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CHANGE OF PHASE UNDER PRESSURE.

II. NEW MELTING CURVES WITH A GENERAL THERMODYNAMIC DISCUSSION OF MELTING.

BY P. W. BRIDGMAN.

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INTRODUCTION.

IN the first paper of this series[1] data were given for the melting under pressure of eleven substances, four of which were found to have new polymorphic forms. The problems offered by polymorphic forms are of great interest and importance; since the writing of the first paper a number of substances have been investigated in this regard, and a number of new forms have been found. This question of polymorphism will be treated in future papers of this series. In the search for new forms a number of substances were investigated without result, whose melting curves lay within the temperature range of this work (0°–200°). These new melting curves are presented in this paper. Complete data are given for nine more substances, and fragmentary data for a few others. In addition, the melting curves of two other substances have been determined, but as these have more than one solid form, the data for them will be reserved for a future paper.

The discussion of melting given in the first paper was almost entirely concerned with the general character of the curve; as to whether it ends

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[1] P. W. Bridgman, PHYS. REV., N. S., Vol. 3, 126–203, 1914.

* Article to be concluded in next issue.

in a critical point, passes through a maximum temperature, or continues rising indefinitely. The data of the first paper seemed to point conclusively to only one conclusion, namely that within the range of at present realizable pressures there is nothing to indicate that the curve does not rise indefinitely. The data of this paper also all point to the same conclusion; the decreasing curvature of the melting curve and the convexity of the ΔV curve toward the pressure axis are shown by these substances also. The other two new substances with polymorphic forms show the same thing. Fig. 24, at the end of the paper, shows in a striking way that the shape of the melting curve is such that there cannot be a maximum temperature, as Tammann has supposed. In this diagram the slope of the melting curve is plotted against temperature. If there were a maximum, the curves would cross the temperature axis vertically. The direction of curvature shows that this cannot be the case at any temperature, no matter how high, unless there is a reversal of direction of curvature beyond the range of pressures at present realizable. If there is a maximum, these curves should be concave, instead of convex, toward the temperature axis. Up to the present, therefore, we have data on twenty two liquids, to four times the pressure range of previous measurements, all indicating the same answer to the question in hand, without exception. I shall, therefore, in future discussion consider this question as settled. It does not seem worth while to gather any more experimental evidence with this point only in view.

Besides the question as to the ultimate course of the melting curve, other questions are presented by the phenomena of melting. One question of interest is how the course of the melting curve is determined by the separate thermodynamic properties of solid and liquid. As is well known, this problem may be readily solved by the use of the thermodynamic potential. It appears that the thermodynamic quantities which determine the course of the melting curve are the differences of compressibility, thermal expansion, and specific heat (C_p) between solid and liquid. We cannot in general determine all three of these quantities from the data already given for the melting curves, but if one of them can be determined in some other way, there are relations which determine the other two. In some cases, at atmospheric pressure, the data are at hand from which all three of these quantities may be determined. Furthermore, at high pressures, it is shown that certain inequalities hold, in virtue of which we are able to make an estimate of the difference of compressibility between solid and liquid which is correct to perhaps 30 per cent. These very rough values for the difference of compressibility are given and discussed.

There are also now at hand data sufficient to allow the comparison of substances of chemically similar constitution; for instance, CCl_4 with $SiCl_4$, or $CHCl_5$ and $CHBr_5$. Some attention is given to the question as to whether the melting curves show any regularly varying behavior with chemical substitutions of this nature.

It must be recognized, however, that any purely thermodynamic discussion cannot carry us very far on our way. What we are searching for ultimately is a description of the construction of the atom so detailed that we can describe how the atoms are put together in a crystal, and how and why they fall apart when they melt. We are very far indeed from such a goal.

The apparatus was the same as that used in the first paper, and the methods of computation are similar. The tables are somewhat fuller, the values of $d\tau/dp$ being included, and the values of the melting temperatures have been smoothed so as to give differences regular to tenths of a degree. In the preceding paper the equilibrium temperatures were read directly from the curves without further smoothing, so there were irregularities in some cases of several tenths of a degree. These irregularities did not affect the values of $d\tau/dp$, however, which were determined and smoothed in another way. The values of ΔV, $d\tau/dp$, and ΔH given in the tables may not always be exactly related by the thermodynamic equations; this is because these three quantities were smoothed independently, after the calculations had been made. Any such discrepancy, however, is always much less than the probable error with which any of these quantities may be determined.

The data for the individual substances follow.

Detailed Data for Nine Substances.

Bromoform.—Specimens of bromoform from two different sources were used. The first was from Eimer and Amend. It was purified by fractional distillation and crystallization at 0°. There was initially some slight amount of volatile impurity present as shown by the fact that boiling began at 60°, but the boiling point very rapidly rose to 148° and remained there while four fifths distilled. The recrystallized substance was slightly yellow, but had a nearly constant melting point at 7.78°. Five points were determined with this sample, between 900 and 7,000 kgm. This sample was lost by an accident to unrelated parts of the apparatus, when only two more points were necessary for the completion of the curve at high pressures. A fresh lot was ordered from Eimer and Amend, but although this was purified by exactly the same process as the first, the impurity remaining was too large for satisfactory results. Another lot was then obtained from the J. T. Baker Chemical Co., made especially to order. This was further purified by the process above, but could not be obtained as pure as the first lot. It melted over a temperature range 0.4° wide, the maximum melting point being 7.62°. The corners of the melting curve were, therefore, somewhat rounded, but not so much as to prevent satisfactory results. The points at nearly atmospheric pressure and the two highest pressure points were determined with this sample. From 40 to 44 gm. were used.

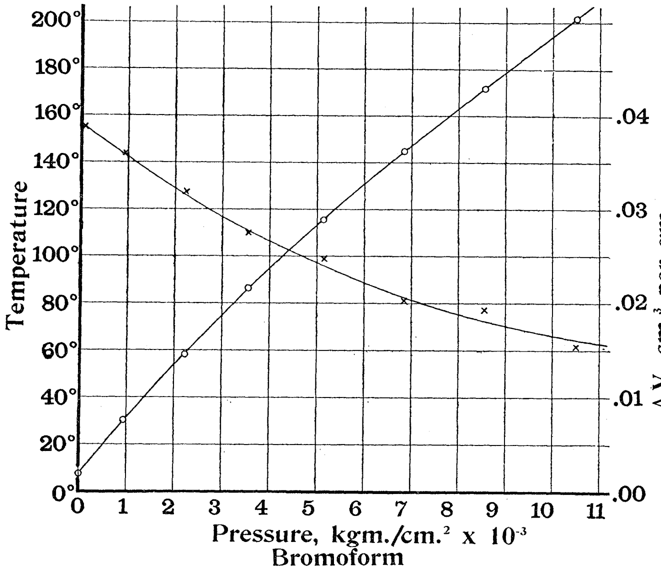

Fig. 1.

Bromoform. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

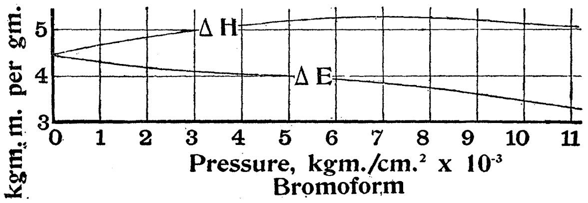

Fig. 2.

Bromoform. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

The second set of measurements was made at an interval nearly six months after the first, with a different manganin coil. The $p - t$ points of the second set fit in smoothly with those of the first set, and the

ΔV points of the two sets are consistent within the limits of error, which are here somewhat larger for ΔV than usual. The experimental results are shown in Fig. 1, the computed values of ΔH and ΔE in Fig. 2, and a summary of the numerical values in Table I.

Table I.

Bromoform.

Pressure.	Temperature. °	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	7.78	0.03906	.0245	4.477	4.477
1,000	31.5	355	230	4.699	4.344
2,000	53.8	322	217	4.852	4.208
3,000	74.9	292	204	4.982	4.106
4,000	94.7	266	192	5.097	4.033
5,000	113.3	243	180	5.217	4.002
6,000	130.8	221	170	5.252	3.926
7,000	147.3	203	162	5.267	3.846
8,000	163.2	188	1565	5.242	3.738
9,000	178.7	176	1535	5.151	3.576
10,000	194.0	166	1515	5.118	3.458
11,000	209.1	157	1500	5.047	3.320

There are several other determinations of the melting point at atmospheric pressure. The earliest is by Thorpe,[2] 2.5°, for what must have been a very impure specimen. Later and better determinations are 7.6° by Steudel,[3] 7.8° by Perkin[4] and 7.5° by Feist and Garnier.[5] The highest of these values, that by Perkin, is in essential agreement with that found above. Perkin remarks at some length on the difficulty of obtaining pure bromoform. He says that it decomposes somewhat on distillation, and that the best method of purification is by repeated crystallization. The density of liquid bromoform is given by Thorpe as 2.8341 at 0° and 2.81165 at 8.56°; by Perkin as 2.90246 for D_{15}^{15} and 2.88253 for D_{25}^{25}, and 2.895 by Feist and Garnier. There seem to be no determinations of the latent heat or the crystalline form.

At room temperature and at 200° no new forms were found between the melting curve and 12,000 kgm. It has been shown by Wahl,[6] however, that at atmospheric pressure there is another modification at low temperature. The reaction to the new form runs only in a narrow interval; the ordinary form may be readily subcooled into a region where

[2] T. E. Thorpe, Jour. Chem. Soc., Vol. 37, 141–225, 1880.

[3] V. Steudel, Wied. Ann., *16*, 369–394, 1882.

[4] W. H. Perkin, Jour. Chem. Soc., Vol. 45, 421–580, 1884.

[5] K. Feist und Ch. Garnier, Arch. Pharm., *249*, 458–463.

[6] W. Wahl, Proc. Roy. Soc., Vol. 89, 331, 1913.

the reaction to the new form does not run. At high pressures the viscous resistance to the reaction increases, and this may be the reason for my failure to find the new form. However, Wahl does not state the temperature of the transition, and as we have no idea whatever as to the magnitude of the change of volume or the latent heat, one cannot tell whether any part of the region investigated above contains the region of stability of the new form.

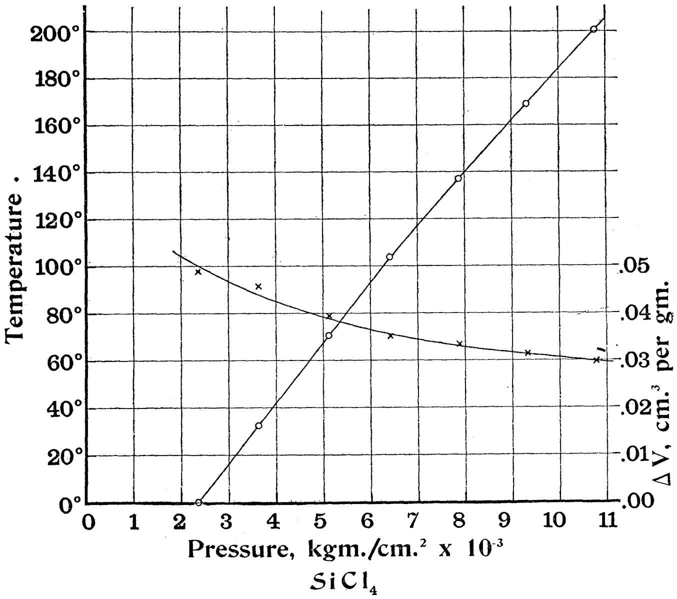

Fig. 3.

Silicon tetrachloride. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

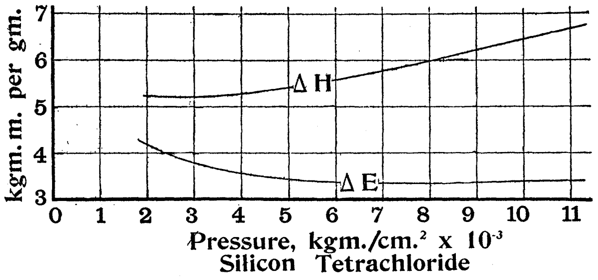

Fig. 4.

Silicon tetrachloride. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

Silicon Tetrachloride.—Measurements were made on only one sample of

$SiCl_4$. This was Kahlbaum's; it is supplied in sealed glass tubes, and was perfectly colorless. No attempt was made to further purify it, as this would require considerable chemical skill, because of its spontaneous decomposition on contact with moist air. The freezing was, nevertheless, gratifyingly sharp, much sharper than appeared likely with a substance of this nature. 21 g. were used.

The experimental results are shown in the curves of Fig. 3, the computed values of ΔH and ΔE in Fig. 4, and the numerical values in Table II.

TABLE II.

Silicon Tetrachloride.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M. Gm.	Change of Energy Kgm. M./Gm.
	°				
2,000	−10.0	.0522	.0273	5.23	4.19
3,000	+16.7	470	263	5.20	3.79
4,000	42.6	428	256	5.28	3.57
5,000	67.9	395	2485	5.42	3.44
6,000	92.5	368	241	5.56	3.35
7,000	116.3	347	234	5.78	3.35
8,000	139.4	330	228	5.97	3.33
9,000	161.8	317	222	6.23	3.38
10,000	183.8	306	217	6.44	3.38
11,000	205.4	297	213	6.67	3.41

Apparently very few measurements have been made on this substance I have found only one value for the melting point, − 89°, quoted in Kaye and Laby's tables from a source not mentioned. But this value must have been obtained from a very impure specimen, because it lies considerably below any value that the curve above would extrapolate to. It has seemed best, therefore, in Fig. 3 not to try to run the melting curve below 2000 kgm. An unforced extrapolation of the melting curve would give − 67° for the melting point at atmospheric pressure. It would probably be safe to accept this, in lack of other experiments, as a better value than − 89°.

No other modifications of the solid were found to 12,500 kgm. at 30° and to 12,400 kgm. at 200°. This was a disappointment, as I had expected other modifications in analogy with CCl_4; in fact this was the only reason for undertaking the investigation of this substance.

Monochlorbenzol.—This was Kahlbaum's purest, further purified immediately before use. The middle third of the distillate obtained with a Hempel fractionating column proved to be sufficiently pure. Seven points on the melting curve were obtained with this substance, all with the same filling of the apparatus. That the purity was sufficient, is shown by the ΔV points, which are fully as regular, if not more so, than usual. 17 gm. were used.

The experimental results are shown in Fig. 5, the computed values of ΔH and ΔE in Fig. 6, and the numerical values in Table III.

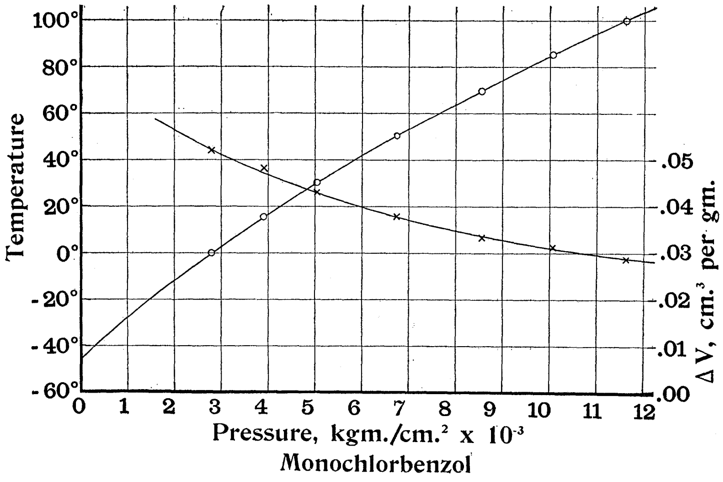

Fig. 5.

Monochlorbenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Very recently, in fact since the measurements above were made, the melting point of CH_5Cl has been determined with particular care at atmospheric pressure by Henning,[7] for use as a fixed point in low temperature thermometry. His value is − 45.5°. This lies very well on the curve passing through the points found above at high pressures. Previous values of the melting point were − 40°, given by Béhal and Valeur,

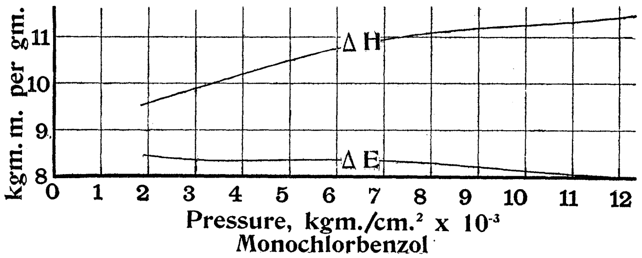

Fig. 6.

Monochlorbenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

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[7] F. Henning, Ann. Phys., Vol. 43, 282–294, 1914.

Table III.

Monochlorbenzol.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	° −45.5		.0184		
1,000	−28.0		167		
2,000	−12.0	.0565	154	9.58	8.45
3,000	+ 2.9	511	1425	9.90	8.36
4,000	16.7	469	133	10.22	8.34
5,000	29.7	432	125	10.47	8.31
6,000	41.9	400	117	10.76	8.36
7,000	53.3	372	111	10.93	8.33
8,000	64.0	349	106	11.10	8.31
9,000	74.4	328	102	11.18	8.23
10,000	84.5	311	099	11.24	8.13
11,000	94.2	297	0965	11.31	8.04
12,000	103.6	285	094	11.42	8.00

− 45° by Schneider,[8] and − 44.9° by Haase.[9] These figures are interesting, because without other evidence one is always inclined to accept the highest listed value of a melting point as most probably accurate, lower values being explained by impurities, whereas here, the more recent and more accurate values are lower. For the density we have by

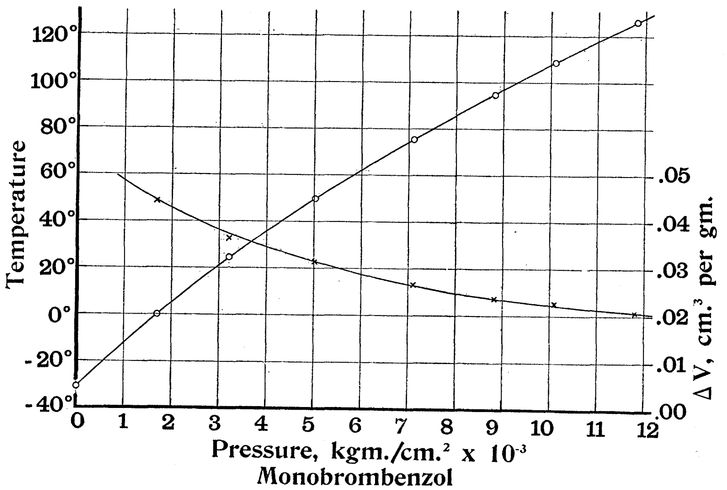

Fig. 7.

Monobrombenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

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[8] B. V. Schneider, ZS. phys. Chem., *22*, 225–240, 1897.

[9] E. Haase, Ber. D. Chem. Ges., *26*, 1052–1054, 1893.

Adrieenz[10] 1.1284 at 0° and 1.1052 at 21.69°, and by Biron[11] 1.1279 at 0° and 1.1064 at 20°. There seem to be no determinations of the latent heat or the change of volume at atmospheric pressure or of the crystalline form. An extrapolation of the above values for ΔV, assuming constant second differences, gives 0.0711 cm.³/gm. Corresponding to this is the value 8.77 kgm.m./gm. or 19.7 cal./gm. for the latent heat.

At 30° and at 100° no new modification of the solid was found to 12,800 kgm. From analogy with benzol, it would not have been surprising if there had been a second form.

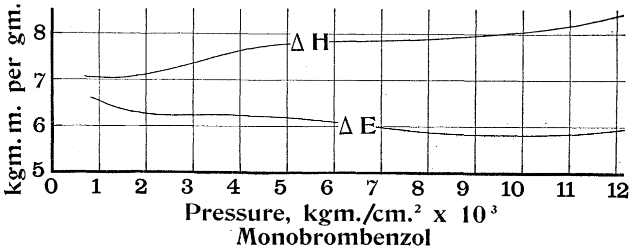

Fig. 8.

Monobrombenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

Monobrombenzol.—Like monochlorbenzol, this was Kahlbaum's purest, and was further purified by fractional distillation. The purity is sufficient as evidenced by the regularity of the points. Seven points were obtained, all with the same filling of the apparatus. 23 gm. were used.

TABLE IV.

Monobrombenzol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	−31.1		0.0197		
1,000	−12.1	0.0486	181	7.010	6.524
2,000	5.3	428	167	7.134	6.278
3,000	21.3	382	1525	7.375	6.229
4,000	35.9	345	140	7.615	6.235
5,000	49.4	315	131	7.756	6.181
6,000	62.0	288	123	7.845	6.117
7,000	74.1	266	118	7.827	5.965
8,000	85.7	248	114	7.868	5.868
9,000	96.9	234	109	7.943	5.837
10,000	107.6	222	105	8.050	5.830
11,000	117.9	212	102	8.127	5.795
12,000	127.9	205	098	8.389	5.929

[10] A. Adrieenz, Ber. D. Chem. Ges., *6*, 441–444, 1873.

[11] E. Biron, Jour. russ. phys. Chem. Ges., *42*, 135–166.

The experimental results are shown in Fig. 7, the computed values of ΔH and ΔE in Fig. 8, and the numerical values in Table IV.

For the melting point at atmospheric pressure we have − 30.5° by Schneider,[8] − 30.7° by Bugarsky,[12] and − 31.3° by Haase.[9] Here, as in the case of chlorbenzol, the lower value, − 31.3°, seems to be probably more accurate, since the curve extrapolates to this without any initial abnormalities in $d\tau/dp$. For the density of the liquid Biron[11] gives 1.5223 at 0° and 1.4953 at 20°, Adrieenz[10] 1.5177 at 0° and 1.4898 at 20.96°, and Wagner[13] 1.5203 at 0° and 1.4945 at 20°. There seem to be no values of change of volume or of latent heat for comparison at atmospheric pressure. We may extrapolate from the values of Table IV. and find at atmospheric pressure 0.0564 cm.^{3}/gm. for the change of volume, and 7.0 kgm. m./gm. for the latent heat. There are apparently no other measurements for comparison at high pressures. The crystalline form has not been determined.

At 25°, no new modification of the solid was found to 12,500 kgm., and at 126°, no new form to 12,700 kgm.

Benzophenone.—This substance was obtained from Eimer and Amend, and was further purified by crystallization at constant temperature in the thermostat. The temperature was so adjusted that crystallization took place very slowly, during 48 hours. Large perfect crystals were obtained. 13 to 18 gm. were used.

Various accidents made necessary measurements at four different times with four different fillings of the apparatus. The benzophenone was placed in an inverted nickel steel shell, instead of the bulb used for substances liquid at room temperature. This shell will be further described in the next paper dealing with solids. With the first filling of the apparatus a complete series of measurements was made over the entire pressure range, but on taking the apparatus apart it was found that the shell had split at some time during the application of pressure, allowing some of the benzophenone to escape. On working up the results, an abrupt drop in the values of ΔV showed that the precise point at which this had taken place was after the determination of the first point. The splitting of the nickel steel shell seems to have been caused by a quite unusual rigidity of this substance under pressure. Of course the values of pressure and temperature found during this first run were quite unaffected by the escape of some of the material; it was the ΔV values that had to be discarded, only the first being good. The second filling was made for a determination of the point at nearly atmospheric pressure;

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[12] Bugarsky, Math. u. Naturw. Ber. aus Ungarn, *26*, 89–151, 1910.

[13] F. Wagner, Lieb. Ann., *221*, 61–107, 1883.

this was accomplished without incident and with unusually sharp freezing. The third filling of the apparatus gave three points with good values of ΔV at 1,200, 3,200 and 2,200 kgm. This set of readings was terminated by the breaking of the lower cylinder into two cleanly divided halves, a rather unusual fracture. Apparently it had been started by an explosion some time previously. The fourth set of readings gave the two points needed to complete the curve at the highest pressures. The data given amount, then, to a double determination of the coördinates of the melting curve, and a single determination of the course of the ΔV curve, but with four different fillings of the apparatus, with different quantities of material.

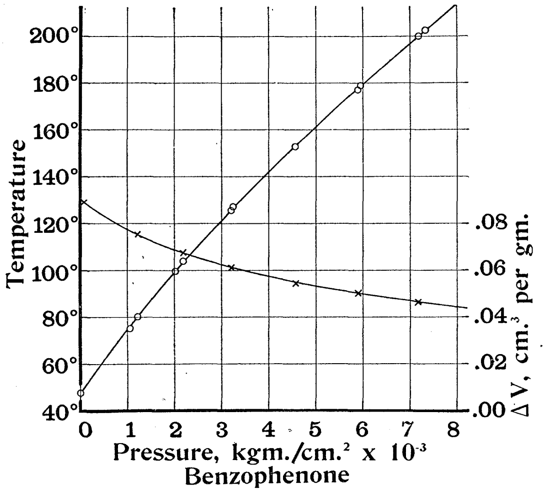

Fig. 9.

Benzophenone. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

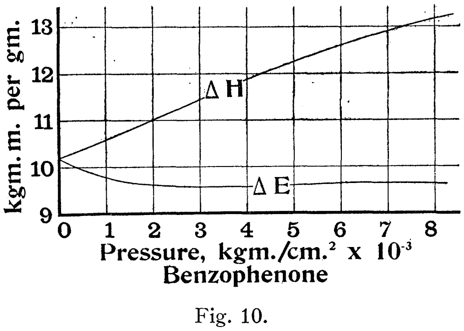

Fig. 10.

Benzophenone. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

The experimental results are given in Fig. 9, the computed values of ΔH and ΔE in Fig. 10, and the numerical values in Table V.

TABLE V.

Benzophenone.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	47.77°	0.0904	.02845	10.20	10.20
1,000	74.6	773	2545	10.56	9.79
2,000	98.9	689	2330	11.00	9.62
3,000	121.3	624	2145	11.48	9.61
4,000	142.0	571	2000	11.85	9.57
5,000	161.3	532	1885	12.26	9.60
6,000	179.6	498	1785	12.63	9.64
7,000	197.0	468	1705	12.90	9.62
8,000	213.7	442	1635	13.17	9.63

There are a number of values for comparison. For the melting point, Tammann[14] gives 48.11° in Kristallisieren und Schmelzen, 47.7° in 1898, and 48.5° in 1899. Linnemann[15] gives 48° to 48.5°, Bruner[16] 48.0°, Hulett[17] 48.10°, and Block[18] 48.1°. The value found directly for the sample above, 47.77°, is evidently too low; the best value selected from the above is probably about 48.11°. For the change of volume Tammann[19] gives 0.0875 to 0.0883 cm.³/gm., and Block[18] 0.0877 against 0.0904 above. For the latent heat, Tammann[19] gives 23.4 from a direct determination and 23.95 cal. calculated from the coördinates of the melting curve. Eykmann[20] determines it as 23.2 from the depression of the freezing point, and Bruner[16] gives the value 23.7. The value that I found above was 23.9; the agreement of all these values is closer than usual. The melting curve found by Tammann at high pressures lies somewhat below that given above, the discrepancy increasing as usual with increasing pressure, but the difference is somewhat less than usual. At 90° my pressure is 20 kgm. lower than his; at 100°, 60 kgm. lower; and at 130°, 160 kgm. lower. Tammann's values for ΔV also drop off with increasing pressure more rapidly than do mine, but the discrepancy is not so much as for many other substances. In addition to Tammann, Hulett[17] has also

[14] G. Tammann, "K. und S.," p. 229. Wied. Ann. *66*, 491, 1898. ZS. phys. Chem., *29*, 51–76, 1899.

[15] Ed. Linnemann, Lieb. Ann., *133*, 1–32, 1865.

[16] L. Bruner, ZS. Chem., *4*, 497–519, 1899.

[17] G. H. Hulett, ZS. phys. Chem., *28*, 629–672, 1899.

[18] H. Block, ZS. phys. Chem., *78*, 385–425, 1912.

[19] G. Tammann, "K. und S.," p. 231.

[20] J. F. Eykmann, ZS. phys. Chem., *4*, 497–519, 1889.

determined the effect of pressure on the melting point up to 300 kgm. His values agree with mine better than with Tammann's. Thus for the initial slope, $d\tau/dp$, Tammann gives 0.0276, Hulett 0.0289, and I find 0.02845.

At 30°, I found no new modification to 12,000 kgm., and at 200° none to 12,500. This result is an interesting one in view of the well known tendency of benzophenone to crystallize in other forms at atmospheric pressure. At least three other, unstable, forms are known at atmospheric pressure. The existence of these unstable forms seems connected in some way with the rather unusual amount of subcooling that benzophenone will allow. If it is allowed to crystallize from the subcooled condition it is likely that an unstable form will appear, rather than the normal stable form. Now in these experiments at high pressures, in which freezing was produced by increasing pressure at constant temperature, it was often necessary to push the pressure considerably beyond the equilibrium value, that is, to produce considerable subcooling, before crystallization could be induced. Yet never did any other than the normal crystal appear, although analogy with the behavior at atmospheric pressure would lead one to expect the sporadic occurrence of unstable forms. The amount of superpressure necessary to produce solidification varied capriciously, as is to be expected, and might be rather large. Once, at 179°, 450 kgm. superpressure was necessary, at 80°, 1,500 kgm., and again at 177°, 2,600 kgm. These values correspond to 9°, 34°, and 46° subcooling. No serious effort was made to obtain regular values for the subcooling; doubtless better values could be found, but there must always be an element of caprice about anything of this kind.

There may be two reasons for the failure ever to observe any of the unstable forms. Tammann has noticed that the unstable forms are much more difficult to produce and that they change spontaneously to the stable form much more readily when there is a metal in contact with the benzophenone than when only glass is used. For these experiments contact with some metal, mercury to transmit the pressure if nothing else, is unavoidable, so that the conditions are never favorable to the appearance of unstable forms. In the second place, there may of course be a specific temperature or pressure effect, the unstable nuclei being less likely to form at the high temperatures. This is not unlikely, and is somewhat borne out by the tendency, in a rough way, for the possible subcooling to become less at high temperatures. At atmospheric pressure, for instance, a subcooling of 100° is possible under the proper conditions. On the whole, then, the chances seem unfavorable for the study of the unstable forms under pressure. No very serious attempt was made to do this in the present work, but it is significant that F. Körber,[21] one of Tammann's pupils, in a recent investigation of the effect of pressure on unstable forms, has not included benzophenone in his list of substances.

The same sluggishness that is manifested in the large amount of possible subcooling has also made possible a rough qualitative examination of the velocity of crystallization under pressure. This is not possible for most substances, because the heat of reaction is the dominating factor for those substances with a normal rate of crystallization, the crystallization proceeding as fast as the heat of reaction can be conducted away through the walls of the pressure cylinder. A consequence of this is that for most substances the melting when the solid is superheated takes place as rapidly as the freezing when the liquid is subcooled in the presence of the solid. The velocity of these reactions is indicated very simply by the rate at which pressure returns to its equilibrium value after it has been displaced to the one side or the other. But with benzophenone the velocity of crystallization is so slow that the heat of reaction has a chance to be dissipated rapidly enough not to entirely mask the normal progress of the reaction. It has been possible to establish the fact for benzophenone that the velocity of crystallization is very much less than that of melting. Careful measurements were made of the rate of spontaneous recovery of pressure from above and below at five different temperatures. Figure 11 reproduces one of these curves for the reaction velocity from above and below. The greater speed of melting is shown by the sharper corner

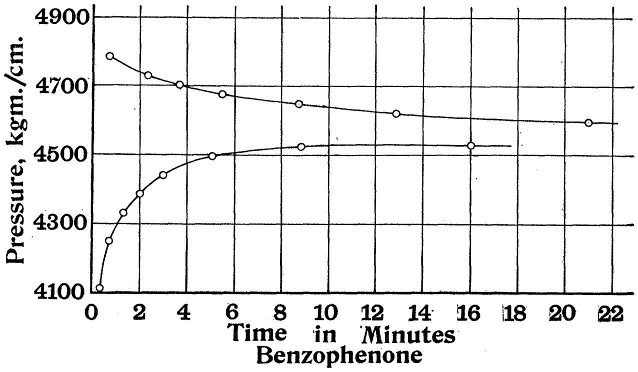

Fig. 11.

Benzophenone at 152°. Shows the recovery of pressure, when pressure has been displaced from the equilibrium value, plotted against time. On the rising curve, the solid is melting, and on the falling curve the liquid is crystallizing. Note that the rate of melting is more rapid than that of crystallization. In the actual experiment, the melting curve was obtained first; in the diagram the freezing curve has been displaced in time for convenience of comparison.

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[21] F. Körber, ZS. phys. Chem., *82*, 45–55, 1913.

of the curve. An examination of all five curves shows that the velocity of melting does not vary markedly with temperature, indicating no large variation in thermal conductivity with rising temperature and pressure along the melting curve. But it does seem probable, although it is not entirely certain, that the velocity of crystallization increases with rising temperature. Because of the impossibility of superheating a solid, the velocity of melting will, of course, always be determined essentially by the heat conductivity of the walls. Irregularity in measurements of this kind is to be expected. For example, if it happened that at higher temperature the crystallization grew from one chance nucleus, while at low temperatures there were two, then the rate of recovery at low temperatures might be greater, although the actual velocity of crystallization might be less. The question of reaction velocity will be considered at greater length in a future paper of this series.

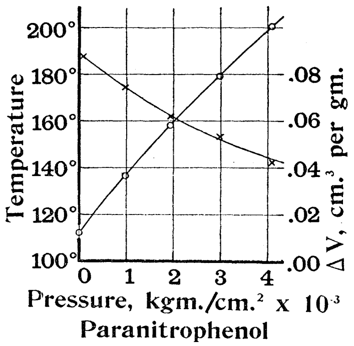

Fig. 12.

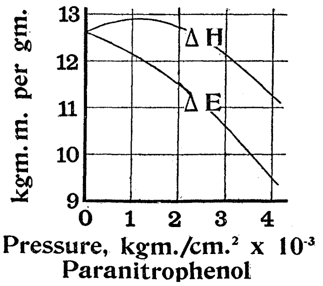

Fig. 13.

Paranitrophenol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Paranitrophenol. The computed values of the latent heat, and the change of internal energy when the solid melts to the liquid.

Paranitrophenol.—Merck's " blue label " preparation was used without attempt at further purification. There was considerable impurity present as shown by the low value of the freezing point and the rounding of the corners of the melting curve. In fact, this is one of the most impure of the substances for which data are given here. Error from the rounding of the corners of the melting curves was largely avoided, however, by running the pressure an unusual distance beyond the freezing point, allowing a better extrapolation.

Two sets of measurements were made; one comprised points at four pressures above 900 kgm., and the other was the usual measurement with the low pressure apparatus at approximately atmospheric pressure. The quantities used were 15.7 and 20.0 gm. respectively.

The observed points are shown in Fig. 12, the computed values of ΔH and ΔE in Fig. 13, and the numerical values in Table VI.

TABLE VI.

Paranitrophenol.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	112.4	.0891	.02720	12.63	12.63
500	125.5	812	2524	12.82	12.41
1,000	137.7	740	2356	12.90	12.16
1,500	149.1	674	2208	12.89	11.88
2,000	159.8	614	2090	12.72	11.49
2,500	170.0	564	2000	12.49	11.08
3,000	179.8	520	1940	12.14	10.58
3,500	189.4	480	1894	11.71	10.03
4,000	198.8	445	1866	11.26	9.48

The normal melting point of this substance is given as high as 115° by the Chemiker Kalendar, but the authority is not stated. The melting point is given as 114° by Schiff,[22] 114° by Wagner,[23] and 111.46° by Mills.[24] The value found above, by an extrapolation of the value at 80 kgm., was 112.4°. For the density of liquid nitrophenol, Schiff [22] gives the formula $1.2809 - 0.00095\ (t° - 114)$, and for the density of the solid at room temperature Schroeder[25] gives 1.468. Assuming the value found above for ΔV, this gives 0.00015 as the value of the mean dilatation of the solid between room temperature and the melting point. At high pressures there are no previous measurements for comparison.

No new modification of the solid was found to 12,000 kgm. either at room temperature or at 200°. The region between atmospheric pressure and 2,000 kgm. was investigated with rather more than usual care at room temperature. The chief reason for undertaking the investigation of this substance at all is that it is usually listed as one with two modifications at atmospheric pressure; in fact the recent Tables of the Société Française marks this substance with an asterisk as a particulary striking example of a polymorphic transition. The low temperature form is supposed to be a bright pink which changes to a nearly colorless form on warming. This is usually stated on the authority of Lehmann;[26] he is sometimes quoted as saying that this transition is enantiotropic and

[22] R. Schiff, Lieb. Ann., *223*, 247–268, 1884.
[23] P. Wagner, Ber. D. Chem. Ges., *7*, 76–78, 1874.
[24] E. J. Mills, Phil. Mag. (5), Vol. *14*, 1–29, 1882.
[25] A. Schroeder, Ber. D. Chem. Ges., *12*, 561–567, 1879.
[26] O. Lehmann, ZS. Kryst., *1*, 43–48, 1877.

sometimes as monotropic. His original statement is monotropic. In the Tables of the French Society his unstable and stable forms have been interchanged. In an attempt to determine whether there is a transition at low pressures, perhaps unaccompanied by a change of color, dilatometric measurements were made in the low pressure apparatus at a constant pressure of 80 kgm. No perceptible volume change could be found between 30° and the melting point.

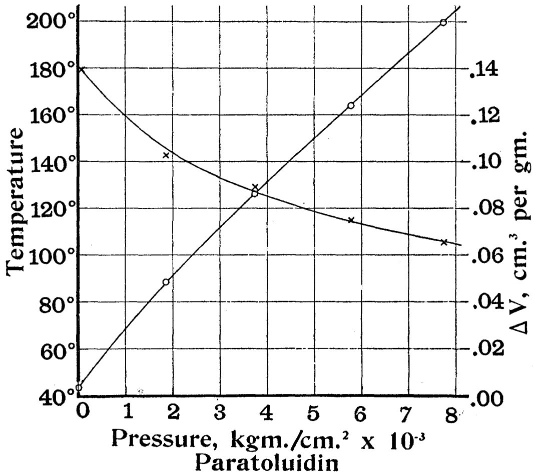

Fig. 14.

Paratoluidin. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Paratoluidine.—This substance was obtained from Eimer and Amend, and was purified by crystallization at constant temperature in the thermostat. Crystals in the form of needles several inches long were obtained. The impurity shown by the rounding of the corners was, however, somewhat more than usual. To avoid errors from this cause in

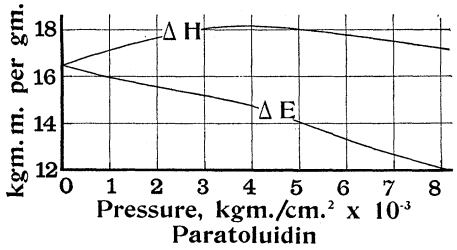

Fig. 15.

Paratoluidin. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid. .

the ΔV determinations, measurements were usually begun 1,500 kgm. beyond the melting point. Only two sets of measurements were made; one of four points at high pressures, and one at 80 kgm. In addition, the melting point was determined at atmospheric pressure. The quantities used were 12 and 16 gm.

The experimental results are shown in Fig. 14, the computed values of ΔH and ΔE in Fig. 15, and the numerical values in Table VII. Especially noteworthy is the rapid approach to linearity of the melting curve at the higher pressures, and the unusually large volume change at atmospheric pressure.

Table VII.

Paratoluidine.

Pressure.	Temperature. °	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	43.6	.1413	.0271	16.51	16.51
1,000	69.0	.1195	238	17.17	15.97
2,000	91.5	.1037	214	17.66	15.59
3,000	112.0	.0931	1977	18.04	15.25
4,000	131.3	.0852	1894	18.19	14.78
5,000	150.0	.0789	1854	18.01	14.06
6,000	168.4	.0736	1831	17.74	13.32
7,000	186.6	.0688	1810	17.48	12.66
8,000	204.6	.0647	1794	17.22	12.04

The melting point at atmospheric pressure of the specimen used above was 43.6°. The Chemiker Kalendar gives 45° for the melting point, but the authority is not cited; probably this is from Brühl.[27] Other values for the melting point are 38.90° by Batteli,[28] 42.89° by Mills,[24] 43.3° by Tammann,[29] 43.73° by Hulett,[17] and 38.7° by Block.[18] The value of Hulett seems to be the best. For the latent heat we have the following values. O. Pettersson[30] gives 37.3 cal. as recomputed by Tammann from Pettersson's value 35.8 at 31° so as to reduce to the melting point. Tammann[29] calculates from his own data 35.6 cal. for the latent heat. Batteli[28] gives 39.3, Eykmann[20] finds 38.6, and I find by calculation from my own data 38.7 cal. For the density Rüdorff[31] gives 1.046 at room temperature, and Brühl[27] 0.9538 for the liquid at 59.1°. For the change of volume, Batteli[28] gives 0.066 cm.^{3}/gm., and Block[18] 0.0877 at atmospheric pressure, against my value 0.1413 above. Tammann[29] gives one

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[27] J. W. Brühl, ZS. phys. Chem., *16*, 193–225, 1895.

[28] A. Batteli, R. Ist. Ven. (6), *3*, 1781–1811, 1884–85.

[29] G. Tammann, "K. und S.," p. 240.

[30] O. Pettersson, Jour. prak. Chem., *24*, 129–168, 1881.

[31] Fr. Rüdorff, Ber. D. Chem. Ges., *12*, 249–252, 1879.

value under pressure, 0.115 at 575 kgm. against 0.1283 above. There must have been some blunder in the values of Batteli and Block, because they would give impossibly low values for the latent heat when combined according to Clapeyron's equation with the values of $d\tau/dp$, in which Tammann, Hulett, and I are in essential agreement. Tammann has determined the coördinates of the melting curve to 3,000 kgm. At 1,000 kgm. his value is 1.3° lower than mine, at 2,000, 2.1° lower, and at 3,000, 3.6° lower. Hulett[17] also measured the effect of pressure on the melting curve up to 300 kgm. His initial value of $d\tau/dp$ is 0.0270 against 0.0271 above.

No new modifications of the solid were found up to 12,000 kgm., either at room temperature or 200°.

Methyl Oxalate.—It is a matter of considerable difficulty to obtain this substance pure, and it was necessary to make several attempts. The first sample was from Eimer and Amend, made especially to my order, and as furnished by them had a melting point of 48°. It was further purified by distilling in air at atmospheric pressure and crystallizing in the thermostat; this raised the melting point to 52.96°. The melting point of the pure substance is listed as 54°. With this sample three points on the melting curve were obtained between 35° and 175°, and also the change of volume at low pressures. There was considerable rounding of the corners of the melting curve, but the results showed conclusively that there was no second modification, a point which will be touched on again later. The series of runs with the first sample was discontinued because of accidental loss of all the purified substance. Another sample, obtained from the ordinary stock of the Harvard Chemical Laboratory, had a melting point of 49°, but no attempt was made to further purify it. A second lot was then obtained from Eimer and Amend, but the same process of purification as that applied to the first sample did not yield a product with so high a melting point. Part of the impurity in these first samples was probably introduced by the process of distillation; it seems certain that some decomposition is caused by heating to 163°, the boiling point at atmospheric pressure. Finally, a special sample was made at the Harvard Chemical Laboratory under the direction of Professor Kohler. The method was not an uncommon one; esterification of pure anhydrous oxalic acid, using pure methyl alcohol and a small quantity of pure sulfuric acid. Especial pains was taken to start with pure reagents; Professor Kohler tells me that it is very difficult to remove the impurities if they have once got into the methyl oxalate, but that one must have purity from the start. This sample came in the form of flakes, which were quite dry and not adherent to each other, whereas the other samples had been obviously impure with some slight moisture. The great purity of this specimen is shown by its high melting point, 54.14° at atmospheric pressure when half melted, as obtained by extrapolation from the melting point at 100 kgm. This seems to be somewhat higher than any value previously listed. This melting point can be counted on with some certainty, because at 100 kgm. it was possible to shut the equilibrium pressure within two values differing by only 3 kgm., the equivalent of 0.07°, when approached from above and below. There was, nevertheless, some slight impurity in this best sample, because it was possible to detect a slight rounding of the corners. At

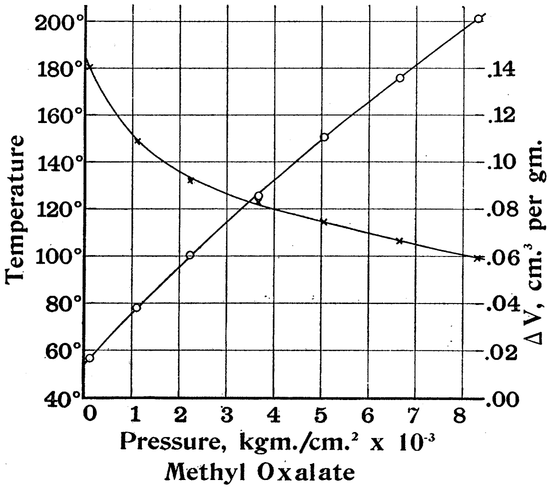

Fig. 16.

Methyl oxalate. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

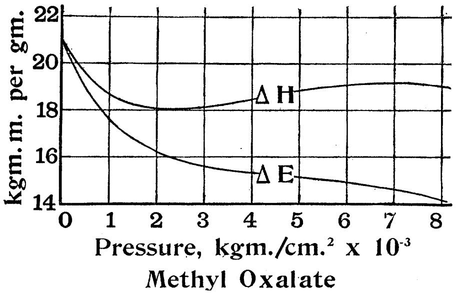

Fig. 17.

Methyl oxalate. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

80 kgm., where the true melting temperature is 56°, this rounding was perceptible at 50°, but was imperceptible at 45°. In this connection it may pay to emphasize the very delicate criterion of impurity afforded by the rounding of the corners. At 50°, the rounding was such as to amount to a premature melting of 0.0082 of the total quantity. This would mean a total depression of the freezing point, if the impurity were uniformly distributed throughout the mass, of 0.10°. We may, therefore, assume 54.24° as the most probable melting point of the absolutely pure substance at atmospheric pressure. The rounding of the corners became somewhat greater at the high pressure end of the melting curve. Evidently the high temperature caused some decomposition under pressure, just as it does when distillation is attempted at atmospheric pressure. The rounding was not large, however, and should not affect appreciaby the correctness of the values for equilibrium pressure and temperature, and only slightly the values for the change of volume.

Two runs, with two different fillings of the apparatus were made; one for all the points at high pressures, and the other for the one point at low pressure.

The experimental values for equilibrium pressure and temperature and the changes of volume are shown in Fig. 16, the computed values of latent heat and change of internal energy in Fig. 17, and the numerical values are collected in Table VIII. In this table the equilibrium temperatures have been corrected by adding 0.10° to the observed temperatures, this correction being obtained from the data above for the rounding of the corners at 77 kgm., and using the assumption that the depression does not change markedly with pressure. The legitimateness of this assumption has been discussed in the first paper of this series.

TABLE VIII.

Methyl Oxalate.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	54.24	0.1453	.02261	21.03	21.03
1,000	75.8	.1115	2078	18.71	17.60
2,000	95.8	.0957	1946	18.13	16.22
3,000	114.7	.0862	1838	18.19	15.60
4,000	132.6	.0798	1747	18.52	15.33
5,000	149.6	.0745	1669	18.87	15.14
6,000	165.9	.0696	1601	19.08	14.90
7,000	181.6	.0650	1544	19.14	14.59
8,000	196.8	.0606	1496	19.03	14.18

The initial rapid decrease of the latent heat is an unusual feature; this accompanies the rapid initial decrease in the change of volume, which may be open to question.

The points obtained with the first impure sample at 135°, 155° and 175°, were all about 5° too low; this is probably to be explained by the escape of some of the methyl oxalate and contamination with the kerosense, as well as by the known initial impurity of the sample. This contamination with kerosene was the accident alluded to above which made necessary the abandonment of this sample; it was not detected until these three points had been measured. The value for the change of volume obtained with the impure substance at low pressure is not affected by the error of the high pressure points, and may be expected to be more nearly correct. This value at 77 kgm. was 0.132 cm.^{3} per gm., which is distinctly lower than that found for the pure sample. This shows the importance of using pure substances if accurate values of the change of volume are expected.

The particular object of working with this substance was that it is one for which Tammann[32] has announced the existence of two modifications. Tammann states that there is a transition point at about 25° at atmospheric pressure; from this point the transition line between the two varieties runs upwards to a triple point at 54.0° and 550 kgm. The domain of existence of Tammann's variety I is, therefore, very restricted in extent. I could find no trace whatever of this supposed second modification. Search was made at 77 kgm. by raising temperature from 13° to the melting point in steps of 5°, and at 40° I could find nothing with increasing pressure to 700 kgm., although Tammann's transition line should be found at 300 kgm. at this temperature. There seems to be little question that this result of Tammann's was due to impurity of his sample, which he states had a melting point from 49.5° to 50.2°. In private correspondence, Professor Tammann has suggested to me that the existence of the second variety may be possible only in the presence of impurity, because cases are known in which an unstable variety is formed only in the presence of impurity. This, however, would demand that Tammann's sample was even more impure than would be indicated by the low value of his melting point. If there really are two modifications, there can be little doubt that the modification of Tammann which is stable over by far the greater portion of his pressure range is identical with the variety which I have measured; that is, Tammann's variety II is the same as that measured above. But Tammann's data would demand that the melting point of II be 46.8° at atmospheric pressure,

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[32] G. Tammann. "K. und S.," p. 265.

which would mean that his sample contained enough impurity to depress the freezing point by 7.3°. That there is some grave fault with Tammann's measurements on this substance is further indicated by the fact that the coördinates which he gives for the melting curve are at 3,050 kgm. more than 33° lower than those which I have found. It is impossible to explain this by the effect of any initial impurity; a possible explanation is that the design of Tammann's apparatus was such as to allow contamination by the fluid transmitting pressure.

Besides the values of Tammann, there are several other values for comparison at atmospheric pressure. For the melting point we have 50° by Kopp,[33] 49.5° by Bruner,[34] 51° by Bartoli,[35] 52.5° by Stohlmann,[36] and 54.0° by Weger.[37] These wide variations of melting point emphasize the difficulty of getting this substance pure. For the latent heat, there is one value by Bruner,[34] who gives 18.30 kgm. m. against 21.03 above. Bruner's sample was very impure, as shown by its melting point of 49.5°. The change of volume at atmospheric pressure has been measured by Block,[11] working in Tammann's laboratory. But his sample was also impure, as indicated by the low melting point, 51.4°; the impurity may have been the same as that of Tammann's sample. He gives for the change of volume 0.0813 cm.^{3} per gm., against 0.1453 above. This enormous discrepancy can be due only to impurity, and emphasizes the necessity for having pure samples for determining the change of volume. It is to be remembered that the value which I obtained with the first impure sample was somewhat lower than that found for the pure one.

Bismuth.—Especial interest attaches to the melting curve of bismuth because, apart from the fact that it is an element, it is one of the few substances whose melting is of the ice type, that is, the volume of the solid is greater than that of the liquid. The question of greatest interest is whether there is a second modification of the solid denser than the liquid analogous to ice III. We are also interested to know whether the melting curve is concave downward, whether the change of volume increases along the melting curve, and whether the latent heat diminishes, as it does for the ice I curve. So far as I know, water is the only other substance of this type whose melting curve has been hitherto determined. The melting curve of bismuth has been previously measured by Tammann[38] and by Johnston and Adams,[39] but the pressure range of these

[33] H. Kopp, Lieb. Ann., *95*, 307–356, 1885.

[34] L. Bruner, Ber. D. Chem. Ges., *27*, 2102–2107, 1894.

[35] A. Bartoli, Gazz. Chim. Ital., *24* (2), 156–172, 1894.

[36] F. Stohlmann, Jour. prak. Chem., (*2*), 40, 341–364, 1889.

[37] F. Weger, Lieb. Ann., *221*, 61–107, 1884.

[38] G. Tammann, ZS. anorg. Chem., *40*, 54–60, 1905.

[39] J. Johnston and L. H. Adams, Amer. Jour. Sci., Vol. 31, 501–517, 1911.

investigators was not high enough to enable them to tell the direction of curvature, and they made no measurements of the change of volume, and so, of course, were not able to calculate the latent heat.

The bismuth was Kahlbaum's purest, used without attempt at further purification. The purity of the specimen was not perfect, because there was some rounding of the corners of the melting curve, but it was only slight.

The previous temperature range of this work has been to only 200°, but the melting point of bismuth at atmospheric pressure is about 270°, so that some modification in the temperature bath became necessary. It was found that the same bath liquid, "Crisco," could still be used for the higher temperatures, provided that a tight cover was placed over the tank to prevent the escape of the stifling smoke into the air of the room. The temperature control was the same as before, by means of a mercury in glass thermostat, which regulated the supply of gas. The temperature regulation by the thermostat was not quite so good at the higher temperatures as it was at the lower ones. The variation of temperature was in some cases as high as 0.7°, or it might be as low as 0.2°. The mean of the extreme values was taken as the temperature of the experiment; this must be very close to the true value at the inside of the heavy steel cylinder. A modification of the method of measuring temperature was also necessary, because the Reichsanstalt calibration of the mercury in glass thermometers used in the previous work reached only to 200°. For this purpose a platinum resistance thermometer was used. This was one that had been constructed by Dr. H. M. Trueblood in this Laboratory for use in his measurements of the Joule-Thomson effect in steam. For this work, I calibrated the thermometer again in ice, boiling water, and boiling naphthalene. For the boiling point of naphthalene and the effect of the barometric pressure upon it, the values of Johnston and Adams[40] were used.

Two sets of measurements were made. The first was with a cylinder which had previously developed a flaw, but which had been patched with apparent success. The flaw redeveloped, however, at about 6,000 kgm. so that the cylinder had to be scrapped. On computing the values for the change of volume from this first run, it appeared that there had always been some minute leak at even the lowest pressures, so that the results had to be discarded. The equilibrium points of this first run up to about 6,000 kgm. were consistently 1° higher than those of the second run. The explanation of this is probably connected with the extreme slowness of the reaction. To meet this difficulty a special method of procedure was

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[40] L. H. Adams and J. Johnston, Amer. Jour. Sci., Vol. 33, 534–545, 1912.

adopted during the second run. The second run, made with a new cylinder, was over the entire pressure range up to 12,000 kgm. and was successful in every way. It was gratifying to find that the cylinder would stand the maximum pressure at the higher temperature. During the seasoning of the cylinder, the pressure was pushed to 13,000 at 220°.

The reaction, whether melting or freezing, was very slow at the upper end of the curve. Part of the explanation of this is to be found in the small slope of the melting curve and the low latent heat, but this does not seem sufficient to entirely explain the unexpected slowness of the reaction. The appearance was as if the heat conductivity of the cylinder has become very much less at the higher temperatures. Whatever the explanation, a source of error was found here which I have never observed before at the lower temperatures. To explain the possibility of error, let us suppose that pressure has just been decreased so as to carry the liquid into the region of the solid. Freezing takes place with rise of pressure, accompanied with setting free of heat and rise of temperature. If now, before equilibrium has been completely attained, the pressure is artificially raised, we may get the reverse reaction, that is, a fall of pressure, at a pressure that is lower than the true melting pressure at the temperature of the bath, because the temperature of the inside of the cylinder is higher than that of the bath. This gives the appearance of having shut the equilibrium pressure within two limits, at one of which the pressure rises while at the other it falls, whereas the fall of pressure would have taken place only at a higher pressure if temperature had been completely attained. To avoid the error, one must take especial pains to wait for complete equilibrium. But this would require a very long time at the higher temperatures of the range, perhaps three or four hours from one side only. Apart from the tediousness of the operation, the error from slight changes in the bath temperature during this interval would more than counterbalance any other gain in accuracy. Another procedure was adopted therefore. Pressure was first lowered far enough beyond the equilibrium line to ensure the reaction running partly, so that both phases were present in the apparatus. By moving the piston, the pressure was then raised back to nearly the equilibrium value, and then further slight changes made until pressures were found at which the pressure would fall or rise after a change. The advantage is that a very slight amount of reaction can be detected in this way and then the pressure altered in the correct direction, before there is time for much of the heat of melting to be set free. By careful work, the equilibrium point, both from above and below, can be found in less than an hour by this method, and very much more accurately than by waiting for the pressure to automatically restore itself over the entire range.

A very striking change in the reaction velocity was found below 250°. Below this temperature the reaction becomes as rapid as a normal melting reaction for metals in this type of apparatus, and no such special procedure was necessary as above. No marked change in the thermodynamic properties of bismuth takes place at 250°, judging from the melting curve; if the effect is due to a change in the properties of the bismuth, it must be some molecular change too far below the surface to affect the ordinary thermodynamic properties. If the effect is due to the bismuth, it is difficult to understand how other experimenters have been able to get a sharp melting point at atmospheric pressure by observing the arrest point in the cooling curve. It seems very possible that the effect is not one inherent in the bismuth, but may be due to a change in the thermal conductivity of the kerosene or the steel cylinder. The steel was of chrome-vanadium steel; the cylinders in both the preliminary and the final runs were made of this, and the effect was found both times. There may be some molecular change in the steel at this temperature. The manufacturers recommend heating the steel to 270° to draw the temper.

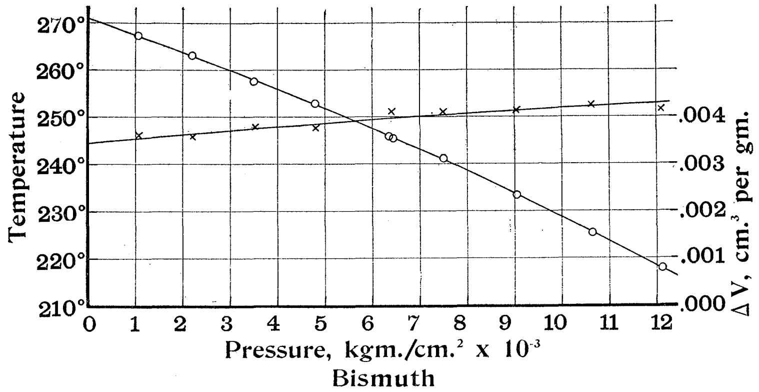

Fig. 18.

Bismuth. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

The observed points and the curves for melting and change of volume are shown in Fig. 18, the computed values for the latent heat and the change of internal energy are shown in Fig. 19 and the numerical values are collected in Table VIII. It is to be noticed that everything is exactly the same as it is for ice I. The melting curve is concave downward, the change of volume curve rises with increasing pressure, and the latent heat and the change of energy become less at the higher pressures. The significance of the rising ΔV curve, unless the dilation relations of solid

TABLE IX.

Bismuth.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat, Kgm. M./Gm.	Change of Energy, Kgm. M./Gm.
	°				
1	271.0	0.00345	−0.00342	5.49	5.49
1,000	267.5	354	357	5.36	5.39
2,000	263.8	362	372	5.24	5.31
3,000	260.0	370	387	5.11	5.22
4,000	256.0	378	403	4.98	5.13
5,000	251.9	386	418	4.85	5.04
6,000	247.6	394	434	4.72	4.96
7,000	243.2	401	451	4.59	4.86
8,000	238.6	407	469	4.44	4.76
9,000	233.8	413	487	4.30	4.67
10,000	228.8	419	506	4.16	4.58
11,000	223.6	424	525	4.01	4.48
12,000	218.3	429	545	3.88	4.39

and liquid are very abnormal, is that the solid is more incompressible than the liquid, although it has a larger volume. It was a matter of great surprise that no other modifications were found. It is almost inconceivable that the liquid should remain permanently of smaller volume than the solid; if we could apply enough pressure we must force the liquid to crystallize into another modification of smaller volume. We must remember, however, that the internal pressure in a metal is already very high, so that we need not be surprised if a very great additional pressure is needed to make it assume another form. It may be mentioned that these experiments show that the effects observed by Ludwig,[41] which he explained by the production of another modification of bismuth under a pressure of 10,000 kgm., must have their explanation in some other direction.

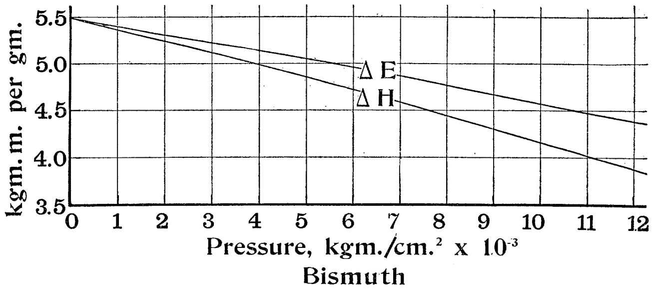

Fig. 19.

Bismuth. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

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[41] A. Ludwig, Jour. Amer. Chem. Soc., Vol. 31, 1130–1136, 1909.

There are several other values for comparison. The melting curves under pressure have been measured by Tammann[38] to 3,000 kgm. and by Johnston and Adams[39] to 2,000 kgm. Tammann gives the melting point at atmospheric pressure as 269.2° and the change of melting temperature with pressure as − 3.9° for 1,000 kgm. Johnston and Adams find for the melting temperature 271.0°, and for the change of melting temperature with pressure − 3.55° for 1,000 kgm. I find by extrapolation 271.0° for the melting point at atmospheric pressure, and for the average slope of the melting curve over the first 2,000 kgm. − 3.60° for 1,000 kgm., agreeing with Johnston and Adams within their limits of error, which they state as 0°.08. Other values of the melting point at atmospheric pressure are: 270.5° on the mercury, and 266.8° on the air thermometer by Person,[42] 271.0° by Vicentini and Omodei[43] on the air thermometer, and 269.2° from an unknown source quoted by Callendar[44] in a table of fixed points. For the change of volume on freezing at atmospheric pressure there are: 0.003 to 0.005 cm.^{3} per gm. by Nies and Winkelmann,[45] 0.0023 by Roberts and Wrightson[46], 0.003 by Lüdeking,[47] 0.00344 by Vicentini and Omedei,[43] and 0.00336 to 0.00340 by Toepler.[48] In criticism of some of these values it may be said that the bismuth of Nies and Winkelmann was admittedly very impure, the individual observations of Roberts and Wrightson show wide variations, and the bismuth of Lüdeking was known to be impure with a small amount of mercury and its melting point was about 260°. There seems to be only one determination of the latent heat of melting, 12.6 gm. cal. by Person.[42] The value given in the table above is 12.7 cal. The agreement is better than one has a right to expect when one considers the known errors in Person's work, which was performed before modern accurate methods in calorimetry had been introduced.

This completes the list of liquids whose melting curves have been systematically investigated. In addition to these, several others were examined without result for other solid forms, and incidentally some of the melting data were collected. These are now given.

Menthol.—This was from Eimer and Amend, purified by distillation. An attempt to further purify it by crystallization in the thermostat failed; the crystal growth does not take place in the form of large single

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42. C. C. Person, Ann. Phys. et Chim., *76*, 432, 1849.

43. G. Vicentini and D. Omodei, Atti Torino, *22*, 28–47 and 712–726, 1886–87; *23*, 38–43, 1887–88.

44. H. L. Callendar, Phil. Mag., Vol. 48, 519–547, 1899.

45. F. Nies and A. Winkelmann, Wied. Ann., *13*, 43–83, 1881.

46. W. C. Roberts and J. Wrightson, Brit. Assoc. Rep., 1880, 544.

47. C. Lüdeking, Wied. Ann., *34*, 21–24, 1888.

48. M. Toepler, Wied. Ann., *53*, 343–378, 1894.

crystals, but confused aggregates of crystals, in appearance like mould, separate out. The melting point was not carefully determined; it was, however, somewhat higher than 42°, because no trace of melting took place at this temperature in 16 hours in the thermostat. The melting point of the pure substance is given as 42.40° by Hulett,[17] and 42.0° by Bruner.[16] The change of volume on freezing at 77 kgm. was found to be 0.0612 cm.^{3}/gm. The latent heat of menthol is given as 18.9 cal. by Bruner.[16] If we combine my value for ΔV with Hulett's value for $d\tau/dp$, ($= 0.0245$), we obtain for the latent heat 18.5 cal. At room temperature no new modification of the solid was found to 12,000 kgm.; no other temperature was tried. Menthol is known to have an unstable modification, and Hulett has determined its melting curve to 300 kgm. This modification did not appear during the present work.

Anethol.—This was from Eimer and Amend, purified by distillation and by repeated fractional crystallization at room temperature. This was possible because the normal melting point is very close to room temperature. In spite of repeated crystallizations, a substance with sharp freezing was not obtained. The melting point was not carefully determined; it was somewhat over 20°, whereas the melting point of the pure substance is given as 21.3° by Schiff,[22] 21.65° by Landolt,[49] and 22.3° by Block.[18] The change of volume found at 77 kgm. was 0.0793 cm.^{3}/gm. Block gives 0.0794 at atmospheric pressure. Eykmann[20] gives 27.9 cal. for the latent heat. Combining this with a value 0.0800 for the change of volume at atmospheric pressure, gives 0.0194 for $d\tau/dp$. The melting pressure at 100° was found to be in the vicinity of 4,200 kgm. At room temperature there were no new modifications to 12,000 kgm. and none between the melting point and 12,000 at 100°.

Naphthalin.—This was Kahlbaum's purest, redistilled. The melting point was not determined. No new modification was found up to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is roughly 4,000 kgm. This agrees with the value extrapolated from Tammann's curves. J. Johnston, at the Geophysical Laboratory in Washington, has recently made a careful measurement of the melting curve of this substance (his results are not yet published), so there was no particular object in repeating the measurements here.

Acetophenone.—It was mentioned in the preceding paper[1] that this had not been successfully purified, so that it was not worth while to attempt the determination of the melting curve. The impurity present was sufficient to depress the freezing point from 20.5° to 19.6°. This impurity was not present in sufficient amount, however, to make it seem

[49] H. Landolt, ZS. phys. Chem., *4*, 349–371, 1889.

useless to try if there were other solid modifications. No other forms were found, however, to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is approximately 11,600 kgm., and the change of volume 0.0454 cm.^{3}/gm.

Antimony Tri-iodide.—This substance was investigated because it is usually listed as showing an enantiotropic transition point at 113°. This is on the authority of Cooke,[50] who is quoted in the Tables of the French Society as stating that the transition is enantiotropic. Cooke really claims two new forms, one with a transition point at 113°, and a rarer one with a point at 125°. Lehmann, however, in his "Molekular Physik," although listing this among substances with enantiotropic modifications, considers that we are not yet sure that the transition is not really monotropic. Furthermore, Groth, in his "Chemische Krystallographie," says that the subject requires further investigation. Groth is of the opinion that Cooke's two forms are monotropic.

The substance used was obtained from Eimer and Amend, and it was not further purified. It contained considerable impurity. No transition under pressure could be found, although unusually careful search was made. At 20° there was none up to 12,000 kgm., and at 150° none from 12,000 down to 600 kgm.; at 90° there was none between atmospheric pressure and 5,500 kgm., and at 120° none between 400 and 8,000 kgm. Furthermore, on heating SbI_3 in the air, no change of color was observed below the melting point. An attempt to make dilatometric measurements was not satisfactory, because the machine oil used as the medium began to attack the SbI_3 at about the supposed transition point with some evolution of gas. However, it was established that there was no large change of volume near 113°.

In the course of the search for the second modification, the melting point at 200.8° was found to be approximately 1,160 kgm., and the change of volume 0.0240 cm.^{3}/gm. The melting point at atmospheric pressure is 163°.

Sodium.—No new measurements were made on this substance, but recently published values by Griffiths[51] for the latent heat of melting at atmospheric pressure allow a very great improvement upon the values listed in the previous paper[1] for the values of ΔH and ΔE at low pressures. Reference is made to pp. 137 and 158 of that paper for the method used in computing the initial value of the specific heat. Broadly speaking, the method was one of compromise between the values indicated by extrapolation from the high pressure measurements, and the direct

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[50] Cooke, Proc. Amer. Acad., Vol. 13, 174, 1877.

[51] E. Griffiths, Proc. Roy. Soc., Vol. 89, 561–574, 1914.

determinations of other observers. At the time of writing that paper, there was only one determination known of the latent heat, that by Joannis at 13.53 kgm.m./gm. The value indicated by extrapolation from my own work was 12.0, and the compromise value adopted was 12.9. Griffiths' recent value has been determined with great care, and is 11.74, close to the value indicated by extrapolation. The value 11.8 is accepted, therefore, as most probably accurate. This will produce an important change in the values of ΔH and ΔE for the first few thousand kgm., and will remove the initial large and abnormal drop of the curves.

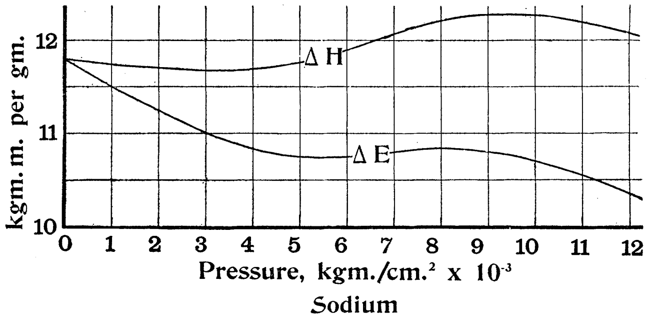

Fig. 20.

Sodium. The latent heat and the change of internal energy when the solid melts to the liquid recomputed from the recent value of Griffiths for the latent heat at atmospheric pressure.

TABLE X.

Sodium [Recomputed Values].

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	97.62°	0.02787	.00860	11.80	11.80
1,000	105.9	2555	816	11.74	11.50
2,000	113.9	2362	778	11.71	11.25
3,000	121.5	2203	744	11.68	11.01
4,000	128.8	2072	712	11.69	10.84
5,000	135.8	1968	684	11.76	10.75
6,000	142.5	1873	654	11.89	10.75
7,000	148.9	1790	626	12.07	10.80
8,000	155.1	1711	600	12.21	10.84
9,000	161.0	1634	578	12.27	10.80
10,000	166.7	1556	558	11.26	10.70
11,000	172.2	1476	540	12.18	10.54
12,000	177.5	1398	522	12.07	10.35

The recomputed curves are shown in Fig. 20, and in Table X. the recomputed numerical values are listed.

It may also be mentioned that the melting point determined by Griffiths, 96.61°, agrees very closely with the two determinations made above, 97.62° and 97.63°. The agreement is closer than that between any other two observers, and 97.62° may, therefore, be accepted as the most probable value.

A remarkable fact discovered by Griffiths is that the specific heat of the liquid at the melting point is less than that of the solid, a result which holds for almost no other substance. See, however, a later discussion for this matter.

(*To be concluded.*)