other Republicans and Garrisonian Abolitionists in calling and in holding a state disunion convention. A call for a national disunion convention was also circulated, Cleveland being the appointed place of meeting, but the financial panic of 1857 prevented the meeting of this convention.

February 2, 1858, John Brown wrote to him, as "an abolitionist" and "a true man," for pecuniary aid in perfecting what Brown considered the most important undertaking of his life. This celebrated abolitionist was already famous, and Higginson says that there was but one way of thinking among the Kansas Free State men as to the most extreme act of John Brown's Kansas career, the so-called "Pottawatomie Massacre." As one of them put it, Brown saw the necessity of some such blow and had the nerve to strike it. "Personally," adds

Higginson, "I have never fully reconciled myself to this vindication of 'the blow,'" and he claims that Brown is to be judged as "a pure enthusiast — fanatic, if you please."

Brown had developed a plan for penetrating Virginia with a few followers, not with a view to an insurrection, but with intent to assemble fugitives, and if unable to protect them in local fastnesses to send them to Canada. In this plan Higginson, Theodore Parker, and others of the anti-slavery leaders co-operated and raised money for its furtherance. The details of the scheme were betrayed, and action on the part of Brown was necessarily postponed. In October, 1859, came the attack on Harper's Ferry, a proceeding on the part of Brown radically different from the plan previously proposed by him, in aid of which the money referred to above had been contributed, and further a proceeding which was opposed by Brown's followers. For a time all those who had been in touch with this fanatical leader and all those who had furnished him with money were under suspicion and were in danger of arrest. Some fled to Canada, but Higginson felt that it was his duty to stand his ground and give Brown his moral support, and he goes on to state that with Brown in confinement there was, of course, an immediate impulse to rescue him from prison. "I do not know how far this extended," he says, "and can only vouch for myself." Brown, however, had absolutely prohibited any such attempt, and unless he could be led to change his opinion any efforts to rescue the inflexible old man would be thrown away. It occurred to Higginson that Brown's wife might, in a personal interview, influence the prisoner to recede from this position, and he went to North Elba and secured her co-operation. The plan failed through the stubbornness of Brown, who refused positively to see his wife. A harebrained effort was shortly afterward started to rescue two of Brown's followers, but the leader chosen for the purpose, after carefully inspecting the ground, pronounced the scheme impracticable. When this proposition was under consideration, Higginson went to Harrisburg to meet the leader of the enterprise, to arrange details, and to take part in the rescue if it should be attempted. On the abandonment of the expedition he returned to his home.

At the outbreak of the war he visited Governor Andrew and volunteered, if provided with the necessary funds, to invade the Virginia mountains with a small force of men selected from the Kansas Free State men, and kindle a back fire there, with a view of distracting attention from the national capital, then in peril. There was no contingent fund in Massachusetts that could be used, but a small sum of money was raised from private sources. Governor Curtin of Pennsylvania was consulted, but events moved so rapidly that the proceeding became unnecessary and even undesirable.

In the spring of 1861 he was offered the command of the 4th Battalion of Infantry, then hastily raised for government service. Notwithstanding the fact that the impending collision had for some time back induced him to turn his reading towards military works, so that he had acquired an academic acquaintance with the theories of attack and defense, he did not feel competent to assume charge in the field of a battalion of troops. Moreover the state of his wife's health at that time was precarious, and she was especially dependent upon him. A third and probably a prevailing reason was the uncertainty of the government position on the slavery question, and the fear that, as commanding officer, he might be compelled to return fugitive slaves to their masters.

By the fall of that year the anti-slavery position of the government had become more clearly defined, and he sought and obtained permission to raise a regiment of which he was to be second in command. After three months of hard labor in raising companies in different parts of the state, and after about half the necessary companies had been raised, an order putting a stop to recruiting rendered all of this preliminary work abortive. Recruiting was renewed in 1862, and he then raised a company for the 51st regiment, of which company he was commissioned as Captain, September 25, 1862. He quotes in his "Cheerful Yesterdays" a popular nonsense rhyme made at his expense about this time which ran as follows:

"There was a young curate of Worcester
Who could have a command if he 'd choose ter,
But he said each recruit
Must be blacker than soot,
Or else he 'd go preach where he used ter."

Very shortly after receiving his commission as Captain in the 51st regiment he was offered by General Saxton, military commander of the Department of the South, the command of a regiment of freed slaves. This offer fulfilled, he says, the dream of a lifetime, and after investigating the circumstances under which the offer was made, he accepted it. November 10, 1862, he became Colonel of the 1st South Carolina volunteers, afterwards the 33d United States colored troops, the first regiment of freed slaves mustered into the United States service. The regiment was stationed near Beaufort, South Carolina. During his connection with it, whether on the march or in camp, he made a close, analytical study of the negro as a soldier, the record of which is to be found in his "Army Life in a Black Regiment." It chanced that he was not engaged in any large battle, but he went on expeditions up the St. Mary's, the St. John's, and the Edisto. While up the St. John's the city of Jacksonville was captured by his command and was held by him until he was ordered back to head-quarters. On the Edisto raid on the 10th of July, 1863, he was wounded. He was shortly thereafter invalided and sent North and, although he thought at one time that he was well enough to resume active service, he found on returning to his regiment that he was not able to bear the exposure of camp life. He resigned in October, 1864.

His wife had meantime, for the sake of her health, gone to Newport to live. He joined her there and resumed literary work. Suggestions as to his life in that place will be found in "Malbone" and in "Old Port Days."

In 1878, shortly after the death of his wife, he took a trip to Europe, where he was cordially received as a representative of American literature, and where he met Froude, Carlyle, Sir Frederick Pollock, Matthew Arnold, Darwin, and many other distinguished Englishmen. On his return to this country he settled at Cambridge, where in February, 1879, he married Mary P. Thacher, herself an authoress of some note.

The numerous services which he performed for the public in Newburyport and at Worcester indicate his sense of civic responsibility and his willingness to give to the public without reward what there was that was available in his still vigorous body and his richly endowed intellect. Though no longer able to endure as much as formerly, still he performed substantially the same rôles at Newport and at Cambridge, renewing his former experiences even to the extent of being dropped from the Newport School Committee, serving as trustee of public libraries, organizing social clubs, and patronizing Shakespeare and Browning Societies. To his connection with the Colonial Club of Cambridge we owe the preservation on canvas of an adequate representation of his person. The picture of the first president of the club graces the walls of the clubhouse. While in Newport and in Cambridge he was for many consecutive years engaged in giving lectures and in editorial works on the "Index" and the "Woman's Journal."

He was elected to the Legislature in 1880 and again in 1881. He served one year as chief of the personal staff of Governor Long. He was three years on the State Board of Education and served seven years as state military and naval historian. He says, indeed, "Looking back fifty years, I cannot put my finger on five years when I myself was not performing some official service for the city or state or both simultaneously." He entered actively the Cleveland campaign in 1888 and reluctantly ran for Congress on the democratic ticket. Although not elected, he was gratified by the vote.

His old age in Cambridge and at his charming summer residence at Dublin, New Hampshire, was peaceful, and his days were full of happiness. The various reforms in which he had been interested were either accomplished or in a fair way of being so. He no longer felt estranged among his fellow Unitarians. They had so nearly reached his own position on the question of religious freedom that he could and did join the congregation of the First Parish in Cambridge. He was blessed with offspring, and, indeed, before he died he was glad to welcome in his household a new member of the family, of a generation twice removed from his own.

With growing years and increasing fame he was accustomed to receive his friends on the recurrence of his birthday, and this custom he kept up to the last whenever his health would permit. These receptions were originally inaugurated on his seventieth birthday, and the scores of persons who annually thereafter took advantage of them to pay their respects to the Colonel bore testimony to the extent of his fame and to the great change in the popular estimate of his character since the days of his personal attack on the Suffolk Court House. They were interrupted by a severe illness which kept him in the house for nearly two years. It was during this period of physical suffering that his "Cheerful Yesterdays" was written. Propped up in bed, leaning against the pillows, he dictated the book, the spirit of which shows that even under those circumstances his to-day as well as his yesterday was cheerful.

He was honored by the Western Reserve and by Harvard Universities with the degree of LL.D. He was Vice-President of the Liberal Congress of Religion, Fellow of the American Academy of Arts and Sciences, Corresponding Member of the Royal Society of Canada, Member of the American Academy of Arts and Letters, and Member of the Massachusetts Historical Society.

A chronological list of his publications was prepared and published in 1906 by the Cambridge Public Library, and in this publication there is also an alphabetical list of books and articles pertaining to his life and career. The information contained therein will be found to be very serviceable to the biographer of Colonel Higginson. It needs, however, to be supplemented with the publications made after 1906. His collected works were reprinted in 1900 in seven volumes. In 1906 a volume was put forth entitled "Part of a Man's Life."

Colonel Higginson died May 9, 1911. He was accorded a military funeral by the Loyal Legion, of which he was a member, and was escorted to his last resting place by a guard of colored men, a fitting tribute on their part to the devotion of his life to the cause of the down-trodden of their race.

When the Colonel entered the field of active life he devoted his energies to three causes : Freedom for the colored race ; freedom from the trammels of the law, for women ; freedom in religious belief from the restraints of dogma. To the first of these causes he sacrificed, in his youth at least, social position and political ambition, and later the chance of military promotion. To a certain extent the championship of the second and third of these causes could only be prosecuted during the same period under similar disadvantages. Coupled with these three reforms, but holding a secondary position in his esteem, was the open advocacy of Outdoor Exercise or Athletics, of Higher Education for Women, and of Temperance for all.

He lived to see the slave released from bondage and to see Woman's Suffrage adopted in several of our states. He attended services in later life in a church where Theodore Parker would have been welcomed in the pulpit. He had but to cast his eyes across the Charles to see, in the Stadium, the evidence of the extraordinary hold upon modern collegiate life developed by athletics and intercollegiate games. The group of buildings made use of by Radcliffe College for the higher education of women in Cambridge he might daily see, and he might also have heard that the preponderant number of women in some of the Western State universities made it questionable in the minds of some philosophic observers whether in the near future it might not prove that there would be a body of highly educated females in these states, while the bulk of the men, absorbed in business and industries, would be found to have contented themselves with a high school education. If in his latter days he had travelled from Maine to the Mexican border he would have found that Prohibition had so far prevailed that a thirsty man would often have to wait for entry into an unprogressive state if he wanted anything stronger than water to drink. There still remained fields in which, if strength had been granted him, he might as a reformer have worked. International arbitration, civil service reform, and the abolition of monopolies are to be found in his list of what remains to be accomplished.

Any man who reads Colonel Higginson's accounts of his personal experiences will realize not only that he was a courageous man, being absolutely devoid of fear, but also that he actually thirsted for adventure. He would have enjoyed being present at the liberation of Shadrach, not alone because the rescue of the slave was in accord with his moral convictions, but because of an impulse in his blood which he describes as "an intrinsic love of adventure." This love of adventure doubtless had voice in all his after proceedings. The story of his army life is tinctured with it. He knows "nothing in life more fascinating than the nocturnal ascent of an unknown river leading far into an enemy's country," or, again, "of going into a region where peril made fascination." At any time, he says, by going into the outskirts at one of his camps, one could have a skirmish which, he adds, was nothing but fun. Such expressions as these betray the soldier rather than the preacher, the lecturer, or the translator of Epictetus and the Sonnets of Petrarch.

At the outset of his appeal to the public through the press he seemed disposed to make use of poetry rather than prose. Twenty titles are given in the chronological list published by the Cambridge Public Library of publications in newspapers in the years 1846–1849 inclusive. Of these fifteen are sonnets, poems, or hymns. Thereafter the poem is the exception, but his "Outdoor Papers" are filled with the aroma of woods and the fragrance of flowers. The cadence of their sentences is so beautifully adjusted that they might almost pass for poems. He seldom ventured into the land of fiction, and once only tried his hand at a novel. A competent critic says that "his writings show a deep love of nature, art, and humanity, and are marked by vigor of thought, sincerity of feeling, and a grace and finish of style."

In 1875 he published "Young Folks' History of the United States," which had a marvellous success in this country, new editions appearing from time to time thereafter, while in Europe the volume was translated into the French, German, and Italian tongues. He also engaged in other historical work, and published in 1885 a "Larger History of the United States"; in 1893 "English History for American Readers," in collaboration with Professor Edward Channing; and in 1905 a "History of the United States," in collaboration with Professor William McDonald, this last being practically an enlarged edition of his "Larger History of the United States."

In Colonel Higginson's sketch of Theodore Parker's life he says, "There may be some whose fame is so ill established that one shrinks from speaking of them precisely as one saw them; but this man's place is secure, and that friend best praises him who paints him just as he seemed." No better suggestion could be made to the biographer of Colonel Higginson than the words which he himself uses concerning the task set for the biographer of Theodore Parker. So far as the person engaged in the memoir of Colonel Higginson is concerned, he is relieved from the necessity of explanation or apology for Higginson's resistance to constituted authorities by the frankness of the Colonel himself, who has revealed his entire career to the world with a sincerity which would permit one who differed from him as to the propriety of the methods of which he at times made use, to appropriate freely from the autobiographical writings which he has left behind him. To a great extent this is what I have done, thus trying to do justice to a friend whom I honored even when I did not agree with him. The story herein given of the career of this aggressive reformer, this outspoken independent preacher, this courageous soldier and scholarly author, this useful citizen and brilliant man, is practically told in his own words. Should it seem that his social charms have been inadequately developed and that there is no sufficient picture of the gentle urbanity of his later years, we must hope that this phase of the Colonel's character will be more forcibly portrayed in the forthcoming life promised at the hand of Mrs. Higginson.

Andrew McFarland Davis.

American Academy of Arts and Sciences

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LIST

OF THE

FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to July 1, 1912.)

FELLOWS. — 323.

(Number limited to six hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 129.

SECTION I. — *Mathematics and Astronomy.* — 30.

Solon Irving Bailey	Cambridge
Edward Emerson Barnard	Williams Bay, Wis.
Lewis Boss	Albany, N. Y.
Ernest William Brown	New Haven, Ct.
Sherburne Wesley Burnham	Williams Bay, Wis.
William Elwood Byerly	Cambridge
William Wallace Campbell	Mt. Hamilton, Cal.
Seth Carlo Chandler	Wellesley Hills
Fabian Franklin	New York
George William Hill	West Nyack, N. Y.
Edward Singleton Holden	West Point, N. Y.
Percival Lowell	Boston
Emory McClintock	New York
Joel Hastings Metcalf	Winchester
Eliakim Hastings Moore	Chicago, Ill.
Edward Charles Pickering	Cambridge
William Henry Pickering	Cambridge
Charles Lane Poor	New York
Arthur Searle	Cambridge
George Mary Searle	Berkeley, Cal.
Vesto Melvin Slipher	Flagstaff, Ariz.

John Nelson Stockwell	Cleveland, O.
William Edward Story	Worcester
Henry Taber	Worcester
Harry Walter Tyler	Boston
Oliver Clinton Wendell	Cambridge
Robert Wheeler Willson	Cambridge
Edwin Bidwell Wilson	Cambridge
Frederick Shenstone Woods	Newton
Paul Sebastian Yendell	Dorchester

Section II. — *Physics*. — 40.

Joseph Sweetman Ames	Baltimore, Md.
Carl Barus	Providence
Louis Agricola Bauer	Washington
Alexander Graham Bell	Washington
Louis Bell	Boston
Clarence John Blake	Boston
Francis Blake	Weston
Percy Williams Bridgman	Cambridge
George Ashley Campbell	New York
Harry Ellsworth Clifford	Newton
Daniel Frost Comstock	Boston
Charles Robert Cross	Brookline
Harvey Nathaniel Davis	Cambridge
Louis Derr	Brookline
Alexander Wilmer Duff	Worcester
Arthur Woolsey Ewell	Worcester
Harry Manley Goodwin	Brookline
George Ellery Hale	Pasadena, Cal.
Edwin Herbert Hall	Cambridge
Hammond Vinton Hayes	Cambridge
William Leslie Hooper	Somerville
William White Jacques	Boston
Frank Arthur Laws	Boston
Henry Lefavour	Boston
Theodore Lyman	Brookline
Richard Cockburn Maclaurin	Boston
Thomas Corwin Mendenhall	Ravenna, O.

Albert Abraham Michelson	Chicago, Ill.
Harry Wheeler Morse	Cambridge
Edward Leamington Nichols	Ithaca, N. Y.
Charles Ladd Norton	Boston
Benjamin Osgood Peirce	Cambridge
George Washington Pierce	Cambridge
Michael Idvorsky Pupin	New York
Wallace Clement Sabine	Boston
John Stone Stone	Boston
Maurice deKay Thompson	Boston
Elihu Thomson	Swampscott
John Trowbridge	Cambridge
Arthur Gordon Webster	Worcester

SECTION III. — *Chemistry.* — 32.

Gregory Paul Baxter	Cambridge
William Crowell Bray	Boston
Russell Henry Chittenden	New Haven, Ct.
Arthur Messinger Comey	Chester, Pa.
James Mason Crafts	Boston
Charles William Eliot	Cambridge
Henry Fay	Boston
Frank Austin Gooch	New Haven, Ct.
Lawrence Joseph Henderson	Cambridge
Eugene Waldemar Hilgard	Berkeley, Cal.
Charles Loring Jackson	Cambridge
Walter Louis Jennings	Worcester
Gilbert Newton Lewis	Boston
Charles Frederic Mabery	Cleveland, O.
John William Mallet	University, Va.
Forris Jewett Moore	Boston
George Dunning Moore	Worcester
Edward Williams Morley	West Hartford, Ct.
Samuel Parsons Mulliken	Boston
Charles Edward Munroe	Washington, D. C.
John Ulric Nef	Chicago, Ill.
James Flack Norris	Boston
Arthur Amos Noyes	Boston
Ira Remsen	Baltimore, Md.

Robert Hallowell Richards	Jamaica Plain
Theodore William Richards	Cambridge
Stephen Paschall Sharples	Cambridge
Francis Humphreys Storer	Boston
Henry Paul Talbot	Newton
William Hultz Walker	Newton
Willis Rodney Whitney	Schenectady, N. Y.
Charles Hallet Wing	Boston

SECTION IV. — *Technology and Engineering.* — 27.

Henry Larcom Abbot	Cambridge
Comfort Avery Adams	Cambridge
Alfred Edgar Burton	Boston
Eliot Channing Clarke	Boston
Desmond FitzGerald	Brookline
John Fritz	Bethlehem, Pa.
George Washington Goethals	Culebra, Canal Zone
Ira Nelson Hollis	Cambridge
Frederick Remsen Hutton	New York
Dugald Caleb Jackson	Boston
Lewis Jerome Johnson	Cambridge
Arthur Edwin Kennelly	Cambridge
Gaetano Lanza	Philadelphia, Pa.
Erasmus Darwin Leavitt	Cambridge
William Roscoe Livermore	Boston
Lionel Simeon Marks	Cambridge
Hiram Francis Mills	Lowell
Cecil Hobart Peabody	Brookline
Andrew Howland Russell	Paris
Albert Sauveur	Cambridge
Peter Schwamb	Arlington
Henry Lloyd Smyth	Cambridge
Frederic Pike Stearns	Boston
Charles Proteus Steinmetz	Schenectady, N. Y.
George Fillmore Swain	Cambridge
William Watson	Boston
Robert Simpson Woodward	Washington, D. C.

CLASS II. — *Natural and Physiological Sciences.* — 102.

SECTION I. — *Geology, Mineralogy, and Physics of the Globe.* — 27.

Cleveland Abbe	Washington, D. C.
Thomas Chrowder Chamberlin	Chicago, Ill.
Henry Helm Clayton	Canton
Herdman Fitzgerald Cleland	Williamstown
William Otis Crosby	Jamaica Plain
Reginald Aldworth Daly	Cambridge
Edward Salisbury Dana	New Haven, Ct.
Walter Gould Davis	Cordova, Arg.
William Morris Davis	Cambridge
Benjamin Kendall Emerson	Amherst
Grove Karl Gilbert	Washington, D. C.
Oliver Whipple Huntington	Newport, R. I.
Robert Tracy Jackson	Cambridge
Thomas Augustus Jaggar, Jr.	Brookline
Douglas Wilson Johnson	Cambridge
Alfred Church Lane	Cambridge
Charles Palache	Cambridge
John Elliott Pillsbury	Washington, D. C.
Raphael Pumpelly	Newport, R. I.
William Berryman Scott	Princeton, N. J.
Hervey Woodburn Shimer	Boston
Charles Richard Van Hise	Madison, Wis.
Charles Doolittle Walcott	Washington, D. C.
Robert DeCourcy Ward	Cambridge
Charles Hyde Warren	Auburndale
John Eliot Wolff	Cambridge
Jay Backus Woodworth	Cambridge

SECTION II. — *Botany.* — 21.

Oakes Ames	North Easton
Liberty Hyde Bailey	Ithaca, N. Y.
Douglas Houghton Campbell	Stanford Univ., Cal.
Frank Shipley Collins	Malden
John Merle Coulter	Chicago

Edward Murray East	Jamaica Plain
Alexander William Evans	New Haven, Ct.
William Gilson Farlow	Cambridge
Charles Edward Faxon	Jamaica Plain
Merritt Lyndon Fernald	Cambridge
George Lincoln Goodale	Cambridge
Robert Almer Harper	New York
John George Jack	Jamaica Plain
Edward Charles Jeffrey	Cambridge
Winthrop John Vanleuven Osterhout	Cambridge
Benjamin Lincoln Robinson	Cambridge
Charles Sprague Sargent	Brookline
Arthur Bliss Seymour	Cambridge
John Donnell Smith	Baltimore
Roland Thaxter	Cambridge
William Trelease	St. Louis, Mo.

SECTION III. — *Zoölogy and Physiology.* — 29.

Joel Asaph Allen	New York
Francis Gano Benedict	Boston
Henry Bryant Bigelow	Concord
William Brewster	Cambridge
Louis Cabot	Brookline
Walter Bradford Cannon	Cambridge
William Ernest Castle	Cambridge
Samuel Fessenden Clarke	Williamstown
William Thomas Councilman	Boston
William Healey Dall	Washington, D. C.
Charles Benedict Davenport	Cold Spring Harbor, N. Y.
Otto Knut Olof Folin	Brookline
Samuel Henshaw	Cambridge
Franklin Paine Mall	Baltimore, Md.
Edward Laurens Mark	Cambridge
Charles Sedgwick Minot	Milton
Silas Weir Mitchell	Philadelphia, Pa
Edward Sylvester Morse	Salem
Henry Fairfield Osborn	New York
George Howard Parker	Cambridge

James Jackson Putnam	Boston
Herbert Wilbur Rand	Cambridge
William Thompson Sedgwick	Boston
John Eliot Thayer	Lancaster
Addison Emory Verrill	New Haven, Ct.
William Morton Wheeler	Boston
James Clarke White	Boston
Harris Hawthorne Wilder	Northampton
Edmund Beecher Wilson	New York

SECTION IV. — *Medicine and Surgery.* — 25.

John Shaw Billings	New York
Edward Hickling Bradford	Boston
Arthur Tracy Cabot	Boston
Harold Clarence Ernst	Jamaica Plain
Reginald Heber Fitz	Boston
Simon Flexner	New York
William Stewart Halsted	Baltimore, Md.
Abraham Jacobi	New York
Elliott Proctor Joslin	Boston
William Williams Keen	Philadelphia, Pa.
Samuel Jason Mixter	Boston
William Osler	Oxford, Eng.
Theophil Mitchell Prudden	New York
Charles Pickering Putnam	Boston
William Lambert Richardson	Boston
Milton Joseph Rosenau	Boston
Theobald Smith	Jamaica Plain
Elmer Ernest Southard	Boston
Henry Pickering Walcott	Cambridge
John Collins Warren	Boston
William Henry Welch	Baltimore, Md.
Francis Henry Williams	Boston
Simeon Burt Wolbach	Boston
Horatio Curtis Wood	Philadelphia, Pa.
James Homer Wright	Boston

CLASS III. — *Moral and Political Sciences.* — 92.

SECTION I. — *Philosophy and Jurisprudence.* — 16.

Simeon Eben Baldwin	New Haven, Ct.
Joseph Henry Beale	Cambridge
Melville Madison Bigelow	Cambridge
Joseph Hodges Choate	New York
Frederic Dodge	Belmont
John Chipman Gray	Boston
Marcus Perrin Knowlton	Springfield
George Vasmer Leverett	Boston
Hugo Münsterberg	Cambridge
Charles Sanders Peirce	Milford, Pa.
George Wharton Pepper	Philadelphia, Pa.
Roscoe Pound	Belmont
Josiah Royce	Cambridge
Arthur Prentice Rugg	Worcester
Samuel Williston	Belmont
Woodrow Wilson	Princeton, N. J.

SECTION II. — *Philology and Archæology.* — 28.

Charles Pickering Bowditch	Jamaica Plain
Franklin Carter	Williamstown
George Henry Chase	Cambridge
Roland Burrage Dixon	Cambridge
Timothy Dwight	New Haven, Ct.
William Curtis Farabee	Cambridge
Jesse Walter Fewkes	Washington, D. C.
Basil Lanneau Gildersleeve	Baltimore, Md.
William Arthur Heidel	Middletown, Ct.
Albert Andrew Howard	Cambridge
Charles Rockwell Lanman	Cambridge
Thomas Raynesford Lounsbury	New Haven, Ct.
David Gordon Lyon	Cambridge
Clifford Herschel Moore	Cambridge
George Foot Moore	Cambridge
Hanns Oertel	New Haven, Ct.

Charles Pomeroy Parker	Cambridge
Frederick Ward Putnam	Cambridge
Rufus Byam Richardson	Woodstock, Ct.
Edward Robinson	New York
Fred Norris Robinson	Cambridge
Edward Stevens Sheldon	Cambridge
Herbert Weir Smyth	Cambridge
Franklin Bache Stephenson	Pittsfield
Charles Cutler Torrey	New Haven, Ct.
Alfred Marston Tozzer	Cambridge
Andrew Dickson White	Ithaca, N. Y.
John Williams White	Cambridge

SECTION III. — *Political Economy and History.* — 19.

Charles Francis Adams	Lincoln
Henry Adams	Washington, D. C.
Thomas Nixon Carver	Cambridge
Edward Channing	Cambridge
Archibald Cary Coolidge	Boston
Andrew McFarland Davis	Cambridge
Ephraim Emerton	Cambridge
Irving Fisher	New Haven, Ct.
Worthington Chauncey Ford	Boston
Abner Cheney Goodell	Salem
Arthur Twining Hadley	New Haven, Ct.
Henry Cabot Lodge	Nahant
Abbott Lawrence Lowell	Cambridge
Alfred Thayer Mahan	New York
James Ford Rhodes	Boston
Charles Card Smith	Boston
Henry Morse Stephens	Berkeley, Cal.
Frank William Taussig	Cambridge
Frederick Jackson Turner	Cambridge

SECTION IV. — *Literature and the Fine Arts.* — 29.

James Burrill Angell	Ann Arbor, Mich
Francis Bartlett	Boston

Arlo Bates	Boston
William Sturgis Bigelow	Boston
Le Baron Russell Briggs	Cambridge
Henry Leland Chapman	Brunswick, Me.
Wilberforce Eames	New York
Henry Herbert Edes	Cambridge
Arthur Fairbanks	Boston
William Wallace Fenn	Cambridge
Kuno Francke	Cambridge
Horace Howard Furness	Wallingford, Pa.
Mark Antony DeWolfe Howe	Boston
George Lyman Kittredge	Cambridge
Gardiner Martin Lane	Boston
William Coolidge Lane	Cambridge
Albert Matthews	Boston
Edward Caldwell Moore	Cambridge
George Herbert Palmer	Cambridge
Robert Swain Peabody	Boston
Herbert Putnam	Washington, D. C.
James Hardy Ropes	Cambridge
Denman Waldo Ross	Cambridge
John Singer Sargent	London, Eng.
William Jewett Tucker	Hanover, N. H.
Williston Walker	New Haven, Ct.
William Robert Ware	Milton
Herbert Langford Warren	Cambridge
Barrett Wendell	Boston

FOREIGN HONORARY MEMBERS. — 54.

(Number limited to seventy-five.)

CLASS I. — *Mathematical and Physical Sciences.* — 16.

SECTION I. — *Mathematics and Astronomy.* — 5.

Arthur Auwers	Berlin
Sir George Howard Darwin	Cambridge
Sir David Gill	London
Felix Klein	Göttingen
Émile Picard	Paris

SECTION II. — *Physics.* — 5.

Oliver Heaviside	Torquay
Sir Joseph Larmor	Cambridge
Augusto Righi	Bologna
John William Strutt, Baron Rayleigh	Witham
Sir Joseph John Thomson	Cambridge

SECTION III. — *Chemistry.* — 4.

Adolf, Ritter von Baeyer	Munich
Emil Fischer	Berlin
Wilhelm Ostwald	Leipsic
Sir Henry Enfield Roscoe	London

SECTION IV. — *Technology and Engineering.* — 2.

Heinrich Müller-Breslau	Berlin
William Cawthorne Unwin	London

CLASS II. — *Natural and Physiological Sciences.* — 17.

SECTION I. — *Geology, Mineralogy, and Physics of the Globe.* — 4.

Sir Archibald Geikie	Haslemere, Surrey
Julius Hann	Vienna
Albert Heim	Zurich
Sir John Murray	Edinburgh

SECTION II. — *Botany.* — 4.

Adolf Engler	Berlin
Wilhelm Pfeffer	Leipsic
Hermann, Graf zu Solms-Laubach	Strassburg
Eduard Strasburger	Bonn

SECTION III. — *Zoölogy and Physiology.* — 5.

Ludimar Hermann	Königsberg
Hugo Kronecker	Bern
Sir Edwin Ray Lankester	London
Elie Metchnikoff	Paris
Magnus Gustav Retzius	Stockholm

SECTION IV. — *Medicine and Surgery.* — 4.

Emil von Behring	Marburg
Sir Thomas Lauder Brunton, Bart.	London
Angelo Celli	Rome
Sir Victor Alexander Haden Horsley	London

CLASS III. — *Moral and Political Sciences.* — 19.

SECTION I. — *Philosophy and Jurisprudence.* — 4.

Arthur James Balfour	Prestonkirk
Heinrich Brunner	Berlin
Albert Venn Dicey	Oxford
Sir Frederick Pollock, Bart.	London

SECTION II. — *Philology and Archæology.* — 7.

Ingram Bywater	London
Friedrich Delitzsch	Berlin
Hermann Diels	Berlin
Wilhelm Dörpfeld	Athens
Henry Jackson	Cambridge
Hermann Georg Jacobi	Bonn
Sir Gaston Camille Charles Maspero	Paris

SECTION III. — *Political Economy and History.* — 5.

James Bryce	London
Adolf Harnack	Berlin
John Morley, Viscount Morley of Blackburn	London
Sir George Otto Trevelyan, Bart.	London
Pasquale Villari	Florence

SECTION IV. — *Literature and the Fine Arts.* — 3.

Georg Brandes	Copenhagen
Jean Adrien Aubin Jules Jusserand	Paris
Rudyard Kipling	Burwash

STATUTES AND STANDING VOTES

STATUTES

Adopted November 8, 1911: *amended May* 8, 1912

CHAPTER I

The Corporate Seal

Article 1. The Corporate Seal of the Academy shall be as here depicted:

Article 2. The Recording Secretary shall have the custody of the Corporate Seal.

See Chap. v. art. 3; chap. vi. art. 2.

CHAPTER II

FELLOWS AND FOREIGN HONORARY MEMBERS AND DUES

ARTICLE 1. The Academy consists of Fellows, who are either citizens or residents of the United States of America, and Foreign Honorary Members. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, and each Class is divided into four Sections, namely:

CLASS I. *The Mathematical and Physical Sciences*
- Section 1. Mathematics and Astronomy
- Section 2. Physics
- Section 3. Chemistry
- Section 4. Technology and Engineering

CLASS II. *The Natural and Physiological Sciences*
- Section 1. Geology, Mineralogy, and Physics of the Globe
- Section 2. Botany
- Section 3. Zoölogy and Physiology
- Section 4. Medicine and Surgery

CLASS III. *The Moral and Political Sciences*
- Section 1. Theology, Philosophy, and Jurisprudence
- Section 2. Philology and Archaeology
- Section 3. Political Economy and History
- Section 4. Literature and the Fine Arts

ARTICLE 2. The number of Fellows shall not exceed Six hundred, of whom not more than Four hundred shall be residents of Massachusetts, nor shall there be more than Two hundred in any one Class.

ARTICLE 3. The number of Foreign Honorary Members shall not exceed Seventy-five. They shall be chosen from among citizens of foreign countries most eminent for their discoveries and attainments in any of the Classes above enumerated. There shall not be more than Twenty-five in any one Class.

ARTICLE 4. If any person, after being notified of his election as Fellow, shall neglect for two months to accept in writing and to pay his Admission Fee (unless he be at that time absent from the Commonwealth) his election shall be void; and if any Fellow resident within fifty miles of Boston shall neglect to pay his Annual Dues for twelve months after they are due, provided his attention shall have been called to this Article of the Statutes in the meantime, he shall cease to be a Fellow; but the Council may suspend the provisions of this Article for a reasonable time.

With the previous consent of the Council, the Treasurer may dispense (*sub silentio*) with the payment of the Admission Fee or of the Annual Dues or both whenever he shall deem it advisable. In the case of officers of the Army or Navy who are out of the Commonwealth on duty, payment of the Annual Dues may be waived during such absence if continued during the whole financial year and if notification of such expected absence be sent to the Treasurer. Upon similar notification to the Treasurer, similar exemption may be accorded to Fellows subject to Annual Dues, who may temporarily remove their residence for at least two years to a place more than fifty miles from Boston.

If any person elected a Foreign Honorary Member shall neglect for six months after being notified of his election to accept in writing, his election shall be void.

See Chap. vii. art. 2.

ARTICLE 5. Every Fellow hereafter elected shall pay an Admission Fee of Ten dollars.

Every Fellow resident within fifty miles of Boston shall, and others may, pay such Annual Dues, not exceeding Fifteen dollars, as shall be voted by the Academy at each Annual Meeting, when they shall become due; but any Fellow shall be exempt from the annual payment if, at any time after his admission, he shall pay into the treasury Two hundred dollars in addition to his previous payments.

All Commutations of the Annual Dues shall be and remain permanently funded, the interest only to be used for current expenses.

Any Fellow not previously subject to Annual Dues who takes up his residence within fifty miles of Boston, shall pay to the Treasurer within three months thereafter Annual Dues for the current year, failing which his Fellowship shall cease; but the Council may suspend the provisions of this Article for a reasonable time.

Only Fellows who pay Annual Dues or have commuted them may hold office in the Academy or serve on the Standing Committees or vote at meetings.

ARTICLE 6. Fellows who pay or have commuted the Annual Dues and Foreign Honorary Members shall be entitled to receive gratis one copy of all Publications of the Academy issued after their election.

See Chap. x. art. 2.

Article 7. Diplomas signed by the President and the Vice-President of the Class to which the member belongs, and countersigned by the Secretaries, shall be given to all the Fellows and Foreign Honorary Members.

Article 8. If, in the opinion of a majority of the entire Council, any Fellow or Foreign Honorary Member shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his membership; and if three fourths of the Fellows present, out of a total attendance of not less than fifty, at a Stated Meeting, or at a Special Meeting called for the purpose, shall adopt this recommendation, his name shall be stricken from the Roll.

See Chap. iii.; chap. vi. art. 1; chap. ix. art. 1, 7; chap. x. art. 2.

CHAPTER III

Election of Fellows and Foreign Honorary Members

Article 1. Elections of Fellows and Foreign Honorary Members shall be by ballot, and only at the Stated Meetings in January and May. Three fourths of the ballots cast, and not less than twenty, must be affirmative to effect an election.

Article 2. Candidates must be proposed in writing by two Fellows of the Section for which the proposal is made. These signed nominations shall be sent to the Corresponding Secretary and shall be retained by him until the fifteenth of the following October or February, as the case may be, when all nominations then in his hands shall be immediately sent in printed form to every Fellow having the right to vote, with the names of the proposers in each case, and with a request to send to the Corresponding Secretary written comments on these names not later than the fifth of November or the fifth of March respectively.

All the signed nominations, with the comments thereon, received up to the fifth of November or the fifth of March shall be sent at once to the appropriate Class Committees, which shall report their decisions to the Council at a special meeting to be called to consider nominations, not later than two days before the meeting of the Academy in December and April respectively.

Article 3. All nominations approved by the Council shall be read to the Academy at a meeting in December or in April, or be sent to the

Fellows in print with the official notice of the meeting, and shall then be posted in the Hall of the Academy until the balloting.

Not later than two weeks after any nomination is reported to the Academy, the Corresponding Secretary shall send to every Fellow having the right to vote a brief printed account of the nominee.

See Chap. ii.; chap. vi. art. 1; chap. ix. art. 1.

CHAPTER IV

Officers

Article 1. The Officers of the Academy shall be a President (who shall be Chairman of the Council), three Vice-Presidents (one from each Class), a Corresponding Secretary (who shall be Secretary of the Council), a Recording Secretary, a Treasurer, and a Librarian, all of whom shall be elected by ballot at the Annual Meeting, and shall hold their respective offices for one year, and until others are duly chosen and installed.

There shall be also twelve Councillors, one from each Section of each Class. At the Annual Meeting in 1912 three Councillors, one from each Class, shall be elected by ballot to serve for one year, three for two years, three for three years, and three for four years. At each subsequent Annual Meeting three Councillors, one from each Class, shall be elected by ballot to serve for the full term of four years and until others are duly chosen and installed. The same Fellow shall not be eligible for two successive terms.

The Councillors, with the other officers previously named, shall constitute the Council.

See Chap. x. art. 1.

Article 2. If any office shall become vacant during the year, the vacancy may be filled by the Council in its discretion for the unexpired term.

Article 3. At the Stated Meeting in March, the President shall appoint a Nominating Committee of three Fellows having the right to vote, one from each Class. This Committee shall prepare a list of nominees for the several offices to be filled, and for the Standing Committees, and cause it to be sent to the Recording Secretary not later than four weeks before the Annual Meeting.

ARTICLE 4. Independent nominations for any office, if signed by at least twenty Fellows having the right to vote, and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted, together with the list of nominees prepared by the Nominating Committee, in the call therefor, and shall be mailed to all the Fellows.

See Chap. vi. art. 2.

ARTICLE 5. The Recording Secretary shall prepare for use in voting at the Annual Meeting a ballot containing the names of all persons duly nominated for office.

CHAPTER V

THE PRESIDENT

ARTICLE 1. The President, or in his absence the senior Vice-President present (seniority to be determined by length of continuous fellowship in the Academy), shall preside at all meetings of the Academy. In the absence of all these officers, a Chairman of the meeting shall be chosen by ballot.

ARTICLE 2. Unless otherwise ordered, all Committees which are not elected by ballot shall be appointed by the presiding officer.

ARTICLE 3. Any deed or writing to which the Corporate Seal is to be affixed, except leases of real estate, shall be executed in the name of the Academy by the President or, in the event of his death, absence, or inability, by one of the Vice-Presidents, when thereto duly authorized.

See Chap. ii. art. 7; chap. iv. art. 1, 3; chap. vi. art. 2; chap. vii. art. 1; chap. ix. art. 6; chap. x. art. 1, 2; chap. xi. art. 1.

CHAPTER VI

THE SECRETARIES

ARTICLE 1. The Corresponding Secretary shall conduct the correspondence of the Academy and of the Council, recording or making an entry of all letters written in its name, and preserving for the files all official papers which may be received. At each meeting of the Council he shall present the communications addressed to the Academy which have been received since the previous meeting, and at the next meeting of the Academy he shall present such as the Council may determine.

He shall notify all persons who may be elected Fellows or Foreign Honorary Members, send to each a copy of the Statutes, and on their acceptance issue the proper Diploma. He shall also notify all meetings of the Council; and in case of the death, absence, or inability of the Recording Secretary he shall notify all meetings of the Academy.

Under the direction of the Council, he shall keep a List of the Fellows and Foreign Honorary Members, arranged in their several Classes and Sections. It shall be printed annually and issued as of the first day of July.

> *See* Chap. ii. art. 7; chap. iii. art. 2, 3; chap. iv. art. 1; chap. ix. art. 6; chap. x. art. 1; chap. xi. art. 1.

Article 2. The Recording Secretary shall have the custody of the Charter, Corporate Seal, Archives, Statute-Book, Journals, and all literary papers belonging to the Academy.

Fellows borrowing such papers or documents shall receipt for them to their custodian.

The Recording Secretary shall attend the meetings of the Academy and keep a faithful record of the proceedings with the names of the Fellows present; and after each meeting is duly opened, he shall read the record of the preceding meeting.

He shall notify the meetings of the Academy to each Fellow by mail at least seven days beforehand, and in his discretion may also cause the meetings to be advertised; he shall apprise Officers and Committees of their election or appointment, and inform the Treasurer of appropriations of money voted by the Academy.

He shall post in the Hall a list of the persons nominated for election into the Academy; and after all elections, he shall insert in the Records the names of the Fellows by whom the successful candidates were nominated.

In the absence of the President and of the Vice-Presidents he shall, if present, call the meeting to order, and preside until a Chairman is chosen.

> *See* Chap. i.; chap. ii. art. 7; chap. iv. art. 3, 4, 5; chap. ix. art. 6; chap. x. art. 1, 2; chap. xi. art. 1, 3.

Article 3. The Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the records of the meetings of the Academy as may seem to them likely to promote its interests.

CHAPTER VII

The Treasurer and the Treasury

Article 1. The Treasurer shall collect all money due or payable to the Academy, and all gifts and bequests made to it. He shall pay all bills due by the Academy, when approved by the proper officers, except those of the Treasurer's office, which may be paid without such approval; in the name of the Academy he shall sign all leases of real estate; and, with the written consent of a member of the Committee on Finance, he shall make all transfers of stocks, bonds, and other securities belonging to the Academy, all of which shall be in his official custody.

He shall keep a faithful account of all receipts and expenditures, submit his accounts annually to the Auditing Committee, and render them at the expiration of his term of office, or whenever required to do so by the Academy or the Council.

He shall keep separate accounts of the income of the Rumford Fund, and of all other special Funds, and of the appropriation thereof, and render them annually.

His accounts shall always be open to the inspection of the Council.

Article 2. He shall report annually to the Council at its March meeting on the expected income of the various Funds and from all other sources during the ensuing financial year. He shall also report the names of all Fellows who may be then delinquent in the payment of their Annual Dues.

Article 3. He shall give such security for the trust reposed in him as the Academy may require.

Article 4. With the approval of a majority of the Committee on Finance, he may appoint an Assistant Treasurer to perform his duties, for whose acts, as such assistant, he shall be responsible; or, with like approval and responsibility, he may employ any Trust Company doing business in Boston as his agent for the same purpose, the compensation of such Assistant Treasurer or agent to be fixed by the Committee on Finance and paid from the funds of the Academy.

Article 5. At the Annual Meeting he shall report in print all his official doings for the preceding year, stating the amount and condition of all the property of the Academy entrusted to him, and the character of the investments.

ARTICLE 6. The Financial Year of the Academy shall begin with the first day of April.

ARTICLE 7. No person or committee shall incur any debt or liability in the name of the Academy, unless in accordance with a previous vote and appropriation therefor by the Academy or the Council, or sell or otherwise dispose of any property of the Academy, except cash or invested funds, without the previous consent and approval of the Council.

See Chap. ii. art. 4, 5; chap. vi. art. 2; chap. ix. art. 6; chap. x. art. 1, 2, 3; chap. xi. art. 1.

CHAPTER VIII

THE LIBRARIAN AND THE LIBRARY

ARTICLE 1. The Librarian shall have charge of the printed books, keep a correct catalogue thereof, and provide for their delivery from the Library.

At the Annual Meeting, as Chairman of the Committee on the Library, he shall make a Report on its condition.

ARTICLE 2. In conjunction with the Committee on the Library he shall have authority to expend such sums as may be appropriated by the Academy for the purchase of books, periodicals, etc., and for defraying other necessary expenses connected with the Library.

ARTICLE 3. All books procured from the income of the Rumford Fund or of other special Funds shall contain a book-plate expressing the fact.

ARTICLE 4. Books taken from the Library shall be receipted for to the Librarian or his assistant.

ARTICLE 5. Books shall be returned in good order, regard being had to necessary wear with good usage. If any book shall be lost or injured, the Fellow to whom it stands charged shall replace it by a new volume or by a new set, if it belongs to a set, or pay the current price thereof to the Librarian, whereupon the remainder of the set, if any, shall be delivered to the Fellow so paying, unless such remainder be valuable by reason of association.

Article 6. All books shall be returned to the Library for examination at least one week before the Annual Meeting.

Article 7. The Librarian shall have the custody of the Publications of the Academy. With the advice and consent of the President, he may effect exchanges with other associations.

See Chap. ii. art. 6; chap. x. art. 1, 2.

CHAPTER IX

The Council

Article 1. The Council shall exercise a discreet supervision over all nominations and elections to membership, and in general supervise all the affairs of the Academy not explicitly reserved to the Academy as a whole or entrusted by it or by the Statutes to standing or special committees.

It shall consider all nominations duly sent to it by any Class Committee, and present to the Academy for action such of these nominations as it may approve by a majority vote of the members present at a meeting, of whom not less than seven shall have voted in the affirmative.

With the consent of the Fellow interested, it shall have power to make transfers between the several Sections of the same Class, reporting its action to the Academy.

See Chap. iii. art. 2, 3; chap. x. art. 1.

Article 2. Seven members shall constitute a quorum.

Article 3. It shall establish rules and regulations for the transaction of its business, and provide all printed and engraved blanks and books of record.

Article 4. It shall act upon all resignations of officers, and all resignations and forfeitures of fellowship; and cause the Statutes to be faithfully executed.

It shall appoint all agents and subordinates not otherwise provided for by the Statutes, prescribe their duties, and fix their compensation.

They shall hold their respective positions during the pleasure of the Council.

ARTICLE 5. It may appoint, for terms not exceeding one year, and prescribe the functions of, such committees of its number, or of the Fellows of the Academy, as it may deem expedient, to facilitate the administration of the affairs of the Academy or to promote its interests.

ARTICLE 6. At its March meeting it shall receive reports from the President, the Secretaries, the Treasurer, and the Standing Committees, on the appropriations severally needed for the ensuing financial year. At the same meeting the Treasurer shall report on the expected income of the various Funds and from all other sources during the same year.

A report from the Council shall be submitted to the Academy, for action, at the March meeting, recommending the appropriation which in the opinion of the Council should be made.

On the recommendation of the Council, special appropriations may be made at any Stated Meeting of the Academy, or at a Special Meeting called for the purpose.

See Chap. x. art. 3.

ARTICLE 7. After the death of a Fellow or Foreign Honorary Member, it shall appoint a member of the Academy to prepare a Memoir for publication in the Proceedings.

ARTICLE 8. It shall report at every meeting of the Academy such business as it may deem advisable to present.

See Chap. ii. art. 4, 5, 8; chap. iv. art. 1, 2; chap. vi. art. 1; chap. vii. art. 1; chap. xi. art. 1, 4.

CHAPTER X

STANDING COMMITTEES

ARTICLE 1. The Class Committee of each Class shall consist of the Vice-President, who shall be chairman, and the four Councillors of the Class, together with such other officer or officers annually elected as may belong to the Class. It shall consider nominations to Fellowship in its own Class, and report in writing to the Council such as may receive at a Class Committee Meeting a majority of the votes cast, provided at least three shall have been in the affirmative.

See Chap. iii. art. 2.

Article 2. At the Annual Meeting the following Standing Committees shall be elected by ballot to serve for the ensuing year :

(i) *The Committee on Finance*, to consist of three Fellows, who, through the Treasurer, shall have full control and management of the funds and trusts of the Academy, with the power of investing the funds and of changing the investments thereof in their discretion.

See Chap. iv. art. 3 ; chap. vii. art. 1, 4 ; chap. ix. art. 6.

(ii) *The Rumford Committee*, to consist of seven Fellows, who shall report to the Academy on all applications and claims for the Rumford Premium. It alone shall authorize the purchase of books, publications and apparatus at the charge of the income from the Rumford Fund, and generally shall see to the proper execution of the trust.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(iii) *The Cyrus Moors Warren Committee*, to consist of seven Fellows, who shall consider all applications for appropriations from the income of the Cyrus Moors Warren Fund, and generally shall see to the proper execution of the trust.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(iv) *The Committee of Publication*, to consist of three Fellows, one from each Class, to whom all communications submitted to the Academy for publication shall be referred, and to whom the printing of the Proceedings and the Memoirs shall be entrusted.

It shall fix the price at which the Publications shall be sold ; but Fellows may be supplied at half price with volumes which may be needed to complete their sets, but which they are not entitled to receive gratis.

Two hundred extra copies of each paper accepted for publication in the Proceedings or the Memoirs shall be placed at the disposal of the author without charge.

See Chap. iv. art. 3 ; chap. vi. art. 1, 3 ; chap. ix. art. 6.

(v) *The Committee on the Library*, to consist of the Librarian, *ex officio*, as Chairman, and three other Fellows, one from each Class, who shall examine the Library and make an annual report on its condition and management.

See Chap. iv. art. 3 ; chap. viii. art. 1, 2 ; chap. ix. art. 6.

(vi) *The House Committee,* to consist of three Fellows, who shall have charge of all expenses connected with the House, including the general expenses of the Academy not specifically assigned to the care of other Committees or Officers.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(vii) *The Committee on Meetings,* to consist of the President, the Recording Secretary, and three other Fellows, who shall have charge of plans for meetings of the Academy.

See Chap. iv. art. 3 ; chap. ix. art. 6.

(viii) *The Auditing Committee,* to consist of two Fellows, who shall audit the accounts of the Treasurer, with power to employ an expert and to approve his bill.

See Chap. iv. art. 3; chap. vii. art. 1 ; chap. ix. art. 6.

ARTICLE 3. The Standing Committees shall report annually to the Council in March on the appropriations severally needed for the ensuing financial year; and all bills incurred on account of these Committees, within the limits of the several appropriations made by the Academy, shall be approved by their respective Chairmen.

In the absence of the Chairman of any Committee, bills may be approved by any member of the Committee whom he shall designate for the purpose.

See Chap. vii. art. 1, 7; chap ix. art. 6.

CHAPTER XI

MEETINGS, COMMUNICATIONS, AND AMENDMENTS

ARTICLE 1. There shall be annually four Stated Meetings of the Academy, namely, on the second Wednesday of January, March, May, and October. Only at these meetings, or at adjournments thereof regularly notified, or at Special Meetings called for the purpose, shall appropriations of money be made, or amendments of the Statutes or Standing Votes be effected.

The Stated Meeting in May shall be the Annual Meeting of the Corporation.

Special Meetings shall be called by either of the Secretaries at the request of the President, of a Vice-President, of the Council, or of ten

Fellows having the right to vote; and notifications thereof shall state the purpose for which the meeting is called.

A meeting for receiving and discussing literary or scientific communications may be held on the second or the fourth Wednesday, or both, of each month not appointed for Stated Meetings, excepting July, August, and September; but no business shall be transacted at any meeting which may be held on the fourth Wednesday.

Article 2. Twenty Fellows having the right to vote shall constitute a quorum for the transaction of business at Stated or Special Meetings. Fifteen Fellows shall be sufficient to constitute a meeting for literary or scientific communications and discussions.

Article 3. Upon the request of the presiding officer or the Recording Secretary, any motion or resolution offered at any meeting shall be submitted in writing.

Article 4. No report of any paper presented at a meeting of the Academy shall be published by any Fellow without the consent of the author; and no report shall in any case be published by any Fellow in a newspaper as an account of the proceedings of the Academy without the previous consent and approval of the Council.

Article 5. No Fellow shall introduce a guest at any meeting of the Academy until after the business has been transacted, and especially until after nominations to Fellowship have been read and the result of the balloting for candidates has been declared.

Article 6. The Academy shall not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its Publications.

Article 7. All proposed Amendments of the Statutes shall be referred to a committee, and on its report, at a subsequent Stated Meeting or at a Special Meeting called for the purpose, two thirds of the ballots cast, and not less than twenty, must be affirmative to effect enactment.

Article 8. Standing Votes may be passed, amended, or rescinded at a Stated Meeting, or at a Special Meeting called for the purpose, by a vote of two thirds of the members present. They may be suspended by a unanimous vote.

See Chap. ii. art. 5, 8; chap. iii.; chap. iv. art. 3, 4, 5; chap. v. art. 1; chap. vi. art. 1, 2; chap. ix. art. 8.

STANDING VOTES

1. Communications of which notice has been given to either of the Secretaries shall take precedence of those not so notified.

2. Fellows may take from the Library six volumes at any one time, and may retain them for three months, and no longer. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.

3. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy without the leave of the Librarian.

RUMFORD PREMIUM

In conformity with the terms of the gift of Sir Benjamin Thompson, Count Rumford, of a certain Fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court of Massachusetts for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of the Rumford Fund, as it now exists, at any Annual Meeting, an award of a gold and a silver medal, being together of the intrinsic value of three hundred dollars, as a Premium to the author of any important discovery or useful improvement in light or heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American Islands; preference always being given to such discoveries as, in the opinion of the Academy, shall tend most to promote the good of mankind; and, if the Academy sees fit, to add to such medals, as a further Premium for such discovery and improvement, a sum of money not exceeding three hundred dollars.

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