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WASHINGTON, D. C., *September, 1893.*

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No. 103

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1893

UNITED STATES GEOLOGICAL SURVEY
J. W. POWELL, DIRECTOR

HIGH TEMPERATURE WORK

IN

IGNEOUS FUSION AND EBULLITION

CHIEFLY IN RELATION TO PRESSURE

BY

CARL BARUS

WASHINGTON
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CONTENTS.

CHAPTER II—Continued.

ILLUSTRATIONS.

PREFACE.

In the following bulletin I have brought together the more important results of experiments in high temperatures, made since the publication of my bulletin on the thermoelectric measurement of high temperatures.[1] Chapter I, in addition to pointing out certain inherent relations between metallic vapor tensions, has a direct bearing on pyrometry. Chapters II and III are of geological importance, and the work was done for Mr. Clarence King. Chapter II shows that in case of the igneous fusion of basic magma, the passage from liquid to solid is one of contraction, and measures the difference of specific volumes at the solidifying temperature. Chapter III contains a full account of the thermal capacity of the same rock under the same conditions, and by aid of Chapter II leads to a numerical value for the relation of melting point to pressure, for silicates.

CARL BARUS.

JUNE 8, 1892.

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[1] Bull. U. S. Geol. Survey, No. 54, 1889, p. 313.

HIGH TEMPERATURE WORK IN IGNEOUS FUSION AND EBULLITION, CHIEFLY IN RELATION TO PRESSURE.

By Carl Barus.

CHAPTER I.

THE PRESSURE VARIATIONS OF CERTAIN HIGH TEMPERATURE (METALLIC) BOILING POINTS.[1]

INTRODUCTORY.

1. *The plan pursued.*—In the following chapter[2] I describe a practical method for the calibration of thermocouples by aid of boiling points, and then apply it in measuring the vapor tensions of zinc, cadmium, and bismuth. During the course of the work a much neglected principle of Groshans[3] is advantageously employed. I must state at the outset that it is not at all my object to furnish accurate values for boiling points. The purpose of this paper is to investigate the probable nature of the relation of boiling point to pressure, throughout very wide ranges of temperature, with the hope of stimulating speculation on the subject somewhat more rigorous than that of Groshans. It is clear that if a law can be found by which the normal (76 centimeters) boiling point of a substance can be predicted from an observed low-pressure boiling point, then there is hope of arriving at a more complete knowledge of high-temperature boiling points than is now available. More than this: By varying pressure, boiling points may be made to overlap each other. Hence a thermocouple calibrated as far as the boiling point of zinc for instance, may be used to measure the low-pressure boiling point of bismuth (say), and the couple then may be further calibrated by making use of the normal boiling point of bismuth at 76 centimeters, predicted by aid of the law in question. The process may obviously be repeated. The couple whose calibration interval has been enlarged in the manner given, may now be used to fix the low-pressure boiling point of some

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[1] The literature of the subject, which is very voluminous, may be omitted here because a full account is given in Bull. No. 54, pp. 1 to 30. At the present stage of progress of the kinetic theory of gases the air thermometer is still the only apparatus available for absolute high temperature measurement, and all data are directly or indirectly derived from it. An account of work of this kind is also given in the bulletin.

[2] Cf. Phil. Mag., (5), vol. 29, 1890, pp. 141–157.

[3] Groshans: Pogg. Ann., LXXVIII, p. 112, 1849.

other suitable metal, and then in turn be further calibrated by means of its boiling point. This is about the idea. It is not wholly illusory, as I think the present paper, which in spite of its approximate character contains considerable work, will show.

2. *The pyrometer.*—Let me say, too, that the platinum/platinum-iridium thermocouple used had on a former occasion[1] been tested for polymerization anomalies by minute comparison with the porcelain air thermometer,[2] and none were found. The alloy contained 20 per cent of iridium. M. Le Chatelier[3] unjustly rejects the platinum-iridium couple because of irregularities of the kind referred to. When the range of temperature is very large the Avenarius-Tait equation is found insufficient; but this equation subserves a good purpose when interpolation between two fixed temperature data, lying anywhere on the scale, but not very far apart, is called for.

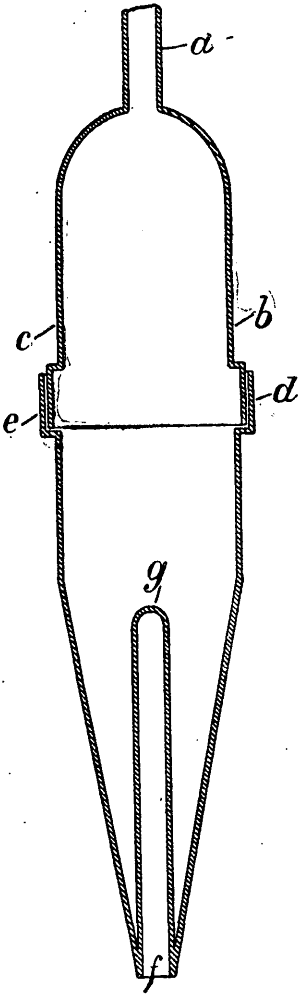

FIG. 1.—Boiling crucible for high temperatures. Scale, ½.

APPARATUS.

3. *Low boiling points.*—Boiling points below 500° may be studied in a closed glass tube *aa* (Pl. I), along the axis of which a thin-walled tube, *dd*, open at both ends, passes quite through. In the bottom of the annular space between the tubes the ebullition liquid, *kk*, is placed, and it is heated by the Gibbs' ring burner, *rr*. A funnel-shaped asbestos screen, *nn*, protects the upper tube against direct radiation. Other screens and jackets, *pp*, are suitably added. The upper end of the tube, *aa*, communicates with the air pump through the tubulure *h*. Finally, $\alpha\ \beta$, the thermocouple to be calibrated, consisting of platinum and platinum-iridium wire, is inserted into the bottom of the central tube, *dd*, with the junction *o* just above the plane of the ebullition liquid, *kk*. The upper part of the tube, *dd*, is closed with asbestos wicking (not shown), extending almost as far down as *o*.

The wires of the couple pass through parallel canals in a rod of fire clay, *xy*, and are thus well insulated. I may add that the boiling points

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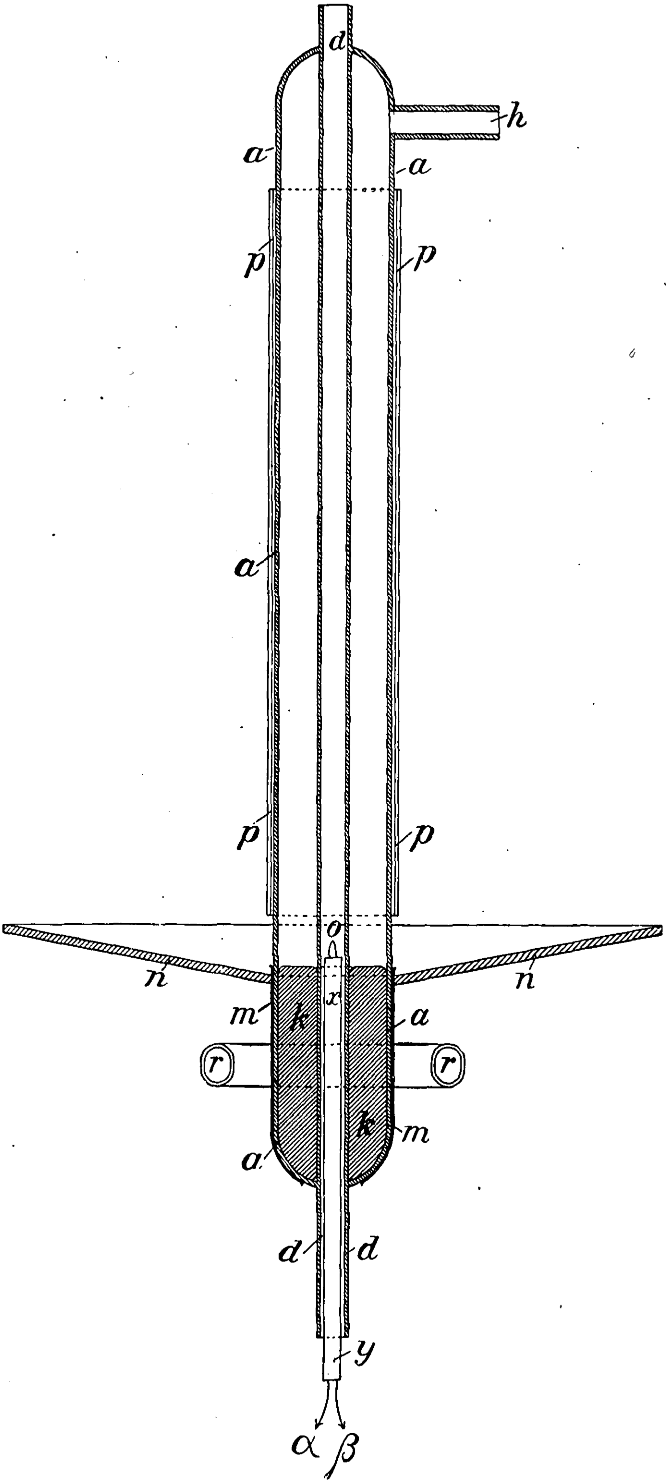
[1] Barus: Bull. U. S. Geol. Survey, No. 54, Chapter IV.

[2] Unfortunately circumstances did not permit me to make use of the former air thermometer comparisons, nor was it expedient to repeat the work.

[3] Le Chatelier: Bull. Soc. Chimique Paris, Vol. 45, 1886, p. 482. Cf. Phil. Mag., (5) vol. 34, 1892, p. 376.



BOILING TUBE AND APPURTENANCES FOR LOW TEMPERATURES. SCALE $\frac{1}{4}$.

of mercury, sulphur, etc., for all pressures compatible with the strength of tube are conveniently obtained in this way. The vacuum boiling point of cadmium is also easily reached. Boiling may be kept up for any length of time.

4. *High boiling points.*—For boiling points above 500° it is more convenient to use glazed porcelain or fire clay crucibles of the form *efd*, *bdc*, (Fig. 1). The ebullition liquid is shown at *kk*, in Fig. 2, and *fg* is the central tube in which the thermocouple, *dd*, is to be introduced. To vary the pressure under which boiling takes place the tube *a* is connected with an air pump. Finally, a tight joint at *ed* is secured by calking with asbestos wicking, and then filling up with fusible metal the annular space or trough left above the asbestos.

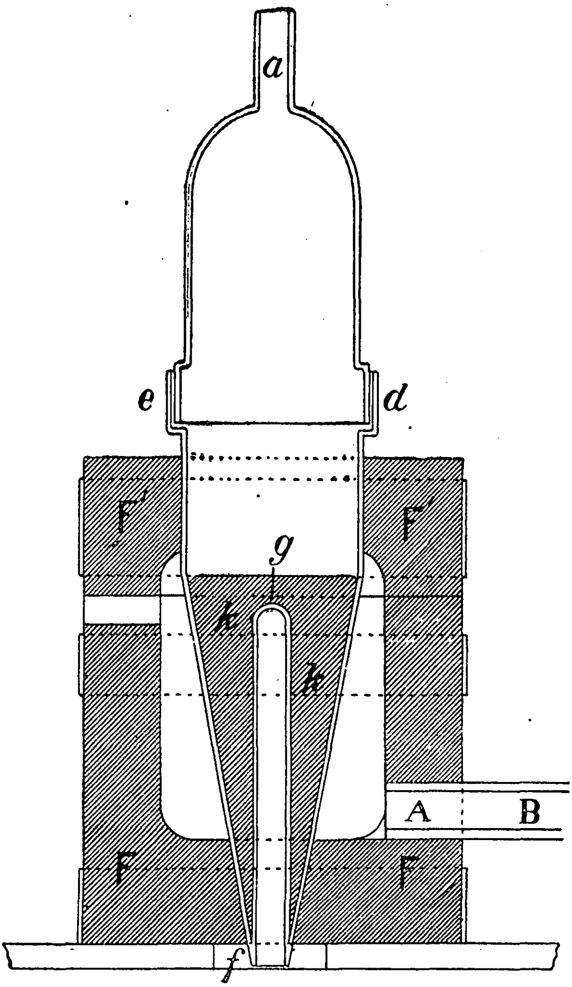


FIG. 2.—Furnace with crucible in place. Scale ½.

The crucible, *efd*, is surrounded by a small furnace of Fletcher's composition, *FFF′F′*, Fig. 2, and heated with one or more blast burners, *AB.* If the flame impinges directly upon the cold crucible it is apt to break it; but such breakage may be quite prevented by surrounding the crucible with a conical shell of asbestos. Unfortunately, the crucibles can be used but once—unless the metal is cautiously poured out before solidifying, an operation which does not always succeed—for they are usually fractured by the solidifying metal, *kk*, on cooling. Nevertheless, the single experiment may be prolonged almost indefinitely; that is, for half a day or more. I found no difficulty in obtaining vacua of two or three millimeters at extreme white heat. In this case the crucibles must be well glazed internally. § 13.

5. *Torsion galvanometer.*—The best method of measurement is doubtless a null method, in which the thermoelectric constants are expressed in terms of a given Latimer Clark's cell. Recalibrations are then rarely necessary. But the computation of observations occurring in great numbers is somewhat inconvenient. In this respect the torsion galvanometer offers decided advantages. A form of apparatus of this kind is shown in Plate II, so that little further description will be necessary. *AA* is the coil of wire, and *BB* the astatic system seen in cross section. The system is suspended by aid of a fine platinum wire *EE;* and inasmuch as *AA* is wrapped on a heavy frame of copper, the motion of the needle is aperiodic. Torsion is imparted by aid of an alidade *DD*, and the amount registered by a large circle graduated in degrees. Fractions of a degree are read off by a mirror and scale adjustment, the parts of which are *C*, *MM* and *S*, *T* being the telescope.

The scale proper *ss* is on transparent glass, and *S* a white diffuse reflector, so that the scale may be more distinct.

The instrument is high enough to be manipulated by the observer standing. When the current passes, the deflected needle is twisted back to a fiducial position, parallel to the windings, and the amount at once read off. Then the current is reversed and a similar reading made. Since the resistance of the coil *AA* is practically the only resistance of the thermoelectric circuit, these deflections are directly proportional to the thermoelectromotive force.

The two magnets *BB′* Plate II, Fig. 1 and 2, of the astatic system each consist of a battery of four flat magnets, about 10 centimeters long, and of glasshard steel, consecutively annealed at 100° both for temper and for magnetic permanence.[1] A square frame of aluminium and hard rubber, embracing the upper half of the coil *AA*, connects the magnets. To this the adjustable mirror is attached. The torsion fiber is a platinum wire, .018 centimeter in diameter. It therefore has considerable strength to resist wear and tear. Finally, the plate-glass doors *xyz*, which close the magnet box, are easily removable, so that the magnet and mirror are conveniently accessible.

The instrument has two zeros: the optical zero of the mirrors, relative to which the reflected scale readings are symmetrical, and the

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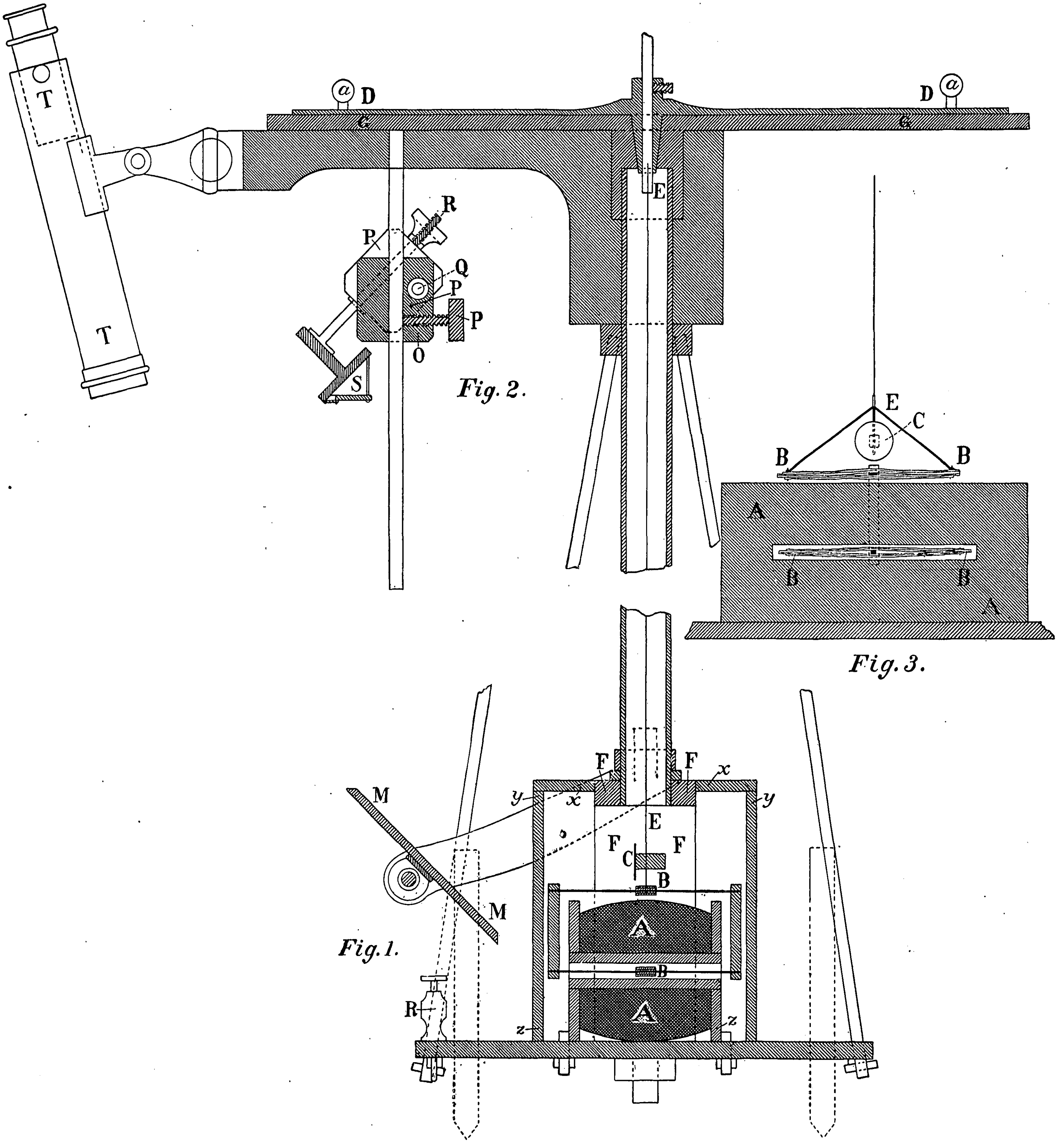
[1] Cf. Bull. U. S. Geol. Survey No. 14, 1885, p. 171. Cf. Chapter VI of the same bulletin.



TORSION GALVANOMETER FOR THERMOELECTRIC PYROMETRY. SCALE $\frac{1}{8}$.

magnetic zero of the astatic system, relative to which the deflections are symmetrical. The two fiducial marks should coincide. The magnetic zero is shown by the fact that the mean of the scale readings on commutation coincide with the zero reading for no current. In case of a system of needles very nearly astatic, the optic zero may be determined by plotting scale readings in terms of twist registered by the alidade without current, and noting the position of symmetry in the circumflexed curve of the chart.

6. It will be seen that by bringing the needle back to zero by twisting the fiber, the effect of the earth's local magnetic field is almost wholly eliminated in an adjusted instrument For let u be the effective magnetic moment of the system and I the intensity of the current, τ the coefficient of torsion and φ the twist necessary to bring the needle back to zero. Then, apart from unnecessary constants,

$$I u + \tau \varphi = 0; \; -\varphi = I u / \tau \qquad (1)$$

Again, in case of deflection φ' in a magnetic field of intensity H parallel to the coils,

$$I u \cos \varphi' + \tau\varphi' + H u' \sin \varphi' = 0.$$

Supposing the deflections very small,

$$\varphi' = I u / (\tau + H u') \qquad (2)$$

Now, in an incidental adjustment I found $\varphi = 4{\cdot}35$; $\varphi' = 4{\cdot}00$. Hence,

$$\frac{\tau}{H u'} = \frac{400}{35} \, .$$

In other words, the magnetic resistance is about one-tenth the torsional resistance to deflection by current. Now, inasmuch as deflections are used only to correct the torsion value, which is increased or decreased in single degrees, the effect of magnetic resistance is quite negligible. In measuring 100°, $\varphi = 4.35$, and the correction must be less than ·6. Hence the magnetic resistance is less than ·06, or less than 1·5 per cent of φ. But inasmuch as the apparatus is primarily intended for temperatures greater than 350°, where $\varphi > 20°$, it follows that the magnetic resistance is usually quite negligible. A little care in the magnetization of the needle will produce the astatic condition much more fully than was done in the above experiment. The same relations apply for finer fibers, where twists are larger.

A few examples of the deflection D for 100° at the hot junction, in case of a thick platinum fiber (diameter .0055 centimeter), and variety of different magnetic fields may be added.

Factor.	D	Remarks.
·893	7·235 7·235	Strong field. Magnetic zero obtained by astasizing magnet.
3·45	7·324 7·319	Astatic needle. Fiducial zero obtained by twisting.
3·08	7·290 7·276	Astatic needle. Coils in its plane.
3·402	7·440 7·437 7·434	Astatic needle, kept in the plane of the coils by twisted fiber.

It follows finally that in the above instrument thermoelectromotive force is expressed only in terms of the torsion of a platinum fiber, supposing the needles to be so tempered and magnetized as not to change their magnetic permanence. Hence thermoelectromotive forces are not only expressed in terms of a fixed standard and therefore comparable with each other after the lapse of time, but the range of measurment is enormous. Any temperature between 100° and the intensest white heat may be measured without further adjustment. These desiderata, added to the convenience of manipulation, and the strength of the instrument against wear and tear, constitute the advantages of the galvanometer described.

In the practical form of this apparatus the torsion circle need not be more than 6 inches in diameter, accurately divided into degrees. The alidade should be provided with a lens. A silk fiber suspension may be put in the case *xy*, so that the needle may at any time be unhitched from the platinum fiber, and attached to the silk fiber. A magnetic position of equilibrium parallel to the coils is thus easily obtained.

Inasmuch as both the internal resistance of the coils, the magnetic movement of the needles and the elasticity of the platinum fiber change with temperature, the torsion galvanometer has a notable temperature coefficient. This, however, is determined at once by measuring the same temperature (hot junction) at two different temperatures of the galvanometer. The boiling point of mercury is a convenient datum for this purpose. Changes of temperature at the galvanometer are to be guarded against by placing a thermometer in the case.

7. *Cold junction.*—From what has been stated, if D be the amount of torsion corresponding in a given instrument to the temperatures T and t of the junctions of the given thermocouple,

$$D=a\,(T-t)+b\,(T^2-t^2)\ldots\ldots(1)$$

Again if $d=a\,(t-20)+b\,(t^2-20^2)\ldots\ldots(2)$

$$D_{20}=D+d=a\,(T-20)+b\,(T^2-20^2)\ldots\ldots(3)$$

Hence a small table corresponding to equation (2) is to be computed, from which the value of d for each value of t between 10° and 35° may be taken. A short preliminary calibration suffices for this purpose. In this way the observer may at once deduce D_{20} from D, where D_{20} is a function of T the temperature of the hot junction only.

By aid of the boiling points of water (100°), mercury (357°), sulphur (448°), cadmium (780°), zinc (930°), bismuth (1,500°), the quantity D_{20} may then be graphically constructed as a function of T, and the points between consecutive boiling points filled in by equation similar to (1).

From a chart of this kind the temperature T, corresponding to any degree of twist D_{20}, may be taken with facility.

OBSERVATIONS.

8. *Mercury.*—In the above apparatus the normal boiling point of mercury is sharply determinable; but there is considerable difficulty in

determining the low-pressure boiling points. Unless the heat be regulated to a nicety the lower layers boil under the pressure of the upper layers. Again, since the agitation of the liquid nearly ceases in approximate vacuo, a flame of moderate intensity presupposed, the rate of evaporation is retarded in relatively greater degree. In the case of a liquid of small specific heat, films of which do not adhere readily to glass, it is therefore to be suspected that both liquid and vapor will be superheated. On the other hand, if the flame of the burner be intensified so as to produce violent ebullition at low pressures, the liquid can be superheated to such an extent that its direct radiation on the junction of the thermocouple may heat it as much as 10° above the boiling point.

Accordingly I was not surprised that the temperatures obtained in the static method by Regnault, Hagen, Hertz, Ramsay and Young[1] are as a rule below the corresponding boiling points of the present dynamic method. It is only by taking great pains in the adjustment of burner and apparatus that my temperatures began to coincide with those of Regnault. But this nice adjustment introduces arbitrary conditions; hence low pressure mercury boiling points are to be rejected. At high pressures the unsatisfactory circumstances mentioned fall away; and the rate at which boiling point changes with pressure is enormously smaller.

In the following tables, 1 and 2, I give instances of my results. The data of Table 1 were obtained at an earlier date, before I became aware of the grave difficulties encountered. T is the boiling point for the pressure P, in centimeters of mercury:

TABLE 1.—*Boiling points of mercury (superheated)*

P	T	P	T	P	T
cm.	°*C.*	*cm.*	°*C.*	*cm.*	°*C.*
44·2	330	·5	194	0.3	198
37·5	325	6·4	256	0.3	184
17·5	290	12·0	280	0.1	183
1·0	195	25·2	310		
0·7	190	47·6	336		
0·5	176	76.2	356		
13·3	279	·2	199		
24·4	304				

In the following table are later results, obtained with great care, relative to the conditions stated at the outset of the present paragraph. The agreement with Regnault's data is very much better, but the temperatures are still high, particularly in the region of low pressure (cf. Fig. 2). D_{20}, the twist corresponding to T, has been added, to show the

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[1] Ramsay and Young; Jour. Chem. Soc., vol. 49, p. 37, 1887; Landolt and Boernstein's tables, p. 56, Berlin, Julius Springer, 1883. I may advert in passing to a discussion between Messrs. Ramsay and Young and Kahlbaum. The former, corroborating Regnault's law, maintain that vapor tensions, whether obtained by static or dynamic mode of measurement, are identical. Kahlbaum believes that he has found a difference. Cf. Beiblätter, vol. 10, 1886, p. 485; ibid., vol. 11, 1887, pp. 88, 430.

delicacy of the apparatus, Pl. II, p. 14. Twist is expressed in degrees of arc:

TABLE 2.—*Boiling points of mercury (superheated).*

P	D_{20}	T	P	D_{20}	T
·1	8·10	164	·2	8·40	168
·2	8·10	164	·3	8·28	166
·2	8·11	165	·5	8·49	170
2·6	11·43	216	2·0	10·84	208
2·7	11·58	218	2·3	11·25	214
2·7	11·62	219	5·2	12·93	239
4·5	12·22	228	9·9	14·98	270
4·6	12·23	229	9·8	14·87	268
12·6	15·44	276	17·2	16·24	288
12·5	15·43	276	17·4	16·23	288
20·7	16·90	297	31·5	18·07	313
20·9	16·95	298	31·8	18·10	314
29·4	17·75	308	50·3	19·69	335
29·4	17·74	308	50·5	19·74	335
47·3	19·58	334	76·43	21·484	358
48·0	19·65	335			
48·5	19·75	336			
76·43	21·323	357			

9. *Sulphur.*—The behavior of sulphur is peculiar. On removing the pressure to about 1^{cm}, the substance soon passes into the treacle state, and the full ebullition observed under atmospheric and other pressures changes into a sticky frothing.

Exact temperature data can not, therefore, here be expected. The following table (3) is an example of the earlier results obtained:

TABLE 3.—*Boiling points of sulphur.*

P	T	P	T	P	T
cm.	°*C.*	*cm.*	°*C.*	*cm.*	°*C.*
·0	218	4·8	298	21·2	374
·0	205	7·0	316	39·8	410
2·4	263	11·2	337	76·0	448

The following table contains results of a later date, obtained by taking great care in guarding against superheating:

TABLE 4.—*Boiling points of sulphur.*

P	D_{20}	T	T *Regnault.*	P	D_{20}	T	T *Regnault.*
55·36	26·57	428	429	4·06	16·80	295	305
55·41	26·59	429	429	....	....	....	....
54·75	26·49	427	428	....	....	....	....
48·30	25·87	420	422	30·69	23·65	389	396
47·78	25·64	416	421	30·70	23·65	389	396
37·59	24·51	402	407	13·01	20·18	342	354
37·57	24·39	399	407	12·93	20·18	342	354
28·67	23·44	386	393	5·61	17·28	302	317
28·80	23·51	387	394	5·91	17·51	305	320
20·68	22·23	370	376	6·14	17·62	306	321
20·70	22·25	370	376	3·29	15·55	278	295
14·37	20·76	349	358	3·44	15·51	277	297
14·49	20·73	348	359	·75	10·76	206	252
11·15	19·66	355	346	1·05	11·33	215	*260
11·25	19·77	336	347	1·39	11·85	223	*266
6·11	18·05	313	321	1·67	11·21	228	*275
6·35	18·20	315	323	75·84	27·976	446	448
6·55	18·30	316	324	75·87	27·999	448	448

*Sulphur sticky.

These results agree fairly well with those of the earlier table. I have added the values of T, exterpolated graphically from Regnault's data, by aid of the Dupré-Bertrand equation. (Cf. § 14.)

Log $p=19{\cdot}10740-4684{\cdot}49/\theta-3{\cdot}40483 \log \theta$, which holds between $\theta=663$ and $\theta=843$ absolute degrees centigrade[1]. It will be seen by comparison of my values with the data predicted by this formula that it is much in error at low pressures. The divergence is largest in the neighborhood of 11^{cm}, and is here greater than 10°.

10. Zinc.—The following table contains data of four sets of experiments for zinc. The first of these were made in the glass tube (Fig. 1) at low pressures. Although in this case there was considerable volatilization, I did not observe any ebullition. In the table, the result marked * is the only datum of this work inserted. Change of temperature with pressure was not very obvious.

The remaining data of this part of the table are legitimate. The criterion of a boiling point is change of temperature with pressure. In the second and third parts of the table I aimed at greater accuracy. Each of the values given is a mean of two or three distinct measurements; † refers to a low position, ‡ to a high position of the thermocouple in the central tube (see Fig. 2).

TABLE 5.—*Boiling points of zinc.*

P	*T*	*P*	*T*	*P*	*T*
cm.	°*C*	*cm.*	°*C*	*cm.*	°*C*
1·0	*582	4·2	710	2·6	675
4·0	710	3·5	699	6·7	731
6·5	732	2·8	684	15·8	792
9·6	757	6·2	736	26·4	833
10·1	772	9·9	758	37·5	864
15·6	785	16·6	802	47·3	884
27·1	837	26·4	838	57·0	904
34·5	857	36·8	863	65·4	916
42·5	873	47·7	884	77·1	933
53·5	897	55·7	900		
76·4	933	65·3	914		
		77·3	†928		
		77·3	‡922		

11. Cadmium.—The first part of Table 6 contains results obtained in a glass tube. Ebullition in vacuum was obvious. But inasmuch as the limit of the power of the ring burner was not much above 500°, the remaining thermal data are too low.

The experiments of the second and third parts of this table were made in the porcelain crucible. They are legitimate, change of temperature taking place with every change of pressure. I was unable to make the crucible satisfactorily tight, so that mean values of fluctuating pressure had to be made use of. Again cadmium is more easily superheated than zinc; so that the present temperatures are probably high.

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[1] I computed the inferior prolongation of the curve and plotted the results. From the chart the values of T were taken to a high degree of accuracy.

A repetition of the experiment failed in consequence of breakage of the crucible. It is interesting to note here that if zinc boils at 930°, cadmium will boil at a temperature not much below 780°.

TABLE 6.—*Boiling points of cadmium.*

P	T	P	T	P	T
cm.	°*C.*	*cm.*	°*C.*	*cm.*	°*C.*
·00	444	2·2	549	6·3	606
2·75	526	2·5	552	8·4	622
5·25	549	2·6	565	22·6	686
7·70	562	3·2	574	27·4	704
		7·5	620	34·2	722
		10·5	639	51·0	752
		15·7	667	56·3	760
		18·9	681	63·6	770
		26·2	702	65·6	772
		29·2	706	75·5	786
		35·5	724	75·5	788
		38·1	729	75·5	781
		48·9	745		
		51·7	750		
		62·4	760		
		64·4	766		
		65·6	766		
		75·6	772		
		75·6	770		
		75·6	774		

12. Bismuth.—Table 7 contains results for bismuth. In the first part of the table temperature does not change with pressure, hence a boiling point is not reached. In the second part of the table temperature certainly oscillates with pressure, hence the temperature corresponding to the lower values of pressure (3 to 4 cm.) are boiling points. The temperatures corresponding to the higher values of pressure (9 to 10 cm.) are below the corresponding boiling points, for I found that on further increasing pressure, the temperature did not increase. These temperatures are therefore at the limit of the heating power of the furnace. At least five minutes must be allowed for each observation. The top of the crucible, moreover, should be filled with asbestos, to diminish loss of heat by radiation.

TABLE 7.—*Boiling points of bismuth.*

P.	T.	P.	T.	Remarks.
cm.	°*C.*	*cm.*	°*C.*	
2·6	1152	3·2	1199	
5·8	1164	8·6	1211	
2·6	1165	9·7	1207	
8·1	1182	3·2	1206	
8·8	1186	3·7	1222	Flame intensified. B. P. criterion satisfied.
2·7	1183	4·2	1215	
9·8	1194	8·7	1247	
2·4	1186	3·9	1213	
		3·4	1204	
		9·5	1236	
		3·4	1207	
		4·0	1217	
		9·7	1260	
		3·4	1206	
		3·9	1221	
		9·6	1258	Limit of the heating power of the burner.
		3·3	1215	
		4·2	1233	

13. Remarks.—In the above tables, 1 to 7, the criterion of boiling point has therefore been change of temperature with pressure. When this was not observed, the data were rejected. The method of obtaining low boiling points from the liquid is doubtless objectionable, because of the liability to superheating. In special measurements made with zinc,[1] however, I found that the error thus introduced is negligible. There seems to be less superheating in case of metals and high temperatures, supposing the temperature of the environment to be reasonably near the boiling point (100° or 200° above it). In case of bismuth and metals of higher boiling points, the difficulties of experiment are such that I do not think a low pressure vapor bath is feasible.

In regard to the crucible used, I may remark that experimentation will be much facilitated by using tubular forms made in a single piece. In this case the trouble experienced in calking the joint of Figure 1 will be obviated. The metal, previously granulated, may easily be introduced through the tube *d*. In this case I have no doubt that very high vacua at white heat will be attainable. It is advisable, moreover, when very high temperatures are to be reached, to place the crucible and lid wholly within the furnace, allowing only a narrow tube to project out of it.

INFERENCES.

14. Available equations.—Equations for expressing vapor tension in terms of temperature have been invented in great number, and among them the simple form of Magnus and the more elaborate exponential devised by Biot and used by Regnault are given in most text books. A remarkably close fitting exponential is investigated and tested by Bertrand.[2] Quite recently M. Ch. Antoine[3] has proposed and applied a new form. Following the early suggestions of Bertrand[4] and of J. J. Thomson,[5] I have used the equation of Dupré,[6]

$$\log p = A - B / \theta - C \log \theta \qquad (1)$$

inasmuch as J. J. Thomson has given it an independent interpretation. The meaning of the equation is clearer in the differential form:

$$dp / d\theta = -p \; (C / \theta - B / \theta^2) \qquad (2)$$

or

$$d\theta / dp = \frac{\theta^2}{p} \; \frac{1 / B}{1 - (C / B) \theta} \qquad (3)$$

with reference to which it is to be observed that C / B is a small quantity (about 1/1000).

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[1] Bull. U. S. Geol. Survey, No. 54, p. 109.

[2] Bertrand: Thermo dynamique, pp. 154 to 162, Paris, Gauthier-Villars, 1887.

[3] Ch. Antoine: C. R., CVII, p. 681, 1888; ibid., pp. 778, 836, 1888.

[4] Bertrand: loc. cit. p. 90 to 102.

[5] J. J. Thomson: Applications of dynamics, etc., p. 158, Macmillan, 1888.

[6] Dupré: Théorie mécanique de la chaleur, pp. 96 to 110, Paris, Gauthiers-Villars, 1869.

15. Constants computed.—Applying equation (1) to the results of the tables 1 to 7, I found the following set of values by direct computation:

TABLE 8.—*Constants. A, B, C, variable.*

Metal.	A	B	C
Mercury	+ 3·583	+3084	− 1·1371
Sulphur	−35·969	− 366·1	−13·066
Cadmium	−30·567	+1391	−11·180
Zinc	+42·265	+11435	+10·022
Bismuth	+24·774	+13495	+ 4·763

These results are grossly irregular, even as to sign. This might have been expected. To get comparable values for constants the observations in case of complex equations must either be very fine or in great number. Other direct methods gave similarly irregular constants, which need not be entered here. Nothing can be learned from them.

Bearing in mind, therefore, that it is my object to detect possible relations, and that my high-temperature boiling points are necessarily somewhat crude, I will facilitate preliminary computation by observing that in Dupré's data the prevailing value of A is nearly 20. Putting $A=20$ the following set of constants were obtained, in which, of course, there is greater degree of uniformity. Water has been added from Dupré:

TABLE 9.—*Constants. B and C, variable.*

Substance.	A	B	C
Water	20·324	2795	3·868
Mercury	20	4345	4·013
Sulphur	20	4379	4·217
Cadmium	20	7467	3·643
Zinc	20	8433	3·603
Bismuth	20	12561	3·456

The results of this table are encouraging. From an inspection of the constants I was led to suspect better agreement in making C constant and A variable. This step is further suggested by assuming, conformably with the indications of table 9, that for any two substances, S and S', the boiling points, θ and θ', corresponding to a given pressure, p, will follow the relation $B\,/\,B'=\theta\,/\,\theta'=n$, where n is constant for the given pair of substances. This virtually postulates a fundamental equation of the form (1) from which all others are derived by substitution, as follows:

$$\log p = A - B/\theta - C\log\theta \ldots\ldots\ldots\ldots\ldots\ldots (1)$$
$$= A - nB/n\theta - C\log n\,\theta + C\log n$$
$$= A' - B'/\theta' - C\log\theta' \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The constants of Table 10 are obtained by supposing C to be constant for all the substances. As to the choice of a value, I noticed that the mean C of Table 9 is almost identical with Dupré's C for water. Hence it was chosen.

TABLE 10.—*Constants A and B, variable.*

	A	*B*	*C*
Water	19·324	2795	3·868
Mercury	19·029	4396	3·868
Sulphur	19·776	4458	3·868
Cadmium	20·63	7443	3·868
Zinc	20·98	8619	3·868
Bismuth	21·51	12862	3·868

The constants might be much improved by successive trials; but further work would be wasted.

16. *Graphic representation.*—In order to clearly exhibit the point of view I have taken, it will be necessary to plot these results graphically. This is done in Plate III, in which the abscissæ are pressures in centimetres of mercury and the ordinates boiling points in degrees centigrade.

The curves passed through the observations are computed for the constants of Table 8. Some points computed by Table 9 are marked; points computed by Table 10 are also marked. The agreement of observed and computed results is quite within the errors of observation, as will at once be evident from an inspection of the chart. In case of mercury I have added the vapor tension results of Regnault, showing that they are uniformly lower than the present data. The reasons have already been given in § 8.

The results for bismuth are particularly interesting. Unfortunately it was impossible for me to calk the crucible tight enough, in order that the low-pressure boiling point of bismuth might overlap the normal boiling point of zinc, which limits the calibration interval of the thermo-couple. The chart shows that the interval of extrapolation is about 270°. This makes the bismuth results less certain. For this reason, perhaps, the normal boiling point of bismuth, as deduced by Groshans's principle is too high, being 1550°. Carnelley and Williams,[1] using a calorimetric method, obtained only 1450° as their maximum value. It is probable, however, that the radiation errors in Carnelley and Williams's experiments would tend to make their data too low; nor have they any sure criterion that ebullition had actually set in. In experiments of my own,[2] using a Fletcher furnace with three blast burners, I signally failed to boil bismuth in a number of trials. The boiling-point criterion in the present results is beautifully exhibited: When pressure increases the group of points *B* on the chart pass into the group of points *A*; hence the group *B* are boiling points. When pressure increases further the group *A* does not increase in temperature; hence group *A* are not boiling points, but merely indicate the maximum heating power of the furnace.

17. *Conclusion.*—I am perfectly aware that the method pursued above, in endeavoring to reach perspicuous results, is forced. Ber-

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[1] Carnelley and Williams, Journ. Chem. Soc., London, vol. 35, 1879, p. 565.

[2] Bull. U. S. G. S., No. 54, pp. 116-118, 124.

trand computes the constants of Dupré's formula for 16 substances, and shows its admirable agreement with the observed data throughout. But the constants in such a case vary largely: A between 4 and 21 (pressures being expressed in centimeters of mercury); C between -9 and $+5$. In any-such grouping of constants as I have attempted, the agreement of the formula would therefore be lost. It is worthy of remark, however, that in 10 out of the 16 substances A lies between 15 and 21·5, and in one-half of the substances C lies between 3·2 and 4·2.

When, however, the errors left in any attempt to group the constants are considered, not so much with reference to the small range of temperatures of a single substance, but rather with regard to the relatively enormous range of temperatures exhibited by these phenomena as a whole, and by a diagram, such as Pl. III, for instance, then the errors in question assume much smaller importance. In the above pages I have presumed to believe that at the outset the wide temperature comparison is the one which ought first to be made, and some fundamental relation applicable to the whole range of temperature investigated. After this has been done, the said relation may then be modified to suit the individual and exceptional case.

I can state this more clearly as follows: Groshans's derivation of his principle is sufficiently simple; for, if vapors have identical coefficients of expansion, 1/273, say, and their densities be expressed relatively to the density at the normal boiling point in each case, then the ratio of absolute boiling temperatures corresponding to any two given pressures will be the same for all vapors. This inference is incorrect just in proportion as the application made of the Boyle-Charles law is incorrect.

However, Dupré in deriving his formula makes virtually the same assumption.[1] Again, J. J. Thomson[2] introduces Boyle's law into the mean value of the Lagrangian function investigated for the present phenomena. Inasmuch, however, as the forms of two arbitrary functions have here to be determined by experiment, the insertion of Boyle's law suffices Thomson's purposes. Following the model of his work, I hoped to find some suggestion as to the modification of Dupré's equation, such that it may be the outcome of an original type for all substances, by inserting Van der Waals's law, $p=R\Theta/(v-b)-a/v^2$, instead of Boyle's law into the proper term. It seemed plausible that Dupré's equation could thus be corrected by aid of constants, the molecular interpretation of which has already been given by Van der Waals. Performing the operations, I find, rigorously,

$$R\theta\log\frac{\rho_0}{\rho}\frac{\zeta-b\rho}{\zeta-b\rho_0}=-R\theta\left(\frac{\zeta}{\sigma}\frac{\rho}{\zeta-b\rho}-b\frac{\rho_0}{\zeta-b\rho_0}\right)+\frac{a\rho}{\zeta^2}\frac{\rho-\sigma}{\sigma}+(w-w')-\Psi(\theta)$$

where a and b are Van der Waals's constants. This equation, though capable of simplification, essentially involves ζ, and is therefore not suggestive.

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[1] Bertrand: loc. cit., p. 101.

[2] Thomson: loc. cit., p. 158.

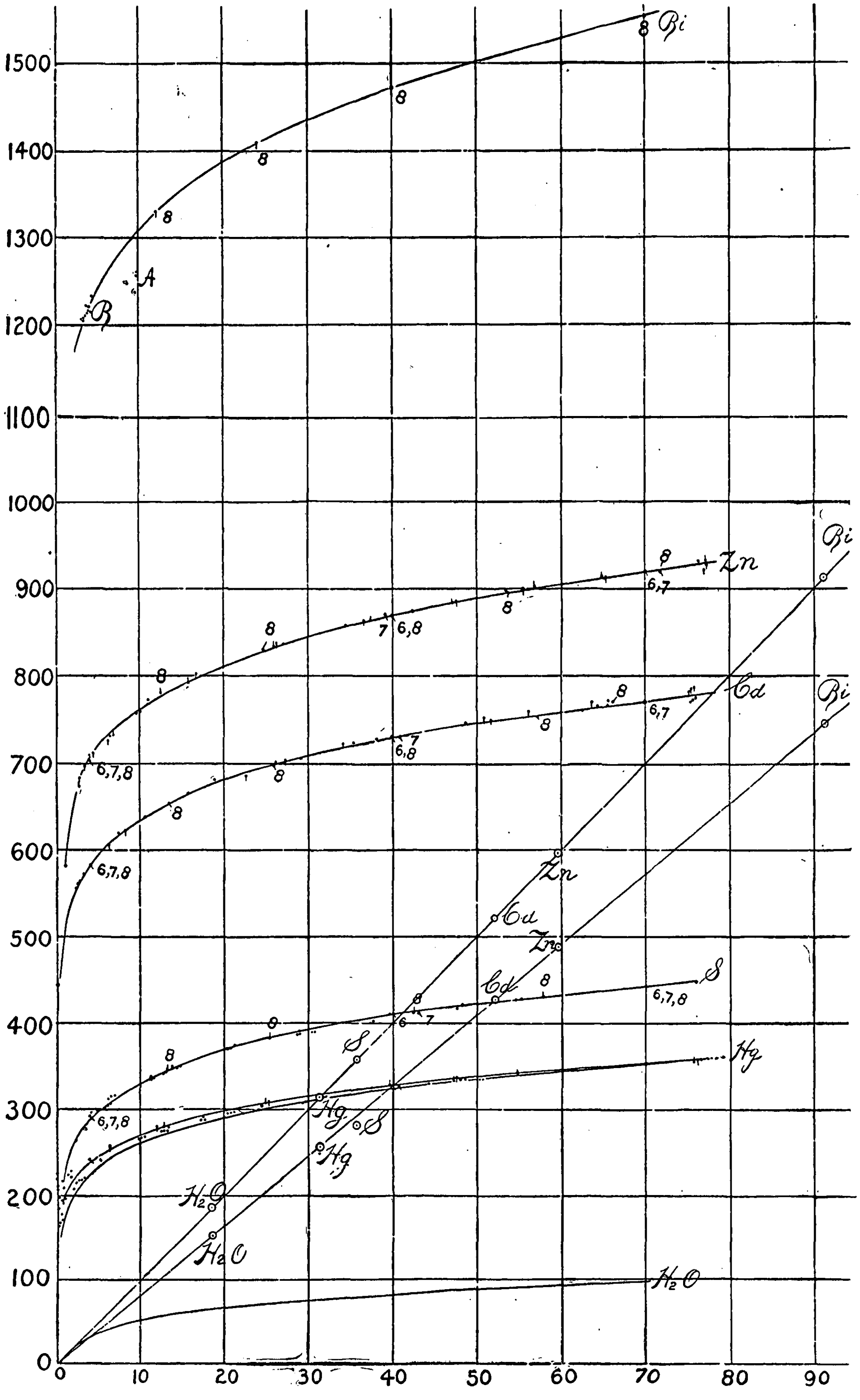

CHART SHOWING THE CHANGE OF BOILING POINT WITH PRESSURE (CENTIMETERS OF MERCURY)

CHAPTER II.

THE CONTRACTION OF MOLTEN IGNEOUS ROCK ON PASSING FROM LIQUID TO SOLID.

INTRODUCTORY.

18. *The rock.*—The following volume measurements were made for Mr. Clarence King, on a sample of diabase which he furnished. The object thus far is to develop the general character of the expansion phenomenon, and for this reason a fusible rock, without action on hot platinum, was selected. In future researches, graded rock magmas, passing from extreme acid to extreme basic, will be operated on.

19. *Literature.*—The importance of the question is well known, but a literary discussion is superfluous here, since Prof. F. Niess[1], of Hohenheim, not long ago made a careful survey of all that has been done on the subject. The reader desiring specific information is referred to this interesting pamphlet. "Es ist ein durch Contraste buntes Bild," says Prof. Niess (loc. cit., p. 36), "welches in der vorstehenden Citatenlese dem Leser zu entrollen war, und aus dem Wirrwarr entgegengesetzter Ansichten heben sich nur zwei Körper: Wismuth und Eisen, heraus, über welche man wohl mit absoluter Sicherheit die Acten als geschlossen bezeichnen kann, und zwar in dem Sinne, dass für sie die Ausdehnung im Momente der Verfertigung als zweifellos bewiesen gelten kann. Die übrigen Metalle stehen noch im Streit, und für sie gilt das Gleiche was wir für die künstlichen Silicate zu fordern hatten * * *" Now, iron, in virtue of the occurrence of recalescence (Gore, Barrett), is scarcely a fair substance to operate upon, and it heightens the confusion to find that Prof. Niess, after carefully weighing all the evidence in hand, is obliged to conclude that rocks expand on solidifying.

The present experiments show beyond question, I think, that at least for diabase this is not true. I find that this rock not only contracts between 3.5 to 4 per cent on solidifying, but that such solidification is sharp and only apparently continuous, and that the fusion behavior throughout is quite normal in character. Hence with certain precautions which I shall specify in the course of this paper, §21, the volume thermodynamic relations which I deduced by acting on organic bodies may be applied to rock magmas.

20. *Effect of fusion* (*polymerism*).—The rock after fusion is changed to a compact black obsidian and quite loses its characteristic structure.

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[1] Niess: "Ueber das Verhalten der Silicate, etc.;" Programm zur 70. Jahresfeier d. k. Würtemb. landw. Academie. Stuttgart, E. Koch, 1889.

It was therefore important to examine the volume relations of this change preliminarily. This is done in Table 11, where the densities obtained with lumps of the rock (mass M), at the temperature t, are given, Δ being the density before, Δ' after, fusion.

TABLE 11.—*Density, Δ, of the diabase, before and after fusion. Massive pieces (not ground).*

A.—BEFORE FUSION.

Sample No.	M	t	D	m	d	Δ	$\frac{\Delta-\Delta'}{\Delta}$	Remarks.
	g	°*C*						
I	22·8950	25	....	....	....	3·0161	....	
II	45·3654	21	....	....	....	3·0181	....	
III	54·7208	21	....	....	....	3·0136	....	
IV	69·4940	21	....	....	....	3·0235	....	

B.—AFTER FUSION.

Sample No.	M	t	D	m	d	Δ	$\frac{\Delta-\Delta'}{\Delta}$	Remarks.
I	60·9330	21	....	....	....	2·7018	·104	Fused in clay crucible. Lump broken out when cold.
II	33·7659	19	3·5013	11·1686	21·021	2·7447	·090	
III	29·9777	19	3·5496	11·2712	(21·00)	2·7045	·103	Fused in a platinum crucible.

The rock was fused both in clay and in platinum crucibles. In the latter case the density d of the known mass m of the platinum crucible had been previously determined, and D denotes the observed density of molten rock and crucible together after fusion. In the case where a clay crucible was used, this was broken away from the glass within and the density of the solid lump (glass) then measured directly.

A few small air bubble cavities were visible on the fresh fractured surface of the glass, due, I presume, to the possibility that most rocks, like most organic liquids, hold gases in solution, which separate on solidification. At some other time I will make sharp vacuum measurements of the density of ground powders both of the rock and of the glass, but I do not believe the results of Table 1 will be seriously changed by such a test.

From Table 1 it appears that the mean density of the original rock is 3·0178. That of the glass after fusion is 2·717, showing that the result of fusion has been a volume increment of 10 per cent. This remarkable behavior is not new nor isolated. Niess (l. c., p. 47), quoting from Zirkel's Lehrbuch, shows even more remarkable volume changes of the same nature in garnet, grossularite, vesuvianite, adularite, orthoclase, augite; but I doubt whether the great importance of this behavior has been sufficiently emphasized. Suffice it to indicate here that it makes an enormous difference into what product the magma is to be conceived as being solidified, and that throughout this paper the molten rock solidifies into an obsidian. I am really only determining, therefore, those volume changes which lie at the margin, as it were, of the more profound but chemically structural volume change, which latter may be reasonably conceived as producible by pressure alone under conditions of nearly stationary (high) temperature.

I may add in passing that, from the magnitude of the chemical change, I shall carry my work on the effect of pressure on chemical equilibrium of solids and liquids and on the solution behavior "solid-liquid" into greater detail than I have hitherto attempted.[1]

APPARATUS.

21. *Temperature measurement.*—In work of this kind, an apparatus for the accurate measurement of high temperatures is the fundamental consideration. I may, however, dismiss this subject briefly here, since I discussed it elaborately in Bulletin No. 54, U. S. Geological Survey. The temperature measurements of this paper were made with thermocouples of platinum and platinum with 20 per cent of iridium, and they had been frequently calibrated by aid of the porcelain air thermometer within an interval of 1100° and tested for freedom from anomalies beyond that interval. Reference to the bulletin cited will show how thoroughly reliable this thermocouple is. Inasmuch as the process consists in expressing thermoelectric force by aid of a zero method in terms of a given Latimer Clark cell, the temperature apparatus is of the same order of constancy as to time as the standard cell.

In order to find, however, how far this work was trustworthy after a lapse of more than four years since it was done, I made fresh check measurements of the boiling points of mercury and of zinc. The latter need only be cited here. My original datum of the boiling point of zinc expressed as thermoelectric force for the couples under consideration was e_{20} = 11,074 microvolts, the cold junction being at 20° C. The new experiments referred to gave me data as follows:

	Microvolts.
Thermocouple No. 35	$e_{20} = 11,168$
No. 36	$= 11,127$
No. 39	$= 11,116$
No. 40	$= 11,136$
Mean	$= 11,137$

agreeing very closely with two subsequent, specially careful measurements, viz:

	Microvolts.
No. 36	$e_{20} = 11,131$
No. 39	$= 11,134$

Thus the difference of values new and old is only 60 microvolts about ½ per cent as regards electromotive force, corresponding to something over 4° at 1000°. In view of the excessive use and abuse to

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[1] Am. Journal, vol. 37, p. 339, 1889; ibid., vol. 38, p. 408, 1889; ibid., vol. 40, p. 219, 1890; ibid., vol. 41, p. 110, 1891; ibid., vol. 42, p. 46 et seq., 1891; Phil. Mag., (5), vol. 31, p. 9, 1891.

which the couples had been put in the meantime, this result is in itself gratifying.

Endeavoring to find, however, where this discrepancy was to be sought, I also made fresh comparisons between the Latimer Clark standard and a normal Daniell of my own (bulletin cited, p. 100), in which the two cells are separate and only joined (with zinc sulphate solution) during the time of use. Supposing the Latimer Clark cell to have remained constant the succession of following values was found:

March,	1886, 20° C.,	L. C., $e = 1·435$	Daniell, $e = 1·138$
August,	1887, 28° C.,	1·435	1·139
September,	1891, 27° C.,	1·435	1·147

If, therefore, instead of regarding the L. C. cell constant, I had assumed the Daniell as constant[1], the thermoelectric difference for the interval of four years would be wiped out. Now my L. C. cells were made by me in 1883, when less was known about the subject than is now available[2]. I conclude therefore that the discrepancy is very probably in the standard cell employed and that my thermocouples have remained absolutely constant.

Apart from this, the new standardization by aid of the boiling point of zinc fixes the scale irrespective of surmises or hypotheses, assuming that zinc boils at 930°.

22. General disposition of apparatus.—This is given in Pl. IV, on a scale of $\frac{1}{2}$, where figures 1 and 3 form a sectional elevation showing the parts chiefly with reference to their vertical height, and figure 2 a sectional plan in which the parts are represented with reference to the horizontal.

The molten rock *ZZ* contained in a long cylindrical platinum tube, largely surrounded by a tube of fire clay, *FF*, is fixed vertically in a long cylindrical furnace, *DD LL*. The heat is furnished by six burners, *BB*, fed by gas and an air blast laden, if need be, with oxygen. These burners are placed at equal intervals along the vertical, three on one side and three on the other (Pl. IV, Fig. 2), and set like a force couple so as to surround the platinum tube with a whirlwind of flame. Suitable holes are cut in the walls of the furnace for symmetrical insertion of the insulated thermocouples, *T*, and also at *S*, for fixing the sight tubes, *A*, near the top and the bottom of the furnace. Parts of the envelopes of the platinum tube are cut away, so that its upper and lower end can be seen in the telescope of an external cathetometer. Thus the expansion of the platinum tube is measured directly. A vertical micrometer, *Kkd*, Pl. IV, Figs. 3 and 4, insulated so as to admit of electrical indications of contact, furnishes a means of tracing the apparent expansion of the rock *ZZ*.

In principle the operations are so to be conducted that under the conditions of slow cooling the magma may be relatively much less

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[1] Our laboratory affords no means for the direct measurement of electromotive force.

[2] See Lord Ragleigh in Phil. Trans., June, 1884, and Jan., 1886; also Carhart, Am. J. Sci., Nov., 1884.

viscous than the practically rigid platinum envelope throughout the work.

The furnace stands on a massive iron base perforated with eight holes, into which vertical iron uprights are screwed, symmetrically surrounding the furnace and at a distance of 4 or 5 centimeters from its circumference. Only one of these is indicated, in part, at *QQ*, in Pl. IV, Fig. 3, the rest with other subsidiary parts being omitted to avoid confusing the figure. Two of these uprights hold the vertical micrometer, two others hold the burners in place. To the fifth the sight tubes are adjustably attached, to the sixth the thermocouple insulators are clamped exteriorly to the furnace, and the remaining two fix the clay holders *H*, *H*, by which the tube *FF* is adjusted vertically. All of these uprights are hollow, and a current of water continually circulates through them with sufficient rapidity to issue finally still cold to the touch. In this way the observer is able to move and change the accessories of the furnace with comfort even when the temperature within is maintained at 1500°. A single stream of water is sufficient, the ends of the uprights being joined by rubber tubing, and this same current additionally flows through the screen *XX* of the vertical micrometer and the high vertical screen of the cathetometer.

23. *The furnace.*—It should be added to the remarks made in the preceding paragraph that all the burners *B*, *B*, Pl. IV, are fed by the same amount of gas and air by properly branching the large supply tubes. A graduated stop cock is at hand for regulating the supply of gas to a nicety, whereas the air blast need not be regulated. Hence the furnace is fed with a mixture of gas and air, and temperatures from 1600° to 400° may be obtained by simply making the influx richer or poorer in illuminating gas. Burner constructions suitable for this purpose are given in Bulletin No. 54, p. 182. For higher temperatures the blast may be made richer in oxygen, but I have thus far had no need of doing this.

The products of combustion are carried off by the two oblique tubes *E*, *E*, in the lid *LL*. Note that the water screen bends around the vertical micrometer in such a way that flames issuing from *E* can do no injury. The central narrow hole in the lid *L*, through which the end piece *dd* of the micrometer passes, is closed by a free plate of fire clay *mm* perforated so as to surround *dd* loosely.

The blast was furnished by a pair of large-sized Fletcher bellows, each with three sheets of rubber above the reservoir. These bellows were set so as to form a double-acting pump, and actuated by aid of a short crank on the axle of a small gas engine. The blast pressure so obtained is considerable, a requisite in the above instances. It can be regulated by lengthening or shortening the crank, whereby the arc of reciprocal motion of the bellows is increased, the frequency remaining unaltered. The efflux pipes of both bellows discharge into a common gas pipe leading to the furnace.

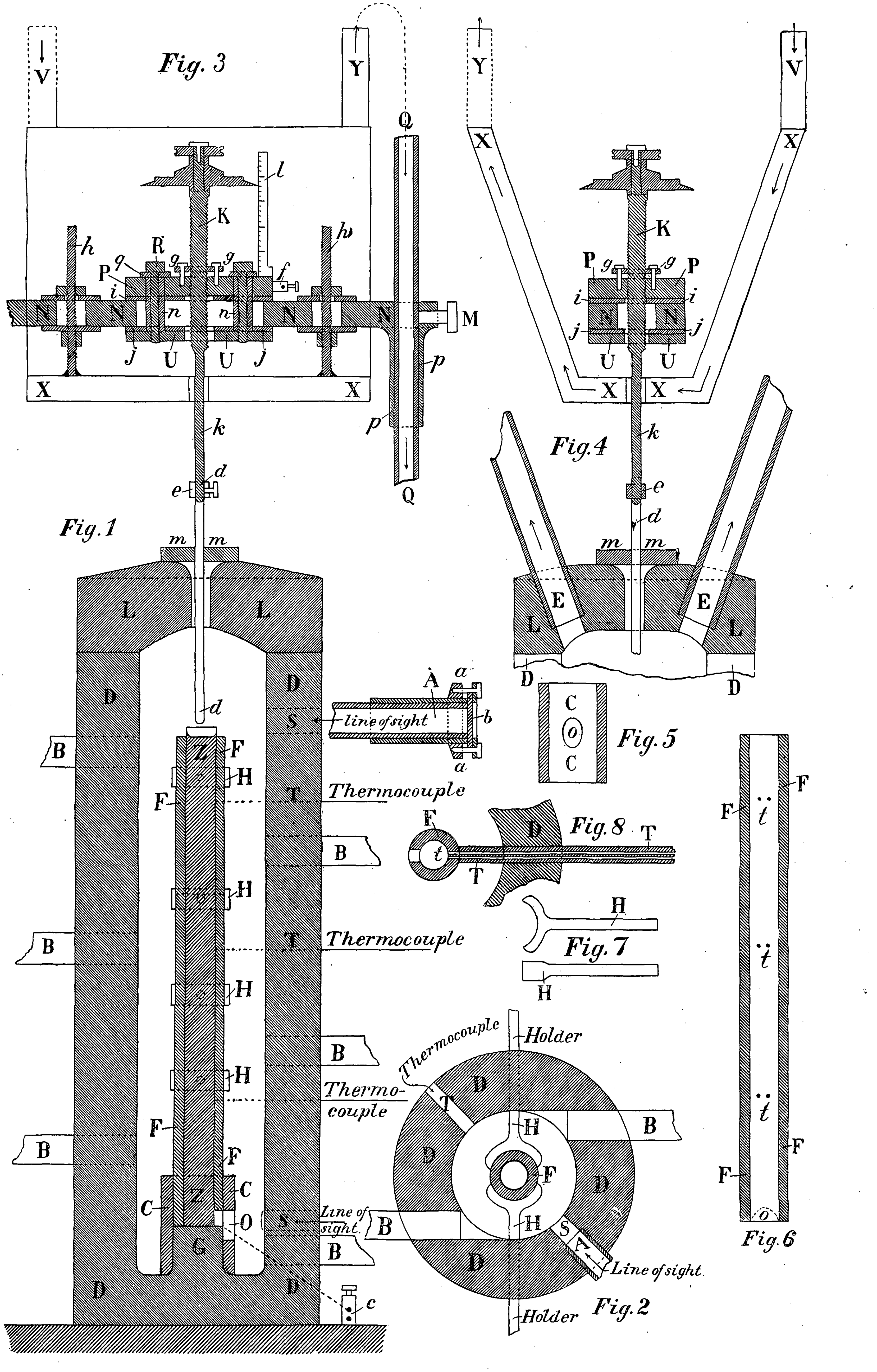
In order to obtain greater constancy of temperature and increase the high temperature efficiency of the furnace at the same time, it is essential to jacket the furnace, *DD*, and lid, *LL*, externally with a coating of asbestos fully ½ inch or more thick. I noted that in these cases the clay parts of the furnace became red hot throughout, whereas the uncovered furnace is not much above 400° externally. This indicates a smaller loss by radiation in the former case.

24. *Fusion tube.*—The platinum tube holding the molten rock, *ZZ*, Pl. IV, was 25 centimeters long and 1·5 centimeters in diameter, with walls about ·02 centimeter thick. It was drawn as accurately cylindrical as possible, and the bottom was plane and at right angles to the axis. To protect this tube from gases and to keep it from bulging in consequence of the pressure of rock within, the platinum tube is surrounded by a fire-clay tube, Pl. IV, *FF*, Figs. 1 and 6, fitting loosely. Care must be taken to allow for shrinkage. Thus a fresh clay tube, after about two hours heating at 1500° shrank from a length of 25·4 centimeters to 24·6 centimeters, i. e., ·8 centimeter or more than 3 per cent. This shrinkage is permanent and uniform in all directions, and is not, therefore, due to viscous sagging; after its full value has been reached, moreover, it ceases and the tube expansion is then normal. If properly sustained in the furnace the clay tube *FF* does not bend or warp. The holders, which I found very serviceable for this purpose, are shown at *H*, *H*, in Pl. IV, Figs. 1, 2, and 7. They are made of fire clay and held in position by suitable clamps on the outside of the furnace (not shown). In this way the fusion tube is to some extent adjustable.

The bottom of the tube, *FF*, is additionally fixed by aid of a perforated fire-clay ring, *CC*, Figs. 1 and 5, which embraces both the tube, *FF*, and a projection in the furnace, *G*.

25. *Thermocouples.*—These are three in number and inserted through the walls of the furnace, *DD*, Plate IV, in the positions given at *T*, in Figures 1 and 2. But Figs. 6 and 8 give a fuller account of the adjustment. The tube, *FF*, is laterally perforated with three pairs of fine holes, *t*, *t*, *t*, corresponding to the two canals in the insulator, *TT*. The wires of the thermocouple are then threaded through *t*, and the insulator in such a way that the junction lies in a small cavity at *t*, immediately in contact with the platinum fusion tube. A hole is cut in the tube, *FF*, opposite *t* (see Pl. IV, Fig. 8) and a similar one in the opposite wall of the furnace to facilitate these operations, the platinum tube being for the time removed. The advantage gained in this way is two-fold, since in the first place no part of the wires of the couple are directly surrounded with flame, and there is no danger of an accidental contact of these wires on the outside of the tube, *FF*. It is known that in the presence of carbon there is danger of passing silicon into the platinum, making the metal relatively fusible. Now, even if the hot gases of the furnace are reducing, they are to some extent stagnant in the insulating tubes, whereas in the flame they are constantly renewed. This I attribute to the protecting effect of the insulators.

The cold junctions of the thermocouples terminate in three pairs of mercury troughs, insulated by hard rubber, and submerged in a bath of



FURNACE FOR MEASURING VOLUME CONTRACTION OF MOLTEN ROCK. SCALE $\frac{1}{4}$.

petroleum. With these troughs the terminals of the zero method, § 21, are connected at pleasure, so that the temperatures at the top, middle, and bottom of the fusion tube are easily determined. Data are given in full below.

26. Sight tubes.—It has been stated, § 22, that the increase of length of the platinum fusion tube, *ZZ*, is to be measured directly. For this purpose Grunow's excellent cathetometer is placed on a suitable pier on the outside of the furnace, so that the prism of the instrument is only about 50 centimetres off from the platinum tube. To obviate the hurtful effect of radiation, however, a tall, flat water screen, 30 centimetres broad, 70 centimetres long, and 1 centimetres thick, and movable on a slide, is placed between furnace and cathetometer. Slots closed by plate glass are cut through the screen to correspond to the two positions of the telescope, and the furnace walls, *DD*, are similarly perforated, at *S*, above and below (see Pl. IV, Figs. 1 and 2), so that the ends of the platinum tube may be seen. The top of the latter projects above *FF;* but this tube and the ring, *CC*, are perforated at *O*, as shown in Figs. 1, 5, and 6. When the furnace is red hot within, the end planes or lines stand out very sharply against the red-hot clay background, in consequence of a difference in the emissive power of the metal and the clay, and hence the measurement is possible with the necessary degree of accuracy.

It is essential, however, to prevent the escape of flame and gas at *S*, and this may be done by closing these holes with sight tubes (only one of which is shown, *A*) of porcelain and about 15 centimeters long. The outer end of these is ground off square and a plate of plate glass, *b*, held against it by aid of the clamping device, *aa*. Surrounding the porcelain tube, *A*, with a layer of asbestos, and cutting a thread on the inner face of the brass ring, *a*, the latter may be screwed on to the soft asbestos, and then serve to secure an iron ring by aid of two machine screws, as shown. The iron ring holds the glass plate, *b*, in place. This joint should be well made, for if there is an escape of hot gases here, the glass is apt to break, though I have had no serious accident of this kind. At first, drops of water collect on *b*, but they disappear as the temperature rises.

27. Vertical micrometer.—Figs. 3 and 4, Pl. IV, give a full account of this instrument, both of which are sectional elevations at right angles to each other. A good millimeter screw, *Kk*, plays easily through the massive block of brass, *PP*, and the fixed lock nut, *gg*, and *l* is the vertical millimeter scale whereby the motion of the graduated head is registered. The block, *PP*, is bolted down to the thick bridge of brass, *NN*, by means of the screws *R*, *R*, and the counter plate *UU*. The ends of *NN* are provided with sleeves, *pp*, and a clamp screw *M*, so that the whole micrometer may slide up or down, or be clamped in any vertical position on the uprights, one of which is indicated at *QQ*.

It has been stated that the registration of the micrometer is to be electric, and hence the screw, *Kk*, must be insulated. This is done by surrounding the screws *R*, *R*, with a layer *n*, *n*, of hard rubber, from which the ends alone project, and insulating the plate, *PP*, and the counter plate of brass *UU*, by interposed sheets of hard rubber *jj*, *ii*, and the washers *q*, *q*.

In order to provide for a certain amount of horizontal adjustment of the micrometer, sufficiently wide slots are cut in the brass bridge *NN*, (see figures) whereby the plate, *PP*, may be shifted about 1 centimetre in any direction and then clamped in position.

In view of the heat which continually rises from the furnace, a V-shaped screen, *XX*, through which water rapidly circulates, nearly envelopes the micrometer below. Water enters and issues through tubes *V* and *Y* at diagonally opposite corners of the top of *XX*. Inasmuch as the micrometer screw, *Kk*, passes through a narrow hole in the bottom of *XX*, this screen must also be capable of lateral adjustment, and this is easily accomplished by aid of two vertical screw hangers *h*, *h*, soldered to *XX* below and passing through wide slots in *NN*, to which they are secured in any horizontal or vertical position by suitably flanged nuts above and below *NN*. Thus it is seen that the micrometer and its water-screen slide as a single piece along the upright *QQ*, an arrangement which greatly facilitates the final adjustment. *Q* and *Y* are connected by a sufficient length of rubber tube, as is merely indicated in the figure. There is a like connection on the other side.

Finally, the end of *Kk* is prolonged by a straight cylindrical tube of platinum *dd*, which may be fixed to the steel rod *k* by aid of the clamp *e* in any position along the vertical. This tube *dd* fits the rod *k* snugly, and should it become bent or warped by accidents, a special steel rod is provided by means of which it may easily be straightened again.

The lower end of *d* is clearly visible in the telescope of the cathetometer through the sight tube *A*. On being screwed down it enters the fusion tube *ZZ* axially, supposing the micrometer and fusion tube to have been properly fixed in position. In how far this has been done can always be seen by temporarily removing one of the efflux pipes *E*, Pl. IV, Fig. 4, when the end of the fusion tube and the motion at the lower end of *d* is visible to the eye. On actuating the micrometer head of *Kk*, the lower end of *d* should show but slight lateral motion in the telescope. Usually the tube *d* becomes coated with an enamel of molten rock, but this is of no consequence, since the increase of length is noted in the measurements.

28. Telephonic registration.—Since it is the object to find how far the meniscus of molten rock *ZZ*, Pl. IV, lies below the plane of the top of the fusion tube, the moment of contact of *ZZ* and *d* is best registered electrically. So long as the interior of the furnace is red hot, the rock is a good electric conductor. Hence, if a current be passed into the screw *Kk*, at the clamp screw *f*, Pl. IV, Fig. 3, it will issue at the bottom at the clamp screw *c*, Pl. IV, Fig. 1, provided, of course, *c* be electrically connected with the bottom of the fusion tube. This is easily done by placing the fusion tube on a plate of platinum above G, and connecting this with c by means of a platinum wire, as is indicated in the figure.

It is, however, very convenient to register the contact of ZZ and d telephonically, and this may be easily done by using the intermittent current of a small inductor like that of Kohlrausch. Contact then evokes a loud roar in the telephone, and the observer's attention is not further distracted. The adjustment is quite delicate, and if the glass ZZ be sticky, the drawing out of a thread is indicated by a gradual cessation of the noise in the telephone, etc. In fact, the character of the fusion may be pretty well inferred in this way. The instrument is available almost as far as 400°, at which time, however, the furnace is dark, and cathetometric measurement is no longer possible.

Care should be taken to secure small sparking distances, for this quantity will vary with the temperature of the gas in the furnace.

If the expansion of the rock be known, and the tube dd sunk deeply into the mass, it is clear that the present method admits of a measurement of the relation of electric resistance and temperature. I mention this, believing that a suitable method for temperature measurement may be thus available.

Elsewhere[1] I have already speculated on the character of the changes of electrolytic resistance referred to temperature. Should a hyberbolic law indeed apply, high-temperature measurement would be effectually promoted.

METHOD OF MEASUREMENT.

29. Consecutive adjustments.—Thus far it has been my object to study the contraction of rock only. For this purpose the graduated faucet is turned on full and the furnace fired as far as 1,400° or 1,500°, when the first measurements are taken. With this end in view the length of the fusion tube is first accurately measured by the cathetometer observations at the bottom and the top. The telescope is then left adjusted for the top and the vertical micrometer (centrally adjusted) screwed down until its lowest point is just in contact with the cross hairs. After this the micrometer is further screwed down until the telephone registers a contact between the meniscus of the molten rock and the platinum micrometer tube. The difference of readings gives the depth of the meniscus below the top plane of the fusion tube. I usually repeated this measurement three times and then raised the micrometer screw again.

Thereupon the temperature measurements were made by connecting the terminals of the zero method consecutively with the upper, the middle, and the lower thermocouple.

Finally the cathetometer measurements of the length of the fusion tube and the micrometer measurement for depth of meniscus were again

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[1] Am. Jour., Vol. XLII, pp. 134-135, 1891.

repeated, the latter three times. Properly uniform heating presupposed, it was permissible to regard the mean of the two sets of length measurements as coincident with the intermediate temperature measurement. This done, I usually waited ten or fifteen minutes to make another complete measurement under better conditions of constant temperature.

The graduated stopcock was then partially closed by a proper fractional amount, and after waiting fifteen minutes or more the same measuring operations were gone through with as before.

This I continued until the slag became sticky and solidification imminent, when longer waiting and greater slowness in changing the temperature is essential. Fortunately the observer can note the state of things very accurately; for when the point of solidification is approached a thread of the magma is drawn out of the fusion tube by the ascending micrometer tube until it breaks to form a rounded coating on the end of the tube. As temperature decreases, even by small amounts, the time that it takes to break and round off increases until finally this pulling out of a thread ceases and the enamel on the end of the micrometer tube does not change its form, being solid. It is at this point (1,095°) that the marked contraction of the molten mass in the tube occurs.

Having waited long enough for the lowest position of the meniscus, temperature may then be varied in larger steps again.

When the inside of the furnace has become dark, measurement is no longer possible. I then allowed the whole arrangement to cool over night, and the next morning determined both the depth of the solid meniscus by ordinary contact micrometric measurement, as well as by filling the top of the tube with water, and computing its bulk. This gives me my fiducial or normal volume.

To fill the fusion tube with rock at the outset of the work is a tedious operation. The material is added gradually in coarse grains, in proportion as the charge melts down, and after the tube is full some time must be allowed to insure the escape of air bubbles. Inasmuch as the fusion tube can at first be easily slipped out of its clay envelope, it is well to pack it as full of rock as possible before heating it.

30. Computation.—Let the linear expansion of the platinum fusion tube be given by $l=l_0\,(1+f(t))$, where l and l_0 are the lengths at t degrees centigrade and at zero, respectively, and where $f(t)$ is a function of temperature. Let λ and λ_0 be the depths of the meniscus below the plane of the top of the fusion tube, and v and v_0 the volume of the inclosed molten magma, at t degrees centigrade and zero, respectively. Then if $(1+f(t))^3$ is nearly enough equal to $1+3f(t)$; if the expansion constants of both platinum tubes be the same; and if in consideration of the small motion of the micrometer tube and the high temperature in the furnace, the air temperature above and outside of the furnace be nearly enough equal to zero, since $v_t/v_0=(l_0-\lambda)\,(1+f(t))^3/(l_0-\lambda_0)$.

$$(1)\ldots\ldots\ldots(v_t-v_0)/v_0=3\,f(t)+(\lambda_0-\lambda)\,(1+3f(t))/(l_0-\lambda_0).$$

Here $3f(t)$ is directly given after each observation as $(l_t - l_0)/l_0$, or it may be computed by some smoothing process from all the data as a whole.

The equation therefore gives the actual expansion of the rock in terms of unit of volume of solid rock at zero. If this be multiplied by the specific volume at zero, the absolute expansion is obtained.

An inspection of the equation shows that in the factor $\lambda_0 - \lambda$, the micrometer value of the lengths λ is to be inserted in both cases, supposing the contour of meniscus to remain similar to itself; whereas in $l_0 - \lambda_0$, the value of λ_0 determined from bulk measurements of the space at the top of the cold tube is suitable, since the tube is squared off below.

With this it is interesting to compare the results to be obtained in case of a float. If A be the height of the column of magma; h the submerged depth of the cylindrical float or bucket with flat base; and if $\delta A = A_t - A_0$, $\delta h = h_t - h_0$, $\delta v = v_t - v_0$, etc., for the temperatures t and t_0 respectively, then

$$(2) \ldots\ldots\ldots\ldots (3\,ft) + \frac{\delta H}{A - h} = \frac{\delta A - \delta h}{A_0 - h_0} + 3\frac{\delta l}{l_0} = \frac{\delta v}{v_0}$$

where δH is the rise of the float and l the length of the fusion tube. From this equation it appears at once that the float shortens the efficient length of the tube. Moreover, there is serious difficulty of properly determining A in this case. Hence, in view of the capillary and other errors encountered by a swimmer in a viscous liquid; the ease with which platinum at white heat welds with platinum vitiating the forms of both tube and swimmer; the tendency of air bubbles to accumulate around the latter and the probable utter failure of this method in indicating the passage from liquid to solid, induced me to prefer the other method. In case of a swimmer the observer does not surely know what he is measuring.

31. Errors.—First among these the lack of uniform temperature from the bottom to the top of the fusion tube may be mentioned. Moreover, only in the case of very slow changes of temperature is this quantity of like value from the axis to the circumference of the tube. I endeavored to meet these conditions. Moreover, since the temperature is actually measured at three points along a vertical, and the platinum tube is surrounded by the relatively nonconducting clay tube, I do not believe that serious discrepancy can here be apprehended. Specific inquiry will be made in the next paragraph in connection with the data obtained. Here I need only remark that it is unfortunate that the tube shows a tendency to be less hot at the top than at the bottom: for it is in the interest of thoroughly compact solidification that the tube cool from below upward. A column which cools first at the top is put into a state of dilitational strain after the manner of a Rupert drop, so that vacuities are left within the mass and the solidification contraction is obtained too small in value. I think a remedy for the difficulty in question will be found by feeding the upper burner from an independent gas supply.

Indeed I have frequently noted lateral funnel-shaped holes several millimeters in diameter and as much as 1 centimeter or more deep, terminating in the smooth surface of the meniscus. It is also possible that bubbles congregate under the surface of the molten magma, without breaking through it, giving rise to these cavities in the cold column. I have already stated that the ejection of gases on solidification is of very common occurrence.

At very high temperatures (say above 1,500°) I found the meniscus to gradually sink in depth even when temperature remained constant or rose in value, § 33. This may be due to the escape of bubbles in the thin liquid, or it may also be due to the fact that the tube is now insufficiently rigid to withstand the pressure of a column of molten rock 25 centimeters high. Examples will be given below, from which it appears that the meniscus, caet. par., does actually sink from day to day conformably with changes of length of the platinum tube. I suspect, therefore, that the clay tube which envelopes the fusion tube, besides acting favorably as a nonconductor, contributes to the high temperature rigidity of the system. After several heatings the platinum tube can no longer be removed trom the clay tube, into which it now fits tightly, without breaking the latter.

It has been assumed that the meniscus remains similar in form at all temperatures. This can only be partially true. The fused rock wets platinum so thoroughly, however, that convex forms of meniscus need never be apprehended. Indeed there is a tendency to flow or creep into crevices. After solidification, however, the meniscus is apt to be drawn down so as to be relatively deep near its center. Here is, therefore, an error which counteracts the tendency to dilitational strain. It is almost futile to make allowance for these discrepancies, but the micrometrically measured depth of the solid meniscus may be as much as ·2 centimeter or ·3 centimeter deeper than the mean surface computed from bulk.

Although too much reliance must, therefore, not be placed on the behavior of the solid state, yet the values are redeemed from the character of mere estimate, because the expansion of the platinum and its solid glass core are so nearly alike. This is a particularly fortunate chance, whereby the strains imposed on both the metal and the glass during cooling do not probably exceed the limits of elasticity of either. (§§ 33, 34 35.) From all of this it follows that the cooling of the furnace must take place so slowly as to give the viscous content of the fusion tube full time to adjust itself free from strain. Particularly are these precautions necessary near the solidifying point. In such a case experiment shows that the platinum tube is not dragged along appreciably by the solidifying magma, and the results retain a degree of trust worthiness much beyond what was to be anticipated, even in the solid state. At the same time dilitational strain is reduced to a minimum. In how far this has been accomplished satisfactorily can always be seen in the degree of uniform contraction of the platinum tube.

Another serious consideration is the allowance to be made for the expansion of the platinum probe *dd* of the vertical micrometer. The expansion as estimated above is too small, for it is not merely the amount by which the probe is lowered that is subject to expansion, but a considerable length of metal above the furnace passes from a lower to a higher temperature. Consecutive values for the depth of the meniscus will thus differ appreciably, the later ones being larger as a rule than the earlier ones. I hope, however, in the future to obtain an estimate of this discrepancy by measuring an amount of thrust through the sight tube with the cathetometer, and comparing this value with the corresponding value to be read off on the vertical micrometer. I have thought of making the micrometer screw hollow and providing it with an internal circulation of water; but this would be difficult to accomplish.

RESULTS.

32. Arrangement of the tables.—In the following tables l_0 and r_0 denote the length and radius of the cold platinum fusion tube, and λ'_0 the bulk value (water measurement) of the mean depth of the meniscus, the measurement being made on the day after the fusion experiments. The temperatures at the bottom, middle, and top of the fusion tube are given under θ_1, θ_2, θ_3, respectively, and θ is their mean value, observed at the time given. For each value of θ two data for the expansion of the rock, the volume expansion of the tube, and the actual expansion $\delta V/V_0$ of the rock are given, and they were obtained before and after the temperature measurement. Here $V-V_0$ is abbreviated δV and V_0 is the volume of the solid rock at zero. The data enclosed in parentheses show that in this case the value applied for the expansion of the tube is obtained as a mean result of all the measurements made. Otherwise the value directly observed was applied.

33. Contraction of diabase. Tables.—The results of my first series, being of inferior accuracy, will be omitted. Table 12 contains the results for the second series of experiments made on October 18, 1891. Here, too, the precaution of alternating volume measurements with the temperature measurements was not yet applied and the values given are less nearly coincident.

TABLE 12.—*Contraction of diabase. Second series.*

$l_0=25{\cdot}49^{cm}$; $\lambda_0={\cdot}86^{cm}$; $r_0={\cdot}75^{cm}$

θ_1 θ_2 θ_3	Mean. θ	Apparent volume expansion of the rock.	Volume expansion of the tube.	$\delta V/V_0$	Mean. $\delta V/V_0$	Time.	Remarks.
°*C*	°*C*					*Minutes.*	
1513	1514	·0442	.0411	....	·0853	0	Liquid. Viscous extension of tube?
1536	....	·0431	....	....	·0842	....	
1492	....	·0421	....	....	·0832	....	
1538	1544	·0379	·0399	....	·0778	25	Liquid.
1566	....	·0374	....	....	·0773	....	
1528	....	·0369	....	....	·0768	....	
1451	1480	·0345	·0378	....	·0721	50	Liquid.
1475	....	·0343	....	....	....	....	
1515	....	·0342	....	....	....	....	
1204	1202	·0302	·0300	....	·0602	75	Solidifying, chilled exteriorly.
1194	....	·0304	(·0290)	....	·0594	....	
1208	....	·0302	·0282	....	·0584	....	
896	872	·0074	·0201	....	·0275	100	Chilled solid.
864	....	·0050	(·0183)	....	·0233	....	
855	....	·0025	·0165	....	·0188	....	
804	770	·0016	·0141	....	·0157	130	Solid.
724	....	....	·0130	....	·0146	....	
783	....	....	·0120	....	·0138	....	
	20	·0000	·0000	....	·0000	Next day	Cold.

Taking each of the three values of $\delta V/V_0$ at 1514°, 1544°, 1480°, it is seen that the members of each set successively become more coincident. Moreover, the sweep downward and to the right of the means of the individual values of $\delta V/V_0$ is such as to indicate either that the tube sagged viscously or that the magma ejected bubbles or changed the figure of its meniscus. It seems to me that the platinum tube underwent stretching until it was finally restrained by the clay tube enveloping it. Rejecting the first datum, the mean volume expansion of the liquid is ·000050 per degree, a value which agrees very well with the subsequent work.

The passage from 1202° to 872° is abrupt, indicating that a melting point has been passed. Moreover, the wide divergence of the three data for $\delta V/V_0$ at 872°, shows that the cooling took place far too rapidly, so that the temperature of the rock must have been much higher than the thermocouples indicate. Finally the mean volume expansion of the solid magma below 872° is about ·000020 per degree, a value which also agrees very well with the work below.

If the solidifying point of the magma be 1095° (the value found in §§ 34, 35) then the contraction on solidifying may be estimated at 3 per cent. Thus it follows with certainty that diabase contracts on solidification and that its fusion behavior must be of a thoroughly normal type.

The amount of solidification contraction is, however, too small if too rapid cooling actually produces a strain of dilatation. For the same reason the values of $\delta V/V_0$ for the liquid state, though correct in their relations to each other, must be uniformly too small, for the factor V_0 used is too large. All this is proved directly by the next two tables, but it may be inferred here from the contraction curve of the platinum tube. This shows reasonable uniformity of contraction as far as 900°, after which, however, there is a break to much smaller rates of contraction, showing I think that the platinum tube has been dragged along by the too rapidly solidifying magma.

34. Contraction of diabase. Tables and chart.—The data of my third series of experiments, made on October 20, 1891, are given in table 13. The precautions for slow cooling were fully taken, and the solidification point is now sharply apparent.

TABLE 13.—*Contraction of diabase. Third series.*

$l_0 = 25 \cdot 466^{cm}$; $\lambda_0 = 1 \cdot 424^{cm}$; $r_0 = \cdot 75^{cm}$.

θ_1 θ_2 θ_3	Mean. θ	Apparent volume expansion of rock.	Volume expansion of the tube.	$\delta V_1/V_0$ $\delta V_2/V_0$	Mean. $\delta V/V_0$	Time.	Remarks.
°C.	°C.					*Minutes.*	
1360	1386	·0452	·0358	·0810	·0811	0	Liquid.
1396		·0454	(·0356)	·0812	(·0809)		
1403				(·0808)			
				(·0810)			
1286	1300	·0437	·0340	·0777	·0778	23	Liquid.
1304		·0438	(·0334)	·0778	(·0772)		
1311				(·0771)			
				(·0772)			
1163	1166	·0406	·0297	·0703	·0704	53	Sticky.
1167		·0409	(·0300)	·0706	(·0707)		
1168				(·0706)			
				(·0709)			
1097	1093	·0376	·0270	·0646	·0646	86	Very sticky.
1093		·0333	(·0281)	·0603			To be drawn out in threads.
1089				(·0657)	(·0657)		Solidifying gradually.
				(.0614)			
1102	1095	·0014	·0273	.0288	·0287	111	Solid.
1095		·0013	(·0282)	.0286	(·0296)		
1088				(.0296)			
				(.0295)			
929	896	·0000	·0211	.0211	·0212	157	Solid.
897		·0002		.0213			
863							
461	468	— ·0004	·0081	·0077	·0079	185	Solid.
433		± ·0000		·0081			
510							
	20	·0000	·0000	·0000	·0000	Next day.	Cold.

Rock, mean actual expansion, solid, 0° — 1000°, ·0000250.
Rock, mean actual expansion, liquid, 1100° — 1500°, ·0000470.
Rock, expansion on fusion (1095°), ·0390.
Rock, mean apparent expansion, solid, 0° — 1000°, ·0000007.
Rock, mean apparent expansion, liquid, 1100° — 1500°, ·0000205.
Tube, mean expansion below 1000°, ·0000240.
Tube, mean expansion above 1100°, ·0000265.

These values are fully represented in the chart, Plate V, where the actual expansion is given by the heavy curve *dcbef*, the ordinates being the volume increments and the abscissæ temperatures. The apparent expansion of the rock is shown by the light curve *lk gh*, the ordinates of the solid contour *lk* being nearly zero, so that the tube and contents expand nearly at the same rate, whereas the liquid contour *gh* follows with a marked jump and shows great uniformity. Finally the expansion of the platinum tube is represented by the dotted curve *dc a i*. The exceedingly small break at *a*, which indicates the amount of drag or shortening of the length of the platinum tube by the solidifying rock, shows how well the operation of cooling has here been conducted, and proves the results to be trustworthy throughout.

One of the important results obtained from the chart is the occurrence of a sharply-defined solidifying point at 1093°. Here, therefore, is a method by which this point of the rock can be defined free from non-intrinsic tests.

Finally, it may be noted that so long as the magma is liquid, the distribution of temperature along the fusion tube is fairly constant, and and is usually hotter at the top. After this the discrepancy increases, probably from lack of convective conduction of the solid magma.

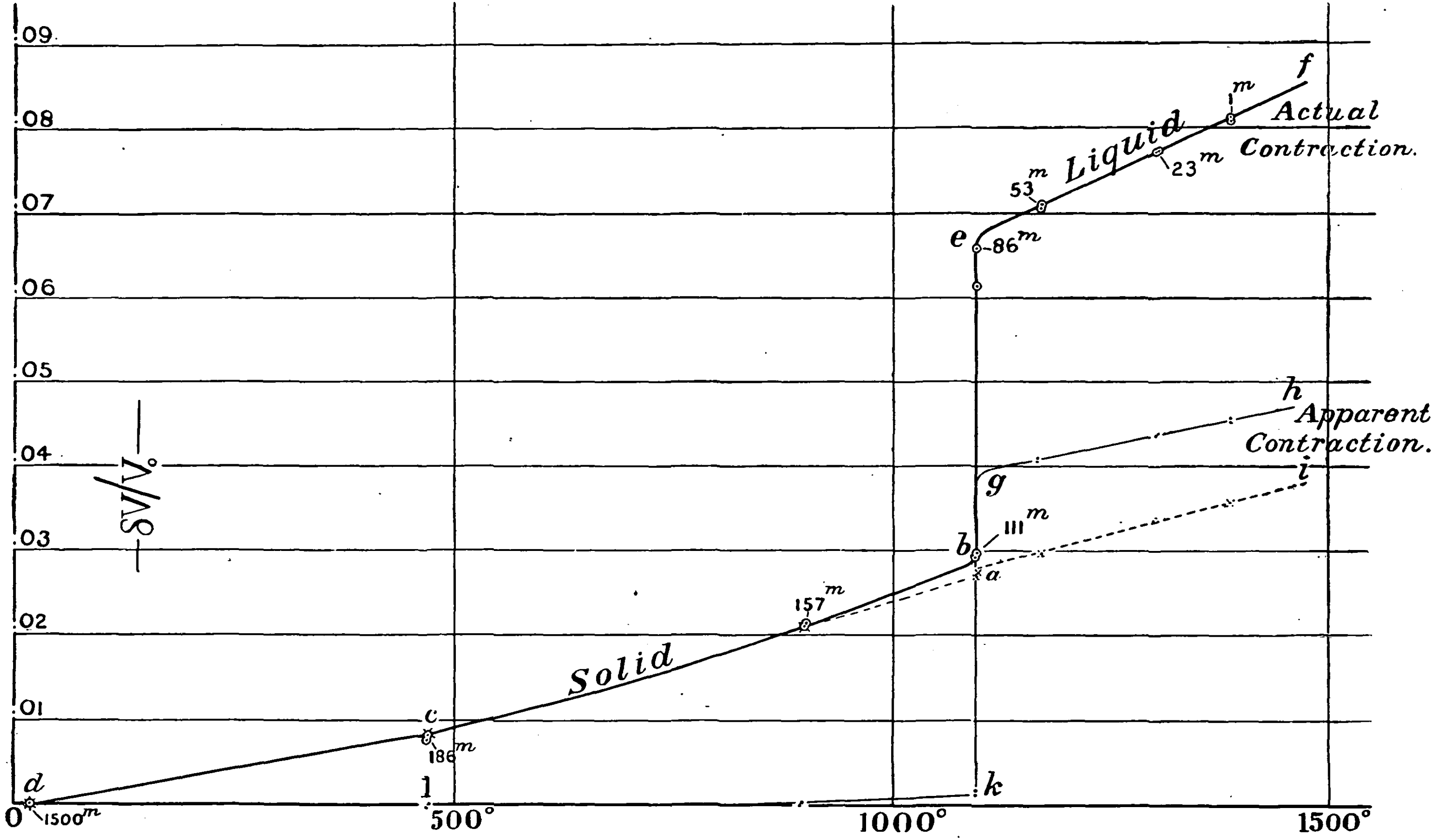
35. *Contraction of diabase. Tables and chart.*—The data of my last series of experiments, made on October 21, 1891, with all precautions necessary, are given in Table 14. Two complete sets of result for each step of temperature are given.

TABLE 14.—*Contraction of diabase. Fourth series.*

$l_0 = 25.447^{cm}$; $\lambda'_0 = 1.220^{cm}$; $r_0 = .75^{cm}$

θ_1 θ_2 θ_3	Mean. θ	Apparent volume expansion of rock.	Volume expansion of the tube.	$\delta V_1 / V_0$ $\delta V_2 / V_0$	Mean. $\delta V / V_0$	Time.	Remarks.
C°.	°C.	—	—	—	—	*Minutes.*	
1374 1394 1395	1388	·0403 ·0404	·0357 (·0356)	·0760 ·0761 (·0759) (·0760)	·0760 (·0760)	5	Liquid.
1415 1431 1417	1421	·0407 ·0409	·0362 (·0364)	·0768 ·0771 (·0771) (·0773)	·0770 (·0771)	20	Liquid.
1318 1324 1315	1319	·0394 ·0387	·0341 (·0339)	·0734 ·0727 (·0733) (·0726)	·0731 (·0730)	50	Liquid.
1304 1308 1304	1305	·0383 ·0390	·0350 (·0335)	·0733 ·0740 (·0718) (·0725)	·0736 (·0721)	65	Liquid.
1204 1189 1176	1190	·0357 ·0355	·0316 (·0305)	·0673 ·0671 (·0662) (·0660)	·0672 (·0661)	90	Sticky.
1177 1158 1153	1163	·0355 ·0349	·0299 (·0299)	·0655 ·0649 (·0655) (·0649)	·0652 (·0652)	105	Very sticky. To be drawn out in threads.
1138 1109 1090	1112	·0339 ·0344	·0286 (·0286)	·0625 ·0630 (·0625) (·0630)	·0628 (·0628)	128	Top encrusted.
1117 1088 1072	1092	·0200 ·0155 ·0091	·0275 (·0280)	·0475 ·0430 ·0366 (·0480) (·0435) (·0371)	·0475 (·0480)	151	Solidifying.
1109 1081 1086	1092	·0032 ·0005	·0282 (·0280)	·0315 ·0287 (·0313) (·0285)	·0287 (·0285)	175	Solidifying.
946 903 893	914	·0013 ·0006	·0213	·0226 220	·0223	198	Solid.
900 827 837	855	·0003 ·0003	·0199	·0202 202	·0202	210	Solid.
20		·0000	·0000	·0000	·0000	Next day.	Cold.

Rock, mean actual expansion, solid, 0°—1000°, ·0000250.
Rock, mean actual expansion, liquid, 1100°—1500°, ·0000468.
Rock, mean apparent expansion, solid, 0°—1000°, ·0000005.
Rock, mean apparent expansion, liquid, 1100°—1500°, ·0000218.
Tube, mean expansion below 1000°, ·0000235.
Tube, mean expansion above 1100°, ·0000260.
Rock, expansion on fusion, (1093°), .0340.



CONTRACTION OF MOLTEN DIABASE, CONTINUOUSLY FROM LIQUID TO SOLID.

These data are given in the chart, Pl. VI, Fig. 1, on the same plan as in the preceding case. The inferences to be derived are identical with those of the preceding paragraph. The sudden contraction of the rock on solidifying is of smaller value here, but this is to some extent compensated by the greater longitudinal compression of the fusion tube, as shown at *a* in the curve *c a i*. It is interesting to note that in both series 3 and 4 the first length measurement of the tube at the solidifying point of its contents, is smaller than the second, showing the end thrust to have diminished in value, while the tube has recuperated from its strain. It is also well to note that the sag of tube, as expressed in the cold lengths 25·49 centimeters in the second series, 25·47 centimeters in the third series, and 25·45 centimeters in the fourth series is small, but quite appreciable.

Regarding the differences of λ_0 (micrometric), and λ'_0 (bulk measurement), which is ·34 centimeter in the fourth series, ·13 centimeter in the third series, and ·38 centimeter in the second series, the remarks made in § 31 apply. Hence the third series is the one in which cooling was slowest, and in this the solidification contraction is largest. Lateral fissures opening into the solid meniscus were present in both these cases. Regarding the depth λ, of the solid meniscus at the outset, and at about the same temperature, 1387°, I found $\lambda = \cdot 50$ centimeter in the third series, and $\lambda = \cdot 62$ centimeter in the fourth series, showing enlargement of the volume of the fusion tube.

Finally, as before, temperatures are hotter at the top or fairly uniform so long as the magma within the fusion tube is very liquid. Near the solidifying point, however, and thereafter, the top is colder. For this reason, since solidification commenced at the top, the data of this paragraph show a smaller solidification contraction than in the last instance.

36. General remarks.—The charts show how important it is to measure the expansion of the fusion tube, which, if neglected, would distort the liquid expansion fully 50 per cent. Moreover I have no doubt that when fusion is made in clay crucibles which are apt to become friable after heating, the clay on cooling is quite at the mercy of the more tenacious slag within, and changes its volume accordingly.

Again even in case of slow cooling solid contraction tends to express itself as a dilatational strain, and if gas bubbles are ejected by rocks on solidifying solid volumes will be found too large and the solid contractions, etc., too small. Hence I place greatest reliance in the solidification contraction given in the third series, the value being 3·9 per cent.

Naturally, I also made special experiments on the floating of solid rocks on the molten magma, cf. § 20. To my surprise such flotation always occurs, notwithstanding the fact that originally the cold rock must be 8 per cent + 10 per cent more dense than the molten rock, since it is both solid and cold as well as possessed of organized rock structure. It soon appeared, however, that the cause of such flotation is crudely mechanical, since the rock in virtue of its weight simultaneously hollows out a cavity and chills it, thus forming a little solid boat in which it floats on the very viscous slag below. This is shown in Plate VI, Fig. 2, where *a* is the body of rock, *AA* the molten magma, and *bb* the solidified bowl-shaped skin. It may be observed that flotation is assisted by viscous friction of the blanket *bb* on the magma *AA* which supports the blanket and keeps it distended. I then attempted to make Niess and Winkelmann's "Fundamental-versuch" by submerging the rock; but here both on account of the intense white glare of the furnace and the tendency to chill at the surface of the magma during the operation I was not able to reach any definite point of view.

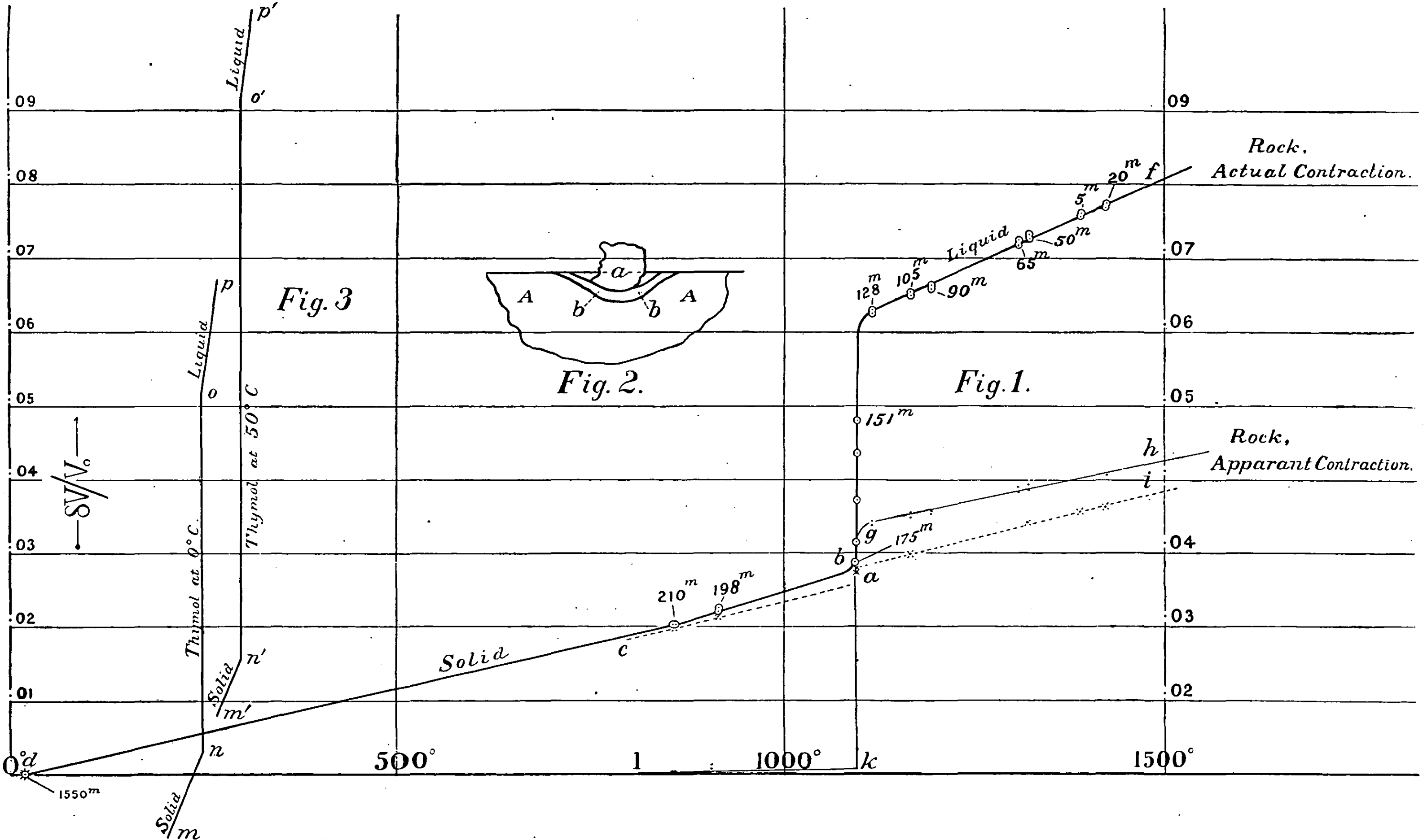
Results for thymol are given in Plate VI, Fig. 3, for comparison. §38.

37. *Fusion and solidification alternating.*—To corroborate the above work, I made some experiments by measuring the expansion on fusion, as well as the contraction on solidification. These are contained in Table 15, where the notation is the same as above. The zero lengths (l_0, λ_0, etc.), were taken from the above work, as was also the expansion of platinum.

TABLE 15.—*Fusion and solidification alternating.*

Time.	θ_1 θ_2 θ_3	Mean θ	$(\delta v/v_0)$ $\times 10^4$	Time.	θ_1 θ_2 θ_3	Mean θ	$(\delta v\ v_0)$ $\times 10^4$
Minutes.	°	°		*Minutes.*	°	°	
20	1139	1158	332	195	1059	1086	302
	1163	....	343		1086	....	300
	1173	....	....		1113	....	....
45	1235	1239	511	225	1097	1067	274
	1246	....	614		1066	....	271
	1234	....	....		1039	....	....
70	1254	1265	664	240	1167	1183	338
	1275	....	671		1190	....	373
	1266	....	....		1192	....	....
95	1285	1286	678	260	1239	1239	538
	1294	....	681		1246	....	595
	1280	....	....		1232	....	....
127	1157	1174	604	280	1087	1113	328
	1176	....	591		1115	....	302
	1188	....	....		1138	....	....
165	1146	1134	425				
	1125	....	404				
	1132	....	....				

The difficulty with these experiments lies in the insufficient time allowed for fusion and solidification (§§33–37). In the former case irregularities are unavoidable, since it is impossible to heat a solid rod of rock uniformly throughout its length. The high solidifying point, here, probably follows from the fact that the fusion was not complete. This is seen in Fig. 3, where the individual data are marked by numerals indicating the time at which the observation was made, and where the first cycle is indicated by a heavy line, the second by a light line. I suspect, therefore, that in rocks melting and solidifying points are different and may be 100° apart. Hence the large contraction at a definite degree of temperature observed above, was due to very slow cooling of an undercooled mass.



CONTRACTION OF MOLTEN DIABASE, CONTINUOUSLY FROM LIQUID TO SOLID.

The amount of volume contraction agrees in both cases with the above data, and this is the chief point at issue.

INFERENCES.

38. Comparison with thymol.—Since the fusion of rocks like diabase is thus thoroughly normal, it follows that melting point must increase with pressure. It is well to examine tentatively into the nature of this relation, and for this purpose I have drawn certain unpublished results of mine for thymol, on the same scale used for the rock. In Pl. VI, Fig. 3, $m'n'o'p'$ shows the contraction of thymol at its melting point, where the substance is liquid along $o'p'$ and solid along $m'n'$. Similarly, $mnop$ shows the contraction of thymol at 0°C. These results indicate that the solidification contraction decreases in proportion as the thermal expansion ($[\delta(V/V_0)/d\theta]_\theta$ where θ denotes temperature) decreases. The solidification contraction of thymol, therefore, like its coefficients of expansion, is larger than the similar variable in the case of rock. The relations are such that if liquid thymol could be cooled down to −25° it would then show the same solidification contraction as the silicate.

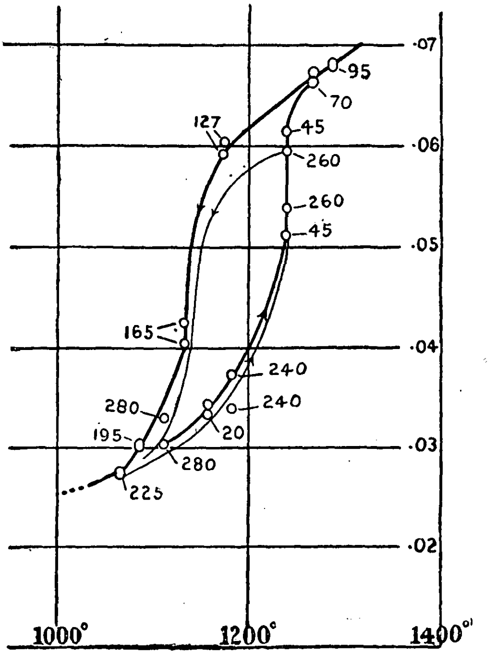


FIG. 3.—Cyclic volume changes produced by alternate fusion and solidification of rock magma (diabase).

39. Lower critical temperature.—Analogously the compressibility of the rock will show decidedly larger values than in organic bodies; and hence it also follows that whereas the lower critical pressure liquid-solid of naphthalene, for instance, should, according to my experiments, lie somewhere in the region of 10,000 atmospheres, the corresponding pressure in the case of rock magma must be indefinitely higher. In other words, the consecutive isopiestics of the magma must lie very much nearer together than the corresponding isopiestics of naphthalene, supposing the pressure to vary in like steps in both cases.

40. Melting point and pressure.—From this, however, it does not by any means follow that the relation of melting point to pressure will be different in the silicate and in the carbon compound. In the latter case, data for normal fusions are available in case of wax, paraffin, spermaceti, and naphthalene, and for these dT/dp, the relation of melting point to pressure, lies within the narrow margin of ·020 to ·036, data moreover which even for the same substance[1] are subject to variation. Thus I found that in naphthalene dT/dp varied from ·027 to ·035, according as melting points or solidifying points were suitably considered. Since, therefore, the fusion both of the organic bodies and the silicate is alike in character, it is probable that the same factor dT/dp will correspond to both cases. The direct consideration of these questions will be the subject of the next chapter.

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[1] See my work on naphthalene, Am. Journal Sci., vol. 42, 1891, p. 144 et seq.

CHAPTER III.

THE THERMAL CAPACITY OF IGNEOUS ROCK, CONSIDERED IN ITS BEARING ON THE RELATION OF MELTING POINT TO PRESSURE.[1]

PRELIMINARY REMARKS.

41. Introductory.—The present experiments are in series with the volume measurements of my last chapter, and the same typical diabase, § 18, was operated upon. Since it is my chief purpose to study the fusion behavior of silicates, more particulurly the relation of melting point to pressure, the observations (700° to 1400°) are restricted to an interval of a few hundred degrees on both sides of the region of fusion. The solid locus found, however, is one which would be nicely tangent to an initial specific heat of about ·2, the value which probably obtains. The liquid locus is again indicative of a transitional temperature.[2]

42. Literature.—Experiments similar to the present, but made with basalt, were published quite recently by Profs. Roberts-Austen and Rücker.[3] In view of the normal behavior occurring throughout my own data, the irregularities obtained by these gentlemen in case of different methods of treatment (heating in an oxidizing or reducing atmosphere, repeated heating, sudden cooling, etc.), the anomalously large specific heat between 750° and 880°, where basalt is certainly solid, and the absence of true evidences for latent heat[4] make their results somewhat startling. Basalt is lithologically so near akin to diabase that one would anticipate a close physical similarity in the two cases. Unfortunately, the account given of the work with basalt is meager, and detailed comparisons are therefore impossible. I will only state that as nobody had then compared the platinum-rhodium couple with the air thermometer, I should not have regarded a standardization by means of a single melting point sufficient.

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[1] Cf. Am. Journal Sci., vol. 43, 1892, pp. 56, 57.

[2] Am. Journal Sci., vol. 42, 1891, p. 145.

[3] Roberts-Austen and Rücker: Phil. Mag., vol. 32, 1891, p. 355.

[4] Supposing basalt to melt below 1200°. The authors state that the specific heat of basalt is greater in the liquid than in the solid state, but no remarks are made as to whether the rock was fused at their higher temperatures or not.

APPARATUS.

43. The rock to be tested.—About 30 grams of diabase were fused in a small platinum crucible, together with which they were to be dropped into the calorimeter. Two of these charged crucibles were in hand and used alternately. After removing the (cold) crucible from the water into which it had been dropped at red or white heat, the surface of the glass usually shows a smooth unfissured gloss. This, however, is only apparent, for after drying and weighing, the mass is often found to have increased in weight fully 5 per cent. I was at first inclined to believe that this was due to water chemically absorbed by the viscous magma; but the water is only mechanically retained, for it passes off completely after twenty-four hours' exposure to the atmosphere, or by drying at 200° for, say, 30 minutes. Hence, at the beginning of each measurement I weighed the crucibles again, having thoroughly dried them at 200°. The solid glass dropped into water at low red heat soon shows a rough and fissured surface, and changes in color from black to brown, possibly from the oxidation of the protosilicate to the sesquisilicate of iron. The effect of this change (if it be a chemical change and not a mere change of the optical character of the surface) is inappreciable, at least by the following calorimetric method.

Throughout the course of the work the charge was neither changed nor replenished.

44. Thermal capacity of platinum.—Since the charge of molten rock and the crucible are submerged together, it is necessary to know the heat given out by the known weight of the platinum. Data for this purpose have been published by Violle.[1] In these the high temperature specific heat at t° is given as $\cdot0317+\cdot000012t$, whence the increase of thermal capacity from zero to the same temperature is $(\cdot0317+\cdot000006t)\,t$. This is the allowance I made per gram of platinum crucible.

45. Furnace.—Inasmuch as heat is rapidly lost by radiation from the white hot slag, it is necessary to transfer the crucible from the furnace into the water swiftly. Trap-door and false-bottom arrangements, which at first suggested themselves, were discarded, because the mechanism clogs the furnace, interferes with constancy of temperature, and is too liable to get out of order.

The furnace adopted is shown in Pl. VII, Figs. 1 and 2, in sectional elevation and plan. The body consists of two similar but independent half cylinders *AA* and *BB* of fire clay, properly jacketed and closed below, which come apart along the vertical plane *cccc*. The lid *LL*, however, is a single piece, fixed in position by an adjustable arm (not shown). Each of the halves of the body of the furnace is protected by a thick coating of asbestos *CC*, *DD*, and by a rigid case of thick sheet iron, *EE*, *FF*; clamp screws *g*; *g*, *g*, *g*, pass through this in such a way as

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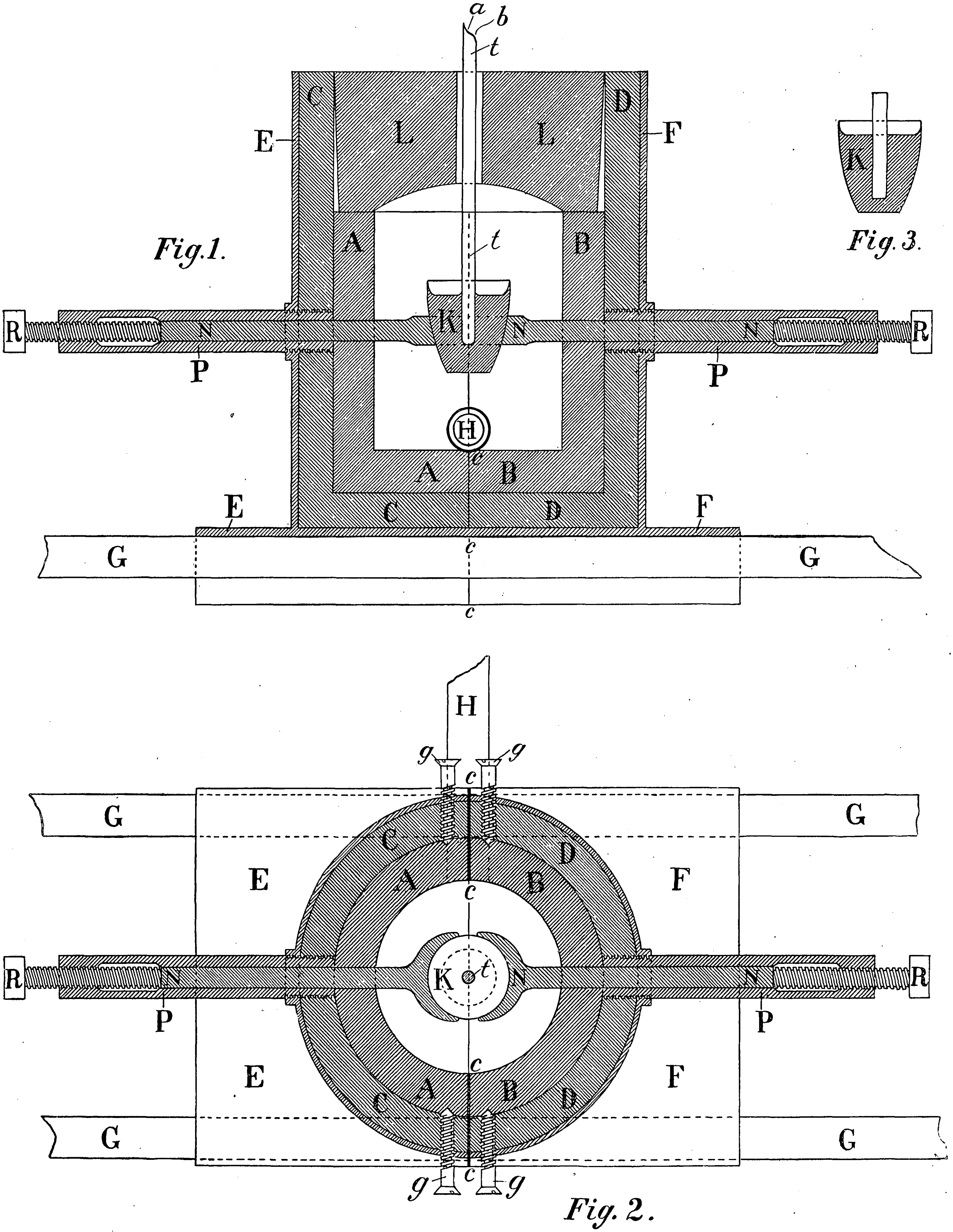
[1] Violle: C. R., vol. 85 1877, p. 543; vol. 87, 1878, p. 981; vol. 89, p. 702, 1879; Phil. Mag., (5), IV, p. 318, 1877.



FURNACE FOR CALORIMETRY, WITH THE BODY K (CRUCIBLE), THE PYROMETER *tt*, AND THE HOLDERS N N IN PLACE. SCALE ⅛.

to hold the fire clay and asbestos firmly in place. The horizontal base of the casing *E*, *F*, is bent partially around the two iron slides *G*, *G*, along which the two halves of the furnace may therefore be moved at pleasure while the lid *L* is stationary, as is also the blast burner *H*, clamped on the outside and entering the furnace through a hole left for that purpose.

The charged crucible is shown at *K*, and is held in position by two crutch-shaped radial arms, *N*, *N*, of fire clay, the cylindrical shafts of which fit the iron tubes *P*, *P* snugly and are actuated by two set screws, *R*, *R*. The two tubes *P*, *P*, moreover, are covered with a non-conductor, and thus subserve the purposes of handles, by grasping which the two halves of the furnace may be rapidly jerked apart. It is by this means that the crucible is suddenly dropped out of the furnace into the calorimeter below. Care must be taken to have the arms free from slag, as otherwise the crucible is not at once released.

46. Temperature.—As in a former case, the temperature of the furnace is regulated at pleasure by forcing the same quantity of air through it at all times, but lading this air with more or less gas supplied by a graduated stop cock. The amount of gas necessary in any case is determined by trial, and observations are only to be taken after fifteen or twenty minutes' waiting, when the distribution of temperature is found to be nearly stationary. It would have been better to have curved the bottom of the furnace cylindrically, so as to surround the crucible with a whorl of flame. The temperature of the crucible is never quite constant from point to point. I therefore measured this datum at three points, near the bottom, middle, and top of the charge. For this purpose the fire clay insulator *t t* of the platinum platinum-iridium thermocouple *ab* passing through a hole in the lid is adjustable along the vertical. Before dropping the crucible the thermocouple is withdrawn from the charge and suspended above it. The cold junction communicates with the terminals of the zero method submerged in a bath of petroleum and provided with a thermometer.

When the charge is solid, a small platinum tube which has been previously sunk into the molten glass before solidification (see Pl. VII, Fig. 3), enables the observer to make the three temperature measurements, as before. In later measurements I also incased the insulator of the thermocouple in a platinum tube, closed below (see Pl. VII, Fig. 1), when making the temperature measurements for the molten charge. Slag at high temperature being a good conductor, it is not impossible that hydro-electromotive forces may enter, slightly distorting the thermoelectric data.

When constancy of temperature is being approached the hole in the lid *L L* is closed with asbestos, and the products of combustion escape by the seam in the side. This facilitates manipulation above the furnace. The crucible is visible in part through the seam in question.

47. *Calorimeter.*—This was a vessel of thin tinned sheet iron, 28 centimeters long and 8 centimeters in diameter, having a water value of 19 g. cal. and holding a charge of about 1,200 grams of water. The inside of the calorimeter was provided with a helical strip running nearly from top to bottom. The vessel, contained within a suitable environment, was supported on a hard rubber stem, which could be grasped below, and served as an axle around which the calorimeter could be rotated from without. In this way the water within was churned. Three small, hard-rubber rowels near the top gave steadiness to the motion. They were fixed to the hollow cylindrical vessel (environment) provided with a hollow hinged lid, through both of which a current of cold water, at constant temperature, continually circulated. Thus the temperature surrounding the calorimeter was at all times given, and the correction for cooling could be found and applied with accuracy. I pass by the description of this apparatus rapidly here, inasmuch as I shall recur to it in connection with other calorimetric work. The box of the calorimeter with its projecting stem was movable on a small tramway, the tracks of which lay at right angles to the slides *G G*. (Pl. VII, Figs. 1 and 2.) Thus when the measurements showed a sufficiently constant temperature in the furnace, the lid of the box was opened and the calorimeter rolled directly under the furnace. After receiving the crucible, the calorimeter was again rolled away and the lid of the box closed, whereupon the temperature measurements were made by aid of a sensitive thermometer inserted through a hole in the lid.

I may add here that should I have occasion to extend the work to other substances, I would have a bullet-shaped platinum crucible provided with a central tube similar to Fig. 3, made at the outset. In this way splashing during the drop of the crucible into water would be to a great extent obviated.

RESULTS.

48. *Method of work.*—While waiting for the temperature of the furnace to become stationary, I made the initial measurements for the cooling of the calorimeter, in time series. Knowing, therefore, the time at which the body was dropped, I also knew accurately the temperature of the water into which it was dropped. Just before this the three measurements for temperature of the charge had also been made in time series. The experiments showed that ten minutes after submergence, the crucible and charge might be safely considered cold, for the minimum temperature of the calorimeter was reached after about five minutes. Hence the time from 10 minutes to 15 minutes after submerging could be utilized for making the final measurements for cooling. Knowing these, I interpolated the rates of cooling for any intermediate times.

Thus while the calorimeter was being constantly stirred, its temperature was measured at the end of every minute. Hence I knew the mean excess of its temperature above that of its environment during the course of every minute, and was able to add the corresponding allowance for radiation at once. How important this is the tables below will fully show. It may amount to 10 per cent of the total temperature increment. The only drawback against obtaining sharp values for the consecutive rates of cooling is to be found in the lag error of the thermometer; but this is eliminated in a long series.

The calorimeter was always weighed before and after the work, but the latter datum was taken. Similarly, as has been stated, the crucible was weighed before and after heating and the latter datum taken. Some charge is always removed or added by the thermocouple.

49. Arrangement of the tables.—There being two crucibles and two tubes (Pl. VII, Fig. 3), they are distinguished by *I* and *II*. In all cases τ is the temperature of the environment, m the mass of the charge, M the water value of the calorimeter (corrected for temperature). Θ is the temperature at the bottom, middle, and top of the charge at the time of submergence, for which a mean value is also given. The temperature observed in the calorimeter at the time specified is given under θ, and a parallel column shows the correction of θ for radiation. Finally, the computed thermal capacity of the platinum crucible and appurtenances (correction h), and the thermal capacity h of the charge given for each of the consecutive times, are found in the last columns. A few obvious remarks follow. All data are referred to gram calories.

50. Tables.—In the data of the first series (Table 16) only one value of Θ occurs for the liquid state. Moreover, the construction of the furnace was somewhat faulty, not being flat-bottomed. Hence these results are of inferior accuracy, and their chief purpose is to bear out the results of Table 17, which are the best I could obtain.

TABLE 16.—*Thermal capacity of diabase. First series.*

Platinum crucible *I*, $11·169^{g}$; platinum tube *I*, $·985^{g}$.
Platinum crucible *II*, $11·271^{g}$; platinum tube *II*, $·654^{g}$.

No.	τ	Time.	Θ	Mean Θ M m.	θ	Correction θ	correction h.	h.	Remarks.
	°C	minutes.			°C		g. cal.	g. cal.	
I	16	25	....	1306°	25·90	....	....	....	Immersion
		26	....	1145^{g}	34·90	·07	16·6	291	Liquid.
		27	....	$33·75^{g}$	36·30	·17	....	342	
		28	....	....	36·60	·27	....	355	
		30	....	....	36·59	·48	....	363	
		33	....	....	36·32	·79	....	364	} 364
		36	....	....	36·04	1·10	....	365	
I	12	5	....	1367°	14·92	....	....	....	Immersion
		6	....	1202^{g}	22·80	·02	17·9	267	Liquid.
		7	....	$33·36^{g}$	25·20	·06	....	355	
		8	....	....	25·50	·11	....	367	
		10	....	....	25·58	·20	....	372	
		13	....	....	25·40	·33	....	370	
		16	....	....	25·25	·46	....	370	} 370
		19	....	....	25·12	·60	....	370	
II	12	26	....	1378°	22·16	....	....	....	Immersion
		27	....	1202^{g}	30·00	·05	20·7	302	Liquid.
		28	....	$29·32^{g}$	31·00	·13	....	346	
		29	....	....	31·70	·21	....	378	
		31	....	....	31·67	·38	....	384	
		34	....	....	31·42	·63	....	384	
		37	....	....	31·21	·87	....	385	} 385
		40	....	....	30·97	1·11	....	386	

TABLE 16.—*Thermal capacity of diabase. First series*—Continued.

No	τ	Time.	Θ	Mean Θ M m.	θ	Correction θ	correction h.	h.	
	°C	minutes.			°C		g. cal.	g. cal.	
I	12	36	....	1337°	14·55	....	....	....	Immersion
		37	....	1196^{g}	22·40	·02	18·0	275	Liquid.
		38	....	$32·22^{g}$	24·00	·07	....	337	
		39	....	....	24·80	·12	....	368	
		41	....	....	24·79	·23	....	371	
		44	....	....	24·68	·39	....	373	}
		47	....	....	24·55	·54	....	375	} 373
		50	....	....	24·40	·69	....	375	}
II	12	9	....	1274°	21·92	....	....	....	Immersion
		10	....	1196^{g}	28·50	·05	17·1	256	Liquid.
		11	....	$29·16^{g}$	29·80	·13	....	312	
		12	....	....	30;60	·21	....	349	
		14	....	....	30·63	·38	....	356	
		17	....	....	30·42	·62	....	358	}
		20	....	....	30·22	·86	....	359	} 358
		23	....	....	29·98	1·10	....	359	}
I	12	15	1199	1166°	14·87	....	....	....	Immersion
		16	1163	1195^{g}	22·60	·03	16·7	271	Solid.
		17	1138	$32·22^{g}$	23·10	·09	....	292	
		18	....	....	23·30	·15	....	302	
		20	....	....	23·37	·27	....	308	
		23	....	....	23·21	·45	....	309	}
		26	....	....	23·15	·63	....	314	} 311
		29	....	....	22·98	·81	....	314	}
II	12	1	1100	1078°	21·16	....	....	....	Immersion
		2	1074	1196^{g}	27·20	·04	16·4	232	Solid.
		3	1060	$29·16^{g}$	27·80	·09	....	259	
		4	....	....	27·90	·15	....	266	
		6	....	....	27·76	·25	....	264	
		9	....	....	27·59	·42	....	264	}
		12	....	....	27·41	·58	....	263	} 263
		15	....	....	27·25	·74	....	263	}
I	11	1	1021	1001°	14·89	....	....	....	Immersion
		2	998	1196^{g}	20·40	·02	13·9	191	Solid.
		3	983	32.23^{g}	21·40	·07	....	230	
		4	....	....	21·58	·11	....	238	
		6	....	....	21·58	·20	....	242	}
		9	....	....	21·45	·34	....	242	} 242
		12	....	....	21·31	·47	....	242	}
II	11	2	1035	1025°	19·76	....	....	....	Immersion
		3	1025	1195^{g}	25·00	·03	15·5	201	Solid.
		4	1015	$29·16^{g}$	25·90	·08	....	240	
		5	....	....	26·20	·14	....	254	
		7	....	....	26·10	·25	....	255	
		10	....	....	25·90	·41	....	253	}
		13	....	....	25·72	·57	....	252	} 253
		16	....	....	25·55	·73	....	252	}
I	11	1	889	880°	16·19	....	....	....	Immersion
		2	880	1198^{g}	21·80	·03	12·0	198	Solid.
		3	872	$32·24^{g}$	21·90	·06	....	203	
		4	....	....	21·94	·10	....	206	
		6	....	....	21·83	·18	....	204	}
		9	....	....	21·70	·30	....	204	} 204
		12	....	....	21·59	·41	....	204	}
II	11	8	827	829°	20·07	....	....	....	Immersion
		9	827	1192^{g}	24·50	·04	12·1	171	Solid.
		10	833	$29·16^{g}$	24·90	·09	....	189	
		11	....	....	24·90	·14	....	191	
		13	....	....	24·85	·23	....	193	
		16	....	....	24·67	·37	....	191	}
		19	....	....	24·51	·51	....	190	} 191
		22	....	....	24·39	·65	....	190	}

TABLE 17.—*Thermal capacity of diabase. Second series.*

Platinum crucible *I*, 11·169g; Platinum tube *I*, ·985g.
Platinum crucible *II*, 11·271g; Platinum tube *II*, ·654g.

No.	τ	Θ	Mean Θ *M* *m*.	Time.	θ	Correction θ	Correction *h*.	*h*.	
	°C.	°C.		minutes.	°C.	°C.	g. cal.	g. cal.	
II	12	1265	1251°	4	18·94	....	....	....	Immersion
		1246	1189g	5	24·60	·04	20·6	236	Liquid.
		1241	26·39g	6	26·05	·10	....	305	
				7	26·52	·16	....	329	
				9	26·61	·30	....	339	
				12	26·45	·50	....	341	340·5
				15	26·25	·69	....	340	
				18	26·08	·88	....	341	
I	12	997	993°	2	14·07	....	....	....	Immersion
		995	1192g	3	20·20	·01	13·8	213	Solid.
		987	32·22g	4	20·56	·03	....	227	
				5	20·80	·05	....	237	
				7	20·80	·10	....	239	238·3
				10	20·75	·16	....	239	
				13	20·61	·22	....	237	
II	12	1260	1251°	3	19·34	....	....	....	Immersion
		1251	1190g	4	26·00	·04	20·8	285	Liquid.
		1243	26·07g	5	27·00	·10	....	333	
				6	27·20	·16	....	345	
				8	27·03	·27	....	342	
				11	26·86	·45	....	343	342·5
				14	26·69	·62	....	343	
				17	26·49	·80	....	342	
II	10	1354	1334°	5	13·78	....	....	....	Immersion
		1333	1190g	6	20·60	·03	22·4	288	Liquid.
		1319	26·27g	7	21·80	·09	....	345	
				8	22·20	·15	....	366	
				10	22·23	·28	....	373	
				13	22·12	·47	....	377	376·6
				16	21·97	·65	....	378	
				19	21·79	·84	....	378	
I	10	954	948°	9	20·24	....	....	....	Immersion
		948	1186g	10	26·00	·05	13·0	201	Solid.
		942	32·22g	11	26·40	·12	....	218	
				12	26·52	·19	....	225	
				14	26·42	·33	....	227	
				17	26·22	·53	....	227	226·6
				20	26·01	·74	....	227	
				23	25·81	·94	....	227	
II	10	1364	1352°	9	17·18	....	....	....	Immersion
		1354	1194g	10	23·70	·04	23·1	277	Liquid.
		1339	26·05g	11	24·80	·10	....	330	
				12	25·20	·16	....	351	
				14	25·42	·29	....	368	
				17	25·19	·49	....	366	367·0
				20	25·01	·68	....	367	
				23	24·82	·87	....	367	
I	10	877	873°	0	14·83	....	....	....	Immersion
		873	1191g	1	19·80	·02	11·9	173	Solid.
		870	32.20g	2	20·30	·06	....	193	
				3	20·60	·09	....	205	
				5	20·48	·16	....	203	
				8	20·38	·26	....	203	202·1
				11	20·23	.36	....	201	
				14	20·13	·46	....	201	
II	10	1176	1166°	5	17·40	....	....	....	Immersion
		1164	1187g	6	24·30	·04	19·2	281	Liquid.
		1158	25·97g	7	24·70	·10	....	301	
				8	24·80	·16	....	308	
				10	24·75	·27	....	311	
				13	24·55	·44	....	309	309·5
				16	24·39	·60	....	309	
				19	24·21	·77	....	309	
II	10	1215	1197°	7	14·38	....	....	....	Immersion
		1191	1192g	8	20·00	·03	19·9	239	Liquid.
		1186	25·95g	9	20·80	·07	....	278	
				10	21·50	·12	....	312	
				12	21·55	·21	....	319	
				15	21·40	·35	....	318	318·5
				18	21·26	·49	....	318	
				21	21·13	·62	....	318	
I	10	782	781°	9	19·36	....	....	....	Immersion
		780	1189g	10	24·00	·05	10·4	163	Solid.
		780	32·19g	11	24·20	·12	....	173	
				12	24·18	·19	....	175	
				14	24·13	·33	....	178	
				17	23·95	·54	....	179	179·7
				20	23·81	·74	....	181	
				23	23·61	·94	....	181	

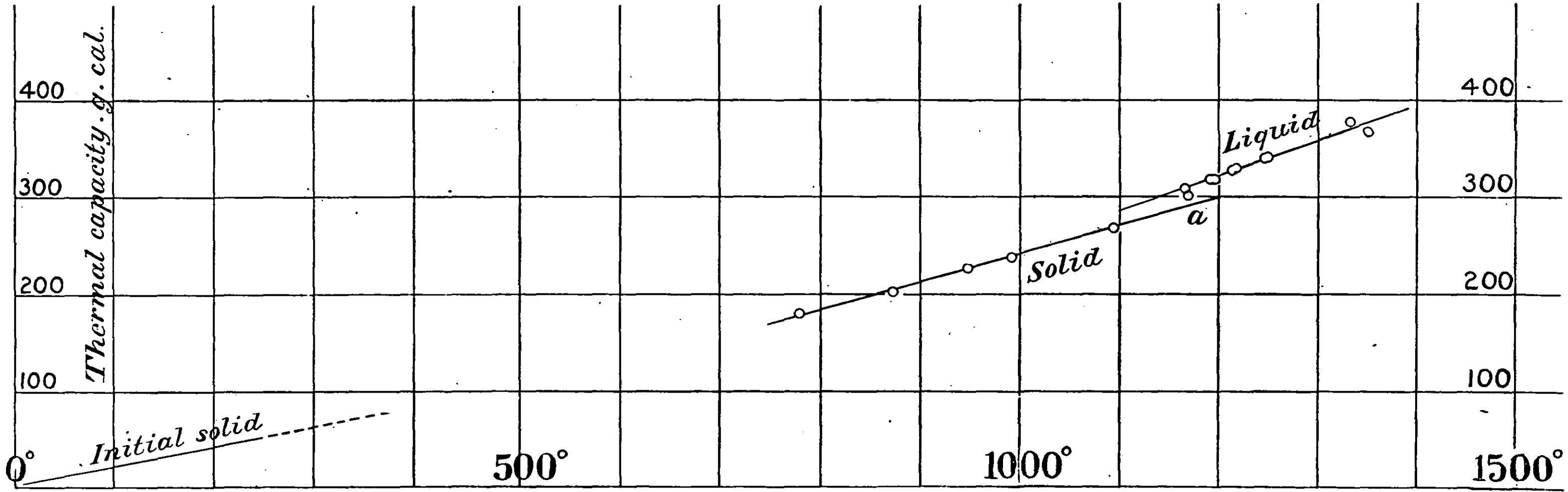
TABLE 17.—*Thermal capacity of diabase. Second series*—Continued.

No.	τ	Θ	Mean Θ *M* *m*.	Time.	θ	Correction θ	Correction *h*.	*h*.	
	°C.	°C.		minutes.	°C.	°C.	g. cal.	g. cal.	
II	10°	1204	1194°	8·5	14·54	....	....	....	Immersion
		1195	1195^{g}	10	21·60	·03	19·9	307	Liquid.
		1183	25·90^{g}	11	21·70	·08	....	314	
				12	21·70	·13	....	316	
				14	21·63	·23	....	318	
				17	21·49	·37	....	318	317·9
				20	21·36	·51	....	318	
				23	21·22	·66	....	318	
I	10	1177	1171°	8	19·88	....	....	....	Immersion
		1170	1192^{g}	9	25·20	·05	16·7	182	Solid.
		1166	32·20^{g}	10	28·20	·13	....	296	
				11	28·30	·21	....	303	
				13	28·07	·37	....	300	
				16	27·95	·62	....	304	301·6
				19	27·62	·86	....	302	
				22	27·37	1·10	....	301	
I	11	1106	1096°	0	16·28	....	....	....	Immersion
		1094	1195^{g}	1	22·70	·03	15·5	224	Solid.
		1088	32·21^{g}	2	23·60	·08	....	259	
				3	23·75	·13	....	266	
				5	23·69	·23	....	268	
				8	23·54	·39	....	268	268·2
				11	23·39	·54	....	268	
				14	23·24	·68	....	268	
II	11	1262	1248°	1	19·72	....	....	....	Immersion
		1244	1191^{g}	2	25·90	·05	21·1	270	Liquid.
		1238	25·49^{g}	3	26·60	·11	....	305	
				4	27·20	·17	....	336	
				6	27·11	·31	....	338	
				9	26·92	·50	....	339	338·8
				12	26·73	·70	....	339	
				15	26·55	·89	....	339	
I	11	1237	1218°	8	13·67	....	....	....	Immersion
		1216	1188^{g}	9	20·60	·02	17·7	263	Liquid.
		1202	29·43^{g}	10	21·40	·07	....	297	
				11	22·00	·12	....	324	
				13	22·05	·23	....	330	
				16	21·90	·38	....	330	330·3
				19	21·75	·54	....	330	
				22	21·60	·69	....	330	
II	11	1224	1215°	5	19·73	....	....	....	Immersion
		1215	1185^{g}	6	25·20	·04	20·4	235	Liquid.
		1205	25·57^{g}	7	26·40	·11	....	293	
				8	26·90	·19	....	320	
				10	26·90	·32	....	326	
				13	26·68	·54	....	326	326·6
				16	26·49	·75	....	327	
				19	26·27	·95	....	326	

For brevity the last observations have been averaged per three minutes, and under *h* the mean for the last 11 minutes is usually given.

Thus in Series I the difference of temperature from top to bottom of the crucible is as large as 61° at 1200°, but falls off pretty regularly to 6° at 829°. In Series II the corresponding mean difference is about 25° at 1300°, 20° at 1200°, 14° at 1100° and 1000°, and 10° at 900° and 800°. The error thus involved can not be greater than 2 per cent in the extreme case; but since the distribution of temperatures is actually measured, the error is probably negligible except at very high temperatures. I was inclined to infer that the greater constancy of the solid distribution as compared with the liquid was due to better conductivity in the former case (solid); but it may result as an equalizing effect of the tube, Pl. VII, Fig. 3.

Considering the observational work as whole, the data are quite satisfactory, seeing that an error of $\frac{1}{10}$° C. in the initial temperature of the



RELATION OF THERMAL CAPACITY (SOLID AND LIQUID) TO TEMPERATURE (°C.). SERIES I.

calorimeter must vitiate the result as far as at least 1 per cent. Hence the great care taken in finding this temperature. It is probable, however, that the real source of error is accidental and is encountered when the body falls out of the furnace into the water, particularly during the latter phase. Splashing, generation of steam, etc., then involve actual losses which can not be accounted for.

INFERENCES.

51. *Digest and charts.*—In Tables 18 and 19 I have summarized the chief data on a scale of temperature. The results are graphically given in the charts, Pls. VIII and IX, in which thermal capacity in gramme calories is constructed as a function of temperature. Straight lines are drawn through the points, showing the mean specific heats for the intervals of observation, solid and liquid. The letter *a* marks the region of fusion.

It will be seen that both in the cases of Pl. VIII and Pl. IX the solid points lie on lines which, if reasonably curved, would be nicely tangent to an initial specific heat of about .2 at 0° C. The grouping, in other words, is so thoroughly regular as quite to exclude the probability of any anomalous feature in the observed or the unobserved parts of the locus. In both charts the solid point near *a* alone lies markedly above the corresponding curve; but inasmuch as in my former work I found solidification to set in at 1,100° it is altogether probable that the occurrence at 1,170° is incipient fusion.

TABLE 18.—*Thermal capacity of diabase. Series I. Digest.*

Mean specific heat, liquid, 1200° to 1400°, ·350.
Mean specific heat, solid, 800° to 1100°, ·304.
Latent heat of fusion, at 1200°, 24^{gcal}; at 1100°, 16^{gcal}.

Solid.		Liquid.	
Temperature.	Thermal capacity.	Temperature.	Thermal capacity.
829	191	1274	358
880	204	1306	364
1001	242	1337	373
1025	253	1367	370
1078	263	1378	385
*1066	311		

*Incipient fusion? Tube sustained in the crucible.

TABLE 19.—*Thermal capacity of diabase. Series II. Digest.*

Mean specific heat, solid, 800° to 1100°, ·290
Mean specific heat, liquid, 1100° to 1400°, ·360.
Latent heat of fusion, 1200°, 24^{gcal}; at 1100°, 16^{gcal}.

Solid.		Liquid.	
Temperature.	Thermal capacity.	Temperature.	Thermal capacity.
°C.	gcal.	°C.	gcal.
781	180	1166	309
873	202	1194	318
948	227	1197	318
993	238	1215	327
1096	268	1218	330
*1171	302	1248	339
		1251	340
		1251	342
		1334	377
		1352	367

*Probably incipient fusion at the base of crucible (1177°).

Quite the same regularity is observable in the liquid loci, remembering that in Pl. VIII only a single datum was taken for temperature, and that in Pl. IX the high-temperature discrepancies above 1300° are within the range given in § 50, and due to distribution of temperature.

52. *Specific heat.*—As regards the mean specific heat between 800° and 1000°, in Tables 18 and 19, it will be seen that the intermediate datum (·304+·290)/2 would satisfy both groups of points about equally well. A tracing of one group of points nearly covers the other, while it is to be remembered that the true locus must be slightly curved. The same remarks may be made for the liquid state. I have discarded elaborate modes of reduction, since the equation of the locus would be arbitrary, and since the values for specific heat are of no immediate bearing on the present inquiry.

53. *Hysteresis.*—Recurring to the suggestion of the preceding paragraph, it appears, since in my volume experiments I was able to cool down the rock to 1095° before solidification definitely set in, whereas, now, evidences for fusion do not occur before 1170° (at *a*, Pls. VIII and IX) that rock fusion must be accompanied by hysteresis[1] of the same nature as that which I observed with naphthaline, § 37. The magnitude of the lag is apparently 70°, and its pressure equivalent may be estimated as 500 atmospheres.

54. *Latent heat.*—In virtue of the fact that the upper end of the solid locus can be carried so near the beginning of the liquid locus, the datum for latent heat is determinable with some accuracy. A difficulty, however, presents itself in the determination of the true melting point, a datum which can only be sharply defined while the temperature of the crucible is quite constant throughout. I, therefore, state the conditions at 1200° and at 1100°, where the latent heats would be 24 and 16 gramme calories respectively, in both of the independent constructions of Pl. VIII and Pl. IX. This coincidence is in a measure accidental.

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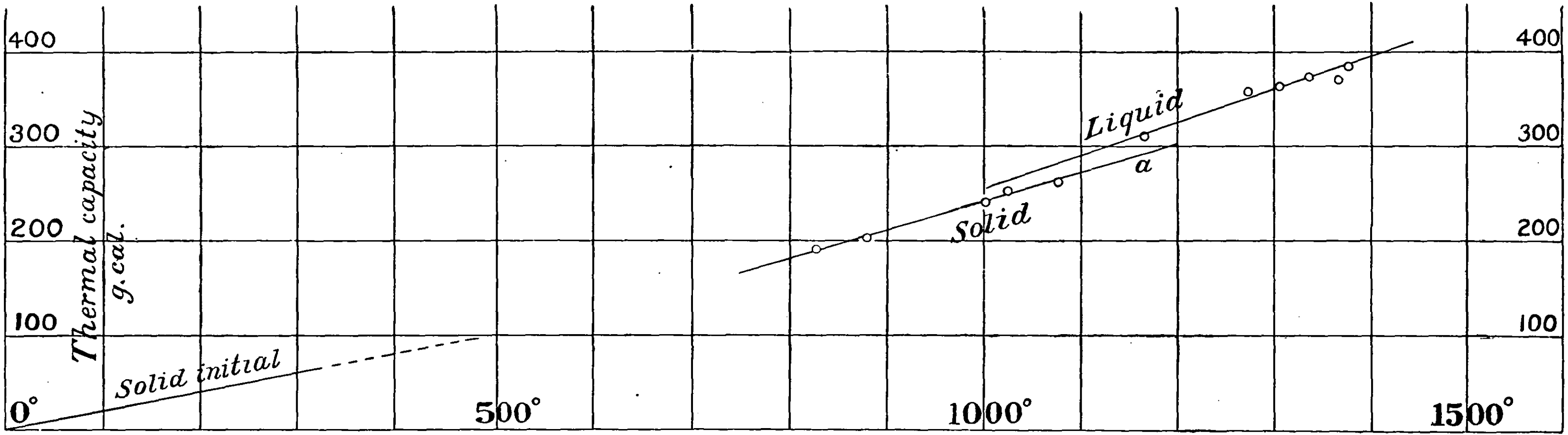
[1] Am. Journal, XLII, p. 140, 1891.



RELATION OF THERMAL CAPACITY (SOLID AND LIQUID) TO TEMPERATURE (°C.). SERIES II.

It may be noticed that a transitional temperature surprisingly near the region of fusion is apparently indicated.

55. *The relation of melting point to pressure.*—The first and second laws of thermodynamics lead to the equivalent of James Thomson's fusion equation, which in the notation of Clausius[1] is

$$\frac{dT}{dp}=\frac{T\,(\sigma-\tau)}{E\,r'},$$

where T is the absolute melting point, $\sigma-\tau$ the difference of specific volumes solid and liquid at T, r' the latent heat of fusion, and E Joule's equivalent. Combining the present series, *I*, with the former series, *III*, of volume measurements,[2] I obtain at 1200°, since $T=1470°$, $\sigma-\tau=\cdot0394/2\cdot72$ (where 2·72 is the density of the solid magma at zero) and $r'=24$,

$$\left(\frac{dT}{dp}\right)_{1200}=\cdot021;$$

and at 1100°, since $T=1370°$, $\sigma-\tau=\cdot0385/2\cdot72$, and $r'=16$,

$$\left(\frac{dT}{dp}\right)_{1100}=\cdot029.$$

Similarly combining the present series, *II*, with the former series of volume measurements,[3] *IV*, at 1200°, since $\sigma-\tau=\cdot0352/2\cdot72$ and $r'=24$,

$$\left(\frac{dT}{dp}\right)_{1200}=\cdot019;$$

and at 1100°, since $\sigma-\tau=\cdot0341/2\cdot72$ and $r'=16$

$$\left(\frac{dT}{dp}\right)_{1100}=\cdot026.$$

Hence the probable silicate value of dT/dp may be taken as ·025, and falls nicely within the margin (·020 to ·036) of corresponding data for organic substances (wax, spermaceti, paraffin, naphthaline, thymol). I may therefore justifiably infer that the relation of melting point to pressure, in case of the normal type of fusion, is nearly constant, irrespective of the substance operated on, and in spite of enormous differences of thermal expansibility and (probably) of compressibility. And in the measure in which this is true in passing from carbon compound to the thoroughly different silicon compound, it is more probably true for the same substance changed only as to pressure and temperature. In other words the relation of melting point to pressure is presumably linear.[4]

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[1] Clausius: Wärmetheorie, I, p. 172, 1876. This is frequently called Clapeyron's equation.

[2] Chapter II, § 34.

[3] Chapter II, § 35.

[4] See my work on the continuity of solid and liquid (Am. Journ. Sci., Vol. xlii, p. 144, 1891), in which these relations are tested for naphthaline within an interval of 2,000 atmospheres.

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