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THE

VOLUME THERMODYNAMICS

OF

LIQUIDS

BY

CARL BARUS

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DEPARTMENT OF THE INTERIOR,
U. S. GEOLOGICAL SURVEY, DIVISION OF CHEMISTRY AND PHYSICS,
Washington, D. C., September 5, 1891.

SIR: I transmit herewith a manuscript by Dr. Carl Barus upon work done in the Physical Laboratory of this division, entitled "The Volume Thermodynamics of Liquids." I recommend that it be published as a bulletin of the Survey.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director.

PREFACE.

In the following chapters, I have commenced a serious study of the volume thermodynamics of liquids and solids. The work is, as yet, confined to volume, pressure, and temperature. Questions involving entropy and energy are also in active progress, but can not be included in the present bulletin.

Accordingly the first and third chapters describe the method of generating and measuring high pressure (i. e., pressures up to 2,000 or 3,000 atmospheres) in full. The second chapter treats of the isometrics of liquids, and it is found that they can be very nearly represented by straight lines (Levy, Ramsay, and Young). The fourth chapter finally traces the isothermals, as yet of but one substance; but the results are none the less noteworthy since they indicate the occurrence of a critical temperature solid-liquid, and show a probable method of coordinating the normal type of fusion with the ice type, in a continuous diagram. The far-reaching importance of hysteresis, as accompanying all changes of molecule, whether chemical or physical, whether induced by stress, magnetization, temperature, or the intervention of affinity, and whether observed electrically, mechanically, or chemically, etc., is emphasized.

The work as a whole is tributary to the geologic views of Mr. Clarence King, by whom the importance of a deeper insight into the volume changes of liquids and solids was pointed out. C. B.

ERRATUM.

In § 74 there is a wrong entry of volume. The effect is such a shifting of the coordinate axes that 0·5016 cm^3 must be added to all the subsequent volumes to correct the results. More rigorously an additional 0·000,011 cm^3 per degree centigrade is to be added, and 0·000,001,32 cm^3 per atmosphere deducted. The relations are therefore practically unchanged, and hence the inferences are sustained throughout.

THE VOLUME THERMODYNAMICS OF LIQUIDS.

By Carl Barus.

CHAPTER I.

METHOD OF OBTAINING AND OF MEASURING VERY HIGH PRESSURES.

INTRODUCTION.

1. Andrews's screw compressor has this advantage that the strains are all brought to bear within the compass of the barrel. In other arrangements, such for instance in which a cylindrical plunger is forced into the barrel, stress must be exerted on the bed plate or applied in a way tending to flexure of the plunger. It seemed to me, therefore, that the screw compressor might well be taken as a model for an apparatus of greater strength and efficiency than was necessary in Andrews's work. Indeed, Andrews himself seems to have been of this opinion,[1] and toward the close of his life devised an apparatus in which screw plungers are an essential part. Hannay and Hogarth,[2] however, were the first to carry a practical improvement of the screw into execution. They reached pressures but slightly short of 900 atmospheres, stating that their reasons for stopping work at this datum are quite apart from the efficiency of their apparatus. With the screw compressor[3] described below I obtain 2,000 atmospheres with facility (§ 17, 23). It is so constructed that a considerable volume of liquid can be operated upon, admitting of compressions of bulk of 5 cubic inches. Finally, special provision is made for the insulation of parts, thus enabling the operator to apply the essential electric methods in studying his test samples.[4]

Particular notice should here be given of the remarkable modification of Desgoffe's differential manometer, by which Amagat[5] succeeded in reaching and measuring more than 3,000 atmospheres of hydrostatic

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[1] See Prof. Everett's account in Nature, vol. 39, 1889, p. 556.

[2] Hannay and Hogarth: Chem. News, vol. 41, 1880, p. 103.

[3] It was constructed for me by the American Tool Company, No. 84 Kingston street, Boston, Massachusetts, Benjamin J. Radford, superintendent.

[4] I here have special reference to Prof. Tait's ingenious device in Trans. Roy. Soc. Ed., vol. 13, 1885-85, p. 2, Cf. Bieblätter, vol. 10, p. 149.

[5] Amagat: C. R., vol. 103, 1884, p. 429. Cf. chap. III.

pressure, but whereas on the one hand Amagat has as yet given only a meager account of his machine, Prof. Tait on the other has so recently described an apparatus on the principle of the "manomètre à pistons libres," that it seems expedient to refer the reader to Prof. Tait's memoir.[1]

THE SCREW COMPRESSOR.

2. *General method.*—The apparatus consists essentially of a strong wrought-iron barrel *ABC*, Pl. I, the head of which *AA* is suitably threaded, so that a steel screw *SSTT* can be forced into it. The piezometer tubes are attached at the end *CC* of the barrel. Barrel and tubes are quite filled with oil.

3. *Special devices.*—It will facilitate comprehension if I state here at the outset the two chief devices used in the construction of the machine. The first of these is the *tinned* screw. This is an ordinary, well-cut machine screw of iron or steel, covered with a uniform thin adhesive layer of solder by dipping it in a vessel of the fused metal, soldering salts being used in the ordinary way. Screws of this kind, when forced into their sockets, secure complete freedom from leakage. Gauges and other appurtenances may thus be attached to the barrel or removed from it with convenience. The other device is the gasket of marine glue[2] or other very viscous liquid. A stuffing box is easily made, by which this substance is kept pressed against the threads of the screw, or against the smooth walls of a cylindrical plunger. The viscosity of marine glue is such that, whereas it easily admits of being shaped by pressure to fill up any cavity, the substance is yet far too viscous to flow through capillary interstices like those between the metallic parts of a well-fitting screw, except after the lapse of an enormous time (months). Thus I found the absolute viscosity of the glue to be 200×10^6. It would therefore require 1,000 atmospheres to force the cement through a capillary aperture $.01^{cm}$ in diameter and 1^{cm} long, at the small rate of only $.05^{cm}$ per hour, supposing (an unfavorable supposition) that its viscosity does not increase under pressure. For larger pressures the rate is proportionately increased. Now, it is the property of the above screw to close the apertures under pressure, since the metallic parts under these circumstances are bound more closely together. This probably further accounts for the insignificant leakage actually observed. I may note in passing that the viscosity of a pitchy substance like marine glue is therefore 20 billion times that of water.

4. *Steel screw.*—To rotate the screw *ST* conveniently, it is provided with a lever and ratchet *LDRR*. The ratchet wheel is shown at *RR* in Pl. I, 1 and 3, and is cut so as to correspond with the right and left click *D*. A pin *E*, sliding in a socket of the lever *L*, and actuated

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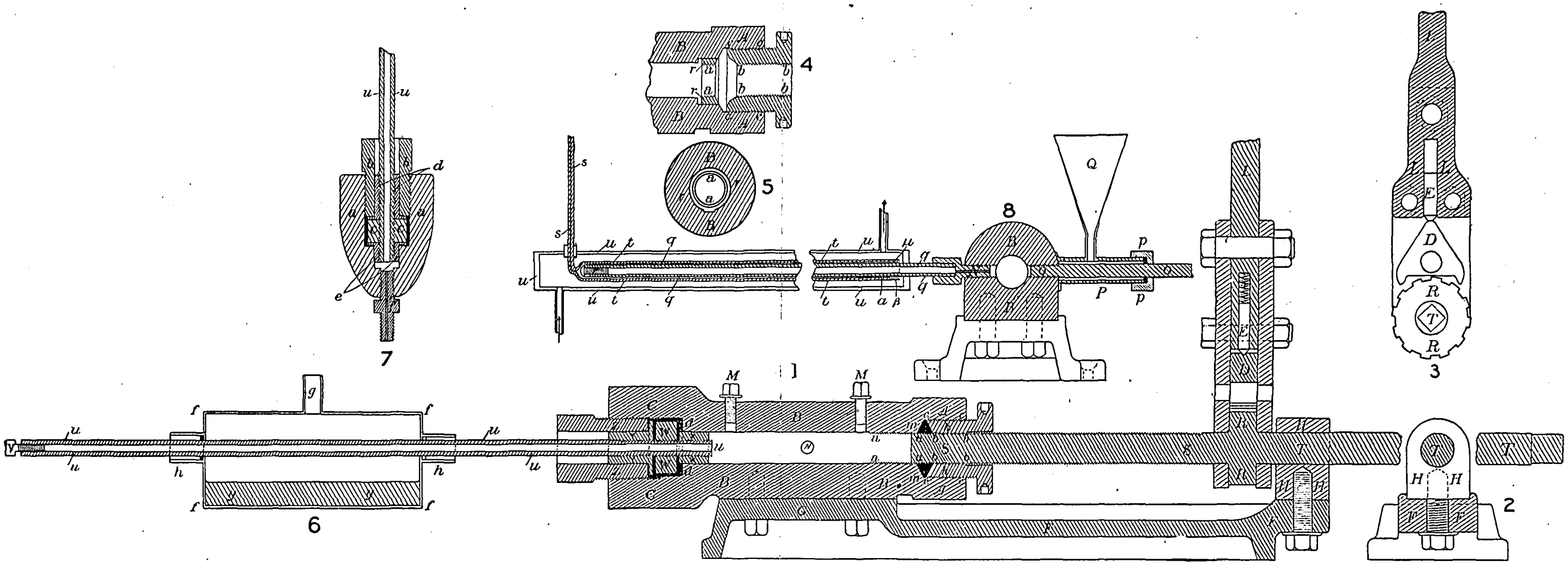
[1] Tait: *Challenger* Reports, 1873-'76, Physics and Chemistry, vol. 2. See Nature, vol. 41, p. 361, 1890.

[2] Supplied by M. Ducretet, of Paris, or by the Société Genevoise. It is a specially prepared mixture of rubber and shellac. It may be thickened by adding shellac.



SCREW COMPRESSOR, WITH PARTS IN PLACE.

by a spring, enables the operator to adjust the ratchet either for forward or retrograde motion of the screw *ST*, or wholly to withdraw the click from the ratchet, as shown in Pl. I, 3. The figure gives a full account of the manner in which the parts of the lever and ratchet are put together. The ratchet wheel is securely forged to the screw. Essential parts are made of steel.

The screw *ST* is 1 inch in diameter. On the front half of it a thread of 12 turns to the inch is cut from the end to about 1 inch of the ratchet wheel. The rear half is a cylindrical shaft held in position by a journal *HHH*. The latter is bolted down to the bedplate *FG*, and additionally secured between slides, as shown in Pl. I, 2.

5. *Barrel. Head.*—The planed front end of the cast-iron bedplate *FG*, the part *FF* of which is hollowed out so as to catch drippings, carries the barrel *BBB* already referred to. It is seen in cross-section in Pl. I, 8, and its flat side is firmly secured to the plane of the bedplate by two bolts. The head *AA* of the barrel carries the stuffing box *kk*, of special construction. The efficiency of the screw depends entirely on this arrangement, and it must therefore be described in detail. *kk* is a hollow steel nut of the form shown, and provided with a large flange for screwing it in place. Both the inner and the outer cylindrical surfaces of the nut *kk* are threaded, with 12 turns to the inch. Moreover, the inner thread *bbbb* of *kk* is a continuation of the thread *aaaa* in the walls of the barrel. And since the thread *cccc* also has 12 turns to the inch, it is clear that the nut *kk* can be forced in or out of the head *AA*, no matter what the position of the screw *ST* may be. In practice *cccc* is cut first and the nut screwed in place. After this the whole thread *bbaaaabb* is cut at one time. To prevent leakage of the oil in the barrel through the threads of the screw, the gasket of marine englue *mm* is inserted and kept firmly pressed against the threads by the gland *kk*. At high pressure the friction is sufficient to hold the nuts in place, thus obviating the need of lock nut.

It is seen that after the screw enters the barrel the chief strain of compression is borne by the thread *aaaa*. The threads *cccc* and *bbbb* hold the material of the stuffing box forcibly in place.

6. *Barrel. Head, improved.*—There is an objection to this form of stuffing box, inasmuch as at very high pressures the threads *aaaa* and *bbbb* tend to act as lock nuts on each other. To obviate this annoyance I devised the method shown in Pl. I, 4 and 5. Here the thread *aa* is movable, being on the inside of a ring *rr* of steel, which fits snugly in a socket of the barrel. The ring *rr*, though capable of moving back and forth, can not rotate, being prevented by a projection corresponding to a slot in the barrel. In this way the material in the stuffing box is not forced into the barrel on actuating *kk*. Note that the thread within *kk* is carried quite to the end, and that the inner face of *kk* is beveled very obliquely, thus allowing the gasket to encircle a greater number of threads of the screw *SS*. The strain is now borne by the thread *bb*. Experiment has shown this to be no disadvantage.

7. *Barrel. Body.*—This is perforated by four or more holes (Pl. I, 1) about three-eighths of an inch in diameter, and threaded to admit the tinned machine screws. Two of these *MM* are vertical, the other two *N*, *O* (Pl. I, 8), horizontal. They are of use in filling the barrel with oil, for attaching gauges and other appurtenances.

8. *Barrel. End with piezometer tube.*[1]—The steel tube *uuu* is inserted in such a way as to insulate it electrically from the barrel end *CC*. A screw is cut on the end of *uuu*, fitting into a cast-iron flange *WW* between two cylindrical jackets *XX* and *YY* of hard rubber or ivory. These parts *Y*, *W*, *X* are screwed to the end of the tube *U*, and the cylinders *Y* and *X* are turned large enough to fit the hole of the barrel and the internal aperture of the steel gland *ZZ* snugly. All space within the head *CC* is filled with marine glue *dd*. This is easily accomplished by melting the cement into the crevices between *Y* and *W*, *W* and *X*, before putting the piezometer in place. A thick gasket *dd* is also inserted. After this the remaining annular space around *W*, through which leakage might occur, is filled by forcing in the nut *ZZ* gradually, and at a temperature not too low.[2] To obviate possible electric contact between *W* and *Z*, the rubber jacket *Y* is flanged.

9. *Piezometer tube. Vapor bath.*—The further end of the piezometer *uu* is closed with a tinned screw *V*. The substance to be examined is inserted in ways which must be specially described for each experiment. As a rule the same tubes are adjusted within the compass of a copper vapor bath *ffff*, Pl. I, 6. This is a hollow cylinder, closed at both ends, through which a suitable thin copper tube *hh* passes somewhat above the middle and from end to end. The liquid *yy* to be boiled is introduced into *ffff* and heated with a large burner. The vapors escaping at *g* are condensed and run back, thus making the ebullition continuous. A number of baths of this kind are at hand, each containing a substance of suitable boiling point. In order to pass from one temperature to another it is merely necessary to slip off one vapor bath *ff* and slide on another. The copper vessels are to be surrounded with thick asbestos jackets in the usual way, and proper provision made to close up the ends of the tube *hh* so that convection currents may be obviated.

10. *Method of filling.*—When the screw is in good adjustment leakages are small and fresh supplies of oil are not frequently necessary. A convenient method of filling the screw with oil is indicated in Pl. I, 8. The steel rod *oo*, threaded at one end and provided with a strong cross

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[1] Weldless cold-drawn steel tubing of any dimension may be obtained from John S. Leng, New York, or of Philip S. Justice, Philadelphia, Pennsylvania. Both gentlemen are agents of English houses whose address is not known to me.

[2] The figure is somewhat diagrammatic here to exhibit the parts. In practice I use hard-rubber cylinders *XX* and *YY*, and two hard-rubber annular disks between *YY* and *WW* and *WW* and *XX*, respectively. When ready for insertion, the cylinders are screwed against *WW*, so that there are mere films of marine glue left between contiguous planes. Finally, the nut *ZZ* is brought in contact with the flange *YY* (disk) by pressure. It is in view of the fact that *YY* is pressed radially inward toward the axis of *UU*, as well as outward by pressure, that the arrangement holds so well. Repacking is only rarely necessary.

handle at the other, is surrounded by a cylindrical tube of brass *P* surmounted by a funnel-shaped inlet *Q*. Both *Q* and *P* are kept full of oil, and to prevent leakage there is an ordinary stuffing box at *pp*. A spring clamp (not shown in the figure) keeps the end of the tube *P* of the filler *PQ* appressed against the barrel *BB*, a leather washer being suitably interposed. To manipulate the filling arrangement, the pressure is taken off and *oo* screwed out without removing it from *P*. The oil in *PQ* will then follow the retreating screw *ST*, Pl. I, 1. To fill the barrel completely, one of the screws *M* may be removed until oil exudes. It is clearly advisable to remove all the air out of the barrel and piezometer tubes, otherwise *ST* must be forced in to a considerable part of its length before the air spaces are sufficiently compressed to sustain high pressure. Ordinary sperm oil or machine oil of a thickish quality, yet sufficiently thin to flow, is available for filling the barrel. It has a great advantage over water in not rusting the barrel, and in keeping the moving parts oiled. Mercury is objectionable, since it would dissolve the tin coating on the bolts, and thus soon produce leakage.

11. *Case for protection.*—Working as far as 2,000 atmospheres, explosions are not infrequent. They occur with slight detonation, scattering thin mists of oil. But there has been nothing of a serious nature. It is necessary, however, to surround the barrel with a case of 2-inch plank, and to put a barricade beyond the end of the piezometer tube. A tin pan, suitably fastened below the bed plate of the screw, is advantageous in catching oil. After filtering this may at once be used over again.

12. *Vertical piezometer.*—An adjustment similar to *CC uu*, but smaller in dimensions, and ending below in a finely perforated screw, may be attached at *M*. The piezometer is thus fixed in vertical position, and is easily adjusted or withdrawn, while the end of the barrel is available for other purposes. (§ 23.) A full view of the vertical piezometer is given in Pl. I, 7, and Pl. III, below, shows the same, with appurtenances.

In Pl. I, 7 *aa* is a hollow pear-shaped piece of steel, which can be attached to the barrel by means of the perforated tinned screw *f*. The piezometer tube of steel is shown at *uu*, and is provided with a steel flange piece *cc*. The hard rubber flanges for insulation are screwed on at *d* and *e*, and the system held in place in a medium of marine glue, by the steel gland *bb*. The advantage of the vertical adjustment lies in the fact that a surface of separation or meniscus of mercury is very much less apt to be broken in the vertical position of the column than is any other. It is also frequently desirable to produce gravitational separation of mixed liquids under pressure. Finally, since the apparatus Pl. I, 7 is complete in itself, the electrical and other adjustments may be made, and all glass apparatus within *uu* fastened before the piezometer is screwed into the barrel. Note that the tube *uu* and the barrel are insulated from each other.

PRESSURE MEASUREMENT.

13. *Tait gauge. Adjustment.*—The gauge connects at *N*, Pl. I, 8, and is shown at *qq*, *tt*, *ss*. The essential part is the steel tube *qq*, closed at one end by the tinned bolt *r*, and connecting at the other with the reducing piece *N*. I added *N* because it is not advisable to cut a deep thread in the tube *qq*. Connection may be made with *N* by a shallow fine thread and solder, and the connecting thread cut in the thick-walled tube of *N*. The tube *qq* is filled with oil. To measure the expansion of *qq* under pressure it is surrounded by a close-fitting glass tube *tttt*, one end of which is joined to the steel tube at $\mu\alpha\beta$ by a layer of marine glue. The other end of *tt* communicates with the vertical capillary tube *ss*, by which the expansions are measured.

It is clear that the shell-like space between the steel tube *qq* and the glass envelope *tt* must be filled with a liquid of small coefficient of expansion. I first tried mercury, but found it almost impossible to fill *tt* in such a way as to entirely exclude air. Moreover, in view of the friction of the mercury thread in *ss*, any trace of air in *tt* will produce irregular motion, and vitiate the experiment. Colored alcohol shows too much thermal expansion. I therefore used water colored with an alcoholic solution of fuchsine. Under these circumstances a sufficient constancy of temperature may be obtained by surrounding *tt* with a jacket *uu* of circulating cold water coming directly from the hydrant. Thus the temperature error may be reduced so as not to exceed 10 atmospheres, reasonably slow motion of the screw presupposed. (See below.) To keep the liquid in *ss* at a given fiducial mark, a special adjustment for moving the meniscus suggests itself; but this is an exceedingly difficult device to apply, seeing that there must be the minimum of water in *tt*, and that obsolutely tight joints are essential. Hence I raise or lower the meniscus and color it, when faded, by inserting filimentary glass tubes into the canal of *ss*. Such tubes are easily made by drawing out a wide glass tube and then covering the open wide end with a rubber cap. Using such tubes there is little difficulty either in adding more liquid to the thread in *ss* or in withdrawing liquid from it.

It is advisable to protect the steel tube *qq* from rusting, either by nickel-plating it or in other ways. I observed, however, that water free from air and containing a little alcohol-does not easily rust iron. After an exposure of several months, bright surfaces were still untarnished. A dilute solution of rubber may possibly be used for coating the tube. Thick coats are to be avoided, because they interfere with the expansion.

In later experiments I made the joint at the closed end of the glass envelope hermetic and rigid, as follows: In Pl. I, 8 *α* is a layer of marine glue between steel and glass, and μ a plug of fusible metal, the whole being surrounded by an external close fitting copper envelope (wired to the glass) β. The latter being a prolongation of the glass tube, the layers a and μ are melted in, while the gauge is held in a vertical position. The effective part of the steel tube qq is about 100^{cm} long, 1^{cm} thick externally, and $\cdot 5^{cm}$ in internal bore. A capillary tube of the rather wide bore $\cdot 07^{cm}$ is then sufficient for measurement, showing a displacement of meniscus of nearly 2^{cm} per 100 atmospheres pressure. Data are given more accurately below. My reasons for using a long tube are these: That the effective length can be more accurately stated. In short tubes the error at the joint μa is much more serious. Again, since the expansion corresponding to a given pressure increases in absolute magnitude with the length of qq, it is clear that a wider capillary tube at ss will suffice when qq is long. A wide capillary ss is obviously convenient, since it can be more easily adjusted for zero in the way just stated, and since the tube qq itself can be more easily filled by aid of the air pump. When the gauge is properly charged and adjusted, it must show no displacement of the fiducial zero during the interval of experiment.

In later experiments I bent the vertical tube ss, Pl. I, 8, horizontally, so that its measuring parts lay close to uu and immediately above a millimeter scale. A somewhat finer capillary corresponding to about 2,000 atmospheres per meter was used with advantage. So constructed the Tait gauge[1] is very much more compact and less fragile.

14. *Tait gauge. Graduation.*—To graduate the gauge I compared it with a large Bourdon gauge, reading from 0 to 1000 atmosphere. The tube of the latter in this case communicates with the barrel through one of the screws M. This comparison with the Bourdon gauge is a check on both instruments, and the statistics are therefore given below. It affords no means of checking the correct value of the standard atmosphere employed. But since both gauges are based on Hooke's law, and provided with scales of equal parts, the relations are well indicated. In the table $2a_0$, $2a_1$, and L, denote the internal, the external diameters, and the length of the steel tube qq, Pl. I, 8, 2ρ, is the bore of the capillary ss.

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[1] The form of steel high pressure gauge based on Hooke's law recommended but not constructed by Prof. Tait (loc. cit.), is somewhat different from the above. I think my form has the practical advantage of greater simplicity, being essentially a single-walled tube. The method of computation is due to Prof. Tait. It was my purpose to make the tube tt of brass, so that the heat of compression would be more quickly dissipated. But I failed to obtain tubing of the proper bore and strength until quite recently.

TABLE 1.—*Comparison of Tait gauge No. 0, and Bourdon gauge.*

[$a_0 = \cdot 27^{cm}$; $a_1 = 1.00^{cm}$; $L = 100^{cm}$; $\rho = .034^{cm}$.]

Time =	15^m^	30^m^	45^m^	75^m^	90^m^
Bourdon.	Tait.	Tait.	Tait.	Tait.	Tait.
Atm.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*
0	1·90	2·10	2·00	2·18	2·16
100	3·58	3·70	3·60	3·85	....
200	5·20	5·50	5·35	5·55	....
300	7·05	7·25	7·20	7·45	7·30
400	8·70	9·00	8·90	9·10	....
500	10·50	10·72	10·70	10·85	....
600	*12·50	12·50	12·45	12·55	12·70
700	14·10	14·10	14·10	14·20	....
800	15·65	15·70	15·70	15·85	....
900	17·22	17·20	17·30	17·45	....
1000	18·80	19·00	19·00	19·10	19·20
900	16·62	16·70	16·80	16·80	....
800	14·65	14·70	14·63	14·70	....
700	12·80	12·80	12·75	12·92	....
600	10·95	11·00	11·00	11·12	11·00
500	9·30	9·28	9·23	9·35	....
400	7·55	7·55	7·50	7·60	....
300	5·95	6·00	6·10	6·15	5·85
200	4·50	4·55	4·60	4·60	....
100	3·04	3·12	3·15	3·20	....
0	1·74	1·90	1·90	2·00	1·60
Rate, in centimeters, per atmosphere...	=.0169	·0171	·0172	·0172	....

* Break in the measurements.

15.—TABLE 2.—*The same gauge comparisons (No. 0 and Bourdon) after long use.*

Large Bourdon.	Tait.	Tait.	Factor.	Mean.	
100	6·35	6·27	·01715	·01722	....
200	8·03	7·96	1725	....	....
300	9·79	9·70	1720	....	....
400	11·48	11·41	1728	....	....
500	13·26	13·16	....	....	....

Small Bourdon.	Large Bourdon.	Tait.	Tait.	Factor.	Mean.
30	31	4·94	5·05	·01722	.01725
120	121	6·42	6·53	1767	....
210	210	8·04	8·05	1667	....
300	300	9·60	9·67	1744	....

TABLE 3.—*High pressure tests.*

$P = 0$	$N_p = 4\cdot 90$	....	....	....	....
2110	40·93	....	....	....	....
0	5·10	....	....	....	....
2160	41·95	....	....	....	....
0	5·20	....	....	....	....

16.—Table 1 contains five series of observations made at the times stated. In the first four series I went up to the maximum and down again gradually, but not slowly. The last I operated as fast as the experiment would permit. To determine the degree of accuracy it is well to consult the rates at the bottom of the table. These show that a mean displacement of $\cdot 0171^{cm}$ of the meniscus takes place in the pressure increasing series for each atmosphere pressure. Consulting data on the same horizontal row it appears that the differences of reading of the new gauge corresponding to a given reading of the Bourdon gauge are greatest in the region of low pressures. At zero the maximum difference observed is ·40cm, equivalent to an error of 24 atmospheres. Again, comparing the two zero readings of the last column, the difference of reading is ·56cm, corresponding to 33 atmospheres. This, therefore, is a maximum index of the inaccuracy of the Tait gauge due to thermal

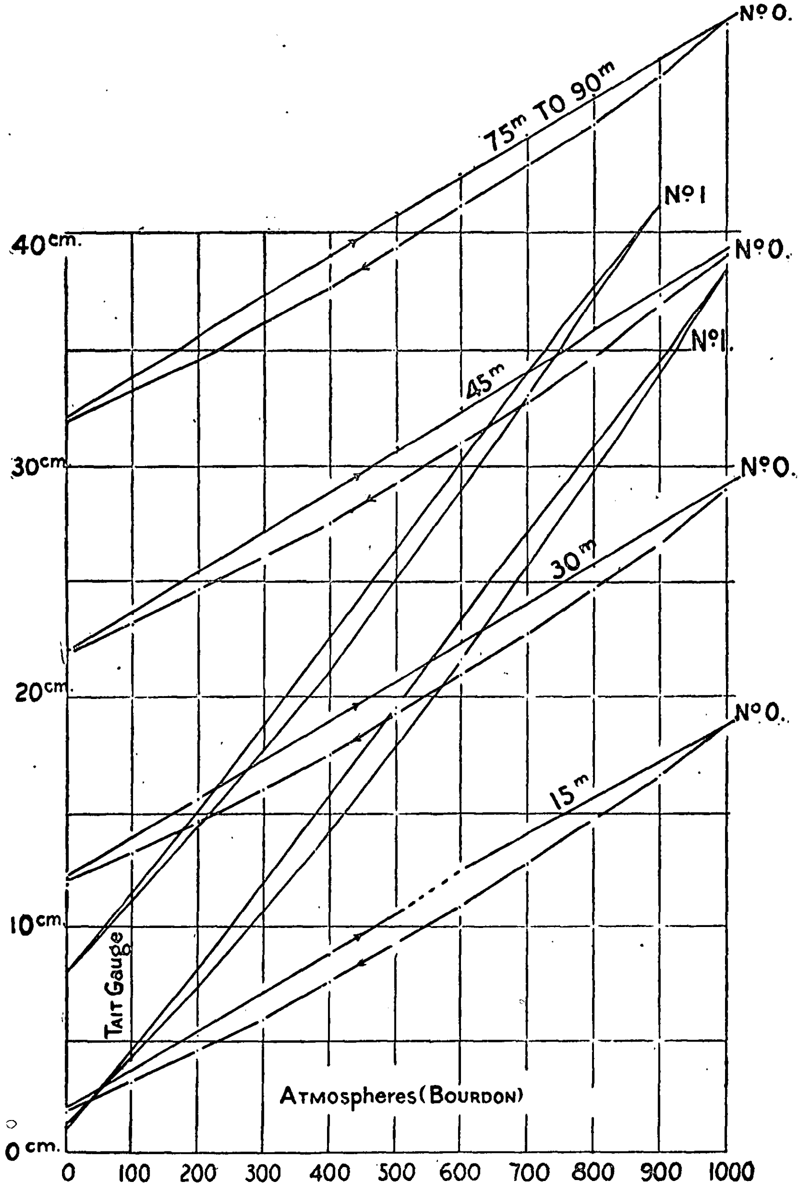


Fig. 1.—Chart showing the bow-shaped cycles obtained in the gauge comparisons.

effects of compression and unreasonably hasty work. To diminish this error further, it is necessary to decrease the bore of the glass tube *tt* in Pl. I, 8, thus making the thermometer property of the gauge of smaller importance. In the above apparatus this tube was 1·15$^{\text{cm}}$ in internal diameter, corresponding therefore to a liquid interstratum ·07$^{\text{cm}}$ thick. Clearly this admits of further reduction. A brass tube would in many respects be preferable to a glass tube, since in this case the heat of compression is more easily dissipated; but I did not find one of the necessary dimensions.

17.—A second point of view is obtained by comparing the data of the pressure "on" and of the pressure "off" phases of the above experiments. For convenience I insert the Chart, Fig. 1, in which the data of Table 1 are inserted. It is seen at once that the degree of accordance in the "on" series is satisfactory. The errors are nowhere larger than 10 atmospheres. The loci, apart for slight circumflexure, are straight lines. In the "off" series, however, this good uniformity is lost. The data lie on consecutive broken lines. The feature of particular importance is, however, this: The observation that the "off" data do not at all return on the lines of the "on" data. Indeed the two lines, "on" and "off," inclose a band the maximum width of which is even 1.5$^{\text{cm}}$, corresponding to 90 atmospheres. Since this band widens at once at 900 atmospheres, and falls off at zero atmosphere, it is clearly due to a *virtual* shifting of the fiducial zero of the mechanism of the Bourdon gauge.

In the present comparisons, therefore, the "on" series of data need alone be considered. It appears for these, slow work presupposed, that the error of the gauge in the above form need not exceed 10 atmospheres, and that it can certainly be reduced decidedly below this limit by diminishing the bore of the glass envelope *tt*, Pl. I, 8.

18.—TABLE 4.—*Comparison of large Bourdon gauge with Tait gauge No. 1.* $p = .0220^{\text{cm}}$. $a_1 = 1^{\text{cm}}$. $a_0 = .27^{\text{cm}}$.

Large Bourdon.	No. 1.	Diff.	Large Bourdon.	No. 1.	Diff.
Atm.	*Cm.*	*Cm.*	*Atm.*	*Cm.*	*Cm.*
0	17·18	....	900	51·27	....
100	21·30	3·49	800	47·12	4·15
200	25·03	3·73	700	43·10	4·02
300	28·85	3·82	600	39·11	4·00
400	32·63	3·78	500	35·12	3·99
500	36·50	3·87	400	31·32	3·80
600	40·35	3·85	300	27·75	3·57
700	44·05	3·70	200	24·31	3·44
800	47·55	3·50	100	21 00	3·31
900	51·25	3·70	0	17·96	3·04

Second comparison. Another thread length.

0	5·96	....	1000	43·40	....
100	9·42	3·46	900	39·00	4·40
200	13·17	3·75	800	34·75	4·25
300	17·00	3·83	700	30·76	4·00
400	20·74	3·74	600	26·75	4·01
500	24·60	3·86	500	22·84	3·91
600	28·45	3·85	400	19·13	3·71
700	32·15	3·70	300	15·74	3·39
800	35·78	3·63	200	12·36	3·38
900	39·57	3·79	100	9·14	3·22
1000	43·36	3·79	0	6·21	2·93

Third comparison. Large Bourbon gauge with Tait gauges Nos. 1 and 3.

[No. 1, $\rho = .0220^{cm}$. No. 3, $\rho = .0336^{cm}$.]

Large Bourdon.	No. 1.	No. 3.	Large Bourdon.	No. 1.	No. 3.
Atm.	*Cm.*	*Cm.*	*Atm.*	*Cm.*	*Cm.*
0	4·72	26·59	1000	43·20	43·28
100	8·29	28·17	900	38·93	41·36
200	12·03	29·81	800	34·58	39·55
300	15·85	31·50	700	30·75	37·87
400	19·48	33·11	600	26·65	36·13
500	23·40	34·82	500	22·68	34·49
600	27·32	36·59	400	19·03	33·00
700	31·04	38·23	300	15·62	31·63
800	34·68	39·81	200	12·24	30·24
900	38·53	41·53	100	8·95	28·86
1000	43·19	43·28	0	6·08	27·60

Cyclic comparisons.

0	6·10	27·92	0	5·98	28·92
100	9·55	29·45	100	9·43	30·50
200	13·27	31·15	200	13·20	32·19
300	17·12	32·64	300	17·05	33·87
400	20·94	34·51	400	20·94	35·51
300	17·13	32·90	500	24·75	37·17
200	13·30	31·29	600	29·00	38·89
100	9·52	29·77	700	32·63	40·39
0	6·08	28·64	800	36·44	42·00
0	6·08	28·64	900	40·18	43·57
100	9·60	30·10	1000	45·10	45·27
200	13·39	31·61	1000	45·13	45·28
300	17·19	33·27	900	40·72	43·43
400	20·96	34·86	800	36·50	41·63
500	24·83	36·54	700	32·49	39·97
600	28·40	38·12	600	28·49	38·35
700	32·30	39·74	500	24·57	36·74
600	28·39	38·07	400	20·86	35·[illegible]4
500	24·35	36·39	300	17·41	33·83
400	20·38	34·77	200	14·00	32·46
....	Accident.		100	10·80	31·16
0	6·02	28·69	0	7·78	29·97

19.—TABLE 5.—*Comparison of Tait gauges Nos. 1 and 4.*

No. 1.	No. 4.	No. 1.	No. 4.	No. 1. atm.	No. 4. atm.
— ·35	10·38	New adjustment of No. 4.			
6·42	13·43				
13·10	16·43	1·39	10·78		
20·20	19·69	7·68	13·54		
30·08	24·09	14·45	16·60		
38·00	27·95	20·54	19·33		
31·49	24·71	28·40	22·85		
23·62	21·23	34·39	25·53		
16·96	18·02	40·07	28·07		
8·96	14·61	46·35	31·05		
1·35	11·22	52·75	34·49		
7·78	14·11	59·02	38·18		
15·67	17·66	63·75	41·62	1761	1783
21·41	20·37	63·53	41·25	1755	1760
28·54	23·56	63·11	41·11	1745	1750
35·31	26·48	56·44	38·26	1564	1579
40·00	28·67	47·36	33·96	1317	1320
32·65	25·35	40·98	31·32	1145	1161
25·86	22·39	33·61	28·10	947	967
19·84	19·69	26·95	25·11	766	787
13·38	16·69	19·24	21·63	557	577
6·25	13·55	13·05	18·80	389	407
·60	11·02	5·54	15·28	185	195
		1·25	12·05	00	00

TABLE 6.—*Calibrations of Tait gauges Nos. 1 and 4.*

No. 1.	No. 4.	Small Bourdon.	No. 1 factor.	No. 4 factor.
— 1·30	12·02	0	3·65	1·63
2·28	13·63	100	3·69	1·67
6·00	15·29	200	3·60	1·67
9·66	16·97	300	3·73	1·61
9·65	16·96	300		
5·90	15·26	200	3·69	1·66
2·20	13·62	100		
— 1·30	12.04	0		

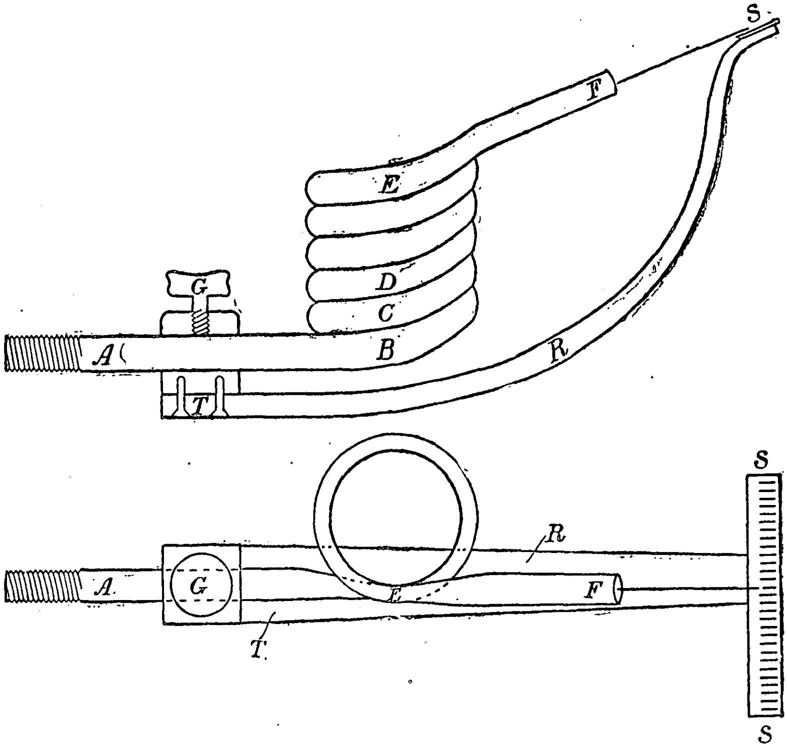
TABLE 7.—*Comparison of Tait gauges Nos. 1 and 4.*

No. 1.	No. 4.	P_1.	P_4.
Cm.	*Cm.*	*Atm.*	*Atm.*
— ·40	12·40	0	0
8·38	16·45	244	252
18·23	20·85	517	525
28·43	25·40	801	807
38·36	29·80	1077	1081
50·04	34·91	1401	1399
59·93	39·41	1675	1678
63·75	41·25	1781	1791
55·03	37·33	1540	1549
42.89	32·06	1202	1221
31·90	27·19	897	919
20·09	21·86	569	588
9·02	16·78	262	272
— ·55	12·30	— 4	6

TABLE 8.—*Calibrations of Tait gauges Nos. 1 and 4.*

Small Bourdon.	No. 1.	No. 4.	Factor No. 1.	Factor No. 4.
Atm.	*Cm.*	*Cm.*		
0	— ·56	12·36	3·57	1·60
100	2·90	13·93	3·73	1·66
200	6·59	15·56	3·58	1·61
300	10·35	17·26	3·51	1·57
300	10·34	17·26		
200	6·68	15·60	3·60	1·61
100	3·18	14·05		
0	— ·33	12·46		

20. *Tait gauge. Volume increase measured and computed.*—With the aid of the above results it will now be easy to compute the volume increase of the steel tube *qq*, Pl. I, 8, per atmosphere of internal pressure, and then compare the datum thus obtained with the result computed by aid of Tait's formula.[1] From the dimensions a_0, a_1, L, ρ given in table 1, it follows that the increase of the external volume of the cylindrical steel tube is $47/10^6$ per unit of volume of *qq*, per centimeter of displacement of the thread in the capillary *ss*. This corresponds to a volume increase of



FIGS. 2, 2*a*.—Direct reading helical Bourdon gauge.

$$v/V = .00000080 \quad . \quad . \quad . \quad (1)$$

per unit of volume of the steel tube, per atmosphere.

Tait shows that in case of internal pressure the changes per unit of length tangentially to a cross section of radius r and longitudinally for any part of the tube, are respectively

$$\frac{\rho}{r} = \frac{\Pi a_0^2}{a_1^2 - a_0^2}\left(\frac{1}{3k} + \frac{a_1^2}{r^2}\frac{1}{2n}\right) \quad \text{and} \quad \frac{d\xi}{dx} = \frac{\Pi a_0^2}{a_1^2 - a_0^2}\frac{1}{3k}$$

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[1] Tait: Challenger Reports, Vol. 2, 1882, Appendix A, p. 26.

Hence the increase, $\frac{v'}{V}$, per unit of volume of the external surface of the tube is

$$\frac{v'}{V}=2\left(\frac{\rho}{r}\right)_{a_1}+\frac{d\xi}{dx}=\frac{\Pi\, a_0^2}{a_1^2-a_0^2}\left(\frac{1}{k}+\frac{1}{n}\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here ξ is the displacement of the point whose position is x centimeters from one end, and ρ the change of a point in a right section, originally distant r centimeters from the axis, Π the internal pressure in atmospheres, and k and n the compressibility and the rigidity respectively, of the steel employed. I take k and n from Everett's tables,[1] as follows:

$$k=1.84\times10^{12} \qquad n=8.2\times10^{11}$$

Inserting these quantities into the equation, there results

$$\frac{v'}{V}=.00000073 \quad . \quad . \quad . \quad . \quad (3)$$

It appears at once that this result is of the same order as (1). The difference is probably due to the constants k and n, which Prof. Everett doubtless found from a high-grade tool steel, whereas the above tubes, being made of low carbon steel, are nearer wrought iron in their properties. Beyond this the absolute gauge atmosphere is not vouched for; nor (being the mean value between 0 and 1000 atmospheres) are the coefficients at the end of table 1 quite free from thermal discrepancy.

When the observations are made for the purpose of measurement, there appears no doubt that equation (2) may actually be utilized to obtain serviceable values of $(1/k+1/n)$. For instance, a_0 may be obtained accurately by filling in vacuo with mercury and weighing, and then from the known specific gravity of the steel tube and its weight when empty, a_1 may be computed. ρ is similarly capable of accurate measurement. Therefore by combining (1) and (2), $(1/k+1/n)$ is measurable with the same accuracy with which Π is known.

21. *Direct reading, Bourdon gauge.*—It is well to insert my endeavors to adapt the Bourdon gauge for high pressures and direct reading. In order to achieve this result it is necessary to multiply the number of coils as well as to work with flat tubes. In Figs. 2 and 2*a*, the latter being the plan, the former the elevation, I have drawn a form of apparatus, with which I obtained some results. It consists essentially of a helix, *A B C D E F*, the spires of which do not touch each other. The end is provided with a needle *F S*, moving over a millimeter scale *S S*, supported by an arm *T R S*. This gauge is screwed directly into the barrel. Being entirely of iron and metal it is very firm. The spires are hammered flat by heating them to redness, the tube being

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[1] Everett: Units and Physical Constants. London, Macmillan, 1879, p. 53.

originally 1^{cm} in external diameter and 5^{cm} in bore. After winding hot, the internal diameter of the helix was found to be somewhat larger than 4^{cm}. There were five spires in all, and the upper one *E F*, with its needle, extended about a decimeter beyond the helix.

The following little table gives the results of a comparison with the Bourdon gauge:

TABLE 9.—*Comparison of Bourdon gauge and the spiral gauge.*

Bourdon.	Spiral.	Bourdon.	Spiral.
Atm.	*Cm.*	*Atm.*	*Cm.*
0	0·00	600	1·28
100	·17	700	1·55
200	·35	800	1·87
300	·54	900	2·30
400	·76	1000	Explodes.
500	1·00	0	1·16

Constructing these results graphically in Fig. 3, it will be seen that between 0 and 300 atmospheres, the permanent set is not appreciable.

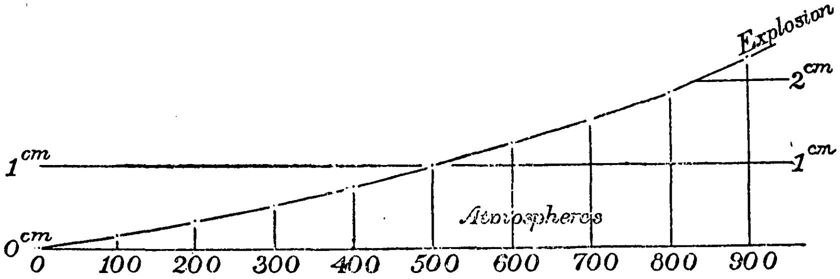

FIG. 3.—Chart showing the action of the helical Bourdon gauge.

When pressure was taken off, the fiducial zero reappeared. Above 300 atmospheres, however, permanent set becomes very marked. The helix was ruptured at 1,000 atmospheres, and the new zero after explosion indicates the large amount of permanent set during the course of the measurement. Connecting the final zero with the point for 900 atmospheres, a line is obtained nearly parallel to the line between 0 and 300 atmospheres. The mean motion of the index was therefore $·0017^{cm}$ per atmosphere. Since high pressure measurement was only contemplated, the gauge would have been serviceable except for the occurrence of permanent set. The chief cause of this insuperable difficulty is the fact that to flatten the gauge it must be heated to redness. By so doing the drawn hardness and resilience is destroyed, and the soft metal of the gauge then becomes useless for measurement. Owing to the rupture of the tube I did not experiment further, since the coiling and flattening is a tedious operation. Clearly the gauge might be used without flattening by suitably attaching a minor index. But this complicates the apparatus.

22. *Concluding remarks.*—I will conclude this description by a few

general remarks on the apparatus used. It is clear that instead of a single barrel, two barrels, the axis of one of which is the prolongation of the other, suggest themselves. The barrels would be used alternately, one being filled while the other is emptied. Again, instead of having the screw enter the barrel, good results must also be obtainable by forcing a cylindrical shaft into the barrel; for the device shown at the end of the barrel *C C*, Pl. I, proves that the gasket of marine glue is quite as serviceable for cylindrical shafts as for screws. In case of a cylinder, however, the strain encountered in forcing in the shaft would be brought to bear on the bed plate, i. e., outside of the barrel. Specially strong devices would therefore have to be resorted to in bolting down the barrel, etc. These would make the apparatus, supposing the horizontal form retained, much more cumbersome. Indeed I conceived it to be an advantage of Andrews's screw, inasmuch as the chief stresses exist within the compass of the barrel. The necessary provision against twisting is much more easily applied. Finally I may state that it was my original object to obviate stuffing boxes altogether, by using a tinned screw *S T*. The maximum of pressure thus obtainable far exceeds the limits of the above screw-compressor with stuffing boxes. The tinned screw would have this disadvantage: it would have to be freshly coated whenever it became necessary to refill the barrel with oil, thus occasioning some loss of time. It is a device however, to be kept in mind, since it obviates the necessity of troublesome metallic gaskets, like those used in Mousson's well-known steel nut, for instance.

23. Cæteris paribus, the labor necessary in producing the above pressures decreases nearly as the fourth power of the diameter of the screw; for friction and leverage both increase as the radius, and the resisting pressure as the square of the radius. Similar advantage is gained by increasing the number of threads to the inch. Hence, by supposing the initial pressures to be produced by a thick screw (diameter 1 inch, say) at one end of the barrel, and the final pressures (above 2,000 atmospheres, when the inclosed liquids have become much more incompressible) produced by a thinner screw (diameter half an inch, say) at the other end of the barrel, the practical efficiency of the screw compressor would be increased. In such a case the piezometer tube must be vertical. (§ 12.) However, in limiting my present work to 2,000 atmospheres, I have by no means exhausted the power of the above machine. My purpose in doing so was to avoid straining the gauges. I add, in concluding, that among the facilities of the above screw compressor is the almost micrometric accuracy with which pressure can be raised to and maintained at a given value for any reasonable length of time.

24. The facility with which the Tait gauge may be replaced by Amagat's manometer, the absolute calibration of the Tait gauge, its availability for the measurement of pressures indefinitely high, and allied subjects will be considered in chapter III.

CHAPTER II.

THE ISOMETRICS OF LIQUIDS.

25. Utilizing the advantages of the screw compressor described in the foregoing chapter, I made the following investigation on the isometrics of liquid matter: The nature of the problem is clearly defined by the results of an earlier paper,[1] where it appears, conformably with the inferences of Dupré, Levy, Ramsay and Young, and Fitzgerald, that liquid isometrics are lines of small curvature.[2] It is thus the purpose of the present work to investigate the amount of deviation from a straight line as accurately as possible.

The word "isometric" is used by J. Willard Gibbs[3] in his researches on graphic methods in the thermodynamics of fluids. It has the advantage of priority if not of expressiveness, and I do not feel the need of withdrawing "isometric" for "isochore," as do Ramsay and Young.[4]

APPARATUS.

26. *Constant volume tube.*—The criterion for constant volume is to be given by a reliable electric contact. The liquid whose isometrics are to be determined is inclosed in a tube of constant volume, of the form shown in Figs. 4 and 5. This tube consists of three parts, a reservoir *ef* and two capillary stems *ed* and *da* separated by an enlarged portion *d*. A platinum wire *c*, passing through the walls of the tube, enters the cavity *d*, for the purpose of securing electric contact, as shown in Fig. 5. The dimensions of the tube are given in Fig. 4, and the choice made is such as to admit of its easy introduction into the steel piezometer tube *uu*, chap. I, Pl. I, Fig. 6.

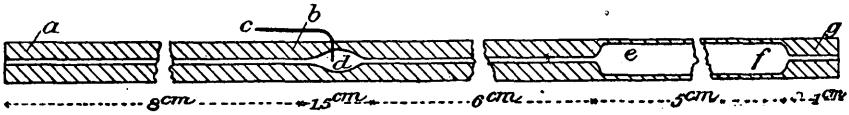

FIG. 4.—Constant volume tube; longitudinal section.

Fig. 5 (diagram) shows the tube ready for use. The end of the tube *g* is sealed, holding the platinum wire *mm*, which passes quite through the reservoir *ef* into the capillary stem. The substance having been

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[1] Bull. U. S. Geol: Survey, No. 92, 1892, chap. I, p. 54.

[2] Am. Jour., 3d ser., vol. 39, 1890, pp. 497 et seq.

[3] Gibbs: Trans. Connecticut Acad., vol. II (2), p. 311, 1873; cf. ibid., p. 382.

[4] Ramsay and Young: Phil. Mag. (5), vol. 23, p. 435, 1887.

introduced into *ef*, completely fills this space and about one-half of the adjoining stem. The remainder of the tube is filled with mercury *hk*, care being taken to guard against inclusions of air.

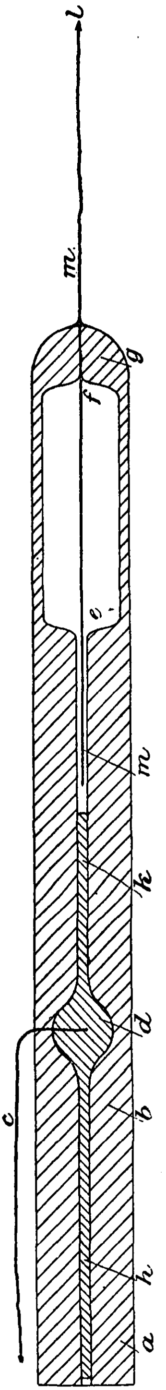

FIG. 5.—Constant volume tube; diagram.

The tube thus adjusted is inserted into the piezometer, and the terminal *c* put in metallic connection with the walls of the steel tube, near *V*, Pl. I. The terminal *ml* is insulated by a glass tube,[1] and after passing through the piezometer into the barrel, is there put in metallic connection with one of the vertical screws *M*. It will be remembered the barrel and piezometer are not in electric contact. A serviceable way of connecting the terminal with the barrel is shown in Fig. 6, where *BB* is part of the wall of the barrel. *S* is a perforated screw, slotted on its upper face, so that it can be inserted or removed easily. The end of the terminal *lo* is passed through the hole in *S*, and then coiled helically, as shown in the figure. The tinned screw *M* is now inserted so as to bind the helix between its lower face and *S*. This insures electric contact. A similar device is utilized at *V*, Pl. I, Fig. 6, and the glass tube is thus held in horizontal position within the steel piezometer tube, by aid of its two tense terminals.

Before introducing the constant volume tube, both piezometer and barrel must be quite filled with oil, and the screws *M* and *V*, Pl. I, are to be so fastened that air may be as far as possible excluded.

27. *Manipulation.*—Supposing the constant volume tube in place, surrounded with oil, the screw *SS* (Pl. I) is forced in. The pressure thus brought to bear uniformly on all parts of the tube, moves the thread of mercury inward by an amount corresponding to the compression of *ef*. Eventually, therefore, the meniscus near *k* and the sharp end of the platinum terminal near *m* come into electric contact. Now, as barrel and piezometer are in a simple circuit, including a suitable galvanoscope and a battery, a deflection in the galvanoscope occurs at the moment of contact.[2] This method of registration is very sharp and thoroughly reliable. Pressure is applied by means of a screw, and can be diminished or intensified with great nicety. Hence the position of the meniscus *k* can be controlled with almost micrometric precision, even when the pressures are as high as 2,000 atmospheres.

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[1] Rubber and other similar insulations are fused or dissolved at high pressure, and are therefore unsuitable.

[2] Devices of this kind have been much used by Weinhold, Crafts, Mendenhall, and others.

When the machine is in satisfactory adjustment contact can be made and broken at *km* without apparent variation of pressure, the difference being in fractions of an atmosphere. The delicacy, however, depends on the relative caliber of capillary tube and reservoir tube.

To avoid breakage of the thread *k* on being forced through *m*, the free end must be made as fine as practicable ($\cdot 01^{cm}$ in diameter, say). Hence it is advisable to weld a fine wire to the relatively thick terminal *m* (diameter $0{\cdot}5^{cm}$).

28. In passing from one constant temperature to another, care must be taken to avoid the mercury thread from being forced either out of the tube or into the reservoir. This may be done by keeping the meniscus *k* always very nearly in contact with *m*. Hence, when a vapor bath is attached and the burner started, pressure is increased in such a way as to keep the contact just made. On the other hand, when temperature decreases, pressure is relieved in such a way as just to keep the contact broken.

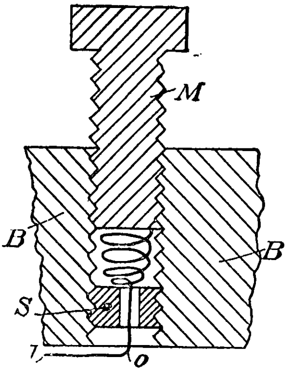

FIG. 6.—Method of fastening the terminals.

29. When the series of isometrics are to be mapped out, the volume of liquid between the meniscus *k* and the sharp end of *m* is suitably changed. This volume may be conceived as either positive or negative. In the latter case the wire *m* penetrates the thread *k*. The advantage of such an arrangement is shown below.

30. *Method of filling.*—When the substance to be compressed (*ef*, Fig. 5) is liquid at ordinary temperatures, like ether or water, the tube may easily be filled without an air pump, by making use of filamentary glass tubes with enlarged funnel-shaped heads. The filamentary end is introduced at *a* and pushed down to the bottom *g*, supposing the tube *ag* to be vertical and *a* uppermost. The liquid is allowed to run throughthe funnel, the top of which is kept filled until the reservoir *ef* and adjoining capillaries *eda* are quite filled. The operation is not stopped however until three or four times as much liquid has run through *ef* as is necessary to fill it.

The tube is now tipped nearly horizontal and mercury passed into the bulb *d* by aid of similar funnel capillaries. The thread is then pushed forward from *d* into *de* by aid of an empty glass filament, by successively draining off small parts of the liquid in *de*, until the meniscus *k* has the desired proximity to *m*.

31. The greatest care must be taken to have all parts of the tube perfectly clean, to use pure, fresh mercury, and *to avoid rubber connections or other material impregnated with sulphur.* I find it desirable to draw off the mercury in *abd* by aid of a fine tube and a jet suction pump, and thus to thoroughly dry out this part of the stem. Fresh mercury is then poured in through the glass filament until the tube is again full.

When the mercury appears dead or fails to move as an unbroken column the tube is worthless. The cause of this by no means infrequent annoyance is usually found in the presence of sulphurous dirt in the tubes or of sulphide in the sample liquid. It is advisable therefore to use fresh tubes only.

32. When the substance is solid like thymol or diphenylamine, it must be introduced by aid of an air pump. For this purpose a wide glass tube about 20^{cm} long is fused to the end *a*, Fig. 5. Into this the solid substance is put, after which the open end of the wide tube is drawn out to a filament and connected with the air pump. After the exhaustion of the system the solid is fused with a burner and allowed to run down into *ef*. The operation must be repeated many times and use made of vacuum ebullition to expel the last traces of air. The thread of mercury is introduced in the way already stated (§ 30), except in so far as it is essential to keep the tube in a warm bath to prevent solidification. When in adjustment it is inserted into a hot piezometer tube. These operations call for much skill on the part of the operator. If solidification occurs the mercury thread is drawn down into the bulb in consequence of the large volume contraction, and the charge is therefore lost.

33. *Vapor baths.*—In order that the isometrics may be sharply traced, temperature must be regulated to a nicety. This is not easy, seeing that the metallic piezometer tube is a good conductor. Hence the forms of vapor baths used in my earlier similar works[1] are not applicable here. It is essential that vapor be directly in contact with the surface of the piezometer tube and that the reservoir of the constant volume tube be at a distance of 3 or more centimeters from the end walls of the bath.

Substances useful for vapor baths are methyl alcohol, 60°; water, 100°; amyl alcohol, 130°; turpentine, 160°; naphthalene, 215°; benzoic. acid, 250°; diphenylamine, 310°; phenanthren, 350°, and others These form a convenient series. They admit of being boiled in a brazed copper vessel and decompose very slowly. The fiducial or initial temperature is obtained by allowing a current of water from the hydrant to circulate around the piezometer tube.

At temperatures above 200°, the form *ffff* shown in Pl. I, 6, is serviceable. The tubulures *hh* through which the piezometer passes may be closed with perforated cork stoppers.[2] At higher temperatures *hh* are screw stuffing boxes, securing asbestos jackets. The vapors issuing from *yy*, the ebullition liquid (usually solid at ordinary temperature), are condensed in a lateral tube (not shown) and run back into the drum *ffff*. The thermocouple is inserted through *g*.

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[1] Bull. U. S. Geol. Surv. No. 92, p. 22; Am. Journal Sci. (3), vol. 39, p. 482, 1890.

[2] Rubber stoppers melt and are otherwise very objectionable above 200°.

34. At temperature below 200°, this form of vapor bath is not convenient, since the substance *yy* is usually liquid and too easily spilt. Moreover the degree of constant temperature obtainable in the drum *ffff* is probably insufficient. I therefore employed the circulating system shown in Fig. 7. Vapor is introduced into the drum *fff* from the boiler *A* and the influx pipe *B*. It is condensed in the tube *C C* carrying the cold water jacket *D D*. The condensed liquid falls into the funnel *E*, which is cylindrical and thus subserves the purpose of a water gauge. The piezometer tube is shown at *U u u U* with the constant volume tube *adeg* in place. *G* and *G* are cold-water jackets surrounding *UU* to prevent the spread of high temperatures along the tube. A single current of water (issuing from the gauge jacket, Pl. I, 8, above) passes through *G*, *D*, and *G*. This current is shunted, so that *G D G* can be cut out at pleasure and the vapor bath removed or replaced by a circulating water bath. It is to be noted that the parts of the vapor bath are rigidly connected, so that it can be rapidly withdrawn as a whole. *H* is a suitable electric clamp, corresponding to the other terminal *K*. All parts of the vapor bath are heavily jacketed with asbestos.

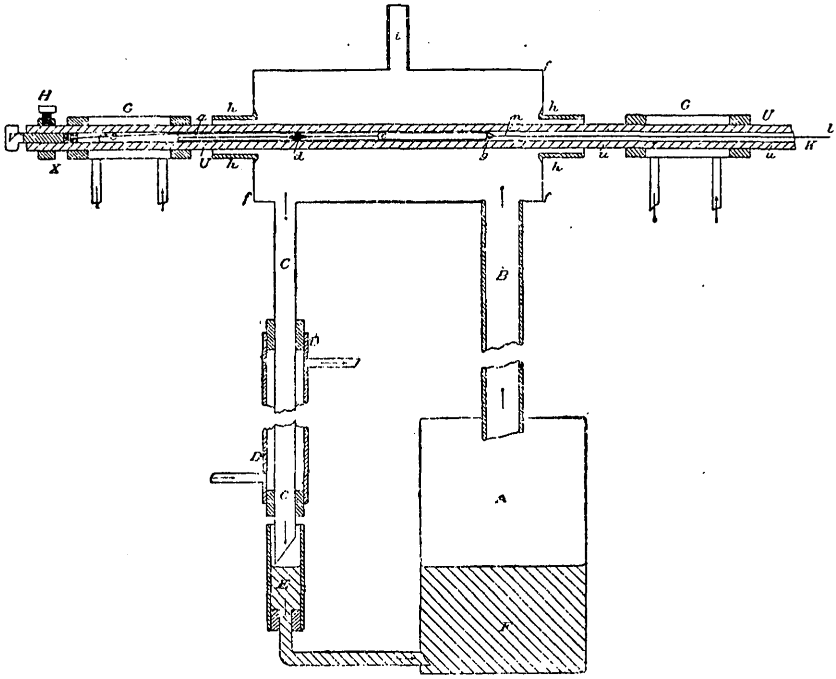

FIG. 7.—Vapor bath and piezometer tube; longitudinal section.

It is necessary that the vapor baths slide off and on easily. Any violent jarring of the piezometer tube will break the thread in the glass tube within.

35. *Method of cooling piezometer.*—To cool the tube *UU* after the vapor bath has been removed, it is convenient to oil the piezometer with vaseline. The jacket *G* may then be slid to and fro very rapidly at first, care being taken to relieve the pressure in proportion as the tube cools.

36. *Method of temperature measurement.*—For the measurement of temperature I used a platinum platinum-iridium thermocouple, the electromotive force of which was expressed in terms of the torsion of the platinum fiber which suspended the given astatic system. The torsion galvanometer serviceable for thermo-electric work I have already described elsewhere.[1] To calibrate this apparatus the boiling points of water and of mercury were first used. Finally I made elaborate comparisons with the reentrant glass air thermometer. §§ 48–50.

37. *Method of pressure measurement.*—Pressure was measured in terms of the expansion of a given cold-drawn steel tube, as detailed in chapter I.

It is needless to say that the factor of the gauge was frequently checked during the course of the work. A small sensitive 300-atmosphere Bourdon gauge with a tinned screw connection is very convenient for this purpose. About twenty or thirty minutes were allowed to secure isothermal conditions both for the gauge and the piezometer tube. Leaks of the apparatus must be so far as possible avoided, inasmuch as continued pumping changes the thermal state of the liquids operated on and is therefore a fertile source of error.

PRELIMINARY RESULTS.

37. *Data for ether.*—The data of Tables 10 and 11 were obtained in the earlier experiments. Although neither the gauge nor the thermocouple was remarkably sensitive, these results bear directly on the matter below and must therefore be inserted. P and θ are corresponding values of pressure and temperature, such that the volume of ether remains constant. Two or three observations were made for each datum, allowing five minutes' time per observation. This is essential where isothermal conditions are to be guaranteed. So far as these observations go, the corrections for volume changes of glass are negligible. During the first five series, extending over an interval between March 14 and 19 the constancy of the fiducial pressure (at about 10°) is to be noted. In the remaining series it was not always possible to regain the fiducial pressure, owing to accidents.

TABLE 10.—*Isometrics of ether. Preliminary results.*

P.	Θ.	*P.*	Θ.
Atm.	°*C.*	*Atm.*	°*C.*
293	11·6	887	66
305	11·6	1237	100
888	66	1242	100
888	66	1247	100
1227	100	284	11·0
1231	100	288	11·2
300	11·6		
301	11·6	287	10·0
885	66	287	10·0

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[1] Barus: Phil. Mag. (5), vol. 29, p. 146, 1890.

TABLE 10.—*Isometrics of ether. Preliminary results*—Continued.

P.	θ.	*P.*	θ.
Atm.	°*C.*	*Atm.*	°*C.*
276	9·4	101	9·8
289	9·9	647	66
		645	67
277	9·8	972	103
1502	127	966	103
1510	128	1080	119
1482	123	1063	121
1480	128	51	10·0
279	9·7	1443	155
		1436	158
		91	10·0
278	10·8		
875	64	80	10·3
868	66	608	66
874	65	611	66
286	9·7	613	66
		614	66
14	9·8	614	65
545	67	925	99
545	67	924	101
859	102	921	101
857	102	920	101
		919	100
65	10·6	84	10·3
595	64	1112	119
602	64	1112	120
597	63	1380	153
		1421	156
71	10·8	1451	161
912	101	1446	162
914	100		
76	10·8	94	11·2
		627	66·5
156	10·8	630	66·4
1087	114	926	98·8
1094	115	924	98·5

TABLE 11.—*Digest of these data.*

Δp	θ	$\Delta\theta$		Δp	θ	$\Delta\theta$	
0	11·5	0		0	9·9	0	
589	66	55		570	66	56	
937	100	89		893	103	90	(3)
				996	120	110	
0	9·8	0	(1)	1369	156	146	
1216	127	117					
				0	10·3	0	
0	10·2	0		530	66	56	
590	65	56		840	100	90	
				1030	120	110	
0	9·8	0		1342	158	148	(4)
531	67	56					
844	102	90		0	11·2	0	
				534	66	55	
0	10·7	0	(2)	831	99	89	
530	64	55					
840	100	89					
0	10·8	0					
934	114	103					

38. *Discussion.*—In the digest, Table 11, the coordinates have been shifted, so that the fiducial pressure and temperature are now zero. The graphic representation, Fig. 8, shows a distribution of points lying very closely along straight lines. So far as these data go, therefore, the linear character of the isometrics is maintained. The rates per atmosphere are respectively ·095°, ·107°, ·106°, ·107°.

DEFINITE RESULTS.

39. *Apparatus improved.*—With the above data in hand I endeavored to carry the discrimination one step further by increasing the sensitiveness of both the pressure gauge and the thermocouple.

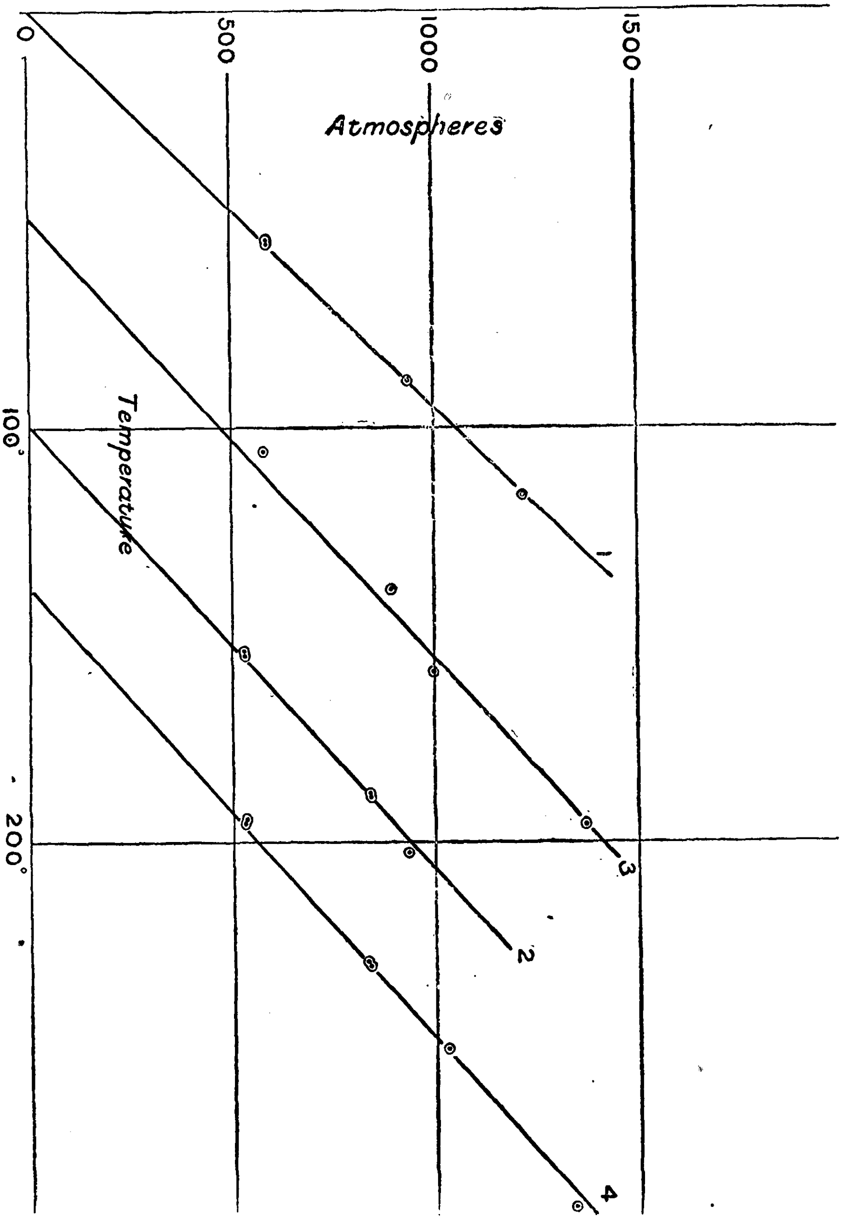

FIG. 8.—Isometrics of ether; preliminary results.

Using the same steel tube for the registration of pressures by Hooke's law, as before, the gauge was made much more delicate by decreasing the caliber of the capillary measuring tube (*ss*, Pl. I, 6), and by making use of a more close-fitting glass jacket *tt* than before. The results have already been shown (§§ 15 to 19). Apart from errors due to viscosity and thermal effects, the gauge was sufficiently sensitive to register fractions of an atmosphere at 2,000 atmospheres.

Particular care was taken to redetermine the initial pressure corresponding to the initial or fiducial temperature (about 15°), before and after each high-temperature observation. This is a certain check on the validity of the results obtained.

Again the temperature measurement was made more delicate by inserting a finer platinum fiber in the torsion galvanometer. Statistics will be given below.

At least ten minutes were allowed for each datum of pressure and temperature given. In proportion as the second of any two measurements made at a given temperature coincides with the first, the inference is warranted that the thermal effects of compression are fully dissipated. The observation at any temperature therefore lasted twenty or thirty minutes.

40. *Notation.*—The notation is as follows:

N'_θ, deflection in degrees of arc observed at the torsion galvanometer;

t, temperature of the cold junction of thermocouple;

n_θ, correction by which N'_θ is reduced to N_θ, the deflection which would be observed at the torsion galvanometer if $t = 20°$;

θ, temperature of the vapor bath surrounding the piezometer tube. θ is computed from N_θ. θ is therefore the temperature of the reservoir of the constant volume tube.

N_p, reading in centimeters observed at the capillary tube of the pressure gauge.

p, pressure corresponding to N_p in atmospheres. Hence p is the pressure bearing on the substance in the constant volume tube;

Δp, $\Delta\theta$, pressure and temperature obtained by shifting the coordinates, so that the initial pressure and temperature may be zero.

41. *Data for ether.*—Table 12 contains fifteen series of observations made with ether. Series in which the constant volume tube and contents were changed are separated by heavy lines. It is necessary to consider these data somewhat in detail. Each series contains at least one observation at the boiling point of water. Since the barometer was also noted, the data for the final reduction of the values θ are at hand—cf. §§ 48 et seq.

The first eight series need but little comment. In the first the gauge reading for $p = 0$ was -1.00^{cm}; in the second, third, fourth, fifth it was -2.00^{cm}; in the sixth, -3.50^{cm}; in the eighth, 1.70^{cm}. Inasmuch as the relation between p and v is nearly linear, the gauge reading for $p = 0$ is of secondary importance. Owing to accidents the fiducial reading was lost at the end of the sixth and eighth series.

42. Comparing the first eight series with the remaining seven, it is seen that the fiducial pressure is very much more constant in the former than in the latter; for the reading at the initial temperature in the one case does not vary more than 5 or 10 atmospheres; whereas in the other the variation is as large as 100 atmospheres. The cause of this discrepancy is a strain permanently imparted to the gauge at the end of the eighth series, where it was necessary to work the machine with great violence and much above the pressure given, to counteract an accidental leak. Hence in constructing Δp for these series (9 to 15) I deduct the fiducial pressure *preceding* and *following* any pair of high temperature data from the first and last of these data respectively. In this way the viscous error of the gauge is eliminated. Of the two values of Δp thus obtained at each temperature, the latter is the more nearly correct, since it has been coordinated with the fiducial pressure immediately following it. As the work proceeds, that is, in the thirteenth, fourteenth, and fifteenth series, the fiducial pressure is again more nearly constant, showing a gradual increase of the viscosity of the gauge.

43. In the ninth and tenth series, $p = 0$ is at $-.70^{\mathrm{cm}}$; in the eleventh, at $-.30^{\mathrm{cm}}$; in the thirteenth, fourteenth, and fifteenth, at $.50^{\mathrm{cm}}$. The last three series (13–15) were obtained with the same tube, and the work, done continuously, was throughout very satisfactory. Moreover the change of fiducial pressure still marked in series thirteen becomes of less prominence in the last two series. These therefore were selected for the digest below.

44. *Method of purifying.*—The ether employed was thoroughly dried with sodium, and then distilled in a small flask at a temperature only slightly above the boiling point. All parts of the condenser tube and flask were fused together, and rubber connections were scrupulously avoided. The distillation was frequently repeated, and the ether then at once used for filling the constant volume tube. I can not guarantee, however, that the ether after being introduced in the tube was quite free from water; for during the necessary manipulations some absorption of water out of the air was unavoidable.

45. *Observations for ether.*—The data for ether are as follows:

TABLE 12.—*Isometrics of ether. Observations.*

N'_θ.	t.	n_θ.	N_p.	θ.	p.	N_θ.	Δp.	$\Delta\theta$.
°	°C.	Cm.	Cm.	°C.	Atm.	°C.	Atm.	
I.	....	....	— ·54	15·1	40	....	0	·0
4·115	22·2	·192	+16·67	67·5	512	4·307	474	52·2
4·132	22·3	·200	+16·86	67·6	517	4·332	479	52·3
....	....	....	— ·70	15·5	36	....	0	·0
7·191	22·3	·200	+27·20	99·5	800	7·391	762	84·0
7·209	22·3	·200	+27·29	99·6	803	7·409	765	84·1
....	....	....	— ·50	15·5	41	....	0	·0
II.	....	....	— ·23	15·4	48	....	0	·0
13·115	23·1	·270	+45·89	157·9	1,312	13·385	1,272	142·4
13·176	23·7	·321	+46·12	158·8	1,318	13·497	1,278	143·3
....	....	....	— ·10	15·5	52	....	0	·0
6·946	24·8	·418	+28·01	99·2	822	7·364	778	83·9
6·890	25·0	·438	+28·00	98·8	822	7·328	778	83·5
3·849	25·0	·438	+17·59	67·2	537	4·287	493	51·9
3·849	25·0	·438	+17·61	67·3	537	4·287	493	52·0
....	....	....	— ·69	15·0	36	....	0	·0

TABLE 12.—*Isometrics of ether. Observations*—Continued.

N'_θ.	t.	n_θ.	N_θ.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
III.	...	...	...	15·9	1.55	44	·0	0
7·132	22·9	+·254	7·386	99·5	28·95	793	83·6	755
7·100	23·0	·262	7·362	99·0	29·03	795	83·1	757
...	...	...	...	15·9	1·20	33	·0	0
IV.	...	...	...	16·2	1·18	32	·0	0
15·337	23·8	·333	15·670	178·7	53·56	1,467	162·5	1,439
15·390	23·8	·333	15·723	179·2	53·65	1,470	163·0	1,442
...	...	...	...	16·2	·90	25	·0	0
V.	...	...	...	15·9	− ·40	44	·0	0
16·403	20·8	·068	16·471	185·7	53·51	1,521	169·8	1,472
16·465	20·9	·076	16·541	186·4	53·38	1,517	170·5	1,468
16·536	21·1	·095	16·631	187·3	53·06	1,509	171·4	1,460
...	...	...	...	15·8	− ·04	54	·0	0
7·297	21·3	·112	7·409	99·8	27·97	821	83·9	767
7·282	21·3	·112	7·394	99·5	27·97	821	83·6	768
...	...	...	...	15·9	− ·08	53	.0	0
VI.	...	...	...	16·0	·00	96	·0	0
7·294	20·7	·059	7·353	98·2	28·59	879	82·2	783
7·294	20·7	·059	7·353	98·2	28·62	880	82·2	784
VII.	...	...	...	16·0	− 1·20	63	·0	0
7·083	22·5	·218	7·301	97·7	26·88	832	81·6	767
7·068	22·6	·226	7·294	97·5	27·01	835	81.4	770
4·065	22·6	·226	4·291	67·1	16·81	556	51·0	491
4·074	22·6	·226	4·300	67·4	16·87	558	51·3	493
...	...	...	...	16·2	− ·97	69	·0	0
VIII.	...	...	...	16·4	+ ·98	73	·0	0
7·144	22·2	·192	7·336	98·1	29·51	854	81·7	781
7·118	22·4	·209	7·327	98·0	29·55	856	81·6	783
20·050	22·8	·243	20·293	219·5	65·31	1,836	203·01	1,763
20·044	22·9	·251	20·295	219·6	65·20	1,833	203·2	1,760
IX.	...	...	...	16·5	+ 4·94	154	·0	0
3·893	23·9	·342	4·235	66·9	23·51	663	50·3	509
3·926	23·9	·342	4·268	67·0	23·73	669	50·4	515
6·890	24·2	·367	7·257	97·4	34·91	976	80·8	822
6·911	24·3	·375	7·286	97·5	35·01	978	80·9	824
...	...	...	...	16·7	+ 6·38	?194	·0	...

N'_θ.	t.	n_θ.	N_θ.	θ.	N_p.	$\Delta\theta$.	p.	Δp.
X.	...	...	...	16·6	1·18	0	32	0
7·303	21·0	·087	7·390	99·5	28·33	83·0	776	740
7·309	21·2	·104	7·413	99·8	28·41	83·3	778	742
...	...	...	...	16·5	1·48	0	40	0
XI.	...	...	...	16·6	1·60	0	44	0
4·206	22·0	·175	4·381	68·0	18·91	51·4	518	465
4·177	22·2	·192	4·369	68·0	18·96	51·4	520	467
7·191	22·2	·192	7·383	99·2	29·14	82·6	798	745
7·180	22·2	·192	7·372	99·0	29·20	82·4	800	747
...	...	...	...	16·6	2·28	0	62	0
XII.	...	...	...	16·6	2·82	0	77	0
4·133	22·4	·209	4·342	67·9	20·10	51·3	551	463
4·136	22·5	·219	4·355	68·0	20·15	51·4	552	464
7·071	22·7	·224	7·295	98·5	30·19	81·9	827	739
7·080	22·8	·243	7·323	98·8	30·34	82·2	831	743
...	...	...	...	16·6	3·58	0	98	0
12·961	23·1	·270	13·231	156·3	50·61	139·7	1387	1289
13·077	23·2	·279	13·356	157·6	50·64	140·9	1388	1208
...	...	...	...	16·7	6·59	0	180	0
15·722	23·3	·287	16·009	182·0	56·74	165·3	1555	1370
15·725	23·4	·296	16·021	182·0	56·71	165·3	1554	1369
...	...	...	...	16·7	6·87	0	189	0
XIII.	...	...	...	17·6	1·61	0	44	0
4·033	23·2	·279	4·312	67·5	17·86	49·9	489	439
4·033	23·3	·287	4·320	67·6	17·88	50·0	490	440
6·896	23·5	·306	7·202	97·5	27·59	79·8	756	706
6·896	23·6	·313	7·209	97·5	27·61	79·8	757	707
...	...	...	...	17·7	2·05	0	56	0
12·834	24·2	·367	13·201	156·2	45·52	138·5	1247	1191
12·822	24·2	·367	13·189	156·0	45·52	138·2	1247	1171
...	...	...	...	17·8	2·78	0	76	0
19·540	24·8	·418	19·958	216·5	62·60	198·7	1715	1639
19·540	24·9	·426	19·966	216·6	62·59	198·7	1715	1611
...	...	...	...	17·9	3·81	0	104	0

TABLE 12.—*Isometrics of ether. Observations*—Continued.

N'_{θ}.	t.	n_{θ}.	N_{θ}.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
XIV.	....	....	....	17·8	3·80	104	0	0
7·147	21·2	·104	7·251	98·2	29·79	816	80·4	712
7·132	21·3	·112	7·244	98·0	29·86	819	80·0	701
....	....	....	....	18·0	4·29	118	0	0
20·080	21·7	·146	20·226	218·8	64·30	1761	200·8	1643
20·071	21·8	·155	20·226	218·8	64·30	1761	200·7	1619
....	....	....	....	18·1	5·19	142	0	0
4·144	22·2	·192	4·336	67·8	21·14	579	49·7	437
4·147	22·3	·200	4·347	68·0	21·14	579	49·9	437
....	....	....	....	(18·1)	(5·20)	(142)	0	0
13·177	22·3	·200	13·377	157·8	49·04	1344	139·7	1202
13·194	22·3	·200	13·394	157·9	49·06	1344	140·0	1196
....	....	....	....	17·9	5·39	148	0	0
XV.	....	....	....	17·4	4·18	114	0	0
20·371	20·0	0	20·371	220·2	64·17	1758	202·8	1644
20·353	20·0	0	20·353	220·0	64·16	1758	202·6	1642
....	....	....	....	17·4	4·23	116	0	0
7·312	20·8	·068	7·380	99·1	30·83	845	81·7	729
7·265	20·8	·068	7·333	98·8	30·84	845	81·4	723
....	....	....	....	17·4	4·45	122	0	0
4·397	21·0	·087	4·484	69·1	21·37	586	51·7	464
4·415	21·0	·087	4·502	69·4	21·35	585	52·0	464
....	....	....	....	17·4	4·43	121	0	0
13·306	21·2	·104	13·410	158·0	48·93	1341	140·6	1220
13·330	21·3	·112	13·442	158·3	48·98	1342	140·9	1209
....	....	....	....	17·4	4·86	133	0	0

46: *Observations for alcohol.*—Table 13 contains data for alcohol corresponding to those already given for ether. The two series, obtained with the same tube on successive days, are satisfactory throughout. The arrangement of data has been already explained.

The alcohol used was kindly furnished me by Dr. Stokes. I redistilled it over lime in small quantities immediately before filling the constant volume tube. Nevertheless some absorption of moisture from the air during the manipulations was not avoidable.

TABLE 13.—*Isometrics of alcohol. Observations.*

N'_{θ}.	t.	n_{θ}.	N_{θ}.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
....	....	....	....	17·2	4·92	135	0	0
4·485	20·3	·025	4·510	69·5	25·46	697	52·3	562
4·491	20·3	·025	4·516	69·7	25·46	697	52·5	556
....	....	....	....	17·2	5·14	141	0	0
7·285	20·7	·059	7·344	98·9	37·67	1032	81·7	891
7·282	20·8	·068	7·350	99·0	37·68	1032	81·8	888
....	....	....	....	17·2	5·27	144	0	0
13·427	21·0	·087	13·514	159·0	63·04	1727	141·8	1583
13·424	21·0	·087	13·511	159·0	63·04	1727	141·8	1575
....	....	....	....	17·2	5·53	152	0	0
....	....	....	....	17·0	4·92	135	0	0
7·377	19·9	—·008	7·370	99·2	37·72	1034	82·2	899
7·356	20·0	±·000	7·356	99·1	37·70	1033	82·3	893
....	....	....	....	16·8	5·12	140	0	0
13·547	20·4	·034	13·581	159·7	63·20	1732	142·9	1592
13·541	20·5	·042	13·583	159·7	63·15	1730	142·8	1582
....	....	....	....	16·9	5·39	148	0	0
....	....	....	....	16·9	5·39	148	0	0
4·100	22·2	·192	4·292	67·4	25·14	689	50·5	541
4·090	22·2	·192	4·282	67·0	25·16	689	50·0	533
....	....	....	....	17·0	5·69	156	0	0
7·106	22·4	·209	7·315	98·9	38·36	1051	81·9	895
7·077	22·4	·209	7·286	98·5	38·36	1051	81·5	884
....	....	....	....	17·0	6·11	167	0	0

47. *Observations for thymol, para-toluidine, and diphenylamine.*— Tables 14, 15, 16 contain results for thymol, para-toluidine, and diphenylamine, arranged on the same plan as Tables 12 and 13. Thymol is particularly convenient since, after firing, it admits of undercooling much below its melting point. Observations can thus be made even at 17°. In case of the other two substances this is possible to a less extent, and it is necessary to insert the constant volume tube into a hot piezometer. A large bath of heated water must be at hand to prevent freezing during the manipulations. (§ 32.)

TABLE 14.—*Isometrics of thymol. Observations.*

N'_θ.	t.	n_θ.	N_θ.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
4·227	20·7	·059	4·286	67·1	32·65	895	49·9	704
4·253	20·8	·068	4·321	67·5	32·69	896	50·3	705
7·259	20.8	·068	7·327	98·8	49·11	1346	81·6	1155
7·235	20·9	·076	7·311	98·6	49·16	1347	81·4	1156
4·282	21·0	·087	4·369	68·1	33·02	905	50·9	714
4·324	21·0	·087	4·411	68·5	33·07	906	51·3	715
....	....	....	....	17·2	6·97	191	0	0
7·230	21·1	·095	7·325	98·9	49·62	1360	81·7	1169
7·221	21·2	·104	7·325	98·9	49·69	1361	81·7	1160
....	....	....	....	17·2	7·35	201	0	0
9·652	21·7	·146	9·798	123·5	62·40	1709	106·3	1508
9·616	21·7	·146	9·792	123·4	62·35	1708	106·2	1495
....	....	....	....	17·2	7·77	213	0	0
....	....	....	....	17·0	7·78	213	0	05
4·306	20·5	·042	4·348	68·0	34.08	934	51·0	721
4·300	20·4	·034	4·334	67·8	34·11	935	50·9	729
....	....	....	....	16·9	7·51	206	0	0
7·288	20·4	·034	7·322	98·9	50·07	1372	82·0	1166
7·315	20·4	·034	7·349	99·0	50·06	1372	82·2	1171
....	....	....	....	16·8	7·34	201	0	0
9·875	20·4	·034	9·909	124·5	62·49	1713	107·7	1512
9·958	20·3	·025	9·983	125·3	62·58	1715	108·5	1506
....	....	....	....	16·8	7·63	209	0	0

TABLE 15.—*Isometrics of para-toluidine. Observations.*

N'_θ.	t.	n_θ.	N_θ.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
4·206	21·5	·131	4·337	67·8	15·34	420	0	0
4·182	21·6	·138	4·320	67·5	15·32	420	0	0
7·147	21·8	·155	7·302	98·5	31·84	872	31·0	452
7·132	21·8	·158	7·290	98·4	31·79	871	30·4	441
4·162	22·3	·200	4·362	68·0	15 69	430	0	0
4·153	22·3	·200	4·353	67·9	15·66	429	0	0
9·578	22·5	·218	9·796	123·5	45·20	1238	55·6	809
9·572	22·6	·226	9·798	123·5	45·24	1239	56·0	799
4·071	22·8	·245	4·316	67·5	16·06	440	0	0
4·100	22·8	·245	4·345	67·9	16·04	439	0	0
13·000	23·1	·270	13·270	156·7	57·51	1576	88·8	1137
13·006	23·2	·279	13·285	157·0	57·50	1575	89·1	1124
4·035	23·5	·306	4·341	67·9	16·45	451	0	0
4·027	23·6	·313	4·340	67·9	16·46	451	0	0

TABLE 16.—*Isometrics of diphenylamine. Observations.*

N'_θ.	t.	n_θ.	N_θ.	θ.	N_p.	p.	$\Delta\theta$.	Δp.
4·035	23·1	·270	4·305	67·5	18·01	493	0	0
4.027	23·1	·270	4·297	67·5	18·02	494	0	0
6·975	23·4	·298	7·273	98·2	36·26	993	30·7	499
6·969	23·4	·298	7·267	98·2	36·30	995	30·1	487
4·051	23·8	·330	4·381	68·1	18·53	508	0	0
4·059	23·8	·330	4·389	68·3	18·54	508	0	0
9·525	24·0	·350	9·875	124·1	51·95	1423	55·8	915
9·587	24·0	·350	9·937	124·9	52·29	1433	57·1	900
3·975	24·2	·367	4·342	67·8	19·46	533	0	0
3·981	24·2	·367	4.348	68·0	19·36	530	0	0

Another zero.

13·200	24·2	·367	13·567	159·6	65·15	1785	92·0	1346
13·171	24·3	·375	13·546	159·5	65·12	1784	91.9	1345
3·949	24·4	·384	4·333	67·6	16·02	439	0	0
3·955	34·4	·384	4·339	67·8	15·93	437	0	0
6·802	24·4	·384	7·186	97·3	33·49	918	29·5	481
6·834	24·4	·384	7·218	97·8	33·48	917	29·7	479
3·985	24·4	·384	4·369	68·1	15·98	438	0	0
4·012	24·4	·384	4·396	68·4	15·98	438	0	0
9·470	24·4	·384	9·854	124·0	49·34	1352	55·6	914
9·534	24·4	·384	9·918	124·8	49·39	1353	56·2	904
4·035	24·4	·384	4·419	68·5	16.39	449	0	0
4·021	24·3	·375	4·396	68·5	16.41	450	0	0

TEMPERATURES CORRECTED.

48. *Behavior of the torsion galvanometer.*—An inspection of the tables shows the temperatures to need correction, for the boiling points (water, for instance) are usually low. The cause of this discrepancy is to be sought in the temperature coefficient and perhaps also in the time coefficient of the magnets of the torsion galvanometer. This error is easily allowed for as follows: It is clear that the magnetic change which obtains affects all deflections (deflections for all temperatures) uniformly. Consequently if N'_θ be the twist corresponding to 100° on any day of observation, and if N_θ be the corresponding twist on the day of calibration, both observed at the same torsion galvanometer, then N_θ / N'_θ is the factor for the reduction of all temperature observations for the former day to the scale of the calibration day.

To test this inference I made two independent calibrations of the same couple about a month apart. The constants a and b given in Table 17, where $N_\theta = a\,(T-t) + b\,(T^2-t^2)$, show considerable variation during this interval.[1] Computing the twists N_θ and N'_θ for different temperatures T, when $t = 20°$, it is found that N_θ / N'_θ is constant within less than 3 per cent for the whole interval 50° to 400°. Clearly this is an error of observation, since the constants a and b never quite faithfully reproduce the calibration interval. Slight reciprocal changes of a and b, for instance, would wipe out the discrepancy $\Delta(N_\theta / N'_\theta)$, without appreciably slighting the observations.

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[1] T, t are the temperatures at the junctions of the platinum platinum-iridium thermo-couple.

TABLE 17.—*Constants of the torsion galvanometer and couple. Comparisons of T, April 20 and May 27.*

April 20 $\left\{ \begin{array}{l} a = .0844, \\ b = .0000717, \end{array} \right.$ May 27 $\left\{ \begin{array}{l} a' = .0829. \\ b' = .0000694. \end{array} \right.$

[Computed from observations at 100° and 357°.]

T.	N_θ.	N'_θ.	N_θ/N'_θ.
°			
50	2·683	2·632	·9810
100	7·440	7·298	·9809
150	12·557	12·311	·9804
200	18·031	17·670	·9800
250	23·865	23·377	·9796
300	30·057	29·430	·9792
350	36·611	35·831	·9787
400	43·520	42·578	·9784

49. *Air thermometers comparison. Apparatus.*—There is a more serious question relative to the degree of truth of the interpolation equation $N_\theta = a\,(T - t) + b\,(T^2 - t^2)$. This can only be decided by direct air-thermometer comparisons, such as are given in Table 18. There are three complete time series and two comparisons in steam.

The air-thermometer bulb used was my reentrant form, combined with the Jolly-Pfaundler stand, by a platinum capillary. The method of work is described elsewhere.[1] Here I need only remark that the metallic fiducial mark at the bulb end of the manometer, being nothing more than the sharpened end of the platinum capillary, the criterion of constant volume was given by an electric contact.

To heat the bulb I made use of a large paraffin bath, being a cylinder about 7 inches long and 7 inches in diameter. This was heavily jacketed with a thickness of about 1 inch of asbestos. At the center of the bath the bulb of the air thermometer was placed; and being of the reentrant form the junction of the thermocouple in its turn was at the center of the bulb.

The paraffin bath, Figs. 9, and 10, needs further description. It consists of two half cylindrical boxes of brazed copper, *d e f* and *g b k*, which fit into each other on their flat sides. These are of thin sheet copper, provided with hemispherical cavities *H* and gutters *t t* adapted to receive the air-thermometer bulb and thermocouple. The figure shows the thermocouple *a o β* and the air thermometer bulb *H H t* in place, the stem of the latter and the insulator of the former issuing in opposite directions. Though filled with paraffin in the present experiments, the apparatus was constructed to be used as a vapor bath at 210° (naphthalene) or 310° (diphenylamine). In such a case the chimneys *N* are prolonged by iron gas pipe into which the vapors distill and condense, falling back into the charge below (indicated by the dotted horizontal line). In this way thoroughly constant temperature may be obtained, and the apparatus is therefore available for standardizing[2] a porce-

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[1] Bull. U. S. Geol. Surv., No. 54, 1889, pp. 168 et seq., 188 et seq.

[2] Cf. Barus: Bull. U. S. Geol. Surv., No. 54, 1889, pp. 22, 208 et seq.

lain (noninglazed) air thermometer, by aid of a glass air thermometer bulb of known constants, through the intervention of (or consecutive comparison with) the same platinum-iridium thermocouple.

In all cases the bath is to be heavily jacketed with asbestos, to a thickness of say 1 inch. Two burners are then sufficient.

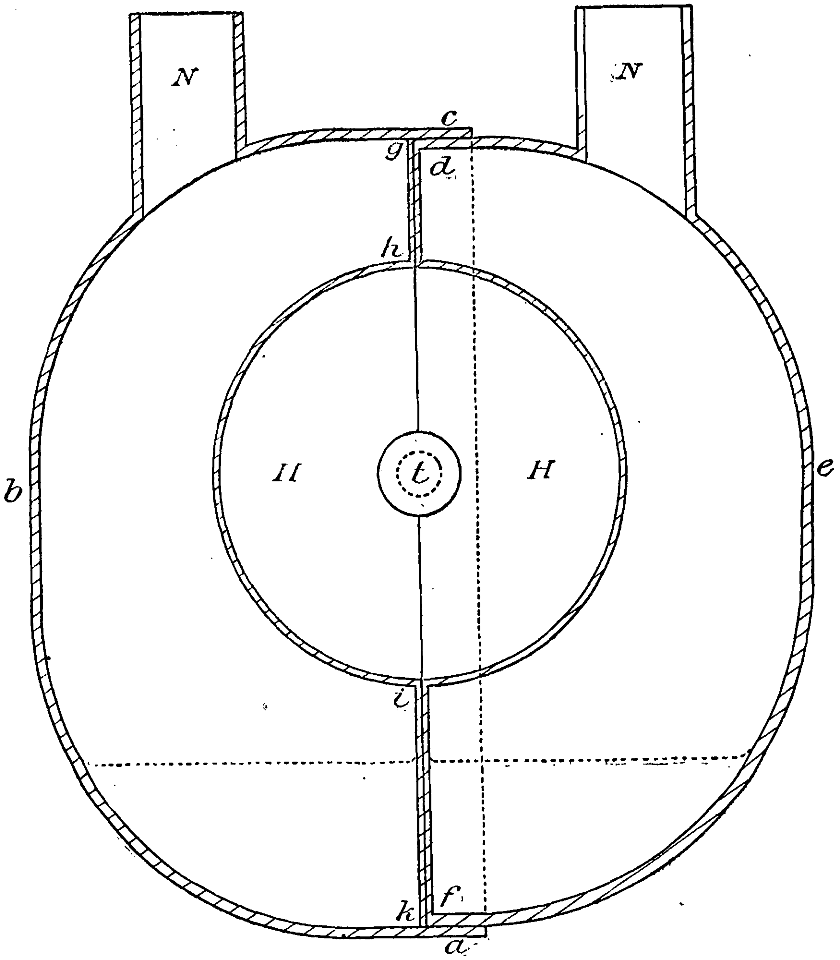

FIG. 9.—Sectional vapor bath, for comparing air thermometer and thermocouple.

50. *Observations.*—Observations were made during the period of cooling, after heating the bath to 300°; cooling must, therefore, take place so slowly that the temperature of the air thermometer bulb and of the thermocouple may be regarded as identical. Whether this is the case can be decided only by trial. Therefore, in making the following comparisons, the first and third series were observed during ordinary cooling; in the fifth series, however, a flat evaporating burner was placed under the paraffin bath to insure slower cooling. The liquid was stirred and paraffin gradually added to compensate for the contraction in cooling. In the table V is the volume of the air-thermometer bulb, v' that of the hot part of the stem, v'' that of the cold stem and of the capillary connections and dead spaces; finally h_0 is the observed pressure for the bulb in melting ice. It is advisable to work with slightly rarefied air, to avoid pressure on the bulb at the high temperatures.

N'_{20} is the twist observed at the torsion galvanometer at the time given, and when the temperature measured by the air thermometer was $T_{a,t}$. From this I computed N_{20}, the twist which would have been observed on the day of calibration (May 27), by the method shown in § 48. Hence I made use of the series II and V (comparisons in steam) and of the *low temperature* comparisons between thermocouple and air thermometer, for here the cooling is so slow that no time lag need be apprehended.

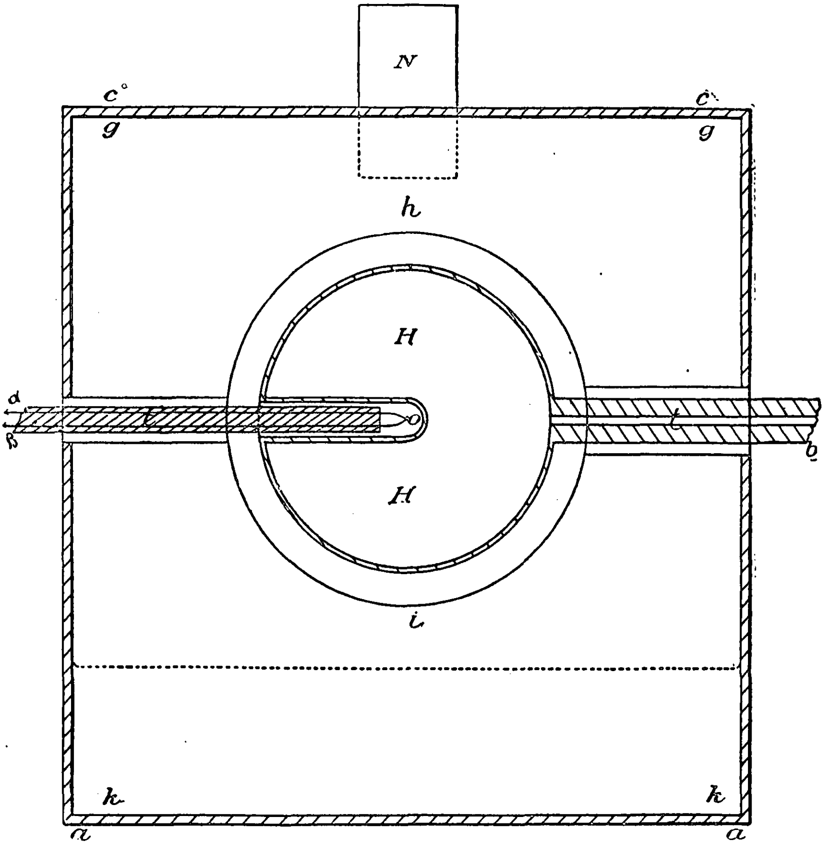

FIG. 10.—Longitudinal elevation of one of the halves of vapor bath, showing the thermometers in place.

From both N'_θ and N_θ, the thermoelectric temperature equivalents $T_{t,c}$ and $T_{t,c}$ were then computed, by aid of the data of Table 17.

TABLE 18.—*Comparison of thermocouple and air thermometer.*

V=239·93^{cc}; v'=·030^{cc}; v''=.694^{cc}; h_0=48·28^{cm}.

Time.	N'_{20}.	T_{at}.	N_{20}.	T_{tc}.	Diff.	T_{tc}.	Diff.
I. 21	28·464	292·1	28·749	291·6	+ ·5	294·0	=1·9
36	25·531	263·5	25·786	267·8	−4·3	270·0	−6·5
44	24·001	251·4	24·241	255·1	−3·7	257·3	−5·9
52	22·648	239·4	22·874	243·6	−4·2	245·6	−6·2
61	20·456	222.1	20·660	224·6	−2·5	226·5	−4·4
7	19·438	213·3	19·632	215·5	−2·2	217.4	−4·1
18	18·052	201·3	18·233	203·1	−1·8	204·7	−3·4
34	16·066	183·2	16·227	185·2	−2·0	186.5	−3·3
45	14·893	171·2	15·042	174·2	−3·0	175·6	−4·4
58	13·571	160·6	13·707	161·8	−1·2	163·2	−2·6
17	12·155	146·9	12·277	148·5	−1·6	149·7	−2·8
34	10·840	134·9	10·948	135·4	− ·5	136·7	−1·8
50	9·912	125·5	10·011	126·4	− ·9	127·4	−1·9
12	8·639	114·0	8·725	113·6	+ ·4	114·5	− ·5
35	7·598	103·8	7·674	103·1	+ ·7	103·8	± ·0
9	6·359	90·4	6·423	90·3	+ ·1	91·0	− ·6
40	5·448	80·9	5·502	80·5	+ ·4	81·1	− ·3
58	4·975	76·4	5·025	75·4	+1·0	76·0	+ ·4
19	4·479	70·9	4·524	70·0	+ ·9	70·5	+ ·4
39	4·075	66·7	4·116	65·7	+1·0	66·1	+ ·6
II.* 0	7·245	100·22	7·317	99·4	+ ·8	100·2	± ·0
20	7·264	100·28	7·337	99·6	+ ·7	100·4	− ·1
III. 34	28·174	286.3	28·456	289·4	−3·1	291·6	−5·3
45	26·136	270·0	26·397	272·8	−2·8	275·0	−5·0
56	24·400	255·0	24·644	258·5	−3·5	260·5	−5·5
7	22·050	235·3	22·270	238·5	−3·2	240·5	−5·2
17	20·731	224·3	20·938	227·0	−2·7	229·0	−4·7
26	19·338	214·5	19·531	214.6	− .1	216·6	−2·1
38	18·036	200·4	18·216	203.0	−2·6	204·8	−4·4
50	16·799	189·2	16·967	192·0	−2·8	193·6	−4·4
6	15·184	176·2	15·336	177·0	− ·8	178·5	−2·3
21	13·899	164·2	14·038	165·0	− ·8	166·4	−2·2
44	12·237	148·9	12·359	149·3	− ·4	150·4	−1·5
IV. 53	29·702	299·6	30·147	301·6	−2·0	305·0	−5·4
5	29·223	295·3	29·661	297·9	−2·6	301·2	−5·9
16	28·744	292·0	29·175	294·0	−2·0	297·3	−5·3
25	28·410	289·1	28·836	291·4	−2·3	294·8	−5·7
33	22·025	236·3	22·355	238·3	−2·0	241·2	−4·9
42	21·492	232·2	21·814	233·6	−1·4	236·5	−4·3
55	20·866	226·9	21·179	228·3	−1·4	231·0	−4·1
9	20·293	222·0	20·597	223·2	−1·2	225·8	−3·8
3	14·334	167·7	14·549	169·0	−1·3	171·2	−3·5
13	13·590	160·9	13·794	162·0	−1·1	164·1	−3·2
24	12·720	153·4	12·911	154·0	− ·6	155·6	−2·2
36	11·897	145·4	12·076	145·9	− ·5	147·7	−2·3
18	9·487	122·5	9·629	122·0	+ ·5	123·4	− ·9
29	8·943	117·2	9·077	116·7	+ ·5	118·0	− ·8
38	8·567	113·1	8·696	113·0	+ ·1	114·3	−1·2
52	7·966	107·1	8·086	106·7	+ ·4	108·0	− ·9
29	6·618	94·0	6·717	93·0	+1·0	94·0	± ·0
39	6·335	90·9	6·430	90·0	+ ·9	91·0	+ ·1
V.† 16	7·205	100·03	7·313	99·0	+1·0	100·1	− ·1
28	7·221	100·09	7·329	99·1	+1·0	100·3	− ·2
37	7·199	100·09	7·307	99·0	+1·1	100·1	± ·0

* Steam, temperature 100·11°
† Steam temperature 99·93°.

TABLE 19.—*Interpolated from the above.*

T_{20} (air thermometer).	50°	100°	150°	200°	250°	300°
N_{20}..............	2·63	7·30	12·47	18·05	23·90	30·20

Tables 17 and 18, or a graphic representation, show at once that throughout every stage of cooling, temperature as registered by the thermocouple is always higher than the corresponding temperature of the air thermometer. Inasmuch as the system cools from the *outside* of the air thermometer bulb, this is precisely what must occur in case of too rapid cooling. It is well, however, to note that in Table 18, series IV, notwithstanding much retarded cooling, the discrepancy between air thermometer and thermocouple retains its original magnitude. Without passing judgment, therefore, I have deduced $T_{a}'{}_{t}$ and N_{20} from all the observations, for use below. See Table 19.

51. *Isometrics corrected as to temperature.*—Applying the corrected temperatures investigated in the foregoing paragraph, I obtained the following data for the isometrics. N_θ is the corrected twist and $\theta_{a}'{}_{t}$ and θ_{tc} its thermal equivalent, as expressed by the air thermometer or the thermocouple (boiling points, H_2O and Hg), respectively. The two data given under $\Delta\ \theta$ are to be similarly interpreted. Δp is the value already met in tables 12 to 16.

It follows from the slight irregularities still observable in the boiling points, that in order to use the torsion galvanometer satisfactorily, check measurements of the boiling point of water must be made before and after any series of temperature observations.

TABLE 20.—*Isometrics of ether.*

N_θ.	$\theta_{t,c}$.	$\theta_{a,c}$.	$\Delta\theta$.	Δp.
....	15·1	15·1	0	0
4·249	67·5	68·2	52·4 53·1	474
4·273	67·8	68·4	52·3 52·9	479
....	15·5	15·5	0	0
7·291	99·9	99·9	84·4 84·4	762
7·309	100·1	100·1	84·6 84·6	765
....	15·5	15·5	0	0
....	15·4	15·4	0	0
13·301	159·4	158·1	144·0 142·7	1272
13·412	160·5	159·2	145·0 143·7	1278
....	15·5	15·5	0	0
7·318	100·2	100·2	84·7 84·7	778
7·282	99·8	99·8	84·5 84·5	778
4·260	67·7	68·4	52·4 53·1	493
4·260	67·7	68·5	52·7 53·5	493
....	15·0	15·0	0	0
....	15·9	15·9	0	0
7·312	100·1	100·1	84·2 84·2	755
7·288	99·9	99·9	84·0 84·0	757
....	16·2	16·2	0	0
15·513	180·1	178·0	163·9 161·8	1439
15·566	180·6	178·6	164·4 162·4	1442
....	16·2	16·2	0	0
....	15·9	15·9	0	0
16·245	186·9	184·5	171·0 168·6	1472
16·315	187·5	185·4	171·6 169·5	1468
16·405	188·4	186·2	172·6 170.4	1460
....	15·8	15·8	0	0
7·308	100·1	100·1	84·3 84·3	767
7·293	99·9	99·9	84·0 84·0	768
....	15·9	15·9	0	0
....	16·0	16·0	0	0
7·300	100·0	100·0	84·0 84·0	783
7·300	100·0	100·0	84·0 84·0	784
....	16·0	16·0	0	0
7·294	99·9	99·9	83·9 83·9	767
7·287	100·0	100·0	84·0 84·0	770
4·287	68·1	68·5	52·0 52·4	491
4·296	68·2	68·6	52·0 52·4	493
....	16·2	16·2	0	0

TABLE 20.—*Isometrics of ether*—Continued.

N_θ.	$\theta_{t,c}$.	$\theta_{a,t}$.	Δθ.	Δp.
....	16·4	16·4	0	0
7·294	99·9	99·9	83·5 83·5	781
7·285	100·0	99·9	83·6 83·5	783
20·177	222·0	219·0	205·6 202·6	1763
20·179	222·1	219·0	205·7 202·6	1760
....	16·5	16·5	0	0
4·251	67·5	68·2	51·0 51·7	509
4·284	67·9	68·5	51·4 52·0	515
7·284	99·8	99·8	83·1 83·1	822
7·313	100·1	100·1	83·4 83·4	824
....	16·7	16·7	0	0
....	16·6	16·6	0	0
7·308	100·1	100·1	83·5 83·5	740
7·331	100·3	100·3	83·8 83·8	742
....	16·5	16·5	0	0
....	16·6	16·6	0	0
4·346	68·6	69·2	52·0 52·6	465
4·334	68·5	69·1	51·9 52·5	467
7·325	100·2	100·2	83·6 83·6	745
7·314	100·1	100·1	83·5 83·5	747
....	16·6	16·6	0	0
....	16·6	16·6	0	0
4·342	68·5	69·2	51·9 52·6	463
4·355	68·7	69·4	52·1 52·8	464
7·295	99·9	99·9	83·3 83·3	739
7·323	100·2	100·2	83·6 83·6	743
....	16·6	16·6	0	0
13·230	158·8	157·4	142·2 140·8	1289
13·356	160·0	158.7	143·3 142·0	1208
....	16·7	16·7	0	0
16·009	184·9	182·7	168·2 166.0	1370
16·021	185·0	182·8	168·3 166·1	1369
....	16·7	16·7	0	0
....	17·6	·17·6	0	0
4·351	68·6	69·4	51·0 51·8	439
4·359	68·6	69·5	51·0 51·9	440
7·267	99.7	99·7	82·0 82·0	706
7·272	99·7	99·7	82·0 82·0	707
....	17·7	17·7	0	0
13·320	159·6	158·2	141·9 140·5	1191
13·308	159·6	158·1	141·8 140·3	1171
....	17·8	17·8	0	0
20·138	221·8	218·5	204·0 200·7	1639
20·146	222·0	218·7	204·1 200·8	1611
....	17·9	17·9	0	0
....	17·8	17·9	0	0
7·274	99·7	99.7	81.9 81·9	712
7·267	99·7	99·7	81·7 81·7	701
....	18·0	18·0	0	0
20·290	223·1	219.9	205·1 201·9	1643
20·291	223·1	219·9	205·0 201·8	1619
....	18·1	18·1	0	0
4·350	68·6	69·2	50·5 51·1	437
4·361	68·6	69·5	50·5 51·4	437
....	(18·1)	(18·1)	0	0
13·420	160·4	159·2	142·3 141·1	1202
13·437	160·5	159.4	142·7 141·5	1196
....	17·9	17·9	0	0
....	17·4	17·4	0	0
20·216	222·4	219·2	205·0 201·8	1644
20·198	222·3	219·0	204·9 201·6	1642
....	17.4	17·4	0	0
7·324	100·2	100·2	82·8 82·8	729
7·277	99·8	99·8	82·4 82·4	723
....	17·4	17·4	0	0
4·450	69·8	70·2	52·4 52·8	464
4·468	69·9	70·4	52·5 53·0	464
....	17·4	17·4	0	0
13·308	159·5	158·1	142·1 140·7	1220
13·340	159·7	158·4	142·1 141·0	1209
....	17·4	17·4	0	0

TABLE 21.—*Isometrics of alcohol.*

N_θ	$\theta_{t,c}$	$\theta_{a,t}$	$\Delta\theta$	Δp
....	17·2	17·2	0	0
4·493	70·1	70·6	52·9 53·4	562
4·499	70·2	70·9	53·0 53·7	556
....	17·2	17·2	0	0
7·317	100·2	100·2	83·0 83·0	891
7·323	100·2	100·2	83·0 83·0	888
....	17·2	17·2	0	0
13·464	160·8	159·6	143·6 142·4	1583
13·461	160·8	159·6	143·6 142·4	1575
....	17·2	17·2	0	0
....	17·0	17·0	0	0
7·337	100·4	100·4	83·4 83·4	899
7·323	100·2	100·2	83·4 83·4	893
....	16·8	16·8	0	0
13·520	161·4	160·0	144·6 143·2	1592
13·522	161·4	160·0	144·5 143·1	1582
....	16·9	16·9	0	0
....	16·9	16·9	0	0
4·310	68·2	68·9	51·3 52·0	541
4·300	68·1	68·8	51·1 51·8	533
....	17·0	17·0	0	0
7·345	100·4	100·4	83·4 83·4	895
7·316	100·2	100·2	83·2 83·2	884
....	17·0	17·0	0	0

TABLE 22.—*Isometrics of thymol.*

N_θ	$\theta_{t,c}$	$\theta_{a\,t}$	$\Delta\theta$	Δp
4·273	67·7	68·5	50·5 51·3	704
4·308	68·2	68·9	51·0 51·7	705
7·305	100·0	100·1	82·8 82·9	1155
7·289	99·9	99·9	82·7 82·7	1156
4·356	68·8	69·2	51·6 52·0	714
4·398	69·2	69·8	52·0 52·6	715
....	17·2	17·2	0	0
7·303	100·0	100·0	82·8 82·8	1169
7·303	100·0	100·0	82·8 82·8	1160
....	17·2	17·2	0	0
9·769	124·9	124·6	107·7 107·4	1508
9·763	124·8	124·5	107·6 107·3	1495
....	17·2	17·2	0	0
....	17·0	17·0	0	0
4·339	68·5	69·1	51·5 52·1	721
4·325	68·4	69·0	51·5 52·1	729
....	16·9	16·9	0	0
7·307	100·1	100·1	83·2 83·2	1166
7·334	100·3	100·3	83·5 83·5	1171
....	16·8	16·8	0	0
9·889	126·1	125·8	109·3 109·0	1512
9·963	126·9	126·5	110·1 109·7	1506
....	16·8	16·8	0	0

About a month later, and after the gauge and appurtenances had been much used during intervening experiments, I repeated the work for thymol again, using the same tube as in Table 22. The results are given in the next table (22 supplement) and will be seen to be in excellent accord with the earlier data. This proves that there can have been no error in the method of measurement between times, and hence the exceptional behaviors noted in case of some of the following substances are actual peculiarities. The constancy of the gauge factors vouched for in this way is gratifying.

TABLE 22 (supplement).—*Isometrics of thymol. Check-work a month after the above.*

N'_θ	t	$n\theta$	$N\theta$	θ	N_p	p	$\Delta\theta$	Δp
....	....	....	....	25·9	6·20	170	0	0
6·513	27·6	·665	7·188	100·0	44·47	1218	74·1	10·48
6·460	27·7	·673	....	100·0	44·50	1219	74·0	10·38
....	....	....	....	26·0	6·60	181	0	0
8·896	28·1	·711	9·607	125·1	57·25	1569	99·1	13·88
8·925	28·1	·711	9·636	125·5	57·25	1569	99·5	13·90
....	....	....	....	26·0	6·55	179	0	0

TABLE 23.—*Isometrics of para-toluidine.*

N_θ	$\theta_{t,c}$	$\theta_{a,t}$	$\Delta\theta$	Δp	N_θ	$\theta_{t,c}$	$\theta_{a,t}$	$\Delta\theta$	Δp
4·328	68·4	69·1	....	....	9·776	125·0	124·8	56·7 55·9	799
4·311	68·2	68·9	0	0	4·307	68·3	68·9	0	0
7·286	99·9	99·9	31·7 31·0	452	4·336	68·5	69·2	0	0
7·274	99·7	99·7	31·1 30·4	441	13·231	158·8	157·4	90·3 88·2	1137
4·352	68·6	69·3	0	0	13·256	159·0	157·8	90·5 88·8	1124
4·343	68·5	69·2	0	0	4·332	68·5	69·0	0	0
9·774	124·8	124·6	56·3 55·4	809	4·331	68·5	69.0	0	0

TABLE 24.—*Isometrics of diphenylamine.*

N_θ	$\theta_{t,c}$	$\theta_{a,t}$	$\Delta\theta$	Δp	N_θ	$\theta_{t,c}$	$\theta_{a,t}$	$\Delta\theta$	Δp
4·323	68·3	69·0	....	....	13·731	163·4	162·2	94·4 92·6	1345
4·315	68·2	69·0	0	0	4·392	69·0	69·6	0	0
7·303	100·0	100·0	31·8 31·0	499	4·398	69·2	69·8	0	0
7·297	100.0	100·0	30·8 30·2	487	7·284	99·9	99·8	30·7 30·0	481
4·399	69.2	69·8	0	0	7·316	100.2	100·2	30·7 30·1	479
4·407	69·4	69·9	0	0	....	(69·5)	(70·1)	....	....
9·916	126·5	126·0	57·1 56·1	915	4·428	69·5	70·1	0	0
9·978	127·0	126·6	58·3 57·2	900	4·455	69·7	70·5	0	0
4·360	68·7	69·4	0	0	9·988	127·1	126·8	57·4 56·3	914
4·366	68·8	69·6	0	0	10·053	127·6	127·3	57·6 56·5	904
13·752	163·7	162·4	94·7 92·8	1346	4·479	70·0	70·8	0	0
					4·456	69·8	70·6	0	0

CORRECTION FOR THE THERMAL AND ELASTIC VOLUME CHANGES OF THE GLASS TUBES.

52. *Thermal expansion of glass.*—The direct measurement of the elastic constants of glass throughout an interval of 300° and 2000 atmospheres is at present out of the question. Hence I selected liquid substances of large compressibility, in order that the discrepancies due to the compressibility of glass might be of smaller magnitude, and could, therefore, be at least in a measure applied by interpolation from known data. It is clear at the outset, moreover, that the correction in question is of smaller moment, because it is differential in character. Rise of temperature expands the glass tube, pressure again diminishes it. If the isometrics of solid glass and the liquids were identical, the correction would be nil. Curiously enough this is nearly the case.

The expansion of glass throughout large intervals of temperature was measured by Dulong and Petit,[1] by Recknagel,[2] and by others. The results of the latter are the larger. For this reason I accept the former, seeing that in the case of compressibility of glass a datum

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[1] Dulong and Petit: Ann. de chim. et phys. (2), VII, 1817, p. 113.

[2] Recknagel: Sitz. Ber. k. Bayr. Acad. (2), 1866, p. 327.

too small must be accepted for want of data on the thermal variations. Dulong and Petit find that from—

0° to 100°, coefficient of expansion, $\beta = 258/10^7$
0° to 200°, coefficient of expansion, $\beta = 276/10^7$
0° to 300°, coefficient of expansion, $\beta = 304/10^7$.

A chart may then be platted from which β may be taken for any interval. It follows that the volumes, V_{20} of the constant volume tube, in terms of the volume at 20°, will be (pressure = 1 atmosphere).

$T =$	20°	50°	100°	150°	200°	250°	300°
$V_{20} =$	1·00000	1·00075	1·00208	1·00350	1·00504	1·00670	1·00856

Again, the corresponding volumes, V_{70} in terms of the volume at 70°, will be—

$T =$	70°	100°	150°	200°
$V_{70} =$	1·00000	1·00080	1·00222	1·00376

53. *Compressibility of glass.*—On the other hand the compressibility of glass, $1/k$, from corroborative results of Regnault and Amagat[1], is $1/4 \times 10^{11}$ in terms of dynes and square centimeters. Bearing in mind, therefore, that no compensation of k in respect to temperature can be made, the volumes of the constant volume tube under any hydrostatic pressure, P will be $1 - P \times 10^6/k$, where

$P =$	500	1000	1500	2000	2500	3000 atmospheres,
$P/k =$	·00125	·00250	·00375	·00500	·00625	.00750

Thus, when the initial temperature is 20°, the volumes will be as follows:

TABLE 25.—*Isometrics of solid glass, in terms of unit of volume at 20° and 1 atmosphere.*

Θ =	20°	50°	100°	150°	200°	250°	300°
P = 1 atm.	1·0000	1·0007	1·0021	1·0035	1·0050	1·0067	1·0086
500 atm.	·9987	·9995	1·0008	1·0022	1·0030	1·0054	1·0073
1000 atm.	·9975	.9982	·9996	1·0010	1·0025	1·0042	1·0061
1500 atm.	·9962	·9970	·9983	·9997	1·0013	1·0029	1.0048
2000 atm.	·9950	·9957	·9971	·9985	1·0000	1·0017	1·0036
2500 atm.	-9937	·9945	·9958	·9972	·9988	1.0004	1·0023
3000 atm.	·9925	·9932	·9946	·9960	·9975	·9992	1.0011

A similar table is easily constructed for unit of volume at 70° and 1 atmosphere.

If these results are represented graphically, the volume changes δv, if the constant volume tubes can be at once obtained for each of the pairs of values of $\Delta\theta$ and Δp given in tables 20 to 24. I have given a full list of the values, δv, in table 27, where the arrangement adopted is such as to correspond to the earlier tables (12 to 16).

54. *Compressibility of the above liquids.*—Having given these data, it is therefore finally necessary to find the pressure equivalent of the

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[1] Amagat: C. R., CVIII, 1889, p. 1199; CVII, 1888, p. 618, or J. D. Everett's Tables (Macmillan, 1879, p. 53).

values δv; in other words, to find the value δp which will annul δv. To do this it is necessary to know the compressibility of each of the liquids under the given conditions of pressure and temperature. The results of my earlier papers[1] are available for this purpose, and from them I take the following mean values.

TABLE 26.—*Correction factors* $\left(d\left(\frac{v}{V}\right)/\,dp\right)_{\theta p,}$ *being compressibilities at* 0° *and* p *atm.*

ETHER. $\Delta\theta = \theta - 20^\circ$.

θ	$10^6 d \; d\left(\frac{v}{V}\right)/dp$	p
70°	100	600
100	95	830
160	80	1340
185	70	1400
220	60	1760

ALCOHOL. $\Delta\theta = \theta - 20^\circ$.

θ	$10^6 d \; d\left(\frac{v}{V}\right)/dp$	p
70°	66	700
100	63	1040
160	51	1730

PARATOLUIDINE. $\Delta\theta = \theta - 70^\circ$.

θ	$10^6 d \; d\left(\frac{v}{V}\right)/dp$	p
100	52	870
136	50	1240
160	45	1580

THYMOL. $\Delta\theta = \theta - 20^\circ$.

θ	$10^6 \times d\left(\frac{v}{V}\right)/dp$	p
70°	46	910
100	44	1360
130	42	1710

DIPHENYLAMINE. $\theta\Delta = \theta - 60^\circ$.

θ	$10^6 \times d\left(\frac{v}{V}\right)/dp$	p
100	43	960
130	40	1390
160	38	1780

Knowing therefore the volume changes of the glass, and the compressibility of the inclosed liquid under the given conditions of pressure and temperature, the correcton δp follows by division. This is fully given in Table 27. Utilizing these values I constructed the final Table 28, in which $\Delta\theta$ and Δp, such as would be observed if the glass tube were absolutely rigid, are inserted. This table 28 exhibits the importance of the correction δp, relative to Δp. For $\Delta\theta$ I give the thermoelectric values only, believing them to be the more nearly correct. The table also contains p_0 and θ_0, which are the initial pressures and temperatures used in constructing Δp and $\Delta\theta$ (cf. Tables 12 to 16). In case of paratoluidine and diphenylamine, p_0 had to be estimated.

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[1] Barus: Am. Journ. (3), XXXIX, 1890, p. 501.

TABLE 27.—*Corrections* (δp) *for thermal and elastic volume changes of glass tubes.*

ETHER.

Δp	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp.$	δp
475	52	+ 100	110	+ 1
765	84	+ 300	95	3
1275	144	+ 700	80	9
780	85	+ 300	95	3
495	53	+ 100	110	1
755	84	+ 300	95	3
1440	164	+ 900	70	13
1470	170	+ 1080	70	15
765	84	+ 280	95	3
785	84	+ 300	95	3
770	84	+ 300	95	3
490	52	+ 100	110	1
780	84	+ 300	95	3
1760	204	+ 1400	60	23
510	52	+ 0	110	0
820	83	+ 100	95	1

$\Delta p, p$	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp$	δp
740	84	+ 350	95	+ 4
465	52	+ 200	110	2
750	84	+ 300	95	3
465	53	+ 150	110	1
740	84	+ 300	95	3
1250	142	+ 600	80	7
1370	167	+ 1150	70	16
490	52	+ 250	100	2
760	82	+ 400	95	4
1250	141	+ 900	80	11
1710	202	+ 1800	60	30
816	82	+ 400	95	4
1760	203	+ 1750	60	30
580	51	+ 200	100	2
1344	142	+ 800	80	10
1760	203	+ 1700	60	+ 28
850	83	+ 350	95	+ 4
590	53	+ 200	100	+ 2
1340	141	+ 800	80	+ 10

ALCOHOL.

Δp	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp.$	δp	$\Delta p, p$	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp$	δp
700	53	— 100	66	— 2	1730	144	— 100	51	— 2
1030	83	— 50	63	— 1	690	52	— 00	66	— 0
1730	143	— 100	51	— 2	1050	83	— 50	63	— 1
1030	83	— 100	63	— 2					

PARATOLUIDINE.

Δp	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp.$	δp	$\Delta p, p$	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp$	δp
870	31	— 300	52	— 6	1580	89	— 300	45	— 7
1240	56	— 410	50	— 8					

THYMOL.

Δp	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp.$	δp	$\Delta p, p$	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp$	δp
900	51	— 500	46	— 11	1710	108	— 950	42	— 23
1350	83	— 750	44	— 17	930	52	— 500	46	— 11
910	52	— 500	46	— 11	1370	83	— 750	44	— 17
1360	83	— 750	44	— 17	1715	110	— 850	42	— 20

DIPHENYLAMINE.

Δp	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp.$	δp	$\Delta p, p$	$\Delta\theta$	$\delta v \times 10^6$	$10^6 \times d\left(\frac{v}{V}\right) / dp$	δp
1000	31	— 450	43	— 10	920	30	— 400	43	— 9
1430	58	— 650	40	— 16	1350	57	— 700	40	— 18
1780	93	— 800	38	— 21					

TABLE 28.—*Isometrics—Digest of probable results corrected.*

Substance.	$\Delta\theta$	$\Delta p'$ $\delta p'$	Δp
Ether........	50·5	437 2	439
$\theta_0 = 18^0$	81·8	701 4	705
$p_0 = 30$ atm ...	142·5	1196 10	1206
	205·0	1619 30	1649
Ether........	52·5	464 2	466
	82·6	723 4	727
$\theta_0 = 17^0$	142.1	1209 10	1219
$p_0 = 30$ atm ...	205·0	1642 28	1670
Alcohol.......	53·0	556 —2	554
$\theta_0 = 17^0$	83·0	888 —1	887
$p_0 = 50$ atm ...	143·6	1575 —2	1573
Alcohol.......	51·2	533 —2	551
$\theta_0 = 17^0$	83·4	889 —1	888
$p_0 = 50$ atm ...	144·5	1582 —2	1580

Substance.	$\Delta\theta$	$\Delta p'$ $\delta p'$	Δp
*Paratoluidine	31·4	441 —6	435
	56·5	800 —8	792
$\theta_0 = 68^0$	90·4	1124 —7	1117
Thymol.......	51·3	710 —11	700
$\theta_0 = 17^0$	82·7	1158 —17	1141
$p_0 = 80$ atm ...	107·7	1495 —23	1472
Thymol.......	51·5	729 —11	718
$\theta_0 = 17^0$	83·3	1171 —17	1154
$p_0 = 80$ atm ...	109·7	1506 —20	1486
*Diphenylamine........	31·3	487 —10	477
$\theta_0 = 68^0$	57·7	900 —16	884
*Diphenylamine........	30·7	479 —10	469
	57·5	904 —18	886
$\theta = 68^0$	94·5	1345 —21	1324

* $p_0 = 400$ atm., approximately.

DEDUCTIONS.

55. *Curvature and slope of the isometrics.*—The deductions to be made from the above laborious investigation can be briefly stated. It conduces to clearness to express graphically both the data of Tables 20 to 24, as yet uncorrected for the volume changes of the glass tube containing the solutions, as well as the data of Table 28, in which this correction has been provisionally added. This is done in Pl. II, 1 and 2, in both of which $\varDelta p$ are fully given, as is also $\varDelta\theta$ in 1. In 2 the change of $\varDelta\theta$ is represented, and the points are connected by straight lines to bring out the contour of the curves.

It is seen at a glance that below 1,000 atmospheres the curves are so nearly linear that they may be accepted as such with an error no larger than 1° or 2° at 1,000 atmospheres. This is quite within the unavoidable errors, as may be seen from an inspection of the individual points. The discrepancy is somewhat greater for toluidine[1]; here, however, the initial temperature is high, being 70°.

Turning first (Pl. II, 1) to ether, the deviation from the right line at 1000 is less than 1° C.; at 1500 atmospheres, the deviation is 9·5° in one case and 10° in the other, showing an abrupt increase of curvature. The slopes of the isometric within the first 1000 atmospheres, are

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[1] Owing to breakage of the tube, I did not repeat toluidine.

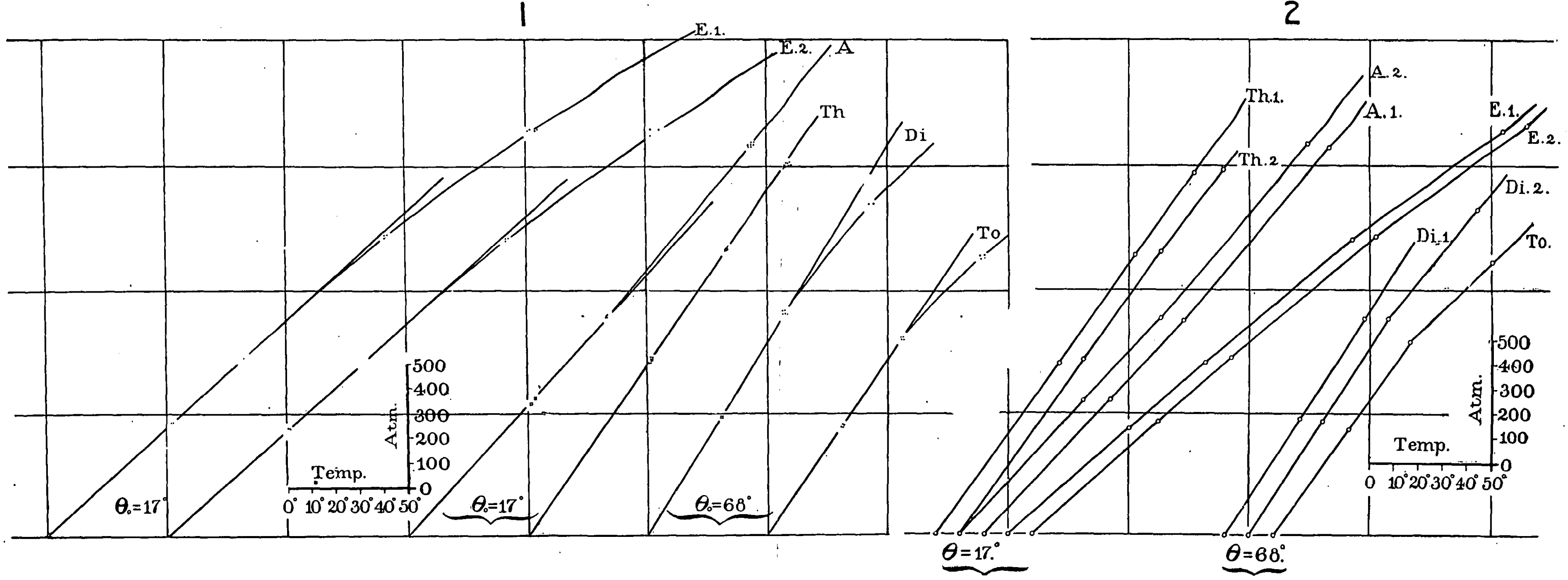

DIAGRAM SHOWING THE ISOMETRICS OF ETHER, ALCOHOL, THYMOL, PARATOLUIDINE AND DIPHENYLAMINE.

104°/1000=·114 in one case and 115/1000=·115° per atmosphere in the other.

Alcohol differs from all the other isometrics, inasmuch as the curvature is upward. The deviation at 1000 atmospheres is nearly 2°. The initial slope of the isometric 95°/1000=·095° per atmosphere.

Thymol, curiously enough, is strikingly near a straight line. The deviation at 1000 is inappreciable. The slope of the isometric 71/1000=·071° per atmosphere.

Diphenylamine deviates from the straight line. The slope is 63/1000=·063° per atmosphere.

In case of toluidine the slope is ·070° per atmospere. In the two latter cases it must be remembered that the initial temperature is 78°, and the initial pressure 400 atmospheres. The deviation from the rectilinear path is an abrupt high-temperature occurrence.

Turning finally to pl. II, 2, the following slopes are found which may be compared with the slope of 1:

TABLE 29.—*Observed initial slopes of the isometrics.*

	Ether.	Alcohol.	Thymol.	Diphenylamine.	Para-toluidine.
	°C. / atm.	*°C. / atm.*	*°C. / atm.*	*°C. / atm.*	*°C. / atm.*
Not corrected for volume changes of glass tubes	·114 ·115	·095	·071	·063	·070
Corrected for volume changes of glass tubes	·116 ·114	·095 ·094	·073 ·072	·065 ·065	·072
Initial temperature	17°	17°	17°	68°	68°
Initial pressure, atmosphere	30	50	80	(400)	(400)
Boiling point	34°	78°	233°	310°	198°
Melting point	....	....	53°	54°	43°

It is seen from this table, as well as from Table 28, that the correction to be applied in consequence of nonrigidity of glass never exceeds 2 per cent. In case of ether and alcohol it may be disregarded. In the other cases the approximation made is probably warranted without elaborate measurements of the elastics of glass.

If the abrupt change of curvature above 1000 atmospheres were due to an unwarranted application of Hooke's law, the curvature of the isometrics would tend to change in similar ways for all curves at the same pressures. This is not the case for the above curves, in which the contour of each preserves an individual character. Even after the gauge had been strained (§ 42) I detected no differences in the factor. Again, the repetition of the thymol work in Table 22 (supplement), made especially to throw light on the present question, shows that no time error in the constants of the pressure apparatus is to be apprehended.

The slopes given in the last table have no absolute value, since these data must vary with the initial volume under consideration. Volume measurements are beyond the scope of the present paper. I may state, however, that when volume measurements are included the complete thermodynamics of liquid matter are expressible in the family of curves obtained with a degree of accuracy which is experimentally the most precise.

56. *Final interpretation.*—For the time being the above results admit of the following interpretation: Whenever a substance passes from the liquid to the gaseous state, no matter whether this takes place continuously above the critical temperature or discontinuously below it, the underlying cause is a change of molecule from a more complex to a less complex type. As long as the molecule remains unchanged the isometrics are straight. When the change of molecule takes place so as to begin with the liquid molecule and pass continuously into the gaseous molecule, the isometrics curve continuously for the linear isometric of the true liquid to that of the true gas. Such an explanation is of course tentative. It rests on evidence purely experimental and therefore of uncertain interpretation; and it is suggested by a controversy which I have summed up elsewhere[1] as follows: "The linear relation was predicted from theoretical considerations by Dupré (1869) and by Lévy (1884)—considerations soon proved to be inadequate by Massieu, H. F. Weber, Boltzmann, and Clausius. Ramsay and Young (1887) established[2] the relation in question experimentally for vapors, but not, I think, very fully for liquids decidedly below their critical points. Reasoning from these data, Fitzgerald (1887) investigated the consequences of the law, viz: (1) specific heat under constant volume is a temperature function only; (2) internal energy and entropy can be expressed as a sum of two terms, one of which is a volume function only and the other a temperature function only. Thus Ramsay, Young, and Fitzgerald arrive substantially at the same position from which Dupré and Lévy originally started."

However, too much care can not be taken in keeping clearly in mind that pressures which, in relation to the usual laboratory facilities, are exceptionally large, may yet be mere vanishing increments when mapped out on the scale of the molecular pressures of liquids and solids.

Some notion of the internal pressures encountered may be gained as follows:

Studying the compression of organic substances throughout an interval of 310° and 600 atmospheres, I found that the isothermal compression v/V could be well represented by an equation $v/V = \ln(1+ap)^{\vartheta/a}$ where ϑ and a are constants and p denotes pressure. Taking this as a basis, I sought the mean values of the constants involved in some fifty-three isothermals, and found $-v/V = \ln(1+9\vartheta)^{1/9}$ to apply within the limits of error of my work. To this extent, therefore, compressibility increases as the reciprocal of the first power of the pressure binomial $(1/9\vartheta+p)$. The interpretation to be given to $1/9\vartheta$ is that of an initial or internal pressure. Computing its value for the above or organic liquids, I found the data of Table 30.

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[1] Am. Jour., Sci. 3d ser., vol. 38, 1889, p. 407.

[2] For a pressure interval not exceeding about 80 atmospheres for a group of isometrics, nor about 30 atmospheres for a single isometric. See Ramsay and Young, Phil. Mag.: 5th ser., vol. 23, 1887, p. 435.

TABLE 30.—*Order of values for internal pressure, assuming* $d\left(\frac{v}{V}\right) dp = \theta \mid (1+9\vartheta p)$.

Subst.	Θ	Internal pressure.	Subst.	Θ	Internal pressure.
	°C.	Atm.		°C.	Atm.
Ether $p_0 = 100$.	29°	673	Para-toluidine $p_0 = 20$.	28°	1,852
	65°	491		65°	1,610
	100°	323		100°	1,262
	185°	110		185°	671
	310°	32		310°	263
Alcohol $p_0 =$ 150..........	28°	1,249	Diphenylamine $p_0 = 0$ ...		
	65°	967		65°	1,709
	100°	703		100°	1,610
	185°	336		185°	1,010
	310°	80		310°	521
Thymol.......	28°	1,683			
	64°	1,481			
	100°	1,146			
	185°	669			
	310°	228			

If, however, compressibility be supposed to vary as the square of the pressure binomial,[1] viz:

$$d\left(\frac{v}{V}\right) / dp = -\mu / (1+\nu p)^2,$$

the internal pressures corresponding, will have about twice the above values. Now it appears, from recent experiments of my own, that the last expression is probably the more nearly true. It follows therefore that at zero centigrade, internal pressures of the order of 1,000 to 4,000 atmospheres are to be taken into account.

57. *Isometrics of solid glass.*—A singularly curious inference is suggested in comparing the approximate isometrics of glass above deduced, (§§ 52, 53), with the liquid isometrics of the present and earlier papers. It appears that for solid glass the slope of the isometric is about 100°/1000 = .1° per atmosphere in its initial course. This coincides very nearly with the slope of the isometrics of the above organic liquids, varying as they do between .07° and .12° per atmosphere. In view of the similarity of glass and the rock producing magma, this degree of isometric similarity is of great interest. In general the proximity of the solid and liquid isometric of compound matter is worthy of note.

The metallic isometrics are different from the above. So far as they can be obtained[2] the slope of the isometric

$$\frac{\theta}{p} = 10^6 \Big/ k\,\beta$$

per atmosphere, where k and β are respectively the resilience of volume and the coefficient of expansion, is only ·014° for steel, ·016° for

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[1] Cf. Barus: Am. Journ. Sci. (3), vol. 39, 1890, pp. 497–506.

[2] Constants k and β are taken from Everett's tables.

iron, and ·011° for copper. They thus preserve an order of magnitude different from that of glass or the above organic liquids.

58. *Conclusion.*—In conclusion I will advert to the easy possibility of obtaining families of isometrics, and from them a complete representation of the isometrics of liquids with a given pressure interval of say, .3000 atmospheres. For this purpose it is merely necessary to change the volume of liquid contained in the glass tubes, and to refer all volumes to the one obtaining at the initial temperature. Thus in the above tube and in case of ether, temperatures pass from 20° to 220°, while pressure varies from 0 to 1,900 atmospheres, say. Suppose, now, that the electric contact is moved in such a way that at 200° the pressure producing contact is not much greater than the vapor tension of the liquid. Clearly, therefore, the isometrics may now be studied between 200° and a temperature between 300° and 400°, while pressure varies between 0 and 2,000 atmospheres as before, etc. Apart from the unavoidable tediousness of the work, the experimental devices suitable for accomplishing this easily suggest themselves.

CHAPTER III.

A COMPARISON OF THE BOURDON, THE TAIT, AND THE AMAGAT HIGH-PRESSURE GAUGES.

HISTORICAL.

59. *The earlier work.*—In my earlier work (chapter II), while investigating the isometrics of liquids, I was obliged to content myself with an investigation of empiric pressure gauges. I found by comparing different Tait gauges with a large Bourdon gauge that so long as pressure continually increased from zero, the relation between the indication of each under like conditions of pressure was linear; but that when pressure again decreased from the high value (1,000 atmospheres or more) to zero, this relation changed to a markedly curvilinear locus, of such a kind that eventually the original zero of both guages was regained. So long as increasing pressures alone were dealt with, either of these gauges could be used with safety. The present work, in which both gauges are directly compared with Amagat's manométre à pistons libres, corroborates this inference, and shows that the bow-shaped cycles[1] represent the actual motion of the free end of the Bourdon tube. From this point of view the present datea are important, for they supply an example of purely mechanical hysteresis, and possibly of metallic volume lag. The data also show that cyclic indications are absent in the steel Tait gauge, and that this instrument may be adopted for the scientific measurement of pressures of any value whatever.

60. *Amagat's manometer.*—The instrument in my possession[2] is constructed for the measurement of pressures as high as 3,000 atmospheres. At this extreme limit the height of the compensating column of mercury (the diameters of the two pistons being $\cdot549^{cm}$ and $12\cdot171^{cm}$ respectively) will be about 464^{cm}. To read so long a column with reasonable convenience, I fixed a long, painter's ladder in a vertical position, and permanently attached to one side of it both the open manometer tube and the long millimetre scale, which I ruled with care on a wide strip of brass. A round leather belt, passing from top to bottom of the ladder and everywhere within easy reach, passed over a pulley adjustment, and was suitably connected with the mechanism for rotating the two "pistons libres." In this way I was able to make this essential adjustment immediately before taking my reading, no matter what my position on the ladder might be.

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[1] Phil. Mag., 5th ser., vol. 30, 1890, p. 338, Ibid., pl. x. In the paper cited I was of the opinion that the cycles were thermal phenomena to be sought for in the Tait gauge.

[2] Marked E. H. Amagat, Lyon, 1890.

I found by trial, that by using the thick mineral machine oil mentioned in my last paper[1], the manometer would be at once connected with my screw compressor, and that the charge of molasses was quite superfluous. I also floated the lower piston in this oil. Thus the same oily liquid for the transmission of pressure is used with advantage throughout the system of apparatus. Once put together, it is ready for use at all times and need not again be touched in years. Care of course must be taken to obtain oil free from grit or dust.

61. *The Bourdon gauge.*—The gauge used was the one to which my earlier measurements apply, having a tube of steel. I made two series of comparisons of this gauge with the manometer. In the first of these the usual Bourdon multiplying gear was used; in the other the excursions of the free end of the Bourdon tube were read off directly with a Fraunhofer microscopic micrometer after the multiplying gear had been detached. Of many experiments of this kind which I made I will give the following typical examples contained in Tables 31 and 32. In Table 1'the Bourdon registry is given at once in atmospheres, the Amagat registry both in centimeters and in the atmospheres reduced therefrom. There are four series of observations, two of them within an interval of 500 atmospheres and the other two within 1,000 atmospheres. Two observations are made at each step of pressure. In Table 32 the micrometer position of the end of the Bourdon gauge is given in cm./40, this being the scale part of the Fraunhofer gauge. In other respects the data are given as in Table 31. Observations were made in triplets, two at the manometer including each one at the Bourdon gauge.

TABLE 31.—*Cyclic comparison of the Bourdon gauge (steel tube) with the Amagat manometer.—Multiplying gear.*

Bourdon.	Amagat.	Amagat.	Bourdon.	Amagat.	Amagat.	Bourdon.	Amagat.	Amagat.
Atm.	*Cm.*	*Atm.*	*Atm.*	*Cm.*	*Atm.*	*Atm.*	*Cm.*	*Atm.*
188	28·65	185	21	2·50	16	465	72·40	468
174	26·80	173	242	37·30	241	458	70.80	458
322	50.30	325	231	35·80	232	650	101·00	653
312	48.60	314	472	73·30	474	645	99·90	647
457	70·90	459	457	71·30	461	855	133·00	860
446	69·20	448	660	102·00	660	838	128·60	832
316	49·50	314	640	99·30	642	985	151·80	982
313	48·10	311	859	131·30	849	977	148·30	960
162	24·30	157	844	128·80	833	964	147·30	954
165	24·50	158	991	151·80	982	950	144·80	937
27	3·60	23	977	148·80	962	840	125.00	809
			847	126·00	815	834	123·90	802
29	3·70	24	837	124·20	804	631	90·80	587
172	26·30	170	651	93·60	606	626	90·00	582
168	25·50	165	646	92·90	601	440	59·60	386
317	49·10	318	475	65·10	421	440	59·60	386
305	47·30	306	475	64·90	420	260	33·30	215
462	71·80	464	262	34·50	223	264	34·40	222
444	69·10	447	263	34·70	225	35	3·30	21
433	67·20	435	28	2·50	16	35	3·80	25
224	33·90	219	28	2·70	17			
225	34·10	221						
83	12·10	78	30	2·90	19			
84	12·10	78	251	38·60	250			
20	2·50	16	245	37·50	243			

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[1] Phil. Mag., 5th ser., vol. 31, 1891, p. 10. I have always found it preferable to use oily instead of aqueous liquids, by which fine parts of steel are liable to rust.

TABLE 32.—*Cyclic comparison of the Bourdon gauge (steel tube) with the Amagat manometer. Fraunhofer micrometer.*

Bourdon.	Amagat.	Amagat.	Bourdon.	Amagat.	Amagat.
Cm./40	*Cm.*	*Atm.*	*Cm.*/40	*Cm.*	*Atm.*
19·09	·00	0	18·92	·10	1
16·04	35·30	228	15·83	37·40	242
16·12	35·10	227	15·87	36·90	239
11·93	80·80	523	11·91	80·80	523
12·19	80·10	518	12·20	79·30	513
8·40	119·30	772	8·86	112·80	730
8·58	118·30	765	9·18	111·30	720
5·23	149·80	969	5·25	149·80	969
5·66	147·80	956	5·70	147·80	956
6·02	141·30	914	6·16	144·50	935
6·12	141·30	914	6·33	139·30	901
7·94	116·30	753	8·20	116·80	756
8·36	116·30	753	8·39	114·30	739
11·20	82·70	535	11·08	83·30	539
11·28	82·60	534	11·08	83·30	539
15·18	38·80	251	14·80	41·80	270
15·18	39·20	254	14·80	42·40	274
18·97	·00	0	19·06	·00	0

DISCUSSION OF RESULTS.

62. *Multiplying mechanism.*—Constructing Table 31 graphically, it appears that within the errors of reading the observations of the first two series lie on a straight line. In series 1 the "on" and "off" measurements possibly suggest a cycle whose maximum divergence is not above 5 atmospheres. The factor of the Bourdon gauge $\left(\frac{\text{Bourdon}}{\text{Amagat}}\right)$ taken from these data is ·998 "on," and ·987 "off." In series 2 this factor has changed to ·984 "on," and ·992 "off." There is no cyclic march. It follows from both series, barring observational errors, that a cyclic march within an interval of 500 atmospheres does not occur.

The third series "on" shows a change of rate above 700 atmospheres; thus the locus is composed of two straight lines. The return march is now distinctly cyclic, and at 500 shows a breadth of almost 50 atmospheres. The zero is regained within 10 atmospheres. The mean factor is ·991 below, and 1·008 above 700 atmospheres in the "on" march. The mean factor of the "off" march is of no interest. In the fourth series, finally, the remarks made relative to series 3 are substantiated throughout. The factor below 700 atmospheres is ·982, and above 700 is 1·072. There is some error in this last result, probably due to unwarrantably vigorous tapping of the gauge. The width of the cycle at 500, about 50 atmospheres.

Hence, the inferences drawn in the earlier paper from a direct comparison of the Bourdon and Tait gauges[1] are valid throughout. It is gratifying to note that even the standard atmosphere formerly used is correct to ·8 per cent. The present results, however, go further in showing that the cyclic march in question is in the Bourdon gauge, whereas the indications of the steel Tait gauge are probably very near the truth. Since I reversed the action of the Bourdon mechanism at different test

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[1] Phil. Mag., 5th ser., vol. 30, 1890, pp. 343 et seq.; ibid., § 18; the breadth of cycles here was about 40 atmospheres.

readings it can not be supposed that these cycles are in the multiplying gear. Nevertheless this test is essential, and the results obtained are given in the next paragraph.

63. *Fraunhofer micrometer.*—Care was taken to fix the axis of the screw parallel to the line of motion of the free end of the Bourdon gauge, which makes an angle of nearly 45° with the tangent at the end of the tube. Table 32 shows the total motion to have been about 4^{cm} per 1,000 atmospheres, where it is to be noted, however, that the solid tapering conoidal plug at the end of the flat tube was about 10^{cm} long. Of the two series given in Table 32, the "on" march of the first shows some convexity upward. The factor is $\cdot 362^{cm}$ per 1,000 atmospheres. The data of the "off" march show distinct convexity downward. Hence the two curves form a cycle whose breadth at 500 atmospheres is about 40 atmospheres, a result agreeing substantially with § 62. The data of the second series, which show rather better agreement among themselves, corroborate the results of the first series throughout. The mean factor in the "on" march is $\cdot 361^{cm}$ per 1,000 atmospheres—nearly identical with the above.

The bow-shaped cycles, therefore, obtained in the present and earlier paper[1] represent a case of actual hysteresis. A certain amount of strain is stored up in the Bourdon tube during the interval of compression, which, during removal of pressure, is always relieved more slowly than pressure decreases. The phenomenon is thus static in character, and I venture to regard it as depending on the occurrence of volume lag in those parts of the tube which are directly influenced by pressure. In other words, the molecules of metal near the inside of the Bourdon tube pass from the original to a second molecular state in proportion as a certain pressure P is approached and exceeded, whereas these molecules pass from the second molecular state back to the first again in proportion as pressure falls below a certain other datum p, where $P>p$. Now, inasmuch as Table 31 shows that within 500 atmospheres there is no appreciable hysteresis, while both Tables 31 and 32 show marked cyclic changes between 0 and 1,000 atmospheres, it follows from the data in question that P must lie somewhere between 500 and 1,000 atmospheres, whereas p may lie below 300 atmospheres. Here, therefore, is a phenomenon very similar to the effect of pressure on an undercooled liquid.

Two other possible explanations of the cyclic changes may be noted. In the first place, it is conceivable that the Bourdon tube is hotter during the "off" march than during the "on" march. To test this directly it would be necessary to submerge the tube in a water bath, which is scarcely feasible without injuring the mechanism. But I hold such an explanation improbable. If it were true the comparison within 500 atmospheres (Table 1) should show a cyclic magnitude pro-

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[1] Phil. Mag., 5th ser., vol. 30, 1890, pp. 344 et seq. See Pl. X. Cf. chap. I, § 16, above.

portional to the cycle corresponding to the interval 1,000 atmospheres, which it does not. Again, the cycles should quite vanish on long waiting (five minutes were allowed per observation in my earlier work), which they do not.

The other explanation, which seems to me equally improbable, is this: There may be two figures of equilibrium of the Bourdon tube, one corresponding to low pressure the other to high pressure, and the figure of labile equilibrium through which the tube passes from the first to the second may be maintained over a relatively large interval of pressure.

In general, therefore, it follows that if the Bourdon gauge is to be used for high pressures, it is necessary to take cognizance of discrepancies inherent in the chemical physics of the metal, in addition to the mathematical difficulties discussed by Lord Rayleigh, Profs. Greenhill and Worthington.

64. *The Tait gauge.*—In Table 33 I give two series of cyclic comparisons of the Tait gauge with the Amagat manometer. The plan of work was similar to that described in section 61. Readings were made in triplets—two at the Amagat manometer, including one at the Tait gauge. An interval of two minutes was allowed for cooling. The Tait gauge used is the same to which my earlier observations apply.[1] The interval of comparison is 1,500 atmospheres. At the end of Table 33 a short résumé of the factors (cm. atm.) corresponding to consecutive pressure intervals is given.

TABLE 33.—*Cyclic comparison of Tait gauge (steel tube) with the Amagat manometer.*

Tait.	Amagat.	Amagat.	Tait.	Amagat.	Amagat.
Cm.	*Cm.*	*Atm.*	*Cm.*	*Cm.*	*Atm.*
12·65	·20	1	12·90	·00	0
21·05	38·30	248	21·30	38·00	246
20·73	37·00	239	20·95	36·40	236
29·35	75·30	487	30·17	76·90	498
28·75	72·30	468	29·25	73·10	484
40·80	124·30	804	38·82	114·80	743
39·72	118·70	768	38·09	111·90	724
51·05	168·00	1,087	50·14	163·50	1057
50·16	163·70	1,059	49·10	159·60	1,033
59·20	201·70	1,305	60·19	206·50	1,335
57·80	195·60	1,266	58·58	200·00	1,294
64·90	225·60	1,460	65·42	228·90	1,481
63·98	221·30	1,432	64·05	222·10	1,437
63·30	218·60	1,414	62·50	216·00	1,398
62·50	215·40	1,394	62·00	213·90	1,384
57·20	192·70	1,247	58·50	199·20	1,289
56·65	190·10	1,230	58·15	197·30	1,277
49·05	157·70	1,020	49·49	160·50	1,038
45·50	155·20	1,004	49·28	159·50	1,022
41·00	123·00	796	40·45	121·30	785
40·72	121·40	786	40·23	120·50	780
31·92	83·30	539	29·86	75·60	489
31·57	82·00	530	29·50	74·20	480
22·44	41·90	271	20·01	32·40	210
22·49	42·10	272	20·06	32·30	209
13·05	·10	1	12·85	—·10	—1
12·85	·10	1	12·93	—·10	—1

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[1] Phil. Mag., 5th ser., vol. 30, 1890, p. 344, § 18, gauge No. 1.

Factors of the Tait gauge.

Series.	Pressure interval.	Factor.	Means on and off.	Mean total.
	Atm.	*Cm. atm.*	*Cm./atm.*	
I, on...	200 to 1,100	·03580		
I, on...	500 to 1,300	3640	·03628	
I, on...	800 to 1,500	3664		
I, off...	800 to 1,400	·03595		
I, off...	500 to 1,200	3577	·03576	
I, off...	300 to 1,000	3555		
				·03596
II, on...	200 to 1,000	·03544		
II, on...	500 to 1,300	3602	·03590	
II, on...	700 to 1,500	3625		
II, off...	800 to 1,400	·03604		
II, off..	500 to 1,300	3591	·03591	
II, off...	200 to 1,000	3579		

65. Table 33 substantiates the inferences of section 62 relative to the absence of cycles in the registry of the Tait gauge. In the first series, "on," the data above 300 atmospheres make up a straight lime. Between 0 and 300 atmospheres the registration of the Tait gauge is too high, being more in error as the pressure zero is approached, where the discrepancy is 30 atmospheres. In the "off" march all the points lie on a straight line, excepting the zero, which is 10 atmospheres too high on the Tait gauge. Thus the locus consists of two straight lines converging at 1,500 atmospheres, and the cyclic character of the data in section 61 does not appear. In the second series, though preserving the general character of series 1, the "off" march practically returns in the line of the "on" march. Thus again true cyclic changes are absent.

As a whole, therefore, the observations lie on a very flat curve, which above 300 atmospheres passes into a straight line. (See Fig 11.) It is difficult to conjecture the cause of this curious low-pressure discrepancy in consequence of the great number of errors which may possibly be encountered, though it may be remarked that the rise of temperature of a liquid per 100 atmospheres of compression may decrease with increasing pressure, since at low pressures compressibility is relatively large. Table 33 shows, finally, that the mean factor derived from all the series is .03596 cm./atm. This is to be increased about 4 per cent, to correct for the temperature of the mercury column of the manometer. Hence the factor is .0361 cm./atm. In my former paper the results[1] were .0360 to .0369 cm./atm., showing that my standard atmosphere must have been less than 2 per cent in error. It is altogether probable that this difference of factor (2 per cent) is the result of the excessive use and abuse to which the gauge was put during the intervening nine months. Regarding the observations as a whole I believe the residual discrepancies to be due rather to unavoidable fluctuations of the temperature of the water jacket than to thermal effects of compression, or viscosity of metal. For this reason I doubt whether any permanent expansion of the metal within 1,500 atmospheres has been registered.

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[1] Phil. Mag. 5th ser., vol. 30, Table IV, p. 345. This table contains cm./atm. instead of cm.×10^2/atm.

SUMMARY.

66.—In the attempt to carry these comparisons above 2,000 atmospheres, I ruptured the stout tube which connected the compressor with the manometer. The above work, however, shows conclusively that the Tait gauge may be perfected so as to be available for precise measurement. It may be permissible to indicate the way in which I am endeavoring to do this here; since many of the experimental contrivances involved have already been tested. The tables have shown that the most annoying difficulty is encountered in maintaining the temperature of the water jacket sufficiently constant. To this end the whole gauge is to be constructed of metal with close-fitting jackets. Furthermore, choice is to be made of as thin walled a steel measuring tube as possible, in order that the volume increase due to pressure, may be large relatively to the simultaneous effects of fluctuations of temperature. There is reason to believe that this can be accomplished by connecting the Tait gauge with the compressor by an interposed "piston libre." In the annexed diagram, Fig. 12, let *B* be the cylindrical piston, consisting of a single piece, of which one end is larger in diameter than the other. Let this piston fit the hollow cylinder *C C C* accurately, so as to be capable of motion to and fro and of rotation, with the minimum of friction. Let the tube *D* be in connection with the compressor, the tube *E* in connection with the Tait gauge, and the whole apparatus be filled with oil. Then it is clear that

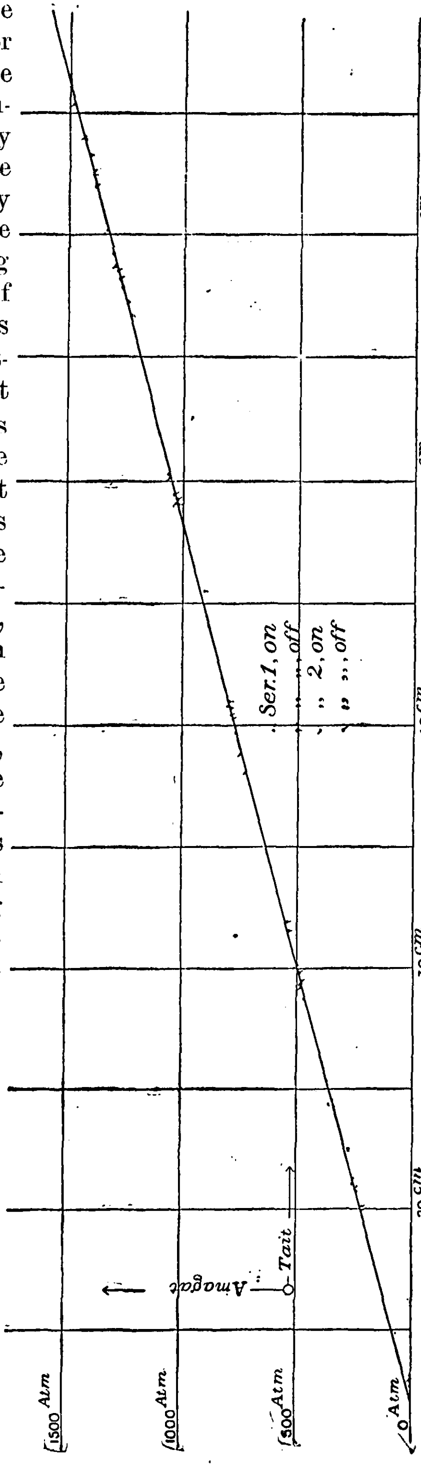

Fig. 11.—Comparison of the Amagat manometer and the Tait gauge.

the exceptionally high pressure, acting only on the shoulder of the piston, can be counterbalanced by a relatively low pressure at *E*. Leaving the essential details of construction out of consideration, a Tait gauge reading to only 1000 atmospheres may thus be made to indicate pressure 2, 3, or more times as large as this at *D*, by selecting suitable dimensions of piston and socket. Hence even very high pressures can be measured by aid of a thin-walled steel tube, the pressure expansions of which are so large that the accompanying thermal fluctuations of the environment dwindle to very small importance. I am far from underestimating the importance of Amagat's manometer as a standard instrument leading at once to absolute results; but it is certainly inconvenient to be obliged to make readings on a column of mercury which may be 5 meters high, even when a stirring arrangement such as that described in § 60 is provided. I doubt, moreover, whether it would conduce to convenience, and certainty if the readings were made by some easily devised electrical method. On the other hand, in case of the Tait gauge, the pressures are read off on a horizontal tube about 1 meter in length and as far as 2000 atmospheres without "pistons libres," and therefore quite without diminution of pressure in consequence of unavoidable leakage. Regarding gauges quite free from leakage, I hope soon to be able to communicate results on the electrical behavior of pure mercury under pressure.

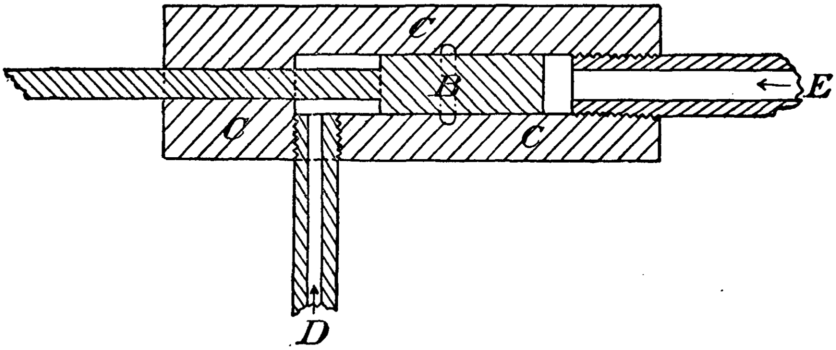

FIG. 12.—"Piston libre," for high pressure.

CHAPTER IV.

THE CONTINUITY OF SOLID AND LIQUID.[1]

INTRODUCTORY.

67. *Scope of the work.*—In my earlier papers[2] I entered somewhat minutely into the volume thermodynamics of fluid matter. The behavior of matter passing from liquid to solid and back again was only incidentally considered.[3] This, however, is the very feature which gives character, or at least a more easily interpretable character, to the whole of the volume phenomena of the substance, and I have therefore reserved it for special research.

The problem may be looked upon from another point of view. Let it be required to find the relation of melting point and pressure. I have long since shown[4] that in a comprehensive attack of this question the crude optical or other methods hitherto used as criteria of fusion (criteria which have no inherent relation to the phenomenon to be observed) must be discarded. In their stead the volume changes which nearly always accompany change of physical state in a definite or simple substance are to be employed.

The present experiments were made with naphthalene only. They are by no means even near the degree of precision of which the applied plan of research admits. My chief object here has been to carry the method quite through to an issue preliminarily and to test it at every point. The data are sufficient, however, to show that the process adopted, though I approached it with much misgiving, can be brought under control throughout, and that the attainable accuracy is only limited by the patience, discernment, and skill of the observer. I was in some degree surprised therefore to find that my method led to new results at the outset.

The literature of the subject I shall omit here, since the more important experiments have entered the text-books and since I shall have occasion to refer to it elsewhere. I need merely mention Sir William

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[1] The geological interpretation of this work is in the hands of Mr. Clarence King, by whom the inquiry was suggested.

[2] Am. Jour. Sci., 3d ser., vol. 38, 1889, p. 407; ibid., vol. 39, 1890, p. 478; ibid., vol. 40, 1890, p. 219; ibid., vol. 41, 1891, p. 110; Phil. Mag., 5th ser., vol. 30, 1890, p. 338.

[3] Am. Jour. Sci., 3d ser., vol. 38, 1889, p. 408; ibid., vol. 39, 1890, pp. 490, 491, 494. Most of my earlier work on this subject has thus far remained unpublished.

[4] Am. Jour. Sci., loc. cit. More pointedly with an indication of methods in Phil. Mag., 5th ser., vol. 31, 1891, p. 14.

Thomson (1850), Bunsen (1850), Hopkins (1854), Mousson (1858), Poynting (1881), Peddie (1884), Amagat (1887), Battelli (1887), and some others (cf. § 95, 96).

68. *Other methods tested.*—In applying this principle I first made direct volume observations on substances inclosed in capillary tubes of glass. In the case of naphthalene and many others I thus obtained satisfactory results[1]. Such work is, however, limited to relatively low pressures (600 or 800 atmospheres); it does not admit of sufficient correction for the volume changes of the glass, and for the small quantity of substance examined and the relatively frequent occurrence of nuclear condensation, volume lags are often obscured. Hence the definition which, after making these experiments, I was inclined to adopt, viz, that a pressure which when acting isothermally for an infinite time will just solidify the liquid and just liquify the solid, stands to the given temperature in the relation of melting point and pressure, is not in accordance with the facts.

In a second method[2] I endeavored to measure the characteristic difference of specific volume by passing current through the thin, hot walls of the tube which contained both the substance and the mercury thread or index. The whole apparatus is in this case surrounded by the oil of the piezometer in which the tube is inserted, and the changes of resistance of the arrangement indicate the motion of the index and hence the degree of compression produced. Here, however, a new and unexpected annoyance was encountered, inasmuch as both the medium of oil and the glass possess seriously large pressure coefficients.[3] Moreover it is only with great difficulty that perfect insulation can be maintained in an apparatus of which water jackets make up an essential part. I therefore abandoned this project.

In a third method similar to the preceding I expressed the motion of the mercury thread or index in terms of the resistance of a very fine platinum wire passing through the axis of the tube. The successive intercepts thus indicated the changes of volume to be observed. This method gave good indications of the pressure positions of the melting points of the sample. It failed, however, to give serviceable values for the fluid volume changes. This is due to the fact that contacts in such a case are essentially loose. Again thermo-currents can only with great difficulty, if at all, be allowed for, seeing that the successive isothermal temperatures are to vary over a large range.

Finally all of the methods above described must necessarily fail after the substance has become solid, for in this case the thread or index is broken and forced into the interstices of the solidified material. Thus it is manifestly impossible to retain a uniform meniscus after solidification has once set in, and it is therefore impracticable both to arrive

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[1] Cf. American Journal of Science, vol. 38, 1889, p. 408.

[2] Phil. Mag., 5th ser., vol. 31, 1891, p. 14.

[3] Ibid., pp. 18 to 24, et seq.

at the behavior of the solid, as well as to rigorously coördinate successive series of experiments.

69. *Advantages of the present method.*—Hence I endeavored to modify Kopp's[1] specific volume flask in a way to make it available under any temperature or pressure. Here the readings are independent of the unbroken character of the meniscus immediately in contact with the solidifying substance, whereas on the other hand, as I shall presently show, the expansion measurements can be made electrically[2] with almost any desirable degree of accuracy. Furthermore, by charging the flask with properly apportioned quantities of substance and of mercury, the error due to the compressibility of the glass may be eliminated in any degree whatever, and an apparatus obtained which is practically rigid in relation to pressure. The data show that from each single series of experiments I thus obtain the isothermals and isopiestics, and therefore also the isometrics, both for the liquid and for the solid; furthermore the relation of melting point and of solidifying point to pressure, and finally the changes of the isothermal specific volumes of solid and liquid at the melting points, with pressure. From these results the character of the fusion and the probable position of critical (§92) and transitional (§94) points can already be pretty well predicted. It is then only necessary to examine a great number of substances, of substances existing under widely different conditions of thermal state, in order to broaden the evidence and possibly to reach results of a uniform bearing on matter in general. This I indicated elsewhere.[3]

APPARATUS.

70. *Temperature.*—Inasmuch as pressure varies at a mean rate of, say, 30 atmospheres per degree, so that temperature is as it were the coarse adjustment and pressure the fine adjustment for the conditions of melting point, it is clear that the method of experiment should be such that temperature may be kept rigorously constant while pressure is made to vary over the necessary interval. To obtain constant temperatures I constructed a set of vapor baths of well-brazed, thin sheet iron heavily jacketed with asbestos. Cf. Pl. III, *pppp*. These were cylindrical in form, 10^{cm} in diameter and 20^{cm} high. Axial tubulures, the upper of which, *ss*, projected outward, the lower, *oooo*, both inward and outward, allowed the vertical tubular piezometer to pass axially through the vapor baths, and suitable stuffing boxes obviated all possibility of leakage. Again the upward projection of the lower tubulure (both of them fit the piezometer snugly) formed an annular trough with the walls and bottom of the vapor bath, in which a sufficient quantity of the ebullition liquid could be placed and boiled by aid of a flat spiral burner

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[1] Kopp, Ann. Chem. u. Pharm., vol. 93, 1885, p. 129.

[2] The absolute expansion and compressibility of mercury being now known § 73.

[3] "Instead of tracing the isothermals of a single substance throughout enormous ranges of pressure, similarly comparable results may possibly be obtained by examining different substances conceived to exist in widely different thermal states." (Am. Journ., loc. cit., p. 510.)

placed below. The top of the vapor bath was provided with two other lateral tubulures, one of which served for the permanent attachment of a vertical condenser and the other for the introduction of a suitable thermometer or thermocouple. Here also the quantity of ebullition liquid present could at any time be tested and its amount increased or diminished, or its quality directly purified by fractional distillation (an operation always necessary when amyl alcohol is used). With a good condenser the boiling may be kept up indefinitely, since the condensed vapors fall back into the trough below. For temperatures below 100° it is expedient to avali oneself of the high latent heat of water and to boil this liquid under diminished pressure. Temporarily attaching Richards's jet pump to the end of the condenser, pressure may be so regulated that any boiling point between 50° and 100° is maintained indefinitely. For higher temperatures amyl alcohol, turpentine, naphthalene, benzoic acid, diphenylamine, phenanthren, sulphur, etc., subserve the same purposes, though less thoroughly. Low latent heats[1] in most of these substances make it difficult to guarantee perfect thermal constancy throughout a length of say 10^{cm}. (Cf. §72, where a view of the apparatus is given.)

Temperature was measured by aid of a Baudin thermometer of known errors and also computed from the vapor tension of steam under known conditions. Thermolectric measurements are similarly applicable.

71. *Pressure.*—To obtain pressures as high as 2,000 atmospheres I used my screw compressor described elsewhere.[2] I made use, however, of a vertical piezometer, identical with the horizontal piezometer there described, except in so far as it could be removed from the barrel as a whole. As before, moreover, piezometer and barrel are insulated. When in adjustment the piezometer was surrounded by the following parts enumerated from bottom to top (see Pl. III): An insulated conical protector or guard preventing spilled water, etc., from reaching the insulation, the lower cold-water jacket, the flat burner, the vapor bath, and finally the upper cold-water jacket. For temperatures below 200° the latter may be dispensed with.

Internally the piezometer was filled with thick petroleum oil, as stated elsewhere.[3]

For pressure measurement I am now able to avail myself of a superb Amagat manomètre à pistons libres, which can be immediately attached to my compressor with advantage.

72. *The volume tube.*—A careful description of this apparatus, together with the operations necessary in standardizing it, is essential here. In one case these preliminary operations have led to a result of an interest apart from the present special purposes.

The tube is shown in the annexed diagram, Fig. 13, while Pl. III

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[1] It is my object in further experiments to boil water under pressure.

[2] Proc. Am. Acad., vol. 25, 1890, p. 93, Chapter I, above.

[3] Phil. Mag., 5th ser., vol. 31, 1891, p. 10, chapter III, above.

shows the tube in place in the tubular piezometer. It consists of an external cylindrical envelope, *A B*, of glass, closed below, open above, about 26^{cm} long and $.4^{cm}$ or $.5^{cm}$ in diameter. Throughout the greater part of its length, the tube *A B* is divided into two coaxial cylindric compartments, by a central glass partition tube, *Ck C*, open at both ends and fused to the tube *A B* along the ring *C C* about 7^{cm} below the open top *A*. This central tube *Ck C* is about 17^{cm} long and $.13^{cm}$ internal diameter, and drawn as thinwalled and as even in caliber as possible, so that the greater part of its lower length may be available for measurement. It extends nearly to the bottom of *A B*.

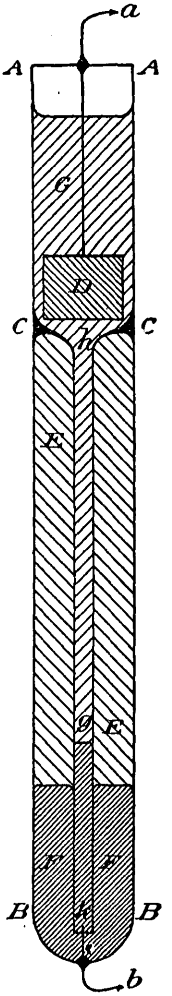

FIG. 13.—Diagram of the volume tube.

The substance to be examined is introduced into the annular space *E E*, care being taken that when fused under the highest temperature to be applied its lower boundary may be 4^{cm} or more above the end *k* of *Ck C*. My fused samples were about 13^{cm} long. Immediately in contact with the substance *E E* and extending upward into the central tube *Ck C* is the plug of mercury *F F* with its free meniscus at *g*. When *E E* is solid *g* must be, say, 2^{cm} above the end *k* of *Ck C*, and when *E E* is liquid at the highest temperature to be applied *g* must still be at about an equal distance below *C C*. The remainder of the tube above *g* is quite filled with a concentrated solution of zinc sulphate *Ghg*, into which an amalgamated zinc terminal, *D*, has been submerged and fixed in position by aid of platinum wire *a*, fused to the sides of the tube *A B*, as shown. The other terminal, *b*, is fused into the bottom of the tube *A* and in metallic connection with the mercury, *F F*, therein contained.

The tube thus adjusted is completely submerged in the oil contained within the tubular piezometer, Pl. III, and pressure is uniformly transmitted to it through the oil. The terminal *a* is put into metallic connection with the insulated piezometer; the terminal *b*, completely insulated therefrom by a coating of glass tube, is in metallic connection with the barrel; the tube *A B* itself is thus held in position by tensely stretching the fixed wires *a* and *b* and so adjusting their lengths that the parts *E E* and *hg*, with reference to which the measurements are made, may lie wholly within the *vapor* reservoir of the cylindrical vapor bath surrounding the piezometer. The method of fastening the ends *a* and *b* is a somewhat delicate operation, which, however, I will not further describe. So adjusted the tube is in position (vertical as shown in Pl. III) for any number of experiments and it is only necessary to attach the vertical piezometer to the barrel by aid of a tinned axially perforated screw.

An inspection of the diagram shows at once that if a current enter the outside of the barrel it will pass through *b*, *k*, *g*, *h*, *D*, and *a* into the outside of the piezometer and thence back to the battery. The only relatively significant resistance encountered in this course need be that between *g* and *h* of the thread of zinc-sulphate solution; but this resistance, cæteris paribus, varies directly with the length of *gh*, and therefore proportionally to the volume contraction of the substance *E E*. Hence the volume variations of the substance to be studied are directly and rigorously measurable in terms of the resistance of the circuit. If Kohlrausch's method[1] of intermittent currents, bridge, and telephone be used for the resistance measurement of the electrolyte, solidification or fusion breaks upon the ear with a loud roar, whereas the ordinary volume changes (solid or liquid) are indicated by mere intensification of sound, sufficiently pronounced to subserve the purposes of measurement.

It is seen that any breakage of the surface of separation between *E E* and *F F* is entirely without influence on this result, and that, even in the case of the solidification of *E E*, when mercury is forced into the interstices left after contraction, the compressibility of *E E* will still be measurable.

The charging of the tube, free from air, is an operation which I have not thus far accomplished satisfactorily. If a volatile substance like naphthalene be filled into *E E* and fused in vacuo, the vapor subsequently condensing in *gh* will soil the tube and interfere with measurement. From the solid *E E* I doubt whether air can be quite eliminated in vacuo. Hence in the present work the substance was not air-free, a condition of things to which I gave less attention because I do not believe the melting points can be appreciably influenced by dissolved air, nor that other of the measurements made are seriously distorted by this error. In the future, however, I will endeavor to meet this difficulty by fusing the end *A A* of the tube *A B* inverted to the top of a barometer tube, in addition to a lateral tubulure leading to a Sprengel pump. If now, after exhaustion, the lower meniscus of the barometric column is adjustable, so that the column as a whole may be raised quite into the tube *A B* or withdrawn from it at pleasure, it is probable that a thorough vacuum filling may be effected. Rubber connections, which corrode and blacken warm mercury, must be scrupulously avoided.

If the whole apparatus be charged with pure mercury in the place of the substance *E E*, the expansion and compression constants of the tube may be found as stated in the next paragraph.

Again, even if the measuring thread in *gh* should break into parts alternating with threads of zinc sulphate (a possibility when the thread is worked up and down many hundred times, particularly in view of the suddenness of solidification), the constants of reduction are not thereby necessarily vitiated, always supposing that the number of

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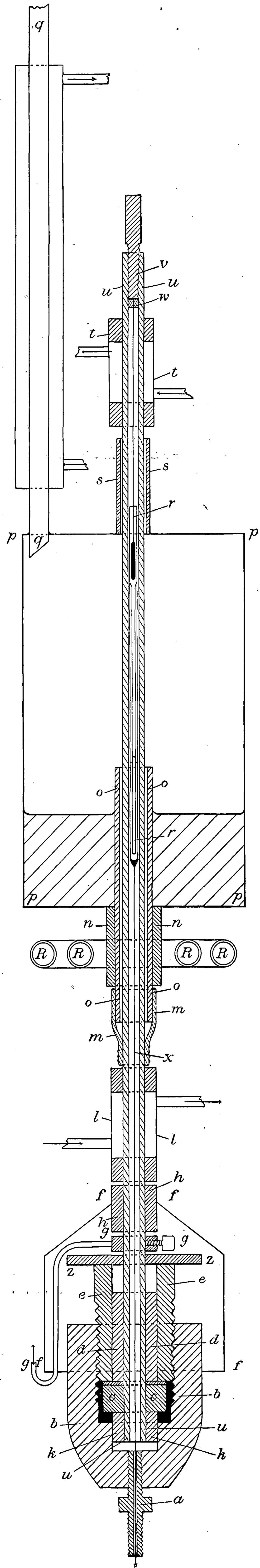
[1] Kohlrausch: Wied. Ann., vol. ii, 1880, p. 653; Long: ibid., 1880, p. 37.



TUBULAR PIEZOMETER, WITH APPURTENANCES.

such breaks is not greater than one or two. Special care, however, must be taken to avoid contact of the mercury thread and the upper zinc terminal. Such an occurrence would either add to or deduct from the length of the thread and produce shifting in the coordination of the volume measurements. The formation of zinc amalgam after the long continued passage of intermittent currents or the possible electric solution of mercury is again to be kept in view, as is also the probable change of compressibility of amalgamated mercury. On all these points I shall make special tests. Solution of mercury, however, can not become of serious consequence, since the column *gh* is continually washed by the zinc terminal *D*.

To give a succinct view of the method of work I will insert Pl. III, which shows the volume tube *rr* in place in the tubular piezometer *uuuu*. The upper terminal *rw* is in contact with the screw plug *v*, where *w* is fastened. The lower terminal *rxx* is completely insulated from *uu* by a glass tube (not shown) and metallically fastened to the perforated connecting screw *a*, by which the piezometer is attached to the barrel (not shown) of the compressor. The insulation of *uu* from *bb* and *a* has been described in section 12 above, *cc* being of steel, *dd* and *kk* of hard rubber, the whole being made tight by a medium of marine glue and secured by the steel gland *ee*. The hard-rubber disc *zz*, prevents the external terminal *ggg* of the piezometer from coming in contact with the metallic parts below and the barrel, while a conical screen or umbrella of sheet iron, *ffff*, additionally protects the lower insulation from water or liquid drippings from above. Note that *ff* is insulated from *nn* by a rubber cork, *hh*. The vapor bath, *pppp*, placed as shown, is heated by the plate burner *rr*, adjustable at pleasure, and an asbestos jacket, *uu*, keeps superfluous heat away from the tube *uu*. The axial tube *oooo* of the vapor bath is sealed below by a piece of rubber hose, *mm*, or by a metallic stuffing box, care having been taken to make *oooo* fit the piezometer tube closely and thus take as little liquid out of the annular ebullition trough already described as possible. The condenser *qq* is connected above with an air pump (not shown). Finally water jackets *tt* and *ll*, through which a current continually circulates. confine the heat to the central parts of the piezometer tube *uuuu*.

METHOD OF MEASUREMENT.

73. *Constants of the tube.*—In order that the present measurements may be carried out absolutely it is necessary to know—

(1) The volume of the charge at a fiducial temperature and pressure.

(2) The volume of the plug of mercury under the same conditions.

(3) The volume of the central or measuring tube *kh* per centimeter of length.

(4) The resistance of the thread of zinc sulphate solution per centimeter of length under all the stated conditions of temperature and pressure. From 3 and 4 there follows at once—

(5) The resistance of the thread of zinc sulphate per unit of volume under stated conditions of temperature and pressure. Thus it is necessary to investigate preliminarily—

(6) The isopiestic relation of resistance and temperature of the given concentrated solution of zinc sulphate and

(7) The isothermal relation of resistance and pressure of the same solution. In other words, it is necessary to know what may be called the isoelectrics relative to temperature and pressure of the measuring electrolyte. Furthermore, it is necessary to find or to know—

(8) The compressibility of glass in its relations to pressure and temperature, and

(9) The compressibility of mercury under the same conditions, and, finally,

(10) The thermal expansion of glass and

(11) The thermal expansion of mercury under the given conditions of pressure.

The measurements 8 to 11 I did not make directly; they are of smaller importance, seeing that the substances on which I operate are all characterized by relatively large volume change. Such measurements are, however, easily feasible, since both the expansion constants and the compression constants of pure mercury (thanks to the recent labors of Amagat, Tait, and Guillaume) are now thoroughly known, and it is also known that the thermal changes of the elastics of glass are of no relative consequence (Amagat), even as far as 200°. I assumed the compressibility of my glass[1] to be ·0000022, that of mercury[2] being ·0000039; moreover, the coefficient of expansion of glass[3] to be ·000025, that of mercury[4] being ·000182 between 60° and 130°.

74. *Volume of the charge.*—Clearly the fiducial conditions to which volume is to be referred are given by the (normal) melting point under atmospheric pressure. By weighing the tube before and after charging I found the mass of naphthalene inclosed to have been ·763 gramme. In a special and duplicate set of pycnometer experiments I furthermore found the density of naphthalene, fused at 82°, to have been ·724. Hence the volume of the charge at 82° is ·552$^{cm^3}$, which I accepted as identical with the volume at the melting point (80°).

75. *Corrections for expansion and compressibility of envelopes.*—The plug of mercury weighed 7·74 grammes. Its volume is therefore ·571$^{cm^3}$ at 20°, and its mean volume between 60° and 130°, being between ·575 and ·582, is sufficiently near ·58$^{cm^3}$.

Thus the volume of the glass tube containing both the charge of naphthalene and mercury was 1·13$^{cm^3}$. Its expansion per degree centigrade ·000028$^{cm^3}$, while the expansion of the actually inclosed mercury per degree centigrade was ·000105$^{cm^3}$, where the apparent expansion

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[1] E. H. Amagat: Ann. ch. et phys., 1891, p. 125.

[2] Ibid., p. 137.

[3] Landolt u. Boernstein's Tables, 1883, p. 69.

[4] Ibid., p. 37.

·000077^{cm3} per degree. Therefore if, in place of the fiducial volume ·552^{cm3} found in §74, the following volumes be substituted, viz,

60°	·5565^{cm3}	100°	·5535^{cm3}
80°	·5550	120°	·5519
90°	·5542	130°	·5311

the tube may be treated as free from thermal expansion. Here at 80° .5550 appears, instead of .5524, to correct for the fiducial volume of the stem *k h* (Fig. 13), as will presently be explained. (§ 83.)

Again, the compression of the 1·13^{cm3} of glass and ·58^{cm3} of mercury will be

100 atm.:	glass, ·00025 ^{cm3};	mercury, ·00023 ^{cm3};	difference, ·00002^{cm3}
500	124	113	11
1000	249	226	23
1500	373	339	34
2000	497	452	45

Thus these corrections, which would individually be appreciable (affecting the increments say 3 per cent), are differentially negligible (0.3 per cent), where they fall below the electrical pressure coefficient of the zinc sulphate solution. (§ 80.) This has already been intimated above (§ 69), and is one of the interesting advantages of the volume tube Fig. 13.

76. *Resistance measurement.*—In making the measurements of resistance of thread it is convenient to use Kohlrausch's interrupter, bridge, and telephone. To facilitate audition I joined the cup of the telephone to a graphophone tube and listened with both ears. The resistances, however, are rather higher than contemplated in Kohlrausch's method, when an ordinary Bell telephone is used. Hence the measurements, particularly near and in the solid state, are far below the limit of attainable accuracy. I shall in future measurements wind telephones specially adapted for my purposes, and endeavor to use both ends of the magnet to actuate diaphragms connected respectively with each ear by an independent tube.

When zinc sulphate is inclosed between terminals of amalgamated zinc a galvanometer is available. In this way I made most of the calibration measurements. Supposing the mercury index to be slightly deadened in its electro-negative qualities by zinc, it may also be used in case of the tube.

77. *Calibration.*—In view of the fact that the central tube *h k* (Fig. 13) is insufficiently uniform in caliber, it is necessary to express volume as a function of length. This I did by weighing threads of mercury whose length in successive parts of the tube had to be measured, obtaining the results of the first two columns of Table 34. The fiducial zero is here arbitrarily placed 2^{cm} below the ring *C C* (Fig. 13), the caliber above this being too variable.

It is next necessary to express the resistance of a filament of the concentrated solution of zinc sulphate as a function of length referred to the same fiducial zero at some convenient (atmospheric) temperature. To do this I drew a zinc wire to a diameter slightly less than the caliber of the tube to be calibrated. Opening the bottom of the tube *A B* (Fig. 13) and closing the top, so as to hold the terminal *D* firmly in position, I inverted the tube and quite filled it with the solution. The tube was then placed in a water bath with the terminal *a* insulated, and the terminal *b* replaced by the zinc wire referred to, and so adjusted that I could slide it up and down the central tube and fix it in any position. Measuring the distance between the ring *C C* (in this case, the neck was quite filled by the fitting terminal) and the free end of the wire with Grunow's cathetometer, and measuring at the same time the resistance corresponding to this length by means of Kohlrausch's Wheatstone bridge (§ 76), I obtained the data necessary for constructing resistance as a function of length for the temperature of the bath. In this way the second and third columns of Table 34 were investigated.

Combining the results of these four columns by graphic interpolation, I obtained the data of the fifth and sixth columns, in which volume is expressed in terms of resistance at 17·8° with regard to the fiducial mark in question.

TABLE 34.—*Volumes per unit of length. Calibration resistance per unit of length, $\theta = 17·8°$. Volume per unit of resistance, $\theta = 17·8°$.*

Length.	Volume.	Length.	Resistance.	Resistance. $\theta = 17·8°$.	Volume. $\theta = 17·8°$.
Cm.	*Cm³.*	*Cm.*	*Ohms.*	*Ohms.*	*Cm³.*
3·00	·0491	—·06	2720	2800	·0000
11·15	·1609	2·13	5780	5530	·0350
		4·75	10190	8850	·0640
		7·96	16200	12530	·0920
4·45	·0715	12·06	24340	16270	·1190
9·79	·1430			20250	·1450
15·42	·2145			24250	·1705
		1·38	4630	28500	·1960
		3·43	7920		
3·30	·0538	6·18	12790		
7·20	·1076	9·00	18220		
11·40	·1614	11·49	23140		
15·60	·2152				
		·11	2930		
2·75	·0470	2·78	7050		
6·10	·0940	Air bubble error.			
9·65	·1410				
13·40	·1880				

78. *Electrolytic resistance and temperature.*—It is next necessary to express the variation of the resistance of the concentrated zinc sulphate solution with temperature. This is a general problem apart from the apparatus used. Nevertheless I made two sets of measurements, in the first of which I measured the resistance of the thread *kh*, Fig. 13, between fixed terminals of zinc, when the whole was kept at successive constant temperatures and under pressure sufficient to keep the thread liquid and to thoroughly condense all polarization gases. The first four columns of Table 35 contains these results, all easily intelligible except the last column perhaps, where under R/R_{100} the relative resistance referred to the resistance at 100° C. is inserted. At 100° the pressures were varied to measure the pressure coefficients discussed in the next paragraph. In the second and third parts of the table the above tube was replaced by a plain straight tube. Resistances are much smaller here, but the column R/R_{100} makes both series comparable.

TABLE 35.—*Temperature coefficients and pressure coefficients of concentrated zinc sulphate solution.*

[First series. Length of thread 10.70^{cm} or 8.7^{cm} from fiducial mark. Diameter of tube .13^{cm}.]

Temperature.	Pressure.	Resistance.	R/R_{100}
°*C*	*Atm.*	*Ohms.*	
6·3	100	26960	6·059
6·5	100	26960	6·059
66·8	140	6178	1·388
67·3	140	6120	1. 376
68·0	140	6050	1·360
67·8	140	6061	1·362
67·8	140	6075	1·365
67·7	140	6075	1·365
100·0	137	4550	1·023
100·0	137	4540	1·020
100·0	479	4470	1·005
100·0	469	4480	1·007
100·0	1019	4370	·982
100·0	996	4380	·985
100·0	1507	4310	·969
100.0	1443	4320	·970
100·0	129	4360	·980
100·0	139	4360	·980
127·6	158	3740	·840
127·8	158	3730	·838
127·8	158	3730	·838
6·5	116	27140	6·100
6·3	116	27000	6·067
[Second series. Plain straight tube, diameter .30^{cm}.			
6·7	72	7280	5·824
....	465	7090	5·672
....	458	7120	5·700
....	906	7020	5·616
....	830	7020	5·616
....	498	7130	5·704
6·7	492	7050	5·640
....	139	7190	5·752
....	147	7160	5·728
99·6	191	1237	.990
°*C*	*Atm.*	*Ohms.*	
....	186	1242	·994
....	471	1222	·978
....	448	1210	·968
....	1011	1198	·958
....	981	1203	·962
....	503	1232	·986
....	507	1232	·986
....	126	1262	1. 010
126·0	157	1062	·850
126·0	157	1062	·850
127·8	149	1058	·846
127·8	149	1058	·846
160.5	154	980	·787
160·5	154	984	·787
160·5	154	984	·787
[Third series. Same tube.]			
16·4	147	4980	3·984
16·4	147	5000	4·000
16·4	147	5020	4·016
6·4	138	7440	5·952
6·4	138	7500	6·000
6·4	138	7500	6·000
61·3	170	1900	1·520
61·3	170	1900	1·520
61·3	170	1913	1·530
85·8	180	1359	1·088
85·8	180	1359	1·088
85·8	180	1364	1·091
99·6	189	1247	1·000
99·6	189	1253	1·002
99·6	189	1253	1·002

If the values R/R_{100} be constructed graphically, as a function of temperature for nearly the same pressures, the results of all the series in Table 35 are found to be in good accord. Moreover the results for the large interval 6° to 160° lie on a locus which in form closely resembles an hyperbola.[1] From this point of view these data are remarkably interesting, for if this be true then a suitable inversion of the locus indicates that the electric conductivity of the electrolyte varies linearly with temperature. Such a result would not only possess theoretic interest, but would make measurements of the kind necessary

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[1] Experiments recently made by Prof. Iddings and myself with diabase (See Am. Journal Sci., XLIV, pp. 242 and 255) showed a geometrical progression of resistances to correspond to an arithmetical progression of temperature, caet. par. Thus the nature of the above locus is exponential.

in the present paper feasible with a high degree of certainty. I must withhold my opinion for the present, however, until I can trace the above locus as far as 300°, and the interpolations of this paper were made empirically.

79. *Volume in terms of resistance.*—With the data of §§ 77 and 78 in hand it is now possible to express the volume of the capillary tube *hk*, Fig. 31, in terms of the resistance of the thread of electrolyte observed at any temperature. This is done in the next table, 36, where the temperatures, θ, are those occurring in the tables of isothermals below.

TABLE 36.—*Relation of volume and resistance at different temperatures.*

Volume.	Resistance.					
	$\theta=63{\cdot}5^\circ$.	$\theta=83^\circ$.	$\theta=90^\circ$.	$\theta=100^\circ$.	$\theta=117^\circ$.	$\theta=130^\circ$.
Cm³.	*Ohms.*	*Ohms.*	*Ohms.*	*Ohms.*	*Ohms.*	*Ohms.*
·0000	1064	818	776	722	636	608
·0350	2101	1615	1532	1427	1255	1200
·0640	3363	2584	2451	2283	2009	1920
·0920	4761	3659	3471	3233	2844	2719
·1190	6183	4751	4507	4198	3693	3531
·1450	7695	5913	5609	5224	4597	4394
·1705	9215	7081	6717	6256	5505	5262
·1960	10830	8322	7895	7353	6470	6185

80. *Pressure coefficient of the electrolyte.*—The divers results of Table 35 for variable pressure and constant temperature are summarized in the small Table 37. Here θ denotes the temperature and k the pressure coefficient, which is negative in sign, showing that pressure decreases the resistance of zinc sulphate. The braces show the manner in which the means were taken, where $k = \delta R / R_0 \, \delta p$. R is the symbol of resistance, p of pressure, and R_0 holds at 0° C.

TABLE 37.—*Pressure coefficients.*

θ.	Pressure.	$k \times 10^5$.	θ.	Pressure.	$k \times 10^6$.
7°	119 479 868	−43 −35	100°	137 474 1007 1475	−43 −35
100°	157 482 996	−64 −49	Mean $k = -{\cdot}000045$		

This table shows that the pressure coefficient is independent of temperature, and that it decreases somewhat with pressure. The results, however, are not quite consistent, and a graphic construction of the detailed results of Table 35 shows a difference of march in the pressure "on" and the pressure "off" movements. I have yet to learn whether this be due to insufficient fixed terminals or to polarization, as well as to find conditions under which the pressure coefficient may be a minimum. As the results stand the mean value $k = -45/10^6$ is probably within 20 per cent of the truth, and hence in the extreme case of 2,000 atmospheres the uncertainty of the pressure coefficient will not affect the volume increments more than 2 per cent.

I may add in passing that the value, investigated in an earlier paper,[1] between 0 and 150 atmospheres was found to be $k = -50/10^6$, agreeing pretty well with Table 37, and I there called attention to the strikingly close proximity of this datum to the corresponding coefficient for mercury, $-30/10$.[2]

The pressure coefficient is of considerable interest, inasmuch as it indicates a certain relation between elasticity and the chemical equilibrium of the solid or liquid operated on.[2] Specially for zinc sulphate compression, which might be regarded as having a concentrative effect on the solution between the terminals, increases the conductivity, whereas the conductivity of a nearly concentrated solution (density >1.29) not under pressure decreases on further concentration.

The admixture of polarization with the pressure coefficient points out the nature of its instability.

RESULTS OF THE MEASUREMENTS.

81. *Arrangement of the tables.*—The following Tables 38 to 43, in which the isothermals of naphthalene are fully given, are constructed on the same plan throughout. The first column contains the time in minutes at which the observation was made, the first date being arbitrary. The (uncorrected) resistance as actually found at the pressure given is shown under *R* in ohms. The factor kp is the correction for pressure coefficient to be added per unit of *R*, after which this datum can be graphically expressed as a volume increment, referred as yet to an arbitrary fiducial zero in the way indicated in §§ 79, 80. To deduce from this the corresponding actual volume (last column of the tables) the initial volume values of § 75 are available, relative to which further explanation will be given in § 83. Two data are given for each step of pressure, the second of which, obtained after long waiting, is more nearly isothermal than the first. The difference is not of seriously large magnitude. In most cases, after the volume has become solid, a small amount of additional volume decrement takes place viscously, or in consequence of gradual decrease of temperature immediately after solidification.

The experiments were made on different days and altogether extended over more than a week. This is somewhat too long a time to employ the tube without special readjustment, and some shifting of coördinates may thus have occurred (§§ 91, 92).

Parentheses occur in the following tables, to show that for the data inclosed the measurement was made along a part of the measuring tube *hk* (Fig. 13), whose caliber is not adequately uniform. Without

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[1] American Jour., vol. 40, 1890, p. 219. This paper was published some two years after the work was done.

[2] Barus: Phil. Mag. (5th ser.), vol. 31, 1891, p. 24 et seq.

knowing the full expansions at the higher temperatures and low pressures, it is, a priori, impossible so to fill the tube that all measurements fall within the calibrated parts and all other calibration conditions are complied with. (§§ 75 et seq.) These approximations, however, refer only to the liquid state, and are therefore of smaller consequence in this paper. (§ 67).)

I may add finally that the melting point of naphthalene in air is 80°, its solidifying point below this; the density of the solid 1·14, and the density of the liquid at 82°, ·724. (§ 74.) Hence naphthalene, if melted in water, sinks or swims, according as its temperature is sufficiently below or above 80°.

82. *Solid isothermal, 63°.*—Since the naphthalene melts at 80°, the isothermal at 63° refers to the solid state. There must clearly be much greater uncertainty in operating on a substance when solid than when liquid. Indeed it is rather remarkable that the solid isothermals are approachable at all. The liquid solidifies to a fissured or honeycombed structure, and it is therefore essential that the mercury should completely fill these interstices before the true compressilbility of the substance can be indicated. Similarly the error due to the compressibility of the envelopes now becomes of much greater importance. It is thus solely by comparing these data with similar solid isothermals obtained at much higher temperatures and pressures that their validity may be inferred (§ 72).

TABLE 38.—*Isothermals of (solid) naphthalene at $\theta = 63·5°$, referred to $·55^{cm^3}$ at the normal melting point.*

Time.	Pressure.	*R.*	$kp \times 10^3$.	Volume.	Time.	Pressure.	*R.*	$kp \times 10^3$.	Volume.
m.	*Atm.*	*Ohms.*		*cm.*^{3}	*m.*	*Atm.*	*Ohms.*		*cm.*^{3}
16	70	7600	3	·4127	38	859	8240	39	·3965
19	68	7430	3	·4156	40	850	8120	38	·3988
20	289	7760	13	·4085	42	972	8310	44	·3945
23	281	7630	13	·4109	44	966	8310	44	·3945
25	491	8160	22	·4003	46	565	7600	25	·4097
29	481	8010	22	·4027	49	565	7600	25	·4097
34	675	8050	30	·4010	51	100	7270	4	·4183
37	662	7880	30	·4039	67	65	7340	3	·4173

With regard to this series it is curious to note that the recoil of volume (pressure decreasing) is more rapid than the compression. The reverse of this would have been anticipated, supposing that mercury lodged in the interstices after compression. Finally I may state that telephonic resistance measurement, when the values are so high, is not unaccompanied by inappreciable errors. (§ 76.)

83. *Liquid-solid isothermal, 83°.*—Table 39 contains three independent series of measurements, the last of which is fragmentary and the second obtained after the experience of the first, probably the best. The solidifying point is here very gradually approached and the locus shows an initial step of James Thomson's double inflections.

It is from these isothermals that I obtained the fiducial zero of the measuring tube *hk*, Fig. 13. For if *R* be constructed as a function of pressure it will be found that pressure zero lies at ·0024$^{cm^3}$ of volume decrement. Hence the value of § 74 (·5524$^{cm^3}$) increased by this correction is the fiducial volume (·555$^{cm^3}$) here to be used and from this the others are derived as already explained. (§ 75.)

TABLE 39.—*Isothermals of naphthalene at θ: =83°, referred to ·55$^{cm^3}$ at the normal melting point.*

Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.	Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm^3.*	*m.*	*Atm.*		*Ohms.*	*cm^3.*
−14	47	2	938	·5490	22	175	8	5493	·4183
−10	45	2	938	·5490	28	179	8	5493	·4183
− 7	164	7	1114	·5404	30	116	5	5061	·4285
− 2	157	7	1100	·5410	36	120	5	5173	·4260
0	259	12	1247	·5340	38	81	4	4263	·4474
+ 7	243	11	4406	·4432	43	86	4	4000	·4540
10	239	11	5667	·4141	49	86	4	3762	·4599
16	238	11	5667	·4142	51	33	1	2448	·4949
18	358	16	5800	·4105	54	36	2	923	·5498
20	355	16	5800	·4105	60	37	2	910	·5505
SECOND SERIES.									
36	39	2	923	·5493	79	129	6	5250	·4241
39	226	10	1183	·5371	81	89	4	4747	·4358
44	221	10	1158	·5382	87	93	4	4348	·4453
46	250	11	1223	·5355	94	93	4	4348	·4453
51	244	11	1198	·5365	96	70	3	3651	·4630
53	267	12	1232	·5348	97	70	3	3256	·4732
59	265	12	1227	·5351	104	74	3	2031	·5062
60	303	13	1288	·5322	115	76	3	1635	·5172
63	322	14	1326	·5306	120	75	3	1480	·5250
64	317	14	5667	·4138	122	49	2	920	·5500
73	299	13	5712	·4128	127	52	2	905	·5508
75	127	6	5250	·4241					
THIRD SERIES.									
9	38	2	910	·5504	21	131	6	1024	·5447
11	135	6	1032	·5444	23	345	15	5450	·4184

84. *Liquid-solid isothermal at 90°.*—Two independent series of results are given in Table 40. In consequence of slight variation of the artificial atmosphere, the temperature of the first is somewhat below that of the second. Thus in series I there is some lack of coincidence in the liquid "on" and "off" march, whereas the two are identical in series II.

TABLE 40.—*Isothermals of naphthalene at θ =90°, referred to ·55$^{cm^3}$ at the normal melting point.*

Time.	Pressure	$kp\times10^3$.	*R.*	Volume.	Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm^3*	*m.*	*Atm.*		*Ohms.*	*cm^3*
−10	83	4	845	·5502	33	346	16	5055	·4205
−8	83	4	842	·5504	34	287	13	4435	·4357
−6	257	12	1049	·5392	36	273	12	4051	·4455
−2	238	11	1016	·5410	41	277	13	3514	·4597
0	434	19	1247	·5296	47	274	12	2969	·4736
+5	425	19	1217	·5309	51	275	12	2677	·4831
7	549	25	5250	·4147	59	272	12	1950	·5042
20	527	24	5329	·4130	62	190	8	923	·5457
22	445	20	5211	·4163	67	192	8	923	·5457
27	446	20	5173	·4172	70	68	3	790	·5532
28	375	17	5100	·4193					

TABLE 40.—*Isothermals of naphthalene at ϑ = 90°, referred to ·55$^{cm^3}$ at the normal melting point*—Continued.

SECOND SERIES, SAME ADJUSTMENT.

Time.	Pressure.	$kp \times 10^3$.	*R.*	Volume.	Time.	Pressure.	$kp \times 10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm*³	*m.*	*Atm.*		*Ohms.*	*cm*³
16	57	3	773	·5542	60	316	14	4618	·4311
18	231	10	972	·5432	65	322	14	4555	·4326
24	222	10	957	·5439	67	280	13	3855	·4504
26	422	19	1188	·5322	73	283	13	2333	·4929
31	406	18	1155	·5338	76	283	13	1985	·5028
33	490	22	1247	·5293	81	278	13	1618	·5152
40	474	21	1232	·5302	83	175	8	897	·5472
42	507	23	1258	·5292	89	179	8	902	·5468
44	532	24	1288	·5276	91	81	4	793	·5530
46	555	25	5250	·4147	95	83	4	802	·5524
57	544	24	5290	·4139					

85. *Liquid-solid isothermals at 100°.*—Table 41 contains four independent series of results, together with some preliminary measurements. These are my earliest result with the above tube and are therefore in greater number. The liquid isothermals should be identical in the "on" and "off" marches. This is, as a rule, very nearly the case, the preliminary series and "on" march of the first alone lying below the others. In the latter the telephone used was more sensitive than in the former.

TABLE 41.—*Isothermals of naphthalene at ϑ = 100°, referred to ·55$^{cm^3}$ at the normal melting point.*

PRELIMINARY MEASUREMENTS.

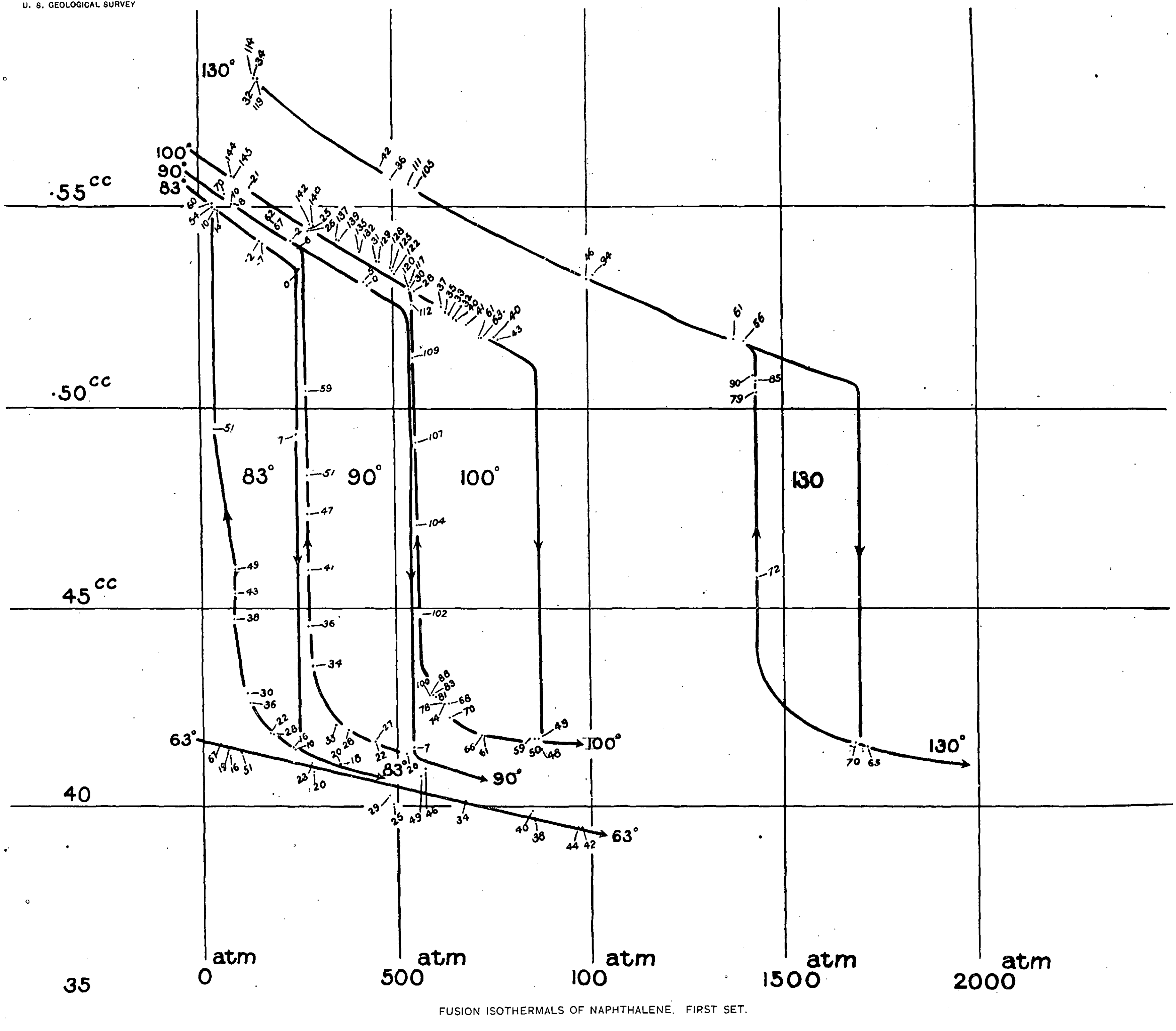
Time.	Pressure.	$kp \times 10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm*³.
5	170	7	780	·5499
10	170	7	780	·5499
13	384	7	1006	·5367
15	355	16	984	·5380
17	593	27	1225	·5255
19	558	25	1209	·5264
21	636	28	1277	·5232
23	610	27	1261	·5239
24	651	29	1301	·5221
27	688	31	1336	·5204
30	196	9	812	·5480
32	176	8	783	·5497

TUBE AGAIN ADJUSTED. FIRST SERIES.

Time.	Pressure.	$kp \times 10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm*³.
21	130	6	707	(·5545)
25	280	13	884	·5436
26	284	13	876	·5441
28	557	25	1169	·5283
30	540	24	1156	·5289
32	655	29	1296	·5222
33	642	29	1279	·5230
35	636	29	1274	·5232
37	622	28	1247	·5245
40	662	30	1307	·5218
41	688	31	1322	·5210
43	769	35	1405	·5172
44	759	35	1392	·5178
48	875	39	4840	·4137
49	862	39	4720	·4169
50	856	39	4720	·4169
59	843	38	4720	·4170
61	720	32	4720	·4177
66	720	32	4720	·4177
68	631	28	4420	·4249
70	633	28	4560	·4225
74	623	28	4420	·4259
78	611	27	4420	·4260
81	600	27	4370	·4274
83	595	27	4370	·4274
88	593	27	4280	·4296
97	592	27	4350	·4278
100	587	26	4350	·4279
102	561	25	3600	·4483
104	556	25	2840	·4708
107	553	25	2150	·4915
109	549	25	1530	·5127
112	545	24	1240	·5250
117	544	24	1120	·5307
120	542	24	1140	·5298
122	503	22	1080	·5327
125	499	22	1068	·5335
128	497	22	1050	·5343
129	461	21	1019	·5360
131	458	21	1019	·5360
132	417	19	978	·5381
135	413	18	978	·5381
137	358	16	921	·5414
139	358	16	924	·5412
140	296	13	862	·5449
142	296	13	866	·5447
144	87	4	660	(·5575)
145	87	4	656	(·5578)

SECOND SERIES. SAME ADJUSTMENT.

Time.	Pressure.	$kp \times 10^3$.	*R.*	Volume.
20	116	5	667	(·5575)
27	116	5	667	(·5575)
29	281	13	852	·5455



FUSION ISOTHERMALS OF NAPHTHALENE. FIRST SET.

TABLE 41.—*Isothermals of naphthalene at $\vartheta=100^\circ$, referred to $\cdot 55^{\mathrm{cm}^3}$ at the normal melting point*—Continued.

Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.
m.	*Atm.*		*Ohms.*	*cm³.*
36	274	12	835	·5464
45	460	21	1020	·5360
47	670	30	1223	·5255
53	653	29	1198	·5266
56	795	35	1331	·5204
63	766	34	1300	·5219
64	808	36	1353	·5195
69	797	36	1353	·5195
75	780	35	1336	·5202
76	818	37	1370	·5185
85	813	36	1370	·5187
91	785	35	1336	·5202
93	856	39	1415	·5167
102	850	38	1410	·5169
107	820	37	1370	·5185
108	908	41	1439	·5155
116	888	40	1439	·5155
121	890	40	1439	·5155
122	921	41	4814	·4141
133	914	41	4882	·4125
148	906	41	4882	·4124
150	769	35	4714	·4175
157	772	35	4714	·4175
159	644	29	4556	·4224
165	652	29	4556	·4224
167	560	25	3808	·4425
168	560	25	3202	·4599
169	562	25	2846	·4707
171	558	25	2279	·4877
173	558	25	1889	·5000
176	558	25	1600	·5102
178	558	25	1416	·5175
180	557	25	1300	·5224
184	552	25	1174	·5280
187	553	25	1160	·5287
208	553	25	1158	·5288
213	546	25	1160	·5287
216	429	19	988	·5375
225	430	19	992	·5375
227	287	13	845	·5459
235	292	13	852	·5454
237	81	4	645	(·5585)
244	86	4	650	(·5583)

THIRD SERIES. SAME ADJUSTMENT.

Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.
7	87	4	653	(·5583)
12	88	4	653	(·5583)
15	274	12	838	·5462
20	267	12	828	·5468
22	489	22	1045	·5345
28	476	21	1008	·5365
31	666	30	1208	·5262
38	649	29	1220	·5256
41	837	38	1375	·5185
47	820	37	1359	·5191
49	874	39	4814	·4143
56	864	39	4883	·4126
70	770	35	4814	·4149
81	760	34	4780	·4159
83	675	30	4714	·4181
88	677	31	4682	·4187
90	578	26	4000	·4371
93	581	26	3975	·4377
96	581	26	3608	·4480
100	580	26	3525	·4503
102	571	26	3255	·4581
107	574	26	2732	·4739
115	569	26	2390	·4845
123	571	26	2087	·4934
131	566	25	1829	·5018
133	557	25	1611	·5097
135	547	25	1380	·5189
136	490	22	1070	·5333
138	484	22	1033	·5351
139	276	13	835	·5464
141	77	4	631	(·5600)
143	80	4	638	(·5590)

FOURTH SERIES. SAME ADJUSTMENT.

Time.	Pressure.	$kp\times10^3$.	*R.*	Volume.
6	72	3	620	(·5605)
9	72	3	622	(·5605)
13	266	12	828	·5468
19	257	12	805	·5481
21	252	11	802	·5483
23	451	20	1008	·5365
33	418	19	957	·5393
36	689	31	1247	.5243
42	642	29	1169	.5280
44	818	37	1353	.5194
50	811	36	1331	.5204
57	853	38	1364	.5188
59	903	40	4882	.4125
65	900	40	4917	.4115
67	1018	45	4988	.4089
73	1005	45	5024	.4080
74	879	40	4882	.4125
79	865	39	4814	.4143
81	690	31	4587	.4213
85	694	31	4587	.4213
87	575	26	4000	.4371
93	581	26	3785	.4430
99	549	25	1631	.5090
105	549	25	1165	.5280
110	539	24	1123	.5306
112	488	22	1041	.5347
120	484	22	1012	.5363
122	294	13	832	.5465
127	295	13	835	.5463
129	89	4	634	(.5595)
135	97	4	647	(.5585)

86. *Liquid solid isothermals at 117°.*—Table 42 contains a series of results. The vapor bath in this case was filled with amyl alcohol, from which the water was not extracted. Hence the peculiarly broken isothermal obtained is in correspondence with the known inconstancy of temperature along the vertical. This feature is, however, of considerable interest, and throws light on certain characters of the other isothermals, inasmuch as it shows the behavior in case of partial solidification.

TABLE 42.—*Isothermals of naphthalene at* $\Theta = 117°$, *referred to* ·55$^{cm^3}$ *at the normal melting point.*

Time.	Pressure.	$kp \times 10^3$	*R.*	Volume.	Time.	Pressure.	$kp \times 10^3$	*R.*	Volume.
m.	*atm.*		*ohms.*	*cm³.*	*m.*	*atm.*		*ohms.*	*cm³.*
4	86	4	408	(·5709)	64	1317	59	4263	·4094
5	86	4	408	(·5709)	66	1055	47	3546	·4325
7	277	13	600	(·5547)	72	1053	47	2448	·4692
12	272	13	585	(·5549)	75	1051	47	2279	·4749
14	496	22	784	·5411	81	1054	47	2175	·4786
20	468	21	740	·5439	84	877	40	1253	·5149
22	689	31	946	·5309	90	877	40	1198	·5174
27	651	29	894	·5339	91	701	31	953	·5307
29	910	41	1123	·5210	95	707	31	938	·5314
35	895	40	1097	·5224	97	517	23	760	·5426
37	1092	49	2257	·4756	102	523	23	765	·5421
39	1086	49	2773	·4579	103	285	13	565	(·5571)
50	1068	48	2704	·4601	107	290	13	572	(·5561)
52	1254	56	4208	·4114	109	96	5	412	(·5699)
58	1226	55	4208	·4115	115	100	5	414	(·5699)
59	1326	60	4263	·4091					

87. *Liquid solid isothermals at 130°.*—Table 43, finally, contains four series of results obtained at 130°. The vapor bath in this case contained amyl alcohol, thoroughly dried by copious distillations. Slight differences in the liquid "on" and "off" march are only apparent in the last series. The temperature of the third series was about 129.6°.

TABLE 43.—*Isometrics of naphthalene at* $\Theta = 130°$, *referred to* ·55$^{cm^3}$ *at the normal melting point.*

FIRST SERIES. SAME ADJUSTMENT.

Time.	$kp \times 10^3$	Pressure.	*R.*	Volume.
m.		*atm.*	*ohms.*	*cm³.*
32	7	151	272	(·5821)
34	7	146	270	(·5821)
36	22	496	522	(·5566)
42	21	461	493	(·5591)
46	45	998	862	·5316
52	45	978	845	·5328
56	63	1403	1119	·5166
61	63	1379	1105	·5171
65	76	1713	3808	·4148
70	76	1686	3785	·4156
72	63	1432	2600	·4578
79	63	1438	1392	·5039
85	63	1433	1326	·5069
90	63	1423	1294	·5081
94	45	1013	847	·5326
102	41	897	786	·5365
105	25	558	548	(·5546)
111	24	540	538	(·5551)
114	7	145	266	(·5821)
119	7	154	275	(·5816)

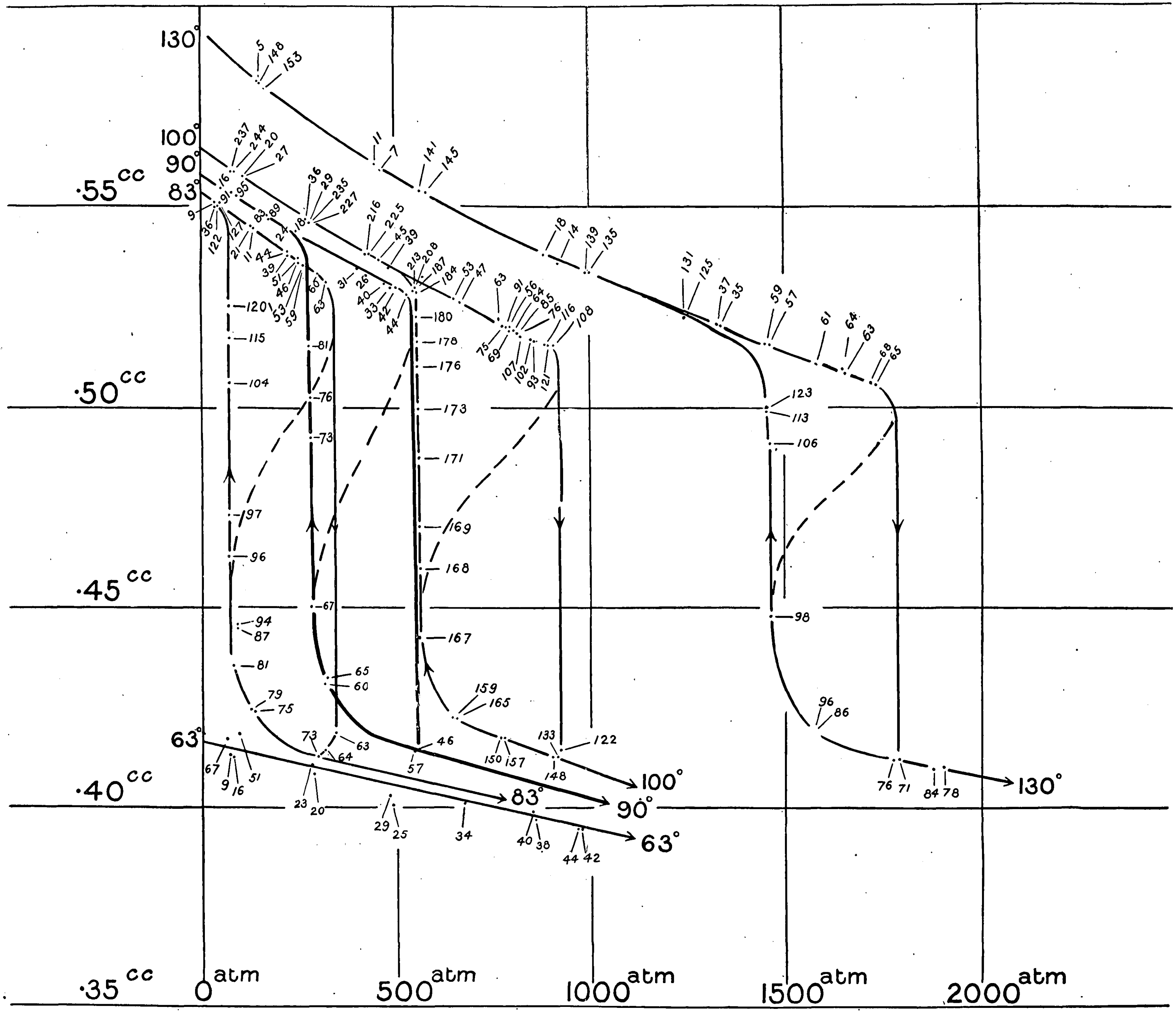
SECOND SERIES. SAME ADJUSTMENT.

5	7	151	276	(·5811)
7	21	464	495	(·5586)
11	20	451	484	(·5601)
14	41	921	808	·5351
18	40	881	770	·5378
35	58	1338	1057	·5200
37	59	1336	1057	·5200
57	65	1464	1132	·5158
59	65	1459	1132	·5158
61	74	1581	1223	·5109
63	74	1656	1278	·5083
64	74	1651	1262	·5091

Time.	$kp \times 10^3$	Pressure.	*R.*	Volume.
m.		*atm.*	*ohms.*	*cm³.*
65	78	1737	1329	·5057
68	78	1723	1320	·5061
71	81	1794	3878	·4119
76	79	1777	3926	·4106
78	85	1907	3926	·4099
84	85	1880	3950	·4091
86	72	1574	3695	·4190
96	72	1575	3695	·4190
98	65	1463	2876	·4480
106	65	1463	1690	·4914
113	65	1458	1481	·5000
123	65	1456	1490	·4996
125	56	1245	1021	·5220
131	56	1244	1021	·5221
135	44	990	845	·5327
139	44	994	850	·5325
141	25	565	565	(·5536)
145	26	580	570	(·5531)
148	7	155	275	(·5811)
153	7	168	289	(·5796)

THIRD SERIES. SAME ADJUSTMENT.

9	6	135	263	(·5831)
12	6	134	263	(·5831)
15	21	468	517	(·5571)
22	21	456	504	(·5581)
28	44	971	845	·5327
31	43	960	825	·5341
34	65	1467	1164	·5143
43	63	1420	1114	·5168
45	72	1579	1242	·5101
50	70	1564	1212	·5116
53	74	1665	3739	·4173
59	74	1632	3762	·4166
61	81	1794	3831	·4135
63	81	1784	3831	·4135
66	70	1564	3651	·4206



FUSION ISOTHERMALS OF NAPHTHALENE. SECOND SET.

TABLE 43.—*Isometrics of naphthalene at $\theta = 130^\circ$, referred to ·55* $^{cm^3}$ *at the normal melting point*—Continued.

Time.	$kp \times 10^3$	Pressure.	*R.*	Volume.
m.		*atm.*	*ohms.*	*cm*^{3}
75	70	1558	3651	·4206
77	67	1484	3405	·4291
83	67	1509	3310	·4324
85	63	1412	2334	·4670
91	63	1416	1217	·5117
100	63	1412	1198	·5126
105	47	1044	855	·5319
111	47	1044	865	·5312
113	26	576	560	(·5536)
120	26	584	560	(·5531)
122	7	146	266	(·5821)
128	7	160	279	(·5801)
FOURTH SERIES.				
45	9	196	320	(·5769)
48	9	196	320	(·5769)
50	19	427	490	(·5591)
55	19	416	480	(·5601)
57	28	626	653	·5465
63	27	611	634	·5479
67	36	801	770	·5379
72	36	789	755	·5389
74	45	1022	930	·5276
84	43	956	845	·5329
87	54	1215	1050	·5206
90	54	1200	1033	·5214
92	65	1432	1203	·5123
96	63	1412	1174	·5139
98	74	1634	1331	·5059
104	72	1606	1320	·5065
108	72	1603	1320	·5067
112	54	1196	1029	·5217
118	54	1199	985	·5240
119	39	859	755	·5387
124	39	862	765	·5381
126	22	498	515	(·5571)
127	22	503	525	(·5561)
134	7	151	282	(·5781)
140	7	160	290	(·5781)

DEDUCTIONS.

88. *Graphic construction.*—To obtain a comprehensive survey over this series of individual data, it will be necessary to resort to the pictorial method and represent volume as a function of pressure, under successive conditions of constant temperature. Moreover it will be expedient to represent the whole group of first series on a single chart, the second series on another chart, etc., and thus obtain about four distinct sets of results, covering the whole interval 60° to 130°, and about 1,900 atmospheres. This has been done in Pls. IV, V, VI, and VII, in which the ordinates are volumes (the fiducial volume being the ·5524$^{cm^3}$ at 80°, arbitrarily chosen), the abscissas are pressures, and in which the temperatures of the isothermals are inscribed at the beginning and end of each curve. Finally the dates or times in minutes at which the individual observations were made are all given by small numerals attached to the points. Thus it is easy to know at once whether an observation was taken during the "on" march or the "off" march of pressure; but to further facilitate inspection arrows are subjoined to the contours of the curves, showing their drift. It is seen from the figures that the solid seems to be comparable as regards compressibility with the liquid, but on this point I shall not now lay much stress, for reasons repeatedly stated in the above paragraphs, §§ 70, 82.

89. *Hysteresis.*—The inherent character of all these curves is pronouncedly cyclic. The isothermal pressure necessary to solidify naphthalene being at all temperatures decidedly in excess of the pressure at which it again liquefies. Then the results which I obtained in other experiments and with other substances some time ago[1] are thus emphat-

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[1] Am. Jour. Sci., vol. 38, 1890, p. 408. The full paper and the deductions there made are as yet unpublished.

ically corroborated. Evidences of the thoroughly static character of these phenomena are abundant and obtained by observing the times of successive points. I need only mention solid isothermal, 100° Pl. IV, where I waited from 50^m to 100^m at a pressure below the solidifying point of the liquid without obtaining fusion; whereas after this with only a slight further reduction of pressure fusion sets in and is complete between 101^m and 112^m; liquid isothermal, 100°, Pl. V, where I waited from 47^m to 121^m at a pressure greater than that at which fusion of the solid takes place without obtaining solidification, which, however, sets in at once (121^m 122^m) when the pressure interval is only slightly increased; same plate solid isothermal 130°, I waited from 86^m to 96^m at a pressure below the solidifying point without any change of volume or fusion whatever; solid isothermal, 130° Pl. VI, where I waited from 66^m to 83^m without obtaining fusion, and from 66^m to 75^m without appreciable change of volume; liquid isothermal, 100°, Pl. VII, where I waited from 36^m to 90^m without obtaining solidification, and from 74^m to 87^m on the solid isothermal without obtaining fusion, etc. If high temperature conditions are unfavorable to lag, the results at 130° are specially good evidence in favor of the point of view taken. I have already pointed out[1] that it is a phenomenon inherent in the passage from one molecular condition to another which lies at the root of all manifestations of hysteresis, whether observed electrically (Cohn, Ewing, Schumann) or magnetically (Warburg, Ewing), or as a purely mechanical result in my work,[2] during fusion, as above, during solution, § 95, etc.

90. *James Thomson's double inflections.*—Solidification almost always sets in at once. This is what one should expect, for, if there be condensation or crystallization at any point, it will form a nucleus for which the whole column will be solidified. Only in one case (Pl. V, liquid isothermal 83°, 60^m to 63^m) did I obtain evidences of curvature, whereas in Pl. IV, at the same temperature, the whole path, though observable (0^m, 7^m, 10^m), is precipitous.

The reverse of this holds true in case of fusion. Here the initial or stable contours of James Thomson's circumflexures are always marked. It is true that fusion rarely takes place instantaneously, because of the difficulty in supplying heat fast enough. Hence it might be plausibly argued that the fusion contours are necessarily more gradual than the solidification contours. It is also supposible that, if temperature be not quite identical throughout the height of the column of substance, fusion will first take place at the hotter planes below and proceed thence to the top. This state of things I have actually observed in glass capillary tubes when the vapor baths were imperfect. In the present experiments, however, the phenomenon occurs with the same uniformity at all temperatures and is quite as pronounced in a

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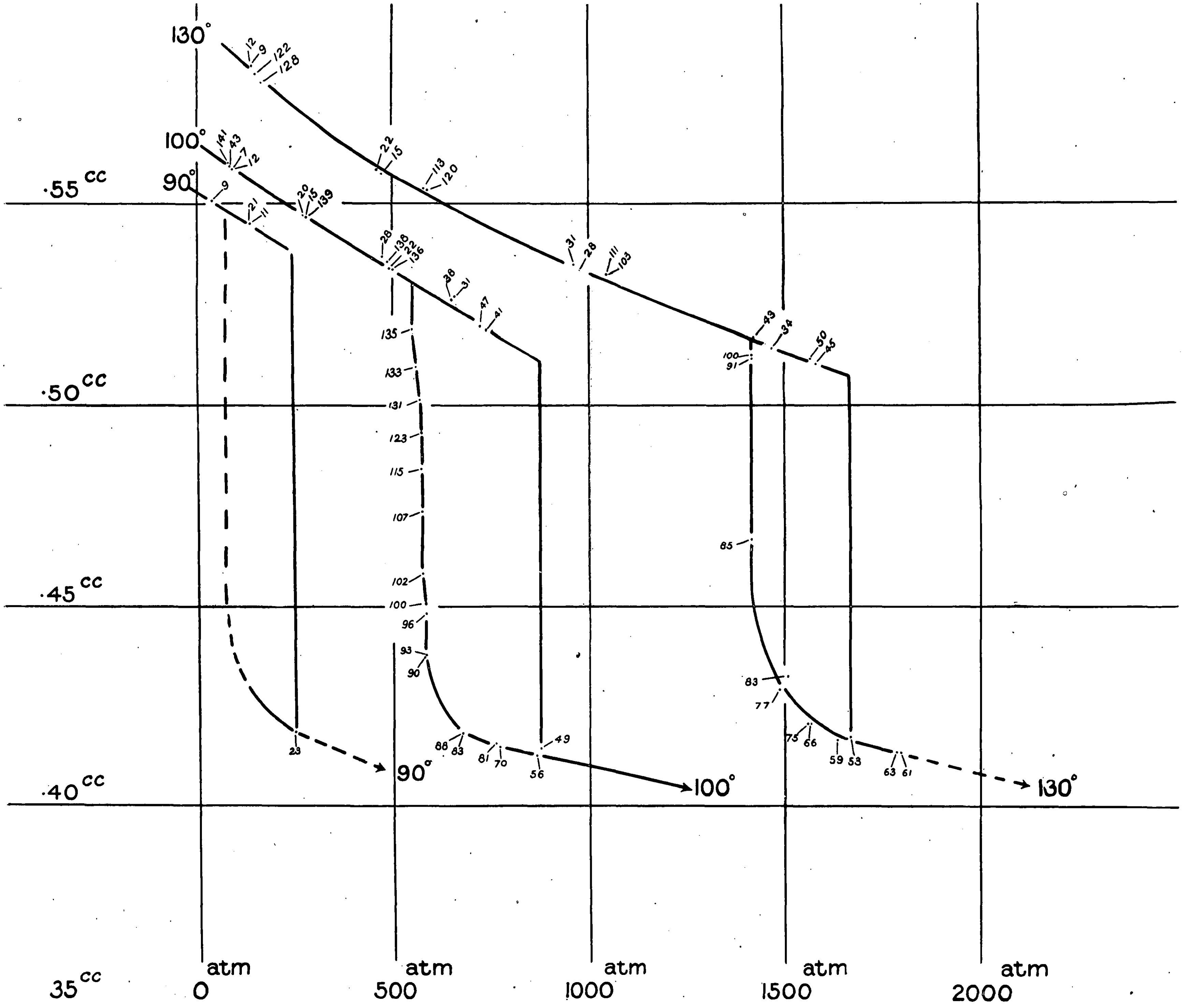
[1] Am. Journal, l. c.; Phil. Mag. (5), vol. 31, 1891, p. 27.

[2] Chapter III, above.



FUSION ISOTHERMALS OF NAPHTHALENE. THIRD SET.

steam bath. Moreover the column is not above 10^{cm} long. Hence, taking this into account in connection with the evidence cited in the foregoing paragraph (89), I conclude that the initial solid contours are static, and hence regard them as evidencing James Thomson's[1] well-known inference relative to the doubly inflected contours of the isothermals accompanying change of physical state. When fusion actually sets in the phenomenon is no longer observable, for the physical parts of the substance now exist in widely different thermal states.

Here I may expediently point out the advantages gained by operating in a thin shell of substance (see Fig. 13 and Pl. III), the heat within which is rapidly dissipated. The conditions, therefore are specially favorable for isothermal work.

91. *The characteristic specific volumes.*—Mere inspection of the charts, Pls. IV to VII, shows that the volume at which solidification takes place decreases with temperature, and the volume after solidification either increases or remains stationary in value. In Table 44 I have inscribed the corresponding values of pressure and volume, observed at the solidification points, in each of the four series; and in Pl. VIII these data have been plotted, volumes being the abscissæ and pressures the ordinates. To distinguish the points they are surrounded by little circles to which the number of the series is attached, and the pressures are given on the right side of the diagram.

TABLE 44.—*Volumes solid and liquid at the solidifying points, varying with the pressure.**

Series.	Temperature 83°.		Temperature 90°.		Temperature 117°.	Temperature 100°.		Temperature 130°.	
	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.
I.	260	260	550	550	....	875	875	1720	1720
	·415	·534	·413	·523	....	·416	·510	·415	·505
II.	320	320	555	550	....	920	920	1790	1790
	·415	·530	·415	·527	....	·413	·515	·412	·505
III.	345	345	550	....	....	870	870	1665	1665
	....	....	·418	....	....	·413	·510	·417	·507
IV.	....	....	....	....	....	900	900	1720	1720
	....	....	....	....	·415	·412	·517	....	·505

* See remarks on Table 46.

A similar and equally important table may be deduced by finding the values of the characteristic volumes at the successive melting points. These are inscribed in Table 45, on the plan of Table 44.

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[1] J. Thomson: Phil. Mag. (4), vol. 42, 1872, p. 227.

TABLE 45.—*Volumes solid and liquid at the melting points, varying with pressure.**

Series.	Temperature 83°.		Temperature 90°.		Temperature 117°.	Temperature 100°.		Temperature 130°.	
	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume. Liquid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.	Solid pressure. Solid volume.	Liquid pressure. Liquid volume.
1	80	80	275	275	....	560	560	1430	1430
	·435	·547	·425	·540	....	·440	·528	·435	·515
2	80	80	280	280	....	560	560	1465	1465
	·450	·548	·440	·541	....	·435	·531	·430	·515
3	....	....	....	....	....	580	580	1410	1410
	....	....	....	....	....	·440	·528	·440	·517
4	....	....	....	....	1050	570	570	....	....
	....	....	....	....	·430	·440	·531	....	....
	....	....	....	....	·515				

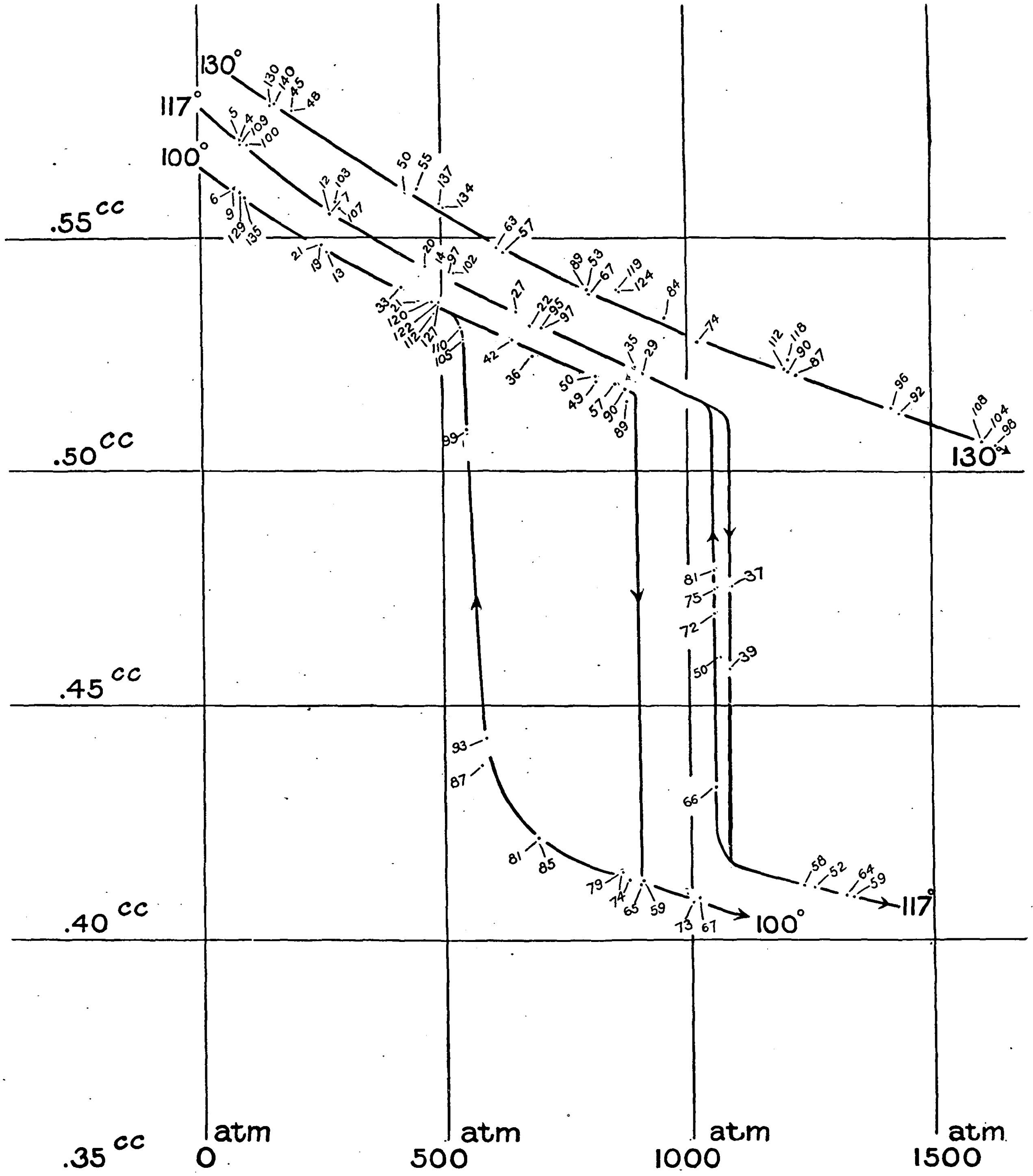
* See remarks on Table 46.

If these data be inscribed in a chart like Pl. VIII, both the solid and the liquid volumes will closely resemble the curves already mapped out for solidifying point; but since the solid volumes can obviously only be approximately given, and since the liquid volumes contain no new feature, I omit them to avoid confusing the figure.

A noticeable part of this diagram is the close accordance of the three groups of points between 0 and 1,000 atmospheres, during which measurements vapor of water was the medium of constant temperature, as compared with the one group of points between 1,000 and 2,000 atmospheres, where vapor amyl alcohol was used. I account for this by supposing the solidification in the latter case (130°) to have been premature, a result to be associated with insufficient constancy of the vapor bath (§ 70, 86, 89), hence the liquid volumes found are too large. There may, however, have been some gradual change in the contents of the tube, which in the lapse of time became appreciable (§76, 81). Thus the zinc gradually deposited by the intermittent currents in the mercury, the possible detachment of the end of the mercury thread in *hk* (Fig. 13) after repeated motion back and forth, changes in the quality of the solution of zinc sulphate, etc., would produce a shifting of the volume constants and a result like that observed in Pl. VIII. Further experiments must decide this point. Regarding the solid volumes, it is clear at once that no device can define them as accurately as the liquid volumes, and the degree of coincidence attained is one of the valuable accomplishments of the present method.

To summarize, therefore, I have in Pl. VIII placed chief reliance on the water points (0 to 1,000 atmospheres) and drawn the locus accordingly.

92. *Critical point.*—The area inclosed by the figure *a b . . . c d*, supposing *b* and *c* eventually to coalesce, has the same signification as Andrews' area of vapor tensions. The same would be true of the similar figure for the characteristic volumes at the melting points, or



FUSION ISOTHERMALS OF NAPHTHALENE. FOURTH SET.

finally to the figure in which the solidification volumes are taken at the solidification points, and the fusion volumes at the melting points. All of these diagrams point out the probable occurrence of a critical point in the region of positive pressure and reached in the direction of increasing temperature, at which point liquid would pass to solid or solid to liquid without paroxysmal change of volume, and consequently without volume log. This position of this point may be conjectured to lie at several hundred degrees centigrade and several thousand atmospheres, naphthalene being the material operated on.

93. *Solidifying points and melting points.*—The cycles as depicted in Pls. IV to VII have two prominent characteristics: They gradually decrease in vertical extent from left to right, and they gradually decrease in lateral extent toward both sides of the chart. Each of these qualities throws important light on the phenomena as a whole.

Table 46 gives the numerical values of the pressures corresponding to solidification and to fusion at the different temperatures, together with other information of importance, as sharply as the statement can be made. Let the solidifying points and the melting points be constructed as a function of pressure. This is done in Pl. VIII, and the points form a long spindle-shaped figure running diagonally across the chart. Points obtained from all the four sets of results (Pls. IV to VII) are inscribed and these points are numbered to show the series to which they belong. The parts of the curves actually observed are given in full lines and the inferential prolongations in dotted lines.

From the nature of the case the solidification points can not be sharply measured. (§ 89.) Thus, if the temperature of the column be not uniform, (and in case of an ebullition liquid of small specific heat and possibly not homogeneous in composition, the tube is sure to be hotter at the bottom than at the top), the colder parts will solidify first, and at once induce solidification throughout the whole length of the column. This is markedly shown in the isothermal for 117°, and given in Pl. VII, where the solidifying and fusing points are practically in coincidence. (§ 86.) Similarly all jarring and percussion, too rapid increase of pressure, a vibratile wire running through the column as in some of my earlier work, etc., will cause the whole labile framework to topple into solidification. Hence the solidifying point must be fairly *crept upon* and surprised, as it were, and hence my present results, in which these precautions were taken, show high solidifying points as compared with my other work. These conditions do not seem to hold in like importance in case of fusion, for the melting points, as a rule, show much greater coincidence.

TABLE 46.—*Showing the relation of solidifying point and of melting point with pressure.—Naphthalene.*

Series No.	Temperature 63°.		Temperature 83°.		Temperature 90°.		Temperature 100°.		Temperature 117°.		Temperature 130°.	
	Solid at—	Fusing at—	Solid at—	Fusing at—	Solid at—	Fusing at—	Solid at—	Fusing at—	Solid at—	Fusing at—	Solid at—	Fusing at—
	Atm.	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*	*Atm.*
I	......	(*a*)	[b]260	[c]80	[e]550	[d]275	[e]875	[d]560	......	....	[e]1720	[f]1430
II	......	....	[g]320	80	[d]555	[d]280	[d]920	[d]560	......	....	[d]1790	[f]1465
III	......	....	[e]345	....	......	....	[h]870	[d]580	......	....	[i]1665	[f]1410
IV	......	....	......	....	......	....	[d]900	[d]570	[j]1090	[j]1050	[e]1720	....
	[k] Factor: Melting point and pressure 80° to 130°, 28·5 atm. °C., or ·0351 °C. / atm. Factor: Solidifying point and pressure 80° to 100°, 36·0 atm./°C., or ·0278 °C./1 atm. Factor: Solidifying point and pressure, 100° to 130°, 29·5 atm./°C., or·0339 1 °C. /1 atm.											

[a] Negative.

[b] Not crept upon. First result at <83°, second and third at >83°. Solidification gradual; other solidifications take place at once.

[c] Fusing very viscously throughout a pressure interval of 50 atmospheres.

[d] Crept upon.

[e] Not crept upon.

[f] Fusion relatively rapid; more-nearly resembling the solidification march than is the case at lower temperatures.

[g] Crept upon. First result at <83°, second and third at >83°. Solidification gradual; other solidifications take place at once.

[h] Intermediate between *a* and *b*.

[i] Intermediate between *a* and *b*. Temperature, 129·6°.

[j] Temperature lower at top than at bottom of the column. Partial fusions. Vapor bath containing aqueous amyl alcohol.

[k] Chiefly with reference to Series II.

In drawing Pl. VIII I have therefore placed chief reliance on the data of Series II, obtained as they were with the experience of Series I, to guide me. The horizontal breadth of the spindle-shaped area indicates the pressure amount of volume lag corresponding to any temperature.

94. *Transitional point.*—If the two curves be prolonged in the direction of increasing temperature, it is clear that they must eventually coalesce. For, at the critical temperature, liquid will pass to solid and vice versa without paroxysmal change of specific volume, and hence there can be no volume lag.

If the curves be prolonged in the direction of decreasing temperature, then the data emphatically indicate the probable occurrence of an intersection in the region of negative pressure. Beyond the point of intersection the substance would solidify at a lower pressure than that at which it fuses, and fuse at a higher pressure than that at which it solidifies. I believe this observation may be interpreted as follows: The normal type of fusion changes continuously into the ice type of fusion, through a transitional type characterized by the zero of volume lag. The position of this transitional type for naphthalene, so far as I can now discern it, may be placed at, say, 50° and —1,000 atmospheres. It may be noted that with the understanding here laid down, the normal type of fusion is reached from the ice type in the direction of increasing temperature.

Throughout the present chapter I have avoided the discussion of the isopiestics, since I shall consider them in detail in connection with special experiments. It is well to state, however, that the transitional temperature is related to the prospective intersection of the prolonged

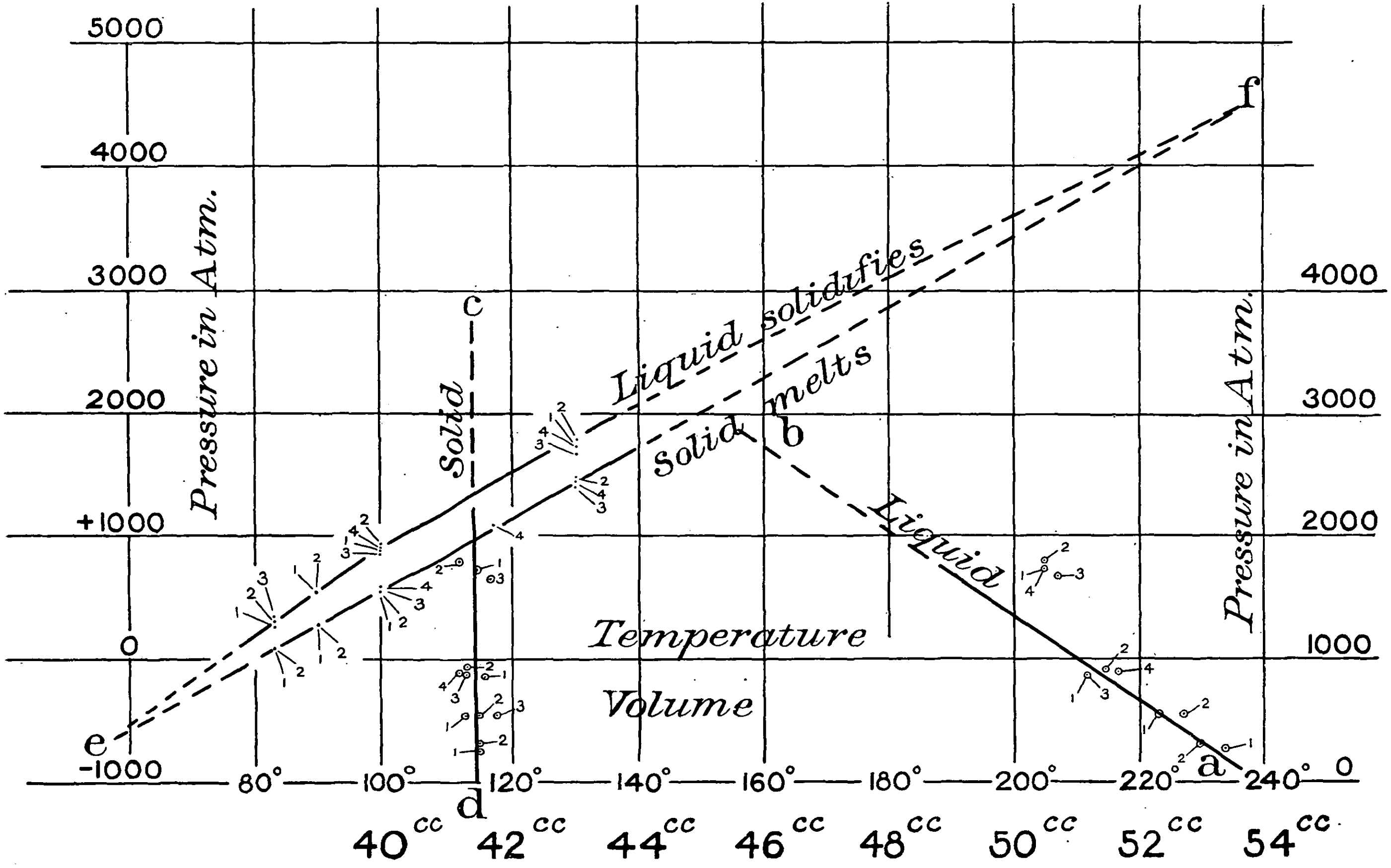


DIAGRAM SHOWING THE CONDITIONS OF FUSION AND SOLIDIFICATION.

liquid and solid isopiestics, of a given substance, at the same pressure in both cases. Thus a reason why hysteresis may vanish is again suggested. A given substance on one side of the transitional temperature need not necessarily differ molecularly from the same substance on the other side.

Practically only one of the states is attainable, for the other implies an application of negative pressure.

If the chart, Pl. IV, is to represent in diagram a field of isothermals for the ice type, the solid and liquid phases of the chart are to be exchanged. The solid march for the ice type takes place along loci of greater specific volumes and the liquid march along loci of smaller specific volumes. Thus the chart of isothermals must show intersecting loci, identical points corresponding, however, to different molecular states. In other respects the character of the figure need not be modified, supposing always that increase of temperature and pressure be taken in the algebraic sense, so that negative quantities are included. Beyond the transitional point I am therefore tempted to look for the proper critical temperature of the ice type in a region of positive external pressures and in the direction of decreasing temperatures.

Thus, curiously enough, the observer is confronted by *periodic relations*, which in all probability will admit of a chemical interpretation. (§§ 95, 96.)

95. *Solubility and pressure.*—In view of the detailed analogy which holds between many characters of fusion and of solution, much that can be investigated for the simpler of these phenomena (fusion apparently) will be applicable to the other. A substance may be transferred from the solid to the liquid state either by heating it or by dissolving it. In general, excess of temperature or of solvent favor the diminution of viscosity here in question. A liquid on the verge of solidification or a concentrated solution is solidified or deposits crystals on cooling; and in both cases the nice adjustment of labile molecular equilibrium is accompanied by volume hysteresis, undercooling, etc., in the one case, supersaturation, etc., in the other. Hence I conclude logically, I think, that if under proper thermal conditions pressure alone can solidify a liquid, it can also under proper solutional conditions induce crystallization, or the deposit of solid from solution.

I am the more justified in drawing these references, as in my article[1] on the solvent action of hot water on glass I already adduced the necessary evidence. Since from one point of view the isothermal compressibility increased proportionally to the time during which the solvent action has been going on, and from another, with the amount of silicate dissolved, to more than three times its original value, the inference is pretty closely at hand that what pressure did in this instance was a mere precipitation of a proportionate amount of dissolved silicate. The volume change thence resulting were put into computation

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[1] American Journal, vol. 41, p. 110, 1891.

as increments of compressibility, for the precipitated silicate is again dissolved when pressure is withdrawn.

Thus the present work bears upon the nature of solution, for I can not believe that what I have ventured to call cohesive affinities[1] can not differ, except in degree, from the affinities which determine valency. At least, proceeding on such an assumption, I am lead naturally to a theory regarding changes of physical state which I will indicate elsewhere.

Finally, in justice to myself let me say that the manuscript left my hands before the kindred deductions of Orme Masson[2] or of Ramsay[3] had reached me. In fact, what these gentlemen have deduced from the solution behavior liquid-liquid I had legitimately derived from the solution behavior solid-liquid, as set forth in my own work. My preceding paper was at fault only in postulating an unnecessary change of hydration of the silicated water (loc cit., p. 116).

It is gratifying to note that evidence of the similar solution behavior solid-solid is forthcoming, and to be found in the work of Osmond, of C. A. Carus-Wilson,[4] and of myself, as I have already pointed out.[5]

CONCLUSION.

96. In the above pages I have merely endeavored to describe the results directly obtained by experiment, and to draw such conclusion, which, in the light of known facts, seemed to be admissible or even obvious. In view of the detailed analogy which holds between many characters of fusion and of solution, I believe that much that can be investigated for the simpler of these phenomena (fusion) will be applicable also to the other. How far the above conclusions as a whole are to stand or fall will depend on similar investigations, which I shall continue to make with a variety of other substances specially selected with reference to their position in a scale of thermal state. How such selection is to be made I am now unable to surmise. Substances, for instance, which fuse continuously, like glass or sealing wax, might at first sight be conjectured to lie near their critical points, but I believe these cases are mere solution phenomena of relatively small interest. At all events the experiments must deal with substances of definite and preferably crystalline character and not with mixtures. I feel confident that in an examination of many types some will be found lying relatively nearer the critical point, while others lie nearer or even beyond the transitional point; and that if the above method be applied with greater rigor than was done in the present paper light will be thrown on the long-neglected department of fusion thermodynamics. From

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[1] American Journal, vol. 41, p. 115.

[2] Masson: Nature, vol. 43, 1891, p. 345.

[3] Ramsay: Nature, vol. 43, 1891, p. 589.

[4] C. A. Carus-Wilson: Phil. Mag., vol. 29, p. 200.

[5] Barus: Phil. Mag., vol. 31, 1891, pp. 26–28.

this stage of progress it will then be possible to approach nearer the next of the kindred phenomena, which I conceive to be nothing less than the kind of hysteresis or higher order of volume lag commonly known as chemical affinity.

To obviate the occurrence of a bald statement like the last, I will indicate my views on the distribution, or successive orders of volume lags. These are to be sought—I, during the passage of a given atom into the next consecutive in a scale of decreasing atomic weights; II, during the occurrence of dissociation of the molecule, including solutions gas-fluid. They are demonstrable, III, the region of Andrews's vapor tensions, including the Alexéef-Masson solutions liquid-liquid; IV, in the region of the solid-liquid phenomena of the present paper, including solutions solid-liquid; V, in the region of solid-solid phenomena categorically distinguishable as "permanent set" (Osmond, Carus-Wilson, Barus). They are to be sought for finally, VI, during the passage of a given atom into the next consecutive in a scale of increasing atomic weights.

The enumeration is systematic, and inasmuch as VI is virtually identical with I, the inherent nature of these changes is periodic. Hence, under suitable thermal conditions and continually increasing pressure, the evolution of atoms, of molecules, of changes of physical state, are successive stages of periodically recurring hysteresis.

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