Second Series. *March, 1914* *Vol. III., No. 3*

THE

PHYSICAL REVIEW.

CHANGE OF PHASE UNDER PRESSURE.[1]

I. The Phase Diagram of Eleven Substances with Especial Reference to the Melting Curve.

By P. W. Bridgman.

Details of Experiment and Computations.

The detailed presentation of data follows. Besides giving the data actually found in this present investigation (which in most cases are shown with sufficient accuracy by the points on the diagrams), the attempt has been made to collect all previous data bearing on the point, and to give some discussion of the most probable values. This would not be necessary if it were the only object of this paper to find the most probable course of the melting curve.

In addition to numerical data, any details of manipulation or of computation peculiar to the individual substances are given; in particular the extent of the region through which search was made for other solid forms.

Potassium.—The potassium was obtained from Eimer and Amend. The first sample used was very carefully purified by the following method. The commercial lumps were placed under gasolene in a glass receiver, the gasolene removed with an air pump, and the potassium melted and run into a connecting vessel. This connecting vessel was constructed so as to form part of a still, from which the potassium was distilled at high vacuum into a third vessel. The third vessel was then sealed off from the still and placed in the thermostat, where about two thirds of the potassium was allowed to crystallize slowly. The liquid metal was then drained off and the pure crystals used for the first run. But subsequent work showed all these precautions to be unnecessary; the commercial metal is pure enough if the scum of oxide is removed by the first of the processes described above.

[1] Continued from page 141.

Three sets of measurements were made; one with each of the three pieces of apparatus. The first set comprises observations to 7,800 kgm. and 150°, the second two observations at atmospheric pressure, and the third five observations between 7,400 kgm. and 12,000 kgm. The direct experimental results are shown in Fig. 2 and the computed values of the latent heat and the change of internal energy in Fig. 3. The numerical values of these quantities are given in Table I.

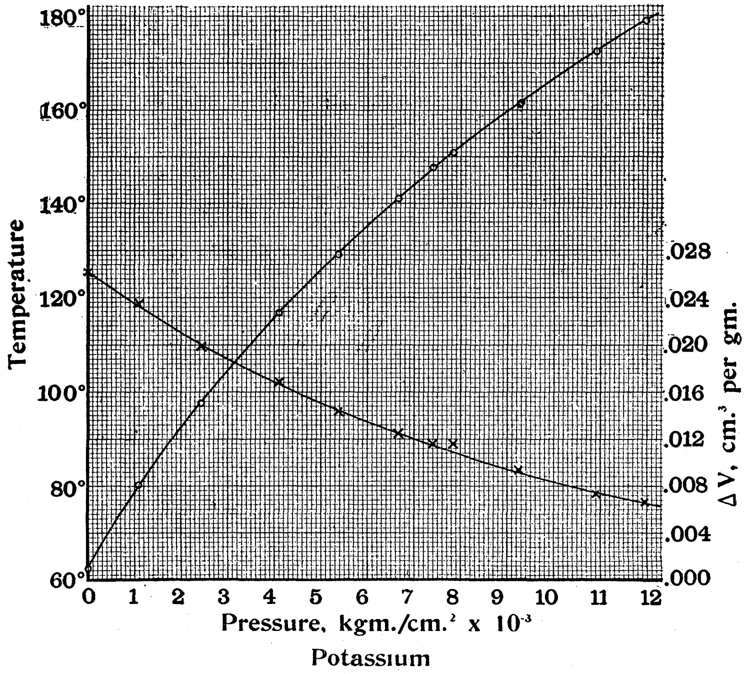


Fig. 2.

Potassium. Freezing curve and the change of volume curve. The observed freezing temperatures are shown by circles, and the observed changes of volume by crosses.

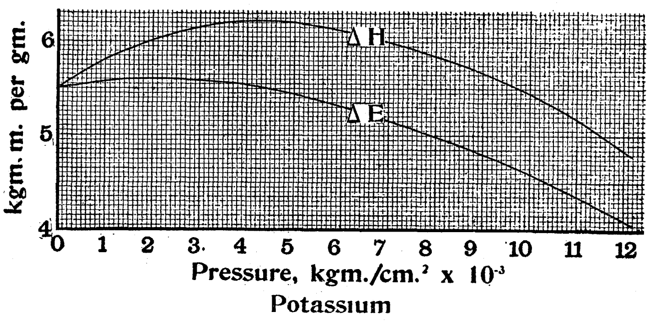


Fig. 3.

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

Table I.

Potassium.

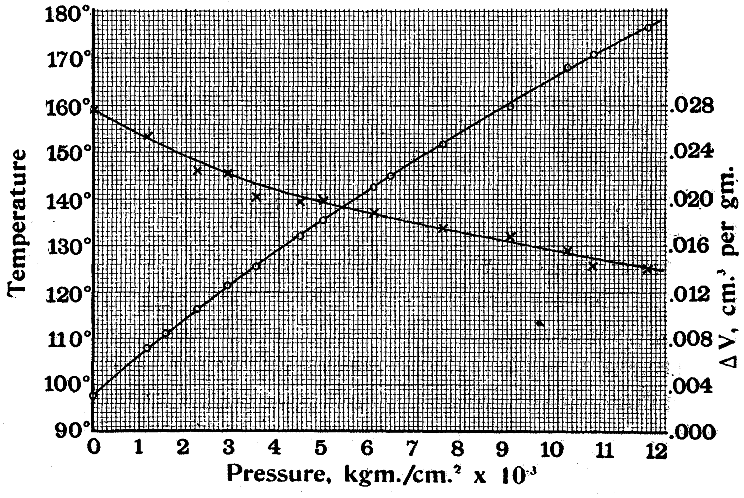
Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	62°.5	0.02680	5.51	5.51
1,000	78 .7	2368	5.81	5.58
2,000	92 .4	2105	6.02	5.60
3,000	104 .7	1877	6.15	5.59
4,000	115 .8	1676	6.22	5.54
5,000	126 .0	1504	6.21	5.44
6,000	135 .4	1347	6.12	5.31
7,000	144 .1	1205	6.00	5.15
8,000	152 .5	1073	5.85	4.98
9,000	160 .1	950	5.67	4.80
10,000	167 .0	838	5.43	4.58
11,000	173 .6	738	5.16	4.34
12,000	179 .6	642	4.83	4.09

These results may first be compared with others at atmospheric pressure. For the freezing point we have: 62.1° by Hagen[19], 62.5° by Holt and Sims[20], and 62.5° by Kurnakow and Puschin[21]. The two present experiments at low pressures gave by an extrapolation 63.3° and 62.8°. As already stated this method does not give accurate results, but the high value is at least evidence of the purity of the metal. The two measurements of the change of volume at atmospheric pressure gave 0.0266 and 0.0262 cm.^{3} per gm. This is considerably lower than the only other values we have 0.0313 by Hagen[19] (this seems to be incorrectly quoted as 0.029 by Tammann[22], and 0.030 by Toepler[23]. The agreement of the two new results makes it probable that they are better than the others. The low value of the melting point given by Hagen would suggest that his potassium was impure, and in all Toepler's work there is one very serious source of error not taken account of. Toepler used a dilatometer method, in which the bulb containing the substance under investigation and its projecting stem were at different temperatures. No correction was made for the thermal expansion of the substance on passing from the one temperature to the other. The effect of the correction would be to decrease Toepler's value. There seems to be only one direct determination of the latent heat, 15.7 gm. cal. per gm. (or 7.00 kgm. m. per gm.) by Joannis[24]. This is considerably higher than the value that was computed from the present data (5.51 kgm. m.), but since the initial slope admits of less adjustment here than for many of the other substances, no attempt was made to bring the two values into agreement. The presumptive error in latent heat measurements is so great that 7.00 could not be accepted without corroboration in any event.

The results at high pressure differ markedly from those of Tammann[25], whose specimen must have been very impure, as shown by its low freezing point, 59.5°, and very slow freezing. Tammann says that he found it particularly difficult to obtain sharp settings with this substance, and had to modify somewhat his usual method. Tammann's results run to only 3,000 kgm. At this pressure he finds an equilibrium temperature nearly 8° lower than that found here. Tammann predicts from his data that a maximum melting point will be found at 10,000 kgm. and 130°. Both of these values are considerably exceeded here, with no indication whatever of a maximum.

Tammann's results must also appear low because of error in his pressure measurement. That this error may be considerable is shown by the fact that he has in his recent work[26] used a gauge giving results at 2,000 kgm., about 100 kgm. lower than the gauge of his previous work. Tammann apparently regards the new gauge as the more reliable of the two. It is unfortunate that he himself had no direct means of calibrating these gauges, but had to rely on the word of the manufacturer.

In the search for other solid modifications, pressure was raised to 12,000 kgm. at room temperature, and to 12,500 kgm. at 142°, but none was found. A comparison of the curves for the change of volume and the latent heat with those for other liquids shows that the behavior of potassium is a little unusual. The change of volume has become an unusually small fraction of its initial value, and the latent heat decreases



Sodium

Fig. 4.

Sodium. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

at the high pressures more than is normal. Both of these considerations would seem to suggest that a new modification of the solid may be at hand.

Sodium.—The material was obtained from Eimer and Amend. That used in the first set of experiments was carefully purified by distilling in vacuo, but this precaution proved unnecessary, and in subsequent work the commercial material, freshly cut under oil so as to avoid all oxide, proved entirely satisfactory. Three sets of measurements were made. The first was with the original apparatus up to 6,400 kgm. This series was terminated by an explosion. The second set comprised two measurements at low pressure, and the third nine measurements with the final apparatus over the entire range up to 12,000 kgm. The experimental results are shown in Fig. 4 and the computed latent heat and the change of internal energy in Fig. 5. The numerical values are given in Table II.

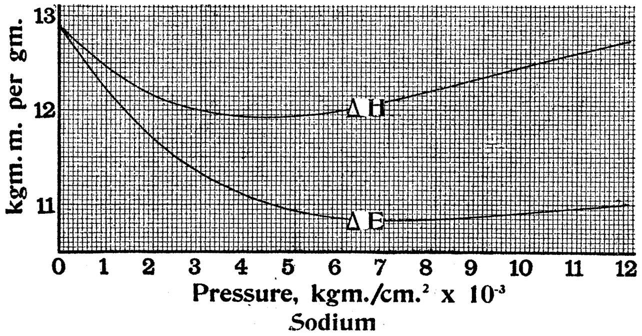


Fig. 5.

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

Table II.

Sodium.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	97°.6	0.02787	12.90	12.90
1,000	105 .9	2555	12.46	12.22
2,000	114 .2	2362	12.16	11.70
3,000	121 .9	2203	12.00	11.33
4,000	129 .1	2072	11.93	11.08
5,000	135 .8	1968	11.94	10.93
6,000	142 .5	1873	11.99	10.85
7,000	148 .9	1790	12.10	10.83
8,000	154 .8	1711	12.22	10.85
9,000	161 .0	1634	12.35	10.88
10,000	166 .7	1556	12.48	10.92
11,000	172 .2	1476	12.60	10.96
12,000	177 .2	1398	12.72	11.00

There are the following data for comparison at atmospheric pressure. For the melting point, 92.0° (evidently a misprint) by Holt and Sims[20], 96.7° by Hagen[19], 97.5° by Kurnakow and Puschin[21], and 97.8° by Tammann[27], against the values 97.62° and 97.63° found here. This evidence makes still further probable the high purity of the sodium used here. For the change of volume we have 0.0264 cm.^{3} per mm. by Toepler[23], and 0.0256 by Hagen[19]. But here again, the low value of Hagen's melting point makes impurity probable in his specimen, and the error already mentioned runs through all Toepler's work. In view of this uncertainty two measurements were made at 60 kg., giving by extrapolation 0.02785 and 0.02789. The agreement of these two values is very good, but is no better than would be expected from the self-consistency of the two individual experiments. There is only one value for the latent heat at atmospheric pressure, 31.7 gm. cal. per gm. (13.53 kgm. m.) by Joannis.[24] The value computed at first from the initial slope of the melting curve, without reference to any other value, was 12.00. But as already explained, the initial slope is open to considerable uncertainty, and therefore it was adjusted, without doing violence to the slope at higher pressures, so as to give 12.90 for the initial latent heat. This is the value shown in the curves.

At high pressures the values of Tammann[28] agree much better with the present values than did those for potassium. At 3,000 kgm. his melting temperature is about 2° below that found here; this is to be explained in part by error in his high pressure measurement. Tammann also gives very rough values for ΔV, with a probable error of 20 per cent., according to his own estimation. Within this limit his values agree with those found here. But Tammann makes a rather daring linear extrapolation from these rough values for ΔV, and hints at a maximum melting point at 8,000 kgm. These data show no evidence whatever of such a point up to 12,000 kgm.

At 40° pressure was raised to 12,000 kgm. and at 170° to 13,000 kgm. but no new solid modification was found.

Carbon Dioxide.—The carbon dioxide was obtained from one of the commercial drums used to supply soda fountains. It was collected in the well-known way in the form of snow by placing a heavy bag over the open valve. The condensation to the solid in this way from the compressed gas acts as a further purifying process, and the carbon dioxide used gave sharper freezing curves than any of the organic substances, almost as sharp as a metal like mercury. A special form of bulb was necessary in placing the carbon dioxide in the apparatus. It is shown in Fig. 6. In general appearance it is much like the bulbs used for other substances except that it is much heavier. The problem was to provide a means of retaining the carbon dioxide in the bulb initially at considerable pressure. This was accomplished as follows. The lower part of the stem was closed by a lead cone *A*, covered with a disc of steel *B*. The cone was driven with a hammer against the conical seat so as to be gas-tight. The bulb was then filled by putting in the snow at the open end, and tamping it into a solid mass with a steel rod. The cap *D* was then screwed into place. This cap was made tight by a ring of solder at *C*, which was forced tightly into all the crevices. When the filling was complete, the entire bulb was of course at the temperature of solid carbon dioxide at atmospheric pressure, − 79°. As the bulb warmed to room temperature, the carbon dioxide liquefied and exerted a pressure, which under the conditions probably rose to 500 kgm. There was at first a slight leak of gaseous carbon dioxide, but this was soon stopped by expansion of the solder gasket. The quantity of carbon dioxide was now determined by weighing the steel bulb. It was about 7.5 gm. The stem of the bulb was then screwed into the mercury cup, *E*, and then placed in the pressure cylinder. Now when pressure in excess of the internal pressure was applied to the exterior of the bulb, the lead cone was forced into the bulb, and perhaps dissolved by the mercury. The rest of the experiment was exactly the same as for other substances. Of course after the lead cone was once dislodged, the pressure could not be allowed to fall below the initial value of about 500 kgm., but in this form of apparatus the friction of the moving piston automatically provided for this.

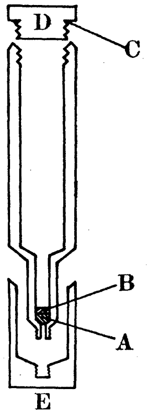


Fig. 6.
The receptacle for containing the carbon dioxide.

In filling the bulb, some care was necessary to prevent condensation of moisture from the air onto the carbon dioxide. This was prevented by placing the closed bulb in a vessel surrounded by solid carbon dioxide, until it came to temperature. The cap was then removed and it was filled from a large funnel fitting the bulb closely. Only the carbon dioxide in the lower part of the funnel passed into the bulb, and there was no chance for condensation on the lower part of the carbon dioxide, since it was protected by the layers above from direct contact with the air.

Only one set of observations was made on carbon dioxide, with the high pressure apparatus, from 3,400 to 12,000 kgm. The results were perfectly regular. It would not have been possible to reach temperatures much below zero without considerable trouble, or even redesigning the apparatus. Since the evidence given by this substance on the main question at issue is perfectly unmistakable, the trouble of reaching lower temperatures did not seem worth while. The experimental results are shown in Fig. 7 and the computed results in Fig. 8. The numerical values are given in Table III.

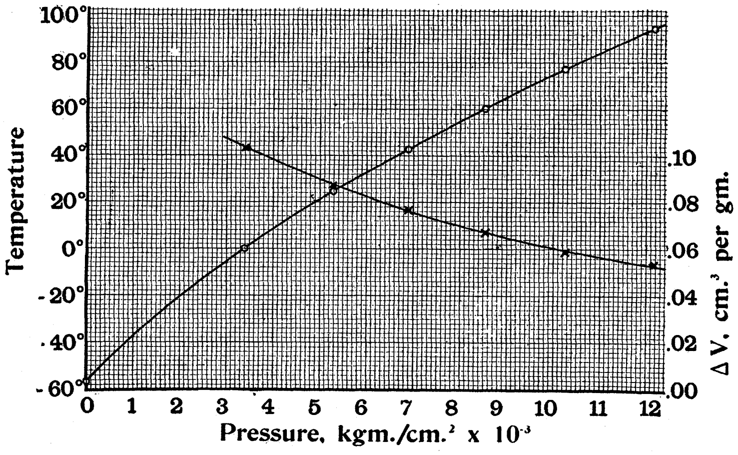


Fig. 7.

Carbon Dioxide. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

There are no results for comparison at low pressures, except a determination of the triple point at 5.2 kgm. and – 56.7° by Villard and Jarry.[29] This value has been used in determining the probable course

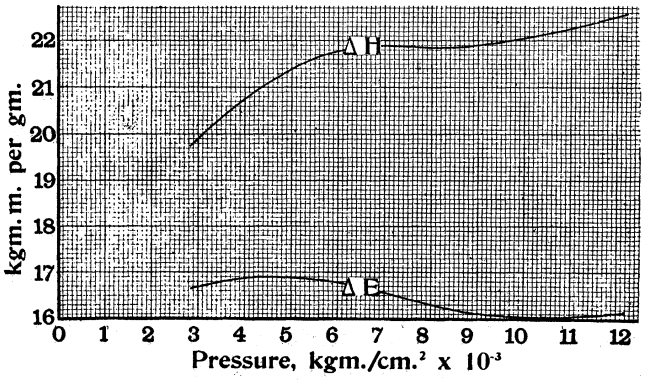


Fig. 8.

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

of the curve below 0°. There are no values at present known for the latent heat or the change of volume at atmospheric pressure, and an extrapolation from the values found here would be too daring. All the indications are, however, that the change of volume at the pressure of the triple point will be found to be unusually high.

Table III.

Carbon Dioxide.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	−56°.6	...	...	...
1,000	−37 .3	...	...	...
2,000	−20 .5	...	...	...
3,000	− 5 .5	.1071	19.92	16.68
4,000	8 .5	.0979	20.77	16.88
5,000	21 .4	896	21.39	16.89
6,000	33 .1	822	21.77	16.79
7,000	44 .2	755	21.90	16.55
8,000	55 .2	697	21.84	16.30
9,000	65 .8	644	21.90	16.10
10,000	75 .4	602	22.06	16.03
11,000	84 .6	564	22.28	16.04
12,000	93 .5	531	22.54	16.12

Comparison with the results of Tammann at high pressures is of little use, because Tammann had no adequate means for keeping the carbon dioxide pure. In his first experiment, described in "Kristallieren und Schmelzen",[30] a solid cylinder of carbon dioxide was wrapped in a piece of parchment paper, and placed directly, with no other protection, in the mixture of glycerine and water serving to transmit pressure. The fact that after release of pressure the paper was found not wet by the glycerine was taken as evidence that there was no contamination of the carbon dioxide. With this apparatus Tammann found irregularities which he accepted as evidence of the existence of another modification of the solid, and carbon dioxide was accordingly listed by him among the polymorphic substances. Later, however, because a recently developed theory of Tammann's indicated that there should be only one solid modification, he repeated his experiment,[31] and came to the conclusion that there was only one solid modification, and that the effects which he had previously explained by two modifications were in reality due to dissolved water or glycerine. His new data are not at all self-consistent, and he represents them within the limits of error between 2,000 and 4,000 kgm. by a straight line. This gives a lower melting point at 2,000 than that found here, and a higher one at 4,000. Tammann did not measure ΔV.

No evidence whatever was found here of the existence of a second solid phase. Search for such a modification was made at 25° to 12,000 kgm. and at 67° to 12,600 kgm.

It is interesting to note in passing that the freezing temperature at pressures above 6,000 kgm. is higher than 31°, that is, higher than the critical temperature between liquid and vapor. It is possible, therefore, by the application of pressure alone to change a gas directly into a crystalline solid. This is the second case for which this has been realized, Tammann[32] having previously shown that such is the case for phosphonium chloride at pressures above 75 kgm.

Chloroform.—This was obtained from Eimer and Amend and purified by fractional distillation just before using. Only one distillation was necessary. The purity was sufficient, as shown by the sharp freezing curve.

Two sets of measurements were made on chloroform. The first set was with the form of high pressure apparatus made entirely of one piece. Three points were obtained with this before the flaw developed that made it necessary to discard the apparatus. The second set was made with the modified high pressure apparatus with connecting tube, and comprises six points between 0° and 107.7°. The quantity of chloroform used was about 25 gm. The experimental results are shown in Fig. 9

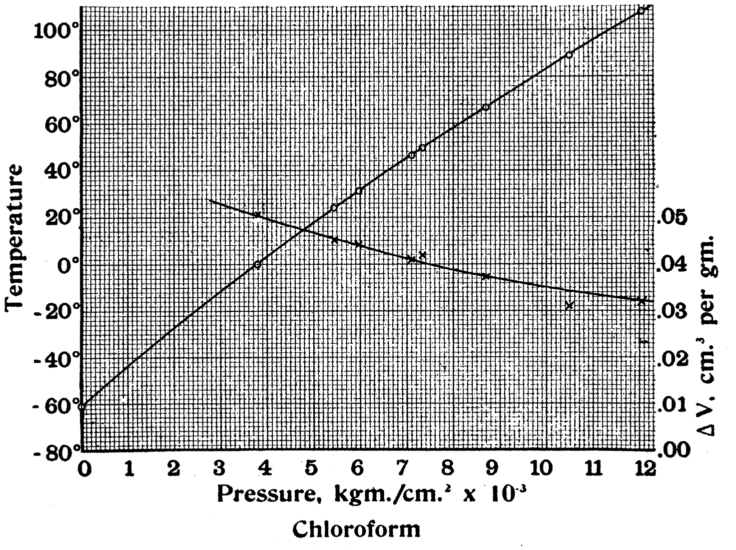


Fig. 9.

Chloroform. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

and the computed values of latent heat and change of volume in Fig. 10. The numerical values are shown in Table IV.

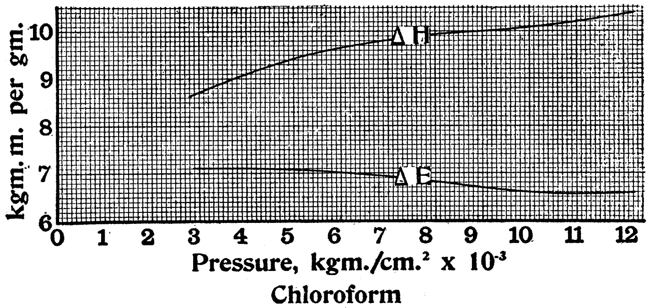


Fig. 10.

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

Table IV.

Chloroform.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	−61°.0	....	....	....
1,000	−45 .7	....	....	....
2,000	−28 .3	....	....	....
3,000	−12 .1	0.0530	8.70	7.11
4,000	3 .4	498	9.10	7.10
5,000	18 .2	467	9.43	7.08
6,000	32 .4	438	9.65	7.01
7,000	45 .6	412	9.81	6.93
8,000	58 .6	389	9.93	6.82
9,000	71 .3	368	10.00	6.70
10,000	83 .7	350	10.08	6.60
11,000	96 .1	334	10.20	6.56
12,000	107 .9	321	10.35	6.59

It had already been shown in another paper that chloroform could be solidified by pressure,[33] and two rough values for the solidifying pressure at 40° and 80° have already been given, which agree rather well with those found here. These two instances, however, seem to be the only previous record we have of the freezing of chloroform under pressure, so there are no other results for comparison at high pressures.

As in the case of carbon dioxide, it was not feasible to make observations below 0°. The freezing of the mercury seal, apart from any other consideration, would demand an essentially different apparatus for readings much below 0°. Over the range investigated, however, the results are just as significant in their bearing on the main question as were the results for carbon dioxide.

There are very few observations on chloroform at atmospheric pressure. For the melting point Beilstein's Handbuch gives – 63.2° and Niescher[34] – 61°. The latter has been accepted for use here as more probably accurate, because higher. For the latent heat at atmospheric pressure we have only the value 19.2 gm. cal. per gm. (8.19 kgm. m.) by Niescher,[34] obtained by indirect means. An examination of the values found here for pressures above 3,000 kgm. shows that they may be extrapolated without great violence to Niescher's value at atmospheric pressure.

Pressure was pushed to 12,000 at 25° and to nearly 13,000 kgm. at 107° in the search for another solid modification, but none was found. Search to 12,000 at a temperature much lower than 25° was not feasible because of the freezing of the mercury. It might be expected by analogy with CCl_4, that chloroform, $CHCl_3$, a substance of much the same chemical constitution, would also show several modifications. It may still be that such is the case, for a glance at the melting curve will show that the explored region is after all comparatively restricted, and that there is room in the unexplored region for several solid modifications of much the same relationship to each other as the modifications of CCl_4. This possibility is still further increased by the rather large subcooling of 2,000–3,000 kgm. that chloroform may support, so that the domain of a new form may have been actually entered, but not far enough to compel its appearance.

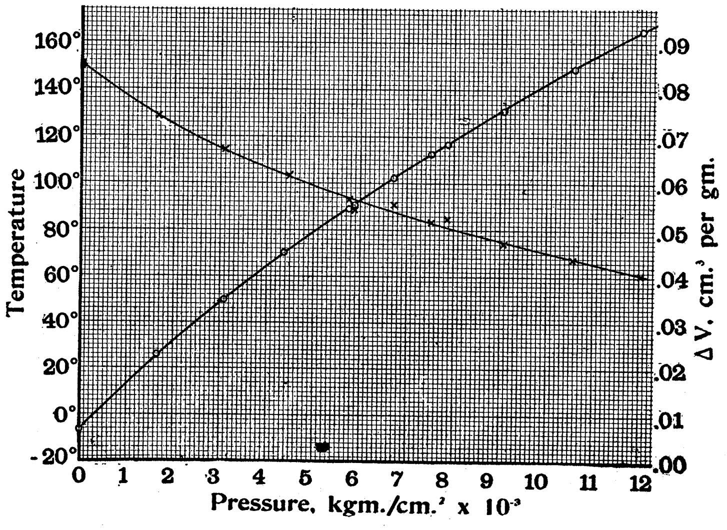


Fig. 11.

Anilin. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

Anilin.—This substance, Kahlbaum's purest, obtained from Eimer and Amend, was purified by distilling, then by crystallization, and then again by a second distillation immediately before making the readings. Measurements on this were made in three series: the first at six temperatures with the first apparatus, the second at approximately atmospheric pressure with the low pressure apparatus, and the third at five pressures up to 12,000 kgm. with the final high pressure apparatus. About 15 gm. of anilin were used. The experimental results are shown in Fig. 11, and the computed latent heat and change of internal energy in Fig. 12. The numerical values are shown in Table V.

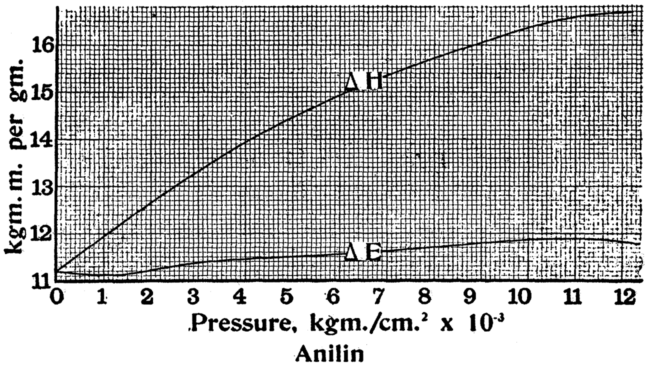


Fig. 12.

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

Table V.

Anilin.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	− 6°.4	0.0854	11.20	11.20
1,000	13 .1	784	11.94	11.12
2,000	31 .6	724	12.66	11.21
3,000	48 .7	673	13.33	11.38
4,000	64 .5	631	13.95	11.45
5,000	79 .0	594	14.48	11.50
6,000	93 .2	561	14.93	11.55
7,000	106 .5	530	15.36	11.62
8,000	119 .1	502	15.73	11.70
9,000	131 .5	476	16.06	11.80
10,000	143 .2	451	16.38	11.87
11,000	154 .7	427	16.60	11.90
12,000	165 .3	405	16.69	11.83

There are only a few results at atmospheric pressure for comparison. For the melting temperature we have – 8.0° by Lucius,[35] – 6.1° by Tammann,[36] – 6.0° in Beilstein's Handbuch, and – 6.45° found here by an extrapolation over about 1.5°. There is only one determination of the latent heat, 20.9 gm. cal. per gm. (8.91 kgm. m. per gm.) by de Forcrand.[37] But the author himself recognizes that the experiment on which this value was founded is probably in error, as is shown by the fact that a specific heat for the solid was found greater than that for the liquid. De Forcrand, from apparently slightly justified theoretical grounds, prefers to replace the experimental value 20.9 by 39.9, rather a large change. The value found here from the initial slope is 11.20. kgm. m. (26.4 gm. cal.), and has been retained, as probably the most accurate value we have.

The results of Tammann[38] up to 2,500 kgm. are somewhat lower than those found here; 1.9° lower at 2,500, 1.1° lower at 2,000, and 0.1° lower at 1,000. This difference may be almost all explained by error in Tammann's standard of pressure. Tammann predicts from his curve to 2,500 a maximum melting point at 9,080 kgm. and 87.2°. Both of these values have been very considerably surpassed here without any sign of a maximum. Tammann does not give values for ΔV.

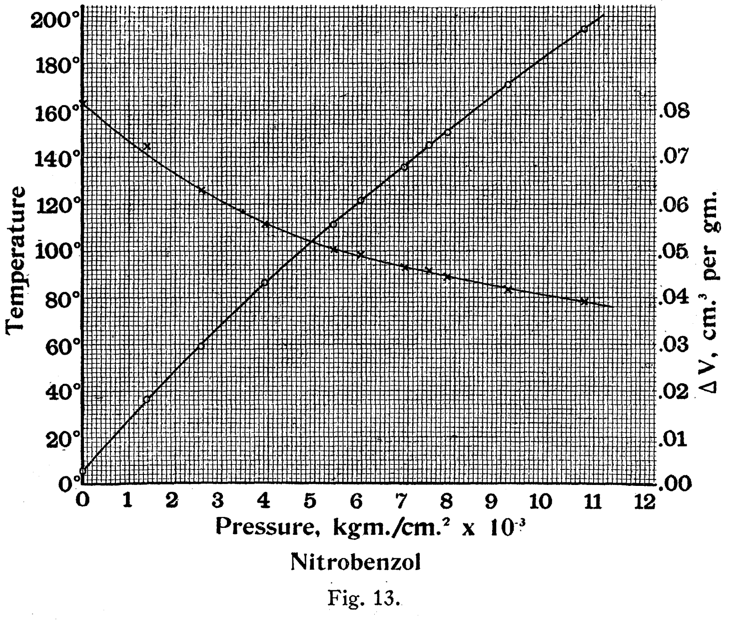


Fig. 13.

Nitrobenzol. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

In the search for another solid modification the pressure was raised to 12,000 kgm. at 25° without result.

Nitrobenzol.—This was Kahlbaum's purest, further purified by fractional distillation, crystallization, and redistillation immediately before using. Three sets of observations were made; the first set comprises six observations with the first apparatus to 7,840 kgm., the second a single observation at approximately atmospheric pressure, and the third four observations with the high pressure apparatus to 10,780 kgm. About 17 gm. of nitrobenzol were used. The experimental results are shown in Fig. 13, and the computed values of latent heat and change of volume in Fig. 14. The numerical values are shown in Table VI.

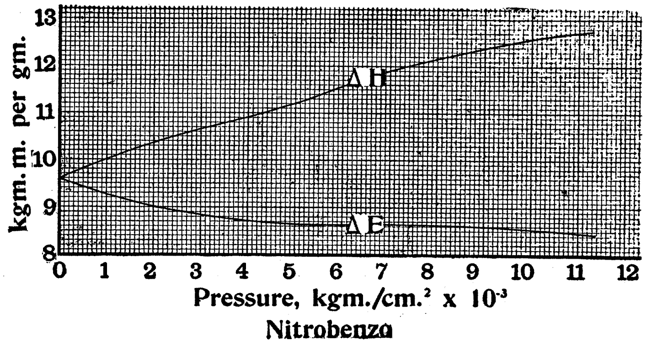


Fig. 14.

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

Table VI.

Nitrobenzol.

Pressure.	Temperature.	ΔV, cm.³/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	5°.6	0.08136	9.60	9.60
1,000	27 .2	7326	10.00	9.26
2,000	48 .1	6639	10.36	9.01
3,000	68 .3	6052	10.66	8.84
4,000	87 .6	5552	10.92	8.71
5,000	105 .5	5172	11.21	8.64
6,000	122 .3	4885	11.58	8.63
7,000	138 .1	4641	11.91	8.64
8,000	153 .8	4415	12.16	8.62
9,000	169 .3	4210	12.39	8.60
10,000	184 .5	4028	12.59	8.53
11,000	198 .6	3864	12.73	8.47

There are a number of values for comparison at atmospheric pressure. For the melting point there is 5.82° by Meyer[39], and 5.67° by Tammann[40]. The directly determined freezing point of the nitrobenzol used in this experiment was 5.67°. For the latent heat we have 30.2 gm. cal. per gm. by de Forcrand[37] (this is certainly greatly in error), 22.30 by Pettersson and Widman[41], and 22.46 by Meyer[39]. The corresponding values in the kgm. m. units of this paper are 12.89, 9.51 and 9.58. The value computed from the present data without any regard to the above values was 10.14. But since, as already explained, the initial slope, and hence the initial latent heat, is open to considerable uncertainty, the slope was corrected so as to give 9.60 for the initial latent heat, which is the value shown in the curves. For the change of volume on freezing there is one value by Meyer[39], 0.0808 $cm.^3$ per gm., against 0.0814 found above. The agreement is better than usual.

Tammann's[42] results at higher pressures run a little low, as we have always found them, the greatest discrepancy being between 2,000 and 3,000 kgm. At 3,000 his curve is 2.0° lower than that given here, at 2,000 it is 0.2° lower, and at 1,000, 0.9° higher. Tammann predicts a maximum melting point at 10,100 kgm. and 124°. The curve has been carried in this work to 11,000 kgm. and 197.8°, with no approach to this supposed maximum.

No other modification of the solid was found. The region explored lies between the melting curve, the isothermal at 25°, out to 12,000 kgm., the isothermal at 200° from the melting curve to 12,800 kgm., and the straight line connecting the point (12,000 kgm., 25°) with the point (12,800 kgm., 200°). Analogy with benzol would lead one to expect that possibly another modification is not far away.

Diphenylamine.—The substance used was Kahlbaum's purest, provided by Eimer and Amend. It comes in the form of fine flakes, such as those familiar naphthalene preparations used for moth preventives. It is of a most dazzling whiteness, but there is some impurity present as shown by the yellow color of the melt. The material used here was further purified by slow crystallization at constant temperature in the thermostat. It was found possible in this way to obtain beautiful perfectly colorless and transparent crystalline plates, sometimes 2 or 3 cm. across.

Three series of observations were made. The first comprises six points with the first apparatus up to 200°. An explosion wrecked the apparatus while obtaining the highest point. The second series consists of two observations at low pressure, and the third of two observations at the upper end of the curve with the high pressure apparatus. In addition, several unsuccessful attempts were made in which the diphenylamine became contaminated with kerosene by the collapse of the steel bulb. The manipulation of starting the experiment required some care, as pressure should not be applied while the diphenylamine was solid because of danger of collapse, and the temperature must not be raised so high in the preliminary melting as to allow any of the diphenylamine to escape from the bulb by temperature expansion. The experimental results are shown in Fig. 15, and the computed values of the latent heat and the change of internal energy in Fig. 16. The numerical values are given in Table VII. The rapid rate of rise of temperature with pressure on the melting curve is worth noticing.

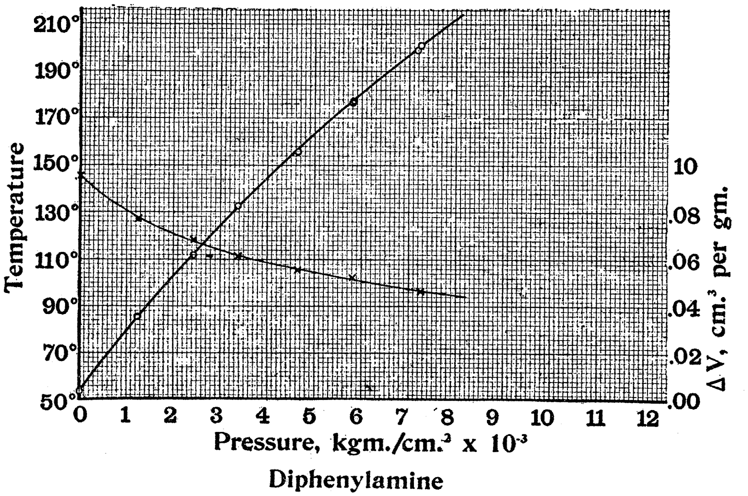


Fig. 15.

Diphenylamine. The freezing curve and the change of volume curve. The observed freezing temperatures are shown by the circles, and the observed changes of volume by the crosses.

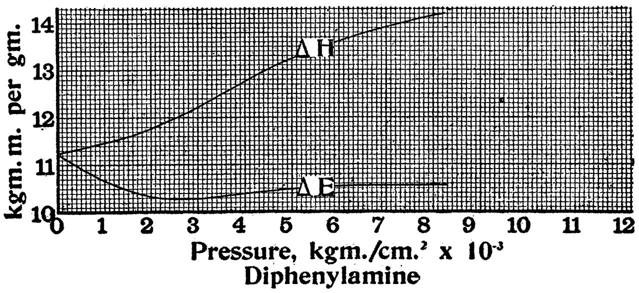


Fig. 16.

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

TABLE VII.

Diphenylamine.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	54°.0	0.0958	11.24	11.24
1,000	79 .1	807	11.47	10.67
2,000	103 .0	708	11.78	10.33
3,000	124 .7	638	12.23	10.29
4,000	144 .9	586	12.77	10.40
5,000	163 .6	541	13.25	10.49
6,000	180 .9	504	13.63	10.54
7,000	197 .3	472	13.92	10.55
8,000	212 .9	448	14.18	10.57

There are the following data for comparison at atmospheric pressure. For the melting point Heydweiller[43] gives 52.6°, Stillman and Swain[44] 54.0°, and Block[45] 53.4°. No direct determination on the purified substance was made in this experiment, but the crystallization from the original impure diphenylamine took place in the thermostat at 53.5°, so that the melting point of the finally purified substance must have been somewhat higher. For the latent heat there are three values. 23.97 gm. cal. per gm. by Stillman and Swain[44], 25.3 by Battelli and Martinetti[46] (because of an obvious misprint this number is quoted in tables of constants as 21.3), and 26.3 by Bogojawlensky[47]. The corresponding values in kgm. m. are: 10.23, 10.79, and 11.18. The number found by computation from the present work was 11.24. Because of the somewhat wide variation of the values by different observers shown above no attempt was made to so adjust the initial slope as to bring this into agreement with the mean of the values above. For the change of volume Block[45] gives 0.0905 cm.^{3} per gm. The first determination of the present work gave a number somewhat higher than this, and the measurement was repeated for greater security. The two values found were 0.0960 and 0.0955, in rather good agreement. The mean of these two was used in the computations.

Tammann's[48] results to 3,000 kgm. are from 2° to 3° lower than those found here; this is probably in part due to impurity, as he himself recognizes that his material was somewhat impure. For the change of volume he gives one value at 455 kgm., 0.0838 cm.^{3} per gm., against 0.0880 found here. As usual Tammann represents his results to 3,000 by a parabolic formula, but in this case does not venture to guess from the constants of the formula what the maximum temperature may be.

At 25° and at 200° the pressure was raised to 12,000 kgm., but no new solid modification was found.

This completes the presentation of data for those substances for which only one solid modification was found.

Benzol.—Kahlbaum's purest benzol was purified by distillation, by crystallization, and be redistilling immediately before use. The original benzol, when tested with sulphuric acid, showed no thiophen, the most likely impurity. Four sets of observations were made on benzol. The first two were with the first piece of apparatus and include eight points; these two sets were both terminated by explosions. There was one obser-

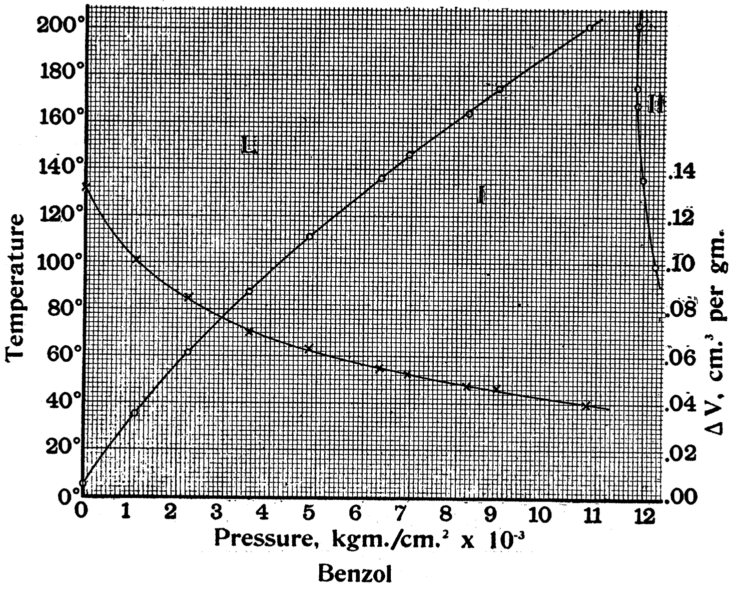


Fig. 17.

Benzol. The phase diagram, showing the equilibrium curves between the liquid and two varieties of the solid, and the change of volume between the liquid and solid *I*. The observed transition temperatures are shown by the circles, and the observed changes of volume by the crosses.

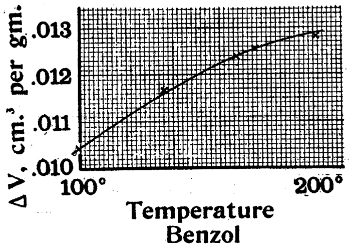


Fig. 18.

Benzol. The change of volume between solid *I* and *II* as a function of the temperature. The curve of transition between these two solids runs so nearly at constant pressure that it would not have been feasible to plot the change of volume as a function of the pressure.

vation at low pressure, and finally eight observations with the new apparatus. The experimental results are shown in Figs. 17 and 18 and the computed values for latent heat and change of internal energy in Figs. 19 and 20. The numerical values are given in Table VIII.

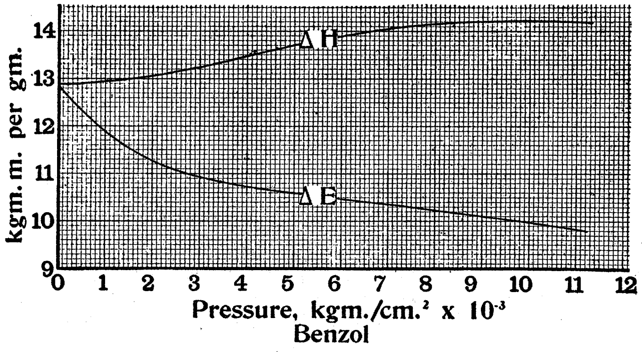


Fig. 19.

Benzol. The computed value of the latent heat and the change of internal energy when the liquid melts to the solid *I*.

TABLE VIII.

Benzol.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	5°.4	0.1317	12.88	12.88
1,000	32 .5	1026	12.94	11.89
2,000	56 .5	872	13.06	11.27
3,000	77 .7	759	13.24	10.93
4,000	96 .6	675	13.47	10.72
5,000	114 .6	614	13.70	10.60
6,000	131 .2	564	13.90	10.47
7,000	147 .2	522	14.05	10.36
8,000	162 .2	485	14.15	10.23
9,000	176 .7	451	14.20	10.10
10,000	190 .5	422	14.21	9.97
11,000	204 .2	394	14.20	9.82

I–II.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
12,260	100°	0.01048	−3.7	−16.6
12,080	120	1110	−3.4	−16.9
11,950	140	1168	−3.0	−16.8
11,860	160	1219	−2.0	−16.5
11,810	180	1262	−0.5	−15.5
11,840	200	1281	1.4	−13.8

Benzol has a second modification of the solid, stable at the very highest pressures reached here. In fact, the transformation line so nearly marks out the arbitrary limit of pressure that had been set for this work that the discovery of the modification can be regarded only as a piece of good fortune. The transformation curve runs nearly vertically (showing low latent heat), convex toward the temperature axis. This seems to be the first example of a curve of this type; the other nearly vertical transformation curves, such as those between the different varieties of ice or the two kinds of phenol,[49] are concave toward the temperature axis. The fact that a transformation between two solids shows such a distinct curvature at so high a pressure seems a bit surprising. It seems natural to think that the properties of a solid at high pressure would vary nearly linearly with temperature and pressure; under these conditions the transformation line would be nearly straight. In fact, it is in any event rather surprising to find a vertical transformation curve, because this means that one solid changes into another of smaller volume with increase of internal energy, and that almost all the work done by the external pressure is stored up within the substance. The internal forces would seem to have become forces of repulsion instead of forces of attraction. It may be that the increased temperature energy of the molecules, corresponding to a greater number of degrees of freedom in the new modification, may account for the absorption of energy. But this seems unlikely, because the indications are that at atmospheric pressure benzol is entirely normal, that is, entirely dissociated into single molecules. In the later part of this paper a possible explanation is given of this increase of energy.

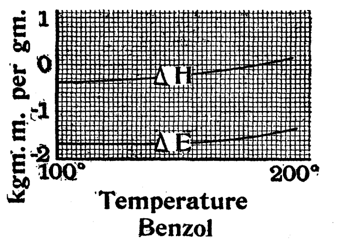


Fig. 20.

Benzol. The computed values of the latent heat and the change of internal energy when the solid *I* changes to the solid *II*, as a function of the temperature of transition. Observe that the internal energy of the form with the smaller volume is greater.

The reaction velocity of the two solid forms shows the same rapid variation with temperature that has been found for the modifications of ice. At the highest temperature, 201.6°, the reaction runs almost immediately, while at the lowest temperature, 99°, the reaction runs so slowly that it was not feasible to wait for complete equilibrium, but the point was approximated to from the two sides. The difference of the two pressures reached from above and below was 100 kgm. The slowness of the reaction increases so rapidly with decreasing temperature that it was not feasible to try for points below 99°, especially since the pressure rises more and more rapidly with falling temperature. Along with the slow reaction velocity at low temperatures goes the possibility of considerably passing over the transformation line without the reaction running. Within the pressure limits set here it was not possible to obtain the second modification at 99°; temperature had to be raised to 135° before it appeared, and the temperature was then lowered to 99° and the readings taken.

At 25°, pressure was raised to 12,500 kgm., but no other modification was found.

The triple point between the two solids and the liquid would apparently lie at about 216° and 12,000 kgm. The temperature was too high above the limit set to make it seem worth while to take the risk of reaching it. At the triple point the transformation line between the two solids has reversed its slope of the lower temperatures, so that pressure and temperature rise together.

There are a large number of data for comparison at atmospheric pressure, inasmuch as benzol has been a favorite substance for investigation because of the comparative ease of obtaining it pure. For the melting temperature we have 5.43° by Demerliac[50], 5.35° by Heydweiller,[43] 5.43° by Ferche,[51] 5.44° by Meyer,[39] and 5.42° by Lachowicz,[52]. The value found here by extrapolation from the determination of ΔV at 60 kgm. was 5.43°. For the latent heat we have 30.38 gm. cal. per gm. by Demerliac,[50] 29.43 by Pickering,[53] 30.18 by Ferche,[51] 29.09 by Pettersson and Widman,[54] 30.39 by Meyer,[39] 30.08 by Fischer,[55] and 30.6 to 31.0 by Bogojawlensky[56]. The corresponding values in kgm. m. are: 12.96, 12.55, 12.87, 12.41, 12.96, 12.83, and 13.05 to 13.22. The value given by these data from the uncorrected initial slope was 12.33. The initial slope was so corrected as to bring the latent heat to 12.88. For the change of volume there are the values 0.1304 cm.^{3} per gm. by Heydweiller,[43] 0.1316 by Ferche,[51] and 0.1333 by Meyer[39]. The result found here was 0.1316, and is in unusually good agreement with the mean of these three.

Tammann's,[57] results up to 3,000 kgm. are considerably lower than those found here; 4.5° lower at 3,000 and 3° lower at 2,000. The discrepancy is not to be entirely explained by impurity.

Tammann as usual fits a parabolic curve to his results. The maximum of the parabola would lie at about 7,100 kgm., although Tammann does not explicitly predict this as the pressure of the maximum point. The data here reach to 12,000 with no tendency to a maximum.

Benzol is one of the few substances for which Tammann attempted measurements of the change of volume over his entire pressure range of

3,000 kgm. His results above 1,500 are considerably lower than those found here, doubtless due to leak around the piston, while his results below 1,500, although showing considerable irregularity, agree with the present ones within the limits of error.

Carbon Tetrachloride.—This was obtained from Eimer and Amend, and was purified by a double fractional distillation. The second distillate showed a constant boiling point. Observations were made in three series; the first with the original apparatus to 183° includes seven points, the second, one point at low pressure, and the third nineteen points with the final high pressure apparatus. The experimental points are shown in Figs. 21 and 22, and the computed values of latent heat and internal energy in Fig. 23. The numerical values are given in Table IX.

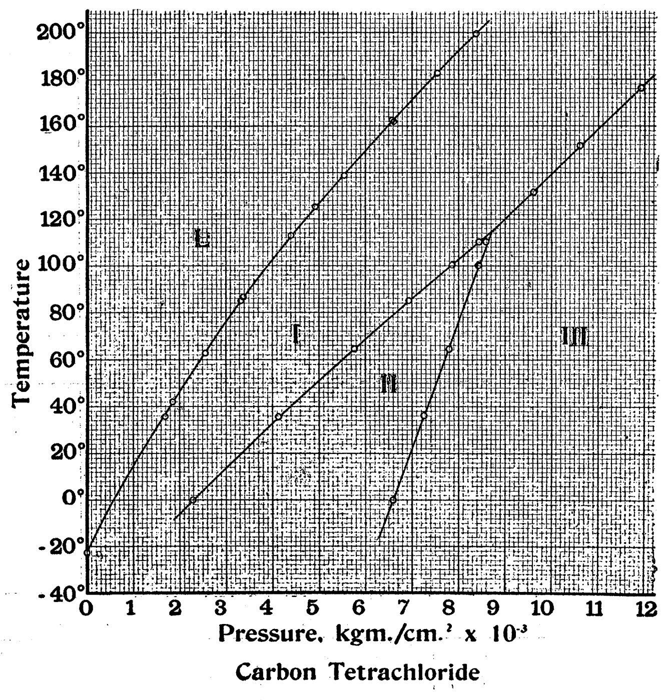


Fig. 21.

Carbon Tetrachloride. The phase diagram of the liquid and three solid forms. The observed transition temperatures are shown by the circles.

Three solid modifications of CCl_4 were found, two of them not known before. This was the first of the four substances studied here for which more than one solid form was found, and the discovery of this was by accident. At 35°, when the experiment was performed for the third time with the high pressure apparatus, pressure was pushed several thousand kilograms beyond the freezing pressure to ensure complete freezing, because the curve for the change of volume liquid-solid had been showing some irregularities. In this way the second modification was found. The third modification was found while working on the transformation curve *I–II*. The first data in which *III* appeared were puzzling until the existence of the new phase had been made certain, because by chance the first readings were taken at almost exactly the temperature of the triple point.

Table IX.

Carbon Tetrachloride.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
		Liquid—I.		
1	−22°.6	0.02580	1.67	1.67
1,000	14 .2	2006	1.72	1.50
2,000	45 .9	1653	1.77	1.41
3,000	75 .8	1401	1.78	1.34
4,000	102 .7	1197	1.76	1.27
5,000	126 .8	1019	1.72	1.20
6,000	149 .5	862	1.65	1.13
7,000	171 .0	730	1.56	1.04
8,000	192 .1	622	1.46	0.95
9,000	211 .9	538	1.37	0.88
		I.–II.		
2,000	− 5°.9	0.02429	3.17	2.68
3,000	13 .8	2343	3.43	2.72
4,000	32 .8	2246	3.68	2.76
5,000	51 .2	2147	3.87	2.78
6,000	68 .6	2042	4.02	2.79
7,000	86 .0	1929	4.12	2.77
8,000	102 .8	1816	4.16	2.71
		I.–III.		
9,000	120°.0	0.02259	4.60	2.55
10,000	139 .4	2229	4.75	2.52
11,000	158 .9	2187	4.87	2.47
12,000	178 .4	2132	4.94	2.39
		II.–III.		
6,500	− 4°.9	0.00555	0.27	−0.09
7,000	21 .8	562	0.30	−0.09
7,500	48 .5	562	0.33	−0.08
8,000	75 .2	555	0.36	−0.08
8,500	101 .9	543	0.38	−0.08

There are no special peculiarities shown by the reactions between the different solid forms. CCl_4 proved itself throughout a particularly pleasant substance to work with because of the sharpness of freezing, and of the speed of reaction, both between solid and liquid and between the two solid phases. We are by this time accustomed to high reaction velocity at high pressure between two solid forms, but in all previous cases the high velocity has been associated with very small latent heat, and the transformation curve has been nearly vertical. In the case

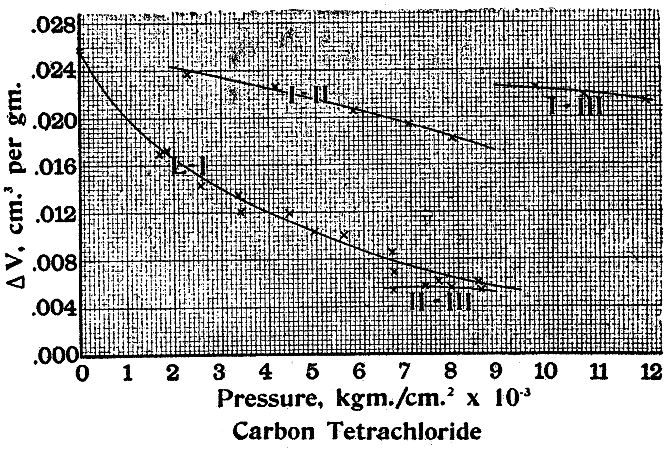


Fig. 22.

Carbon Tetrachloride. The change of volume curves for the liquid and the three solid modifications. The observed values are shown by the crosses.

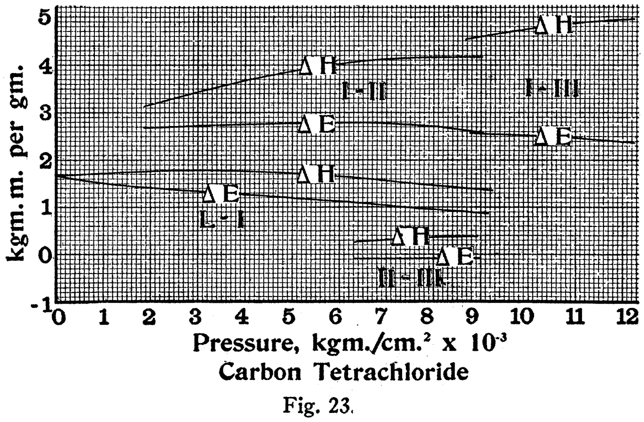


Fig. 23.

Carbon Tetrachloride. The computed values for the latent heat and the change of internal energy for the various transitions between the liquid and the three solid forms.

of these new modifications of CCl_4 the reaction between solids is noticeably rapid, much more rapid than between solid and liquid, but nevertheless does not approach the explosive rapidity that we have found previously. The reaction velocity between *II* and *III* is notably less than that between *I* and *II* or between *I* and *III*. Evidently the fact that there is here considerable heat of reaction is sufficient to prevent the reaction from becoming explosive, because time must elapse for the heat of reaction to be conducted away. But the converse, namely that explosive rapidity is brought about by zero heat of reaction, is not true, as is shown by the enormous slowing down of an explosive reaction by lowering the temperature a few degrees. The reaction velocity between these modifications of CCl_4 remained sensibly independent of temperature over the extent of the transformation curve investigated here. This is contrary to the behavior of those solids which show explosive velocity. This suggests, as will also be suggested by the behavior of o-kresol, that the explosive rapidity of reaction between two solids is something that is essentially brought about by the nearness of the liquid phase; we never find it except in the neighborhood of a triple point with a liquid.

It was found possible to superheat *III* with respect to *II*; in this respect, therefore, two crystalline phases are essentially different from a liquid and a solid. Previous examples of this are not common. But no case was found of the superheating of either *II* or *III* with respect to *I*.

The phase diagram of CCl_4 is different from that of most other substances with which we are familiar in that the various reactions from one solid to another go on with no apparent relation to the liquid. It is usual for the new solid form to replace the original solid at high pressures, forming a new equilibrium with the liquid, so that the new solid has the appearance of having been made necessary in some way by new conditions in the liquid. But in the case of CCl_4 it is quite different; it is evident that if there is a triple point between the liquid and *I* and *III* it is probably at pressures at least twice as high as those reached here. The necessity for the new solid forms seems to have been here brought about almost solely by the action of forces operative within the crystalline phase, independent of the liquid.

It should be possible to realize the phase *II* at atmospheric pressure at low enough temperatures. Such an attempt was made by cooling CCl_4 in carbon dioxide snow to − 80°, but the depression of temperature was not sufficient to overcome the viscous resistance to the reaction.

The two forms found here at high pressures seem to be entirely new, but there are hints by Tammann and Amagat, who have both worked with CCl_4 under pressure that there are other solid forms. Amagat[58] used an apparatus with glass windows, and was able to obtain photographs of the CCl_4 crystallizing under pressure. He found crystals of different shapes, and assumed the existence of allotropic forms. But such an inference, without careful measurements of the crystalline angles, is dangerous, as shown by the varied appearance of snow flakes, for example. Amagat certainly did not obtain a modification of CCl_4 with a freezing point different from that of the ordinary variety, which makes it exceedingly probable that his crystals of different shapes were only crystals of the same crystalline system, but of different crystalline habit from the common form. Tammann's[59] evidence for other forms is also by no means convincing, being chiefly certain inconsistencies that he found in his determinations of ΔV. He was not able to find two distinct melting temperatures at the same pressure, as would be expected if he really had two distinct forms of the solid, but apparently he found exactly the same equilibrium temperature and pressure for two supposedly different forms. Tammann's inclination to explain these discrepancies by new allotropic modifications apparently is a bias left from his interpretation of some erroneous results that he had obtained in 1898.[60] His original experiment was performed on a very impure specimen of CCl_4 with a melting point 3° below that used here. An error in recording the temperature had led Tammann to think that his specimen was unusually pure. Irregular results were obtained with this impure liquid that were explained by the existence of three polymorphic forms. But the properties of these supposed modifications were so remarkable, such as ability to exist indefinitely in contact with the liquid without the reaction running, that Tammann reëxamined the question, and in "Kristallieren und Schmelzen" retracted his former results. He still explained the outstanding irregularities, however, by the existence of two polymorphic forms. But there now seems to be some doubt in Tammann's own mind as to the reality of the existence of his second modification, for in a recent paper[61] he marks it with an interrogation point.

There are few other data for comparison at atmospheric pressure. For the melting point there is a value $-24°$ by Niescher,[34] and $-22.6°$ by Bugarszky.[62] Tammann's specimen melted at $-22.96°$. The specimen used in this work melted at $-22.6°$, determined by extrapolation from data at 60 kgm. There seems to be only one value for the latent heat, 4.2 gm. cal. per gm. or 1.79 kgm. m., determined by Niescher[34] by an indirect method. The value computed from these data is 1.67, in close enough agreement with Niescher's somewhat doubtful value to make unnecessary any adjustment of the initial slope of the melting curve. The exceptionally small value of the latent heat should be noticed. No other values of ΔV at atmospheric pressure are known; 0.0258 cm.^{3} per gm. was found here.

As might be expected from the probable impurity of Tammann's[63] sample, his results up to 3,000 kgm. are considerably lower than those found here, 6.6° lower at 3,000, 5.4° lower at 2,000, and 3.5° lower at 1,000. The change of volume was measured by Tammann at three points. The change found at 700 and at 2,000 for his supposedly second modification is not in violent disagreement with the values found here, but his value at 700 for the so-called first modification is much too high.

O-Kresol.—This substance was Kahlbaum's purest, supplied by Eimer and Amend. It was further purified by twice crystallizing at constant temperature in the thermostat. The crystals were obtained in the form of large transparent needles. The original substance came in the form of a powder of about the same coarseness as granulated sugar, and was somewhat impure, as shown by the yellow color of the melt. Three series of observations were made; the first with the original apparatus comprises 15 points up to 7,500 kgm., the second one point at low pressures with the low pressure apparatus, and the third nine points with the final apparatus. The experimental results are shown in Fig. 24, and the computed latent heat and change of internal energy in Fig. 25. The numerical values are given in Table X.

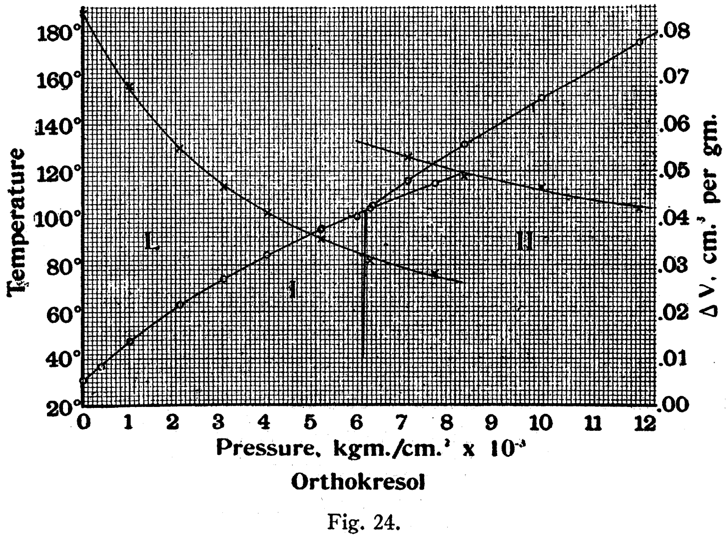


Fig. 24.

Orthokresol. The phase diagram for the liquid and two forms of the solid, and the change of volume curves between the liquid and the two solid forms. It was not possible to find experimentally values for the change of volume between the two solids, because of the extreme slowness of the reaction. The observed transition temperatures are shown by the circles and the observed changes of volume by the crosses.

Table X.

Orthokresol.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	30°.8	0.0838	14.38	14.38
1,000	47 .4	678	14.10	13.41
2,000	61 .9	557	14.10	13.00
3,000	74 .2	471	14.28	12.94
4,000	81 .8	406	14.50	12.88
5,000	94 .5	359	14.61	12.80
6,000	102 .9	319	14.60	12.70
7,000	110 .8	288	14.61	12.61
8,000	118 .1	264	14.72	12.59
		Liquid—II.		
6,000	102°.7	0.0559	14.88	11.50
7,000	116 .4	529	15.57	11.85
8,000	129 .3	499	16.08	12.07
9,000	141 .4	475	16.43	12.12
10,000	153 .7	454	16.73	12.14
11,000	164 .6	436	17.05	12.22
12,000	175 .9	422	17.42	12.33

O-kresol has two solid modifications. The second modification was not found during the first set of experiments, although two equilibrium points between the liquid and solid *I* were found in the domain of stability of solid *II*. The new modification requires a good deal of urging to appear. At 80°, pressure on solid *I* was raised to 12,500 kgm., 6,500

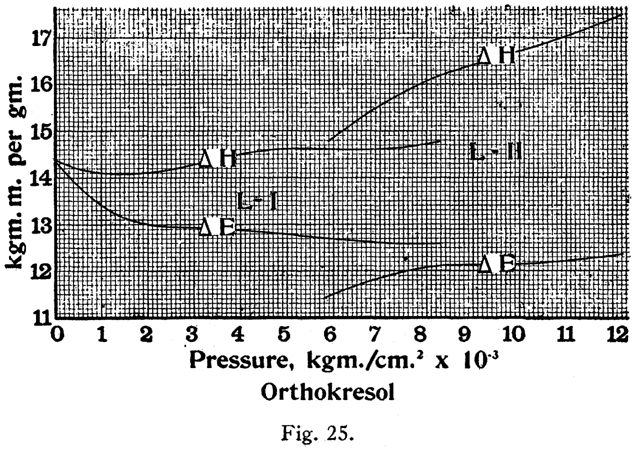


Fig. 25.

Orthokresol. The computed values for the latent heat and the change of internal energy when the liquid melts to one or the other of the two solid forms.

kgm. beyond the transformation point, without the appearance of *II*, which was obtained only by raising the temperature at 12,500 kgm. to 195° and waiting for some little time. All of the reactions with o-kresol were abnormally slow, both between the liquid and either modification of the solid or between the two solids. A high degree of subcooling of the liquid was also possible. On one occasion pressure on the liquid at 130° was raised to 12,500 kgm., 4,500 kgm. beyond the freezing pressure, and 50° below the freezing temperature, without solidification. The temperature had to be lowered at this pressure to induce solidification. The sluggishness of the reaction between the two solids was so great that only one point could be found on the transformation curve *I–II*. At 95.4°, 7.8° below the triple point, the reaction was so slow that absolutely no progress of the reaction within a region 500 kgm. wide could be detected in four hours, while 5.4° higher, 2.4° below the triple point, the reaction velocity had become great enough so that it was possible to shut the equilibrium point in between two values differing by only 70 kgm. in the course of an hour. This is the most striking example yet found of the enormous variation of reaction velocity between two solids as the triple point with the liquid is approached. The sluggishness of the solid reaction is not to be explained by the heat of reaction, because the transformation line between the two solids is almost vertical and the latent heat abnormally low.

During the experiment, pressure was raised to 12,500 at 25° without the appearance of any other solid form.

The two points found in the first series of observations in the domain of stability of *II* are interesting as the second example we have of the possibility of prolonging a transformation curve between solid and liquid to higher temperatures into the region of another solid. The other example is the prolongation of the ice *III*—water curve into the domain of ice *V*, but the effect was not nearly so persistent there as here; in fact it was obtained only once, by accident. On the other hand, several cases are known in which it has *not* been found possible to so prolong the curve to higher temperatures into an unstable region.

The following seem to be the best values at the triple point: pressure, 6,100 kgm. and temperature, 103.2°; $\Delta V(L\text{–}I) = 0.0317$; $\Delta V(I\text{–}II) = 0.0238$, $\Delta V(I\text{–}II) = 0.0555$ cm.³ per gm., and $(d\tau/dp)_{I\text{–}II} = 0.700$. That is, the transformation curve *I–II* rises 700° for an increase of pressure of 1,000 kgm.

O-kresol is a substance for which Tammann[64] claims two solid modifications. His solid form has no relation with that found here, but entirely disappears beyond 640 kgm. and 38.8°, and at atmospheric pressure at temperatures below 22.5°. (See Fig. 26 for the domain of existence of this supposed modification.) This means that if liquid o-kresol is cooled at atmospheric pressure, it solidifies at about 30° to a solid which has a very limited region of stability, passing over at 22.5° to the form stable throughout the most of the phase diagram. Tammann gives the coördinates of five points on the transformation curve between the two solid forms. However, he apparently did not measure the magnitude of the change of volume between the two phases, and gives no hint as to what order of magnitude to expect, as he might if the reaction had been clean cut. Most careful search was made during this present investigation for such another modification, but none was found. Two different methods were employed in the search. First, the equilibrium pressure and temperature was determined at eight points at pressures both above and below the supposed triple point, but no discontinuity in the curve could be found. These points are shown in Fig. 26 together with the points of Tammann. Secondly, measurements were made on the solid at 60 kgm. from 15° to the melting point at about 31°. Absolutely no discontinuity was found on passing over the supposed transformation point at 22.5°. The evidence seems unquestionable that at least in the present work there was only one low pressure variety present. If there are really two low pressure varieties, then the measurements given here must have been on the second of Tammann's varieties (that is, the low temperature variety). But this possibility is ruled out by the high melting point of the modification used here. The melting point of Tammann's variety should be about 26°.

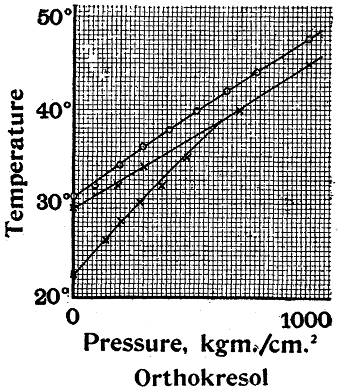


Fig. 26.

Orthokresol. Equilibrium temperatures at low pessures (circles), together with Tammann's points (crosses). It will be noticed that in this work no trace could be found of a second solid form at low pressures.

There seems little room for doubt that Tammann's two varieties are only the apparent effect of impurities. The melting point of his o-kresol was about 1.2° lower than that used here. One is the more inclined to accept this explanation since Tammann has himself retracted announcements of new modifications which he later found to be due to impurities. Examples of this are CCl_4, carbon dioxide, æthylendibromid, p-xylol, and trimethylcarbinol. At the same time, it must be admitted that the evidence against there being two varieties is not so absolutely conclusive as it has been in other instances. If there are two modifications at low pressures, they must be very much indeed alike.

There are practically no measurements at atmospheric pressure for comparison. The melting point has been determined to be 30° by Béhal and Valeur.[65] The directly measured melting point of the substance used here was 30.75° to 30.78°, showing that this sample was probably purer than any on which measurements have been previoulsy made. There seem to be no measurements of the change of volume or of the latent heat.

In view of the impurity of Tammann's sample we should expect his values to be considerably lower than those found here. His results are about 3.5° low at 2,500 kgm. He predicts from his data a maximum melting point at 4,700 kgm. The data here show that this temperature may be considerably exceeded with no suggestion of a maximum before the second phase appears.

Phosphorus.—The purest commercial stick phosphorus (yellow) from Eimer and Amend was used. For the first experiment this was further purified by slow crystallization in the thermostat, giving colorless and transparant crystalline plates 2 cm. across and perhaps 8 mm. thick. Subsequent work, however, showed that this careful purification is not

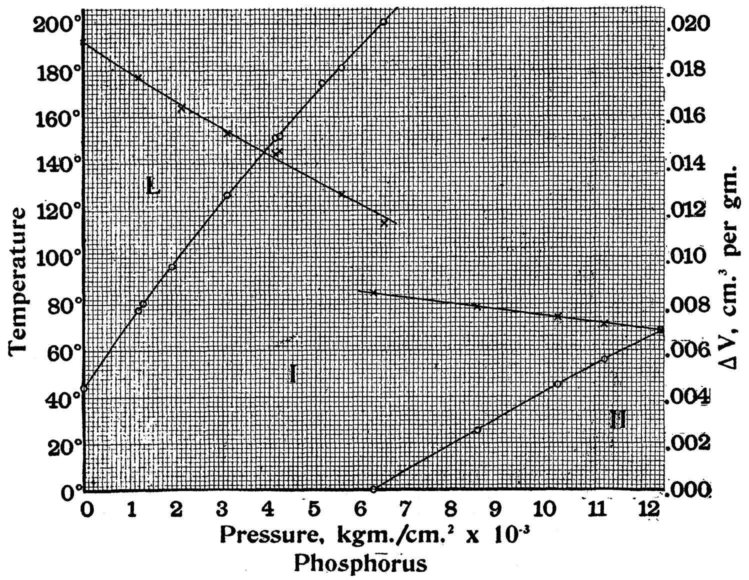


Fig. 27.

Phosphorus. The phase diagram and the change of volume curves for the liquid and ordinary solid yellow phosphorus, and for the yellow and another variety of the solid. The observed transition temperatures are shown by circles, and the observed changes of volume by crosses.

necessary; the commercial material without further treatment is good enough. Four sets of readings were made; the first comprises six observations with the original apparatus, the second one observation at low pressure, the third eight observations with the final apparatus, and the fourth was a redetermination of one slightly doubtful point of the previous work. The experimental results are shown in Fig. 27 and the computed latent heat and the change of internal energy in Fig. 28. The numerical values are given in Table XI.

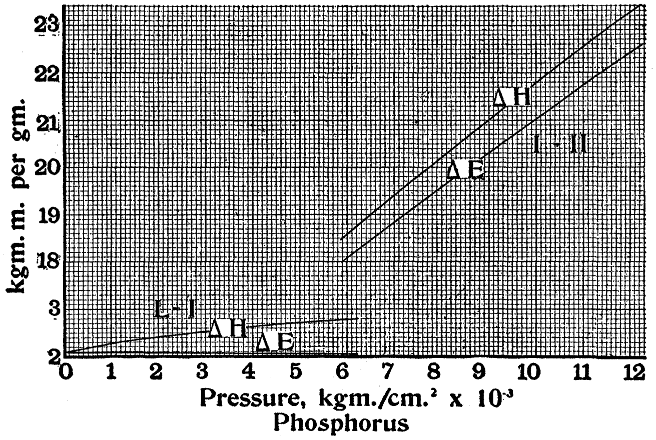


Fig. 28.

Phosphorus. The computed values for the latent heat and the change of internal energy between the liquid and the two forms of the solid.

During the third series of observations the second modification of the solid was found, and the equilibrium curve and the changes of volume determined. This second form is of interest because yellow phosphorus is itself unstable with respect to red, so that we have here a reversible reaction between two unstable varieties. There is no possibility of the new modification being the ordinary red phosphorus, because the change of volume is not nearly great enough, and all indications point to the reversible change between yellow and red taking place only at high temperatures, if indeed it takes place at all. The reaction velocity between these two solid forms was slower than that between any other two solid forms studied, except between the two varieties of o-kresol. The reaction is unlike that of o-kresol, however, in that it will run to completion if enough time is allowed, so that it was possible to reach the same equilibrium pressures from above and below. But this takes many hours. To expedite matters, the equilibrium pressure was found here by observing the progress of the reaction with time from above and below during melting or freezing, and extrapolating for the equilibrium pressure. In very few cases did the possible error of such a proceeding amount to as much as 10 kgm. There is no marked change in reaction velocity from one end to the other of the equilibrium curve.

TABLE XI.

Phosphorus.

Liquid—I.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
1	44°.2	0.01927	2.09	2.09
1,000	72 .7	1792	2.27	2.08
2,000	99 .3	1667	2.41	2.07
3,000	124 .4	1549	2.52	2.07
4,000	148 .2	1436	2.63	2.06
5,000	170 .5	1326	2.72	2.05
6,000	191 .9	1218	2.78	2.04

I.–II.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.	Latent Heat, kgm. m./gm.	Change of Energy, kgm. m./gm.
6,000	−2°.4	0.00851	18.61	18.10
7,000	9 .6	825	19.43	18.86
8,000	21 .4	799	20.24	19.61
9,000	32 .7	772	21.04	20.34
10,000	43 .7	746	21.82	21.06
11,000	54 .4	720	22.58	21.77
12,000	64 .4	694	23.29	22.44

Interesting effects were also found at the higher temperatures of the equilibrium curve between solid and liquid, particularly during the first series of readings. Perfectly satisfactory readings had been made up to 150°, the freezing being as sharp as for metals, and some preliminary work had been done at 175° with every promise of sharp freezing here also, when suddenly the character of the melting changed completely to that of an impure liquid, the freezing taking place over a long interval of pressure, and varying with the quantity of liquid present. When the apparatus was taken apart, the phosphorus was found to be of a brilliant scarlet color, which has survived the melting of the phosphorus and been stable for six months since. The explanation that suggested itself was that at the high temperature some of the yellow phosphorus had been transformed into red, which is presumably the stable form, and had dissolved in the yellow. For some unknown reason the reaction did not run further. The amount transformed to red, if this is the explanation, must have been slight, because the change of volume was too small to be detected with certainty. Of course it was natural to fear that the same effect would make it impossible to reach the higher temperatures on the repetition of the experiment. However, the effect did not show itself again, and it was found possible to make satisfactory readings of the change of volume up to 200° with only slightly greater rounding of the corners than found at the lower temperature.

Nevertheless, it was felt that the transformation to red phosphorus might be possible, and in searching for this the most interesting fact of all connected with phosphorus was discovered. At 150° the pressure was raised to 12,000 without effect, and again at 200° to 12,000 without immediate effect. Some irregularity in the working of the apparatus made it desirable to keep the pressure at the maximum longer than would have been done naturally. After about fifteen minutes there was a sudden drop of pressure to about 4,000 kgm., a truly remarkable drop, for which the only explanation seemed to be a leak. But no leak could be found. 4,000 kgm., it will be observed, is considerably below the melting pressure of yellow phosphorus at 200°, so that if there were a leak the phosphorus must have melted. Pressure was now raised to 9,500 kgm. (the limit set by the stroke of the piston), with no sign of the liquid freezing to the solid again, as it almost certainly would under a super-pressure of 3,000 kgm., and then the pressure was lowered again to about 1,000 kgm. without any transformation taking place. The only apparent explanation was that red phosphorus had been formed.

On taking the apparatus apart the next morning it was found that the phosphorus had been transformed indeed, but not to the familiar red form, but to another modification that is apparently quite new. The new form is grayish black like graphite, breaks with a similar greasy looking fracture, and will mark on paper. It is stable in the air although slightly deliquescent, is ignited with difficulty by a match, and cannot be exploded by a blow from a hammer, as red phosphorus can. It is a conductor of electricity and a rectifier. The most definite characteristic is its high density, 2.69 against 2.34 for the red variety, and 1.9 for the yellow. The experiment was repeated twice, successfully each time. Once it was necessary to go to nearly 13,000 kgm. to start the transformation. The time necessary to force the reaction to start may also vary considerably. An attempt to similarly transform the commercial powdered red phosphorus into the new variety by subjecting it to 200° and 13,000 kgm. for over half an hour was without result. If the gray phosphorus is sealed into a heavy glass capillary and heated, it sublimes and condenses to yellow and red phosphorus in the colder parts of the tube, exactly as red phosphorus powder does under the same circumstances.

The discovery of this new modification reopens the whole puzzling question of the relationship of the various phosphorus modifications. It makes very improbable the correctness of Roozeboom's suggestions as to the relationship of the red and yellow forms. Probably, judging from the greater density, gray phosphorus is more stable than either red or yellow at atmospheric temperatures. The problem is one that requires further experimental investigation, but it is not necessary to investigate it further for the purposes of this paper, since we are here concerned only with reversible reactions. We may emphasize, however, that this is apparently the first instance of a permanent transformation for which a high pressure is essential. For at low pressures this new modification is not produced by the action of high temperatures alone, even up to a red heat.

Returning now to the ordinary yellow phosphorus, there are a number of data for comparison at atmospheric pressure. For the melting point we have 44.10° by Hulett,[66] 44.2° by Person,[67] 44.4° by Pisati and de Franchis,[68] and 44.27° by Lussana.[69] The melting point of the phosphorus used in this experiment was not directly determined. The rough value found by extrapolation from the determination of ΔV at 60 kgm. was 43.8°. For the latent heat there are apparently only two determinations: 5.05 gm. cal. per gm. by Pettersson,[70] and 4.71 by Person [67] (these values in kgm. m. are 2.15 and 2.01). Tammann [71] quotes Person's value as 5.03; the authority for this other number is not clear. The value computed from the present observations was 2.09, almost exactly the mean of Pettersson and Person. Hence no adjustment of the initial slope was necessary. For ΔV we have 0.0190 cm.^{3} per gm. by Hess,[72] 0.01894 by Kopp,[73] 0.0179 by Damien,[74] 0.01939 by Pisati and de Franchis,[68] and 0.0191 by Leduc.[75] The value found here was 0.01926.

Tammann's [76] results are about 6° lower than the present ones at 3,000 kgm. and about 2.5° lower at 2,000. His results show a sudden change in the direction of the melting curve above 2,000; below 2,000 his curve is nearly linear. The explanation is doubtless to be found in an error in Tammann's high pressure measurements, which we have seen on other grounds to be probably the case.

Besides the data already given, the attempt was made to find the melting curve of two other substances, which, however, proved to be too impure. Nevertheless, some fragmentary data were obtained which may be worth giving.

Monochloracetic Acid.—This was purified by slow crystallization, and was apparently in a state of sufficient purity initially. No trouble was found in making the low pressure measurement, for which it was enclosed in a glass bulb. At the high pressures it was necessary to enclose it in a steel bulb; and under pressure the acid attacks the steel slowly, becoming after several hours' use too impure to give results worth while. The results that were obtained are shown in Table XII. The corners were very much rounded by the impurity in obtaining the value at 139°. There is no reason, however, why the value at atmospheric pressure should not be as good as the values found for any of the other substances.

Table XII.

Approximate Values for Monochloracetic Acid.

Pressure.	Temperature.	ΔV, cm.^{3}/gm.
1	62°.53	.1070
7,540	151°.7	.0414
9,320	164°.8	.0281
6,350	139°.4 ±	.....

Acetone.—Another attempt was made with this, the purest acetone "from Bisulfite" of Kahlbaum being twice distilled. But it was still too impure, and no better results could be obtained than were obtained previously in the work on the thermal properties of twelve liquids.[17] At 40°, the freezing pressure is in the neighborhood of 10,000 kgm.

Discussion.

Shape of Experimental Curves.—Before proceeding to the main question as to the probable character of the melting curve, it will pay us to examine the results for the different substances to find what characteristics they have in common.

The melting curve itself first concerns us. One universal feature strikes us: that the concave side is always toward the pressure axis. This is true for the liquid-vapor transition as well as for liquid-solid. We should not expect, therefore, that the direction of curvature of the melting curve would of itself give us much information about the particular mechanics of the change from the liquid to the solid.

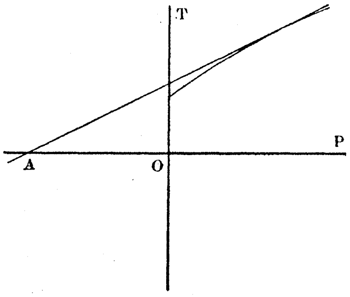


Fig. 29.

Diagram to show the significance of a freezing curve concave toward the pressure axis.

A geometrical interpretation of the thermodynamic quantities involved throws some light on the question, and suggests the reason for the universal direction of curvature. From Fig. 29 it is obvious that the intercept of the tangent on the negative pressure axis (AO) will increase with increasing pressure if the curve is concave downwards. And conversely, if the curve is convex downwards, the intercept AO will decrease with increasing pressure. Now AO has a simple thermodynamic interpretation. It is at once obvious that

$$AO = \tau \frac{dp}{d\tau} - p.$$

But

$$\Delta E = \Delta V \left(\tau \frac{dp}{d\tau} - p. \right).$$

That is, AO is the factor by which ΔV is multiplied to give the difference of energy between the two states. Now ΔE may be thought of as due to two things. In the first place, the internal forces do work as the molecules come closer together during change of state. And in the second place, the temperature energy of a liquid molecule may be different from that of a solid molecule, so that there may be an absorption or liberation of energy when change of state occurs. Let us for the moment consider the effect of only the first factor. As the molecules are brought closer together with increasing pressure, we should expect the intensity of the force of attraction between them to increase, so that the change of energy for a given decrease of volume would increase. That is, the factor by which we multiply the change of volume to obtain the change of energy would increase as the volume decreases, or as the pressure increases. Now we have just seen that this is equivalent to the melting curve being concave downwards, and this is actually what happens. The argument is not altered by considering the change of temperature energy, if we suppose, as does not seem unlikely, that passage from solid to liquid means an increase in the number of degrees of freedom per unit volume. If the change in the number of degrees of freedom does not decrease too rapidly with increasing temperature on the melting curve, then the temperature change of energy will increase with increasing temperature (increasing pressure) and the factor by which ΔV is to be multiplied to give the part of ΔE due to temperature effects will also increase, and the curve will be concave downwards for this reason also.

The direction of curvature of all the curves is just what we should expect on general reasoning, therefore, and cannot be used as evidence in support of any particular hypothesis.

The melting curves also all show a decreasing curvature with increasing pressure; at the higher pressures many of the curves have become nearly straight lines. This is also what we would be inclined to expect, since in general at high pressures physical properties vary more nearly linearly with pressure than at low pressures. But the curves given here do not reach to high enough pressures to justify speculation as to whether they would ultimately become asymptotic to a straight line either inclined or horizontal, or whether the curvature would continue, as in a logarithmic curve.

The curves for the change of volume also all have a common curvature, convexity toward the pressure axis. This is opposite to the curvature of the melting curves. The fact that all these curves are convex to the pressure axis constitutes the most important new evidence of this paper. Tammann's data were not accurate enough to justify him in assuming anything else than a linear relation, and there is little other experimental evidence on the point. The only other measurements are those previously made by the author[15] on water and mercury with apparatus like that used here. The evidence of water is not of much value at low pressures, because of abnormalities, but at high pressures, where all the evidence points to water becoming as normal as other liquids, there is a reversal in the direction of the ΔV curve, and it becomes convex to the pressure axis. The universal direction of curvature found here verifies most gratifyingly a prediction that was ventured in the paper on water; that the convex curvature would be found to be the normal curvature for all liquids. The only exception found so far is for mercury, which is concave up to 12,000 kgm. But the variation of ΔV for mercury over this range is very small (about 8 per cent.) in comparison with the variation found for other substances. The apparently abnormal behavior of mercury need not disturb us, therefore; there is chance enough for the curve to reverse its curvature at higher pressures. But the fact that mercury is exceptional makes it hazardous to extrapolate to find the point where ΔV might become zero, as van Laar[16] has done. He finds this pressure to be about 35,000 kgm.

It is not by any means impossible that the curvature shown by mercury is the normal curvature for all liquids at low pressures. The variation of ΔV with pressure is unusually slow for mercury; for most of the substances investigated here ΔV has decreased by more than 8 per cent. in less than the first thousand kilograms, that is, in the region not reached here by direct measurement. It is therefore possible that there may be a point of inflection on all the ΔV curves below 1,000 kgm. Special experiment would be necessary to show it.

The curves for latent heat and change of internal energy do not show a common curvature for all substances, but there are individual variations. But the fact is striking, as shown in Fig. 30, that there is on the whole comparatively little change with pressure. It would perhaps be fair to say that the general tendency is for the latent heat to increase with rising pressure, and for the change of energy to decrease. This agrees with Tammann, who found that the latent heat showed little tendency to change along the melting curve.

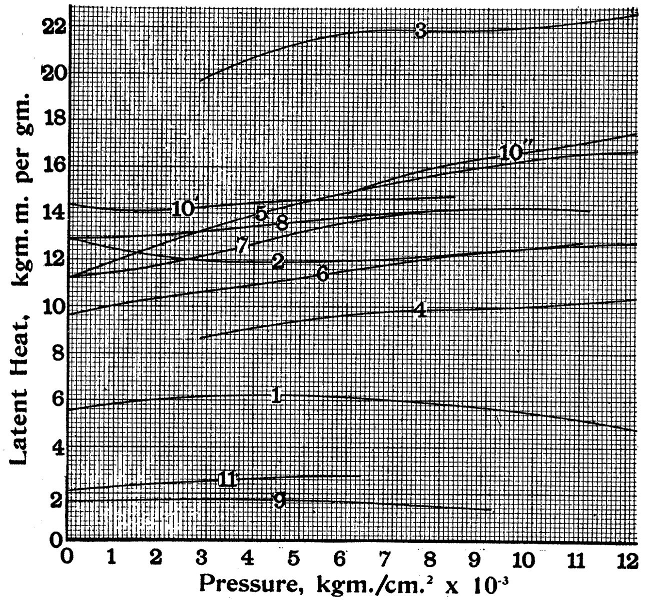


Fig. 30.

Collected curves for the latent heat between the liquid and the solid for the various substances experimented on in this paper.

The substances referred to by the numbers on the curves are as follows: *1*, potassium; *2*, sodium; *3*, carbon dioxide; *4*, chloroform; *5*, anilin; *6*, nitrobenzol; *7*, diphenylamine; *8*, benzol; *9*, carbon tetrachloride; *10′*, orthokresol (liquid to the first variety of the solid), *10″*, orthokresol (liquid to the second variety of the solid); *11*, phosphorus (the ordinary liquid to the ordinary yellow solid phosphorus).

Thermodynamics Cannot Determine Shape of Melting Curve.—Before applying the evidence of these results to discussing the shape of the melting curve, it will pay us to emphasize again that there is no purely thermodynamic evidence as to the probable shape of this curve; this must be entirely determined by the special mechanism involved in the change from a liquid to a crystal. It is easy to prove that no particular shape of the melting curve is made impossible by either the first or second laws of thermodynamics. It may also be proved that no restriction is placed by one fact of experience, which we have come to regard as a law, although it does not seem to be thermodynamically necessary. This is the more worth mentioning because Tammann's thermodynamics on this point seems to be faulty. It is our experience that in a great many cases when a change in a system is produced by an external agency there is an automatic reaction in the direction opposite to that of the applied force. Thus if we compress a substance by raising the pressure, and thus raise the temperature, as time passes the pressure will drop slightly as the substance regains the temperature of the surroundings. Or, if we suddenly stretch a wire and hold it stretched by a fixed amount, the force necessary will gradually become less in virtue of elastic after-effects. In the same way, if we suddenly compress a mixture of a solid and a liquid in equilibrium, and keep the mass as a whole adiabatic, we expect the increment of pressure will gradually drop as equilibrium is reëstablished between liquid and solid. Tammann[77] discusses this question, and concludes that if the adiabatic lines of solid and liquid are steeper than the melting curve, then the secondary pressure reaction will be a still further increase, instead of the decrease that we have come to expect. But this would be the case in the neighborhood of a maximum, where the curve is nearly horizontal. Tammann expected both of the following phenomena to be shown at high pressures; a maximum in the melting curve, and a secondary pressure increase following a primary increase, instead of the secondary decrease with which we are familiar. He states, however, that up to 3,000 kgm. he was never able to find such an increase. It may also be stated that such an effect was never found in the present work up to 12,000 kgm.

If Tammann's analysis were correct, we should have here a small piece of presumptive evidence from thermodynamic grounds alone making the maximum melting point improbable. But detailed analysis will show that Tammann's thermodynamics was much too off-hand and simple. The problem may be rigorously formulated as follows. Given a mixture of liquid and solid in equilibrium on the melting curve. Pressure is suddenly applied adiabatically. The temperature of both solid and liquid changes because of the compression, the change in the liquid being in general different from that in the solid. The mass as a whole is now kept adiabatic and at constant volume until internal equilibrium is restored. The process of restoration of equilibrium is irreversible. We require that during this process the entropy of the system shall increase (the second law), and that the pressure shall drop, but not below its initial value. The analysis is complicated, and will not be given in detail; merely the results will be stated. The second law will be satisfied if the condition

$$\left\{\frac{c_p}{\tau}\left(\frac{\partial v}{\partial p}\right)_\tau + \left(\frac{\partial v}{\partial \tau}\right)_p^2\right\}\left\{\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\left(\frac{\partial v}{\partial \tau}\right)_p\frac{d\tau}{dp} - \left(\frac{\partial v}{\partial p}\right)_\tau\right\} < 0$$

is satisfied by the liquid and the solid separately, where $d\tau/dp$ is the slope of the melting curve. Now the first factor is equal to $(\tau/c_p)(\partial v/\partial p)_s$ and is always negative, because c_p and τ must be positive, and $(\partial v/\partial p)_s$ is negative if the substance is stable. The condition requires, therefore, that the second factor shall be always positive. But this is true, for it may be shown by a differentiation that the minimum value of the factor is $-(\partial v/\partial p)_s$, which is intrinsically positive. This shows, therefore, that a mixture of a solid and a liquid together in equilibrium will always satisfy the second law, no matter what the shape of the melting curve, provided that both liquid and solid separately satisfy the conditions of internal stability.

Now the condition that the mixture of liquid and solid shall together be stable, that is, that the final pressure after the above operation shall be greater than the initial pressure, is:

$$\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\left(\frac{\partial v}{\partial \tau}\right)_p \frac{d\tau}{dp} - \left(\frac{\partial v}{\partial p}\right)_\tau > 0 \qquad \text{(A)}$$

which must hold for liquid and solid separately. But this is exactly the second factor above, which we have just proved to be always positive. The mixture of liquid and solid is stable, therefore, if the liquid and solid are stable separately.

Finally, the condition that the secondary pressure reaction shall be a decrease, and not an increase is that

$$\frac{c_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\left(\frac{\partial v}{\partial \tau}\right)_p \frac{d\tau}{dp} + \frac{\tau}{c_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2 > 0 \qquad \text{(B)}$$

shall hold for liquid and solid separately. Now the difference between (A) and (B) is $-(\partial v/\partial p)_\tau - (\tau/c_p)(\partial v/\partial \tau)_p^2$, which we have just seen is precisely the minimum value of (A). That is, in the most unfavorable case the value of (B) is zero, and in all other cases positive. The secondary pressure reaction, therefore, is never an increase, no matter what the shape of the melting curve, provided only that liquid and solid are each separately stable, as of course they must be. The condition, therefore, that our ordinary experience continue to be valid at high pressures imposes no condition of shape whatever on the melting curve.

Although we might find it difficult to give a rigorous proof, we conclude that the presumption at present is very great that thermodynamics alone cannot determine the shape of the melting curve. The question must be settled by experimental evidence in addition to pure thermodynamics.

We proceed to examine the bearing of the new experimental evidence presented above on the two theories in possession of the field.

As to a Critical Point.—It must be emphasized at the outset that our present knowledge of the atomic structure of liquids and solids is not sufficient to enable us to decide in the light of pure reason whether a critical point exists or not. Tammann has made this mistake. His argument against a critical point consists in saying that our conception of the atomic structure of crystals makes unthinkable a continuous transition from the chaos of the liquid to the orderly array of the solid. The answer to this is that many men have not found such a continuous passage unthinkable, men like Poynting, Planck, Ostwald, Weimarn, and van Laar. Van Laar in particular indicates a possible mechanism for such a continuous passage, and the author[78] has also made another suggestion to the same end. In our present state of ignorance we must be content, therefore, to find from experiment whether a critical point exists, and from this to reason back to a probable mechanism of solid and liquid.

The evidence of these experiments may be stated almost immediately. If there is to be a critical point, thermodynamics demands that the latent heat and the change of volume vanish together. But an examination of the curves shows no tendency toward any such effect; the change of volume decreases while the latent heat remains sensibly constant. What is more, the change of volume decreases in such a way that there is no necessity that it should ever vanish, and we have not even the first condition for a critical point satisfied, quite apart from any possible change in the behavior of the latent heat at pressures very much higher than those reached here. The hope left to van Laar by the previous data on mercury is taken away by these new data.

One must have been struck on reading the history of the subject to notice how the pressure at which a critical point was looked for was pushed higher and higher into the region of as yet unreached pressures by each new experiment. It is hoped that these experiments will give the final push to this supposed critical pressure, so that it will disappear in the limbo of the infinite.

As to a Maximum.—The argument as to a maximum will be concerned almost entirely with Tammann's work, because this is essentially his theory; the only other evidence for it by Damien resting entirely on fallacious experiments. Tammann seeks by two lines of reasoning to make a maximum plausible. The first is from the shape of the melting curve. The melting curves are universally concave toward the pressure axis, as they would be if there were a maximum. Furthermore, Tammann found that within his limits of accuracy the curves could be represented by a second degree equation ($t - t_0 = ap + bp^2$), as might be expected for any curve of slight curvature. But now Tammann, firm in his belief of a maximum, assumed that the position of the maximum given by the equation must be near the actual maximum, and he computed the probable maximum for many of his substances in this way. But it should be noticed that this is properly not an argument for a maximum, but merely an argument for the probable position of the maximum, granting that it exists. Tammann himself recognizes that the maximum as predicted by the second degree equation would probably be too low. This was indicated by a few rough experiments which he performed at pressures higher than he could measure. Nevertheless, he thought the maximum given by the formula sufficiently good to make it worth while tabulating in a good many cases.

As regards the effect of Tammann's experimental error on the shape of his melting curves, it will be found on plotting his points that there are numerous irregularities. Furthermore, there is in all probability a constant source of error in the high pressure measurements which makes the temperature appear too low at the higher pressures, thereby increasing the curvature of the melting curves, and bringing the maximum too low.

Tammann's second line of argument is from measurements of the change of volume during freezing. His experimental means of measuring this quantity were not very good, as he could never entirely avoid leak, and for many of his substances he did not attempt it. On plotting the values of ΔV it will be seen that they are much more irregular than the points on the melting curve.[1] The data do show without question, however, that ΔV decreases with increasing pressure, and Tammann assumed that the relation was linear with the temperature (or the pressure), which he was justified in doing in view of the rather large experimental error. But just here is the crux of the whole matter. Shall we regard the relation between ΔV and p as actually linear, or is the linear relation merely an approximation within the region of the experiments? Tammann chose to think that the relation would actually be a linear one. The rest is easy. By extrapolation, the pressure may be found at which ΔV vanishes; this is the maximum point, unless it should happen that the latent heat should vanish also. But computation by Clapeyron's equation from the slope of the melting curve and the observed values of ΔV shows that the change in the latent heat is relatively slight, the tendency being toward an increase. Hence the existence of a maximum.

It is significant that Tammann has been able to give no "atomistic"

---

[1] See "Kristallisieren und Schmelzen," p. 66.

argument in favor of the maximum melting point, especially since he invokes such an argument in making the critical point seem improbable. This is a matter of no small difficulty, and is doubtless responsible for much of the intuitive mistrust with which Tammann's theory is viewed. Whether we find it easy or difficult to conceive a mechanism making continuous passage from the solid to the liquid probable, we find it much more difficult to conceive a mechanism by which the usual volume relations of liquid and solid are reversed at high pressures, so that the orderly arrangement of the solid comes to occupy more space than the haphazard disorder of the liquid. No one seems to have succeeded in forming a molecular picture of how this might occur.

In answer to Tammann's first argument from the shape of the melting curve, the data here show that the curvature of all the curves decreases rapidly with increasing pressure, and that there is no tendency to turn over toward a maximum. The curves found here almost invariably lie above those of Tammann and show less curvature than his, even in his own range of pressure. The differences, which become accentuated toward 3,000, are doubtless to be explained by impurities and by the error in his pressure measurements. The details of the disagreement have been given under the discussion of the separate liquids. For almost every substance investigated the pressure and temperature assigned by Tammann as the probable maximum have been exceeded with no sign whatever of a maximum.

Tammann's second argument, from the variation of ΔV, is fully answered by an inspection of the curves given here. The curves present the results of complete measurements over the entire range for all the substances (except for carbon dioxide and chloroform at low pressures). The experimental error is very much less than Tammann's, because a means was found of avoiding Tammann's most fruitful source of error, leak past the piston. The ΔV curve is not linear with pressure, but is convex toward the pressure axis. This universal convexity is sufficient to invalidate Tammann's entire argument, for up to at least 12,000 kgm. there is no tendency for ΔV to become zero, and the direction of curvature is such that ΔV need never become zero. Certainly an unprejudiced observer, examining the curves on their own merits, would not be justified in predicting that the curves would ever cross the axis.

The conclusion to be drawn is that there is at present no evidence for either a maximum or a critical point, that the melting curve rises indefinitely, and that along this curve the change of volume becomes less but does not become zero for any finite pressure, while the latent heat changes only slightly and usually increases.

Possible Mechanism.—The facts we have just seen to be very simple. It may perhaps be permitted to indicate a very simple conception of the mechanism of crystallization which would lead us to expect just these simple facts. The fundamental idea is the same as that which was strongly suggested by the previous work on the thermodynamic properties of liquids,[79] namely that at high pressures we must begin to take account of the intrinsic shapes of the molecules. Now it seems almost axiomatic to suppose that the arrangement of a large number of similar objects which will occupy the least possible space is in general an order in which the same grouping of the fundamental units will constantly recur at regular intervals, that is, an order which repeats itself in space. But a crystal is just such an aggregate of similar elements arranged in a repeating order in space. (It is not *universally* true that the smallest possible volume is that occupied by a repeating order, for it is possible to set up examples for which this is not true.) We would expect in general, therefore, that at any temperature, no matter how high, a pressure so high could be applied that the molecules would be forced to take up the smallest possible space (that is, to crystallize) in spite of the deorienting forces of temperature agitation. Also as pressure increases the unoccupied space left by the uncoördinated motion of the molecules of the liquid would be expected to become smaller, so that the change of volume on freezing would become less as pressure increases. On the other hand, at low pressures, there are probably orienting forces tending to produce crystallization quite apart from the tendency to crystallize in virtue of the effort to assume the smallest possible volume. It may well be that the crystalline shape that would be demanded by these two sets of forces is not the same; that at low pressures the orienting forces of the molecules build up the molecules in their own characteristic shape, but that at high pressures the molecules are constrained to take up quite another crystalline form, the one occupying the minimum volume. In this way we may account for allotropic forms. It may be that there are several symmetrical arrangements possible, corresponding to the degree to which the natural orienting forces are compelled to yield to the demands of external pressure. Furthermore, it seems natural that the crystalline form assumed under the free action of the orienting forces is one in which the potential energy of the attractive forces is a minimum, that is, that the local centers of attraction within the molecule have approached as close as possible to each other. If the molecules are forced to assume a different arrangement, even one occupying less volume, these centers of attraction must be pulled apart, and work done against the attractive forces while decreasing the volume. That is, the internal energy of the form with the smaller volume will be the greater. This may well be the case with the two modifications of benzol, for example.

This hypothesis assumes that any particular crystalline phase, thermodynamically considered, is characterized by the same grouping of the molecules throughout its region of existence; in other words, that a given crystalline phase belongs to the same crystalline system throughout its region of stability, no matter how pressure and temperature vary. It is perhaps worth while to make an explicit statement of the question at issue, because the result seems to have often been assumed (correctly) without clearly formulating the question. The question is this: is it possible by subjecting a crystal to hydrostatic pressure or to changes of temperature to so change the type symmetry that it no longer belongs to the same crystalline system? The question is not utterly foolish; a cubic crystal, for instance, when subjected to a tensile pull no longer has the symmetry of the cubic system, and nearly every crystal when subjected to hydrostatic pressure undergoes changes of angle as well as change of absolute size. May the change of shape be such as to alter the type of symmetry of the original crystal, and so change the crystalline system? The answer is provided by examining, in the light of the theory of elasticity, the effect of hydrostatic pressure when applied to each of the nine elastically different types of crystal. It will be found that in general the effect of hydrostatic pressure (so long as Hooke's law holds) is to alter unequally the length of unequal crystallographic axes, but to leave the angle between the *axes* unchanged. That is, hydrostatic pressure may change the numerical values of the index numbers of a crystal, but cannot change the crystalline system. The only apparent exception is the triclinic system, in which hydrostatic pressure does alter the angle between the axes, but this evidently does not mean in this case a change of crystalline system, since the triclinic system is merely the class of left-overs, which have no symmetry at all. The analysis for the effect of changing temperature is much simpler than for the effect of hydrostatic pressure, and leads to the same result. The crystalline system cannot be changed, therefore by variations of temperature or of hydrostatic pressure (within the domain of Hooke's law), and we are justified in thinking of a single crystalline phase as being characterized by the crystalline system to which it belongs.

The Existence of New Polymorphic Forms.—A discussion of the several new allotropic forms may well be left to a future paper, when more data have been collected. One point may be mentioned, however, because the data are sufficient to definitely settle the question. Tammann[80] has recently developed a theory of the prediction of new allotropic forms.

His theory is that the cause of the reversible transformation of one crystalline phase to another is to be found in different molecular association in the two phases. At the triple point between the liquid and the two solid phases we would have, therefore, a liquid capable of crystallizing into either of two differently associated forms. It seems natural to suppose that in the liquid itself there are molecules of different degrees of association; at the lower pressures the one kind of molecule crystallizes out, while at higher pressures the other kind of molecule separates. If, therefore, a liquid is to crystallize to more than one crystal form, it must be a liquid showing association. Now there are various criteria for the association of a liquid. Perhaps the best known is that of Eötvös, dealing with the temperature coefficient of the capillary constant. From this point of view carbon tetrachloride and benzol are perfectly normal liquids, and therefore Tammann has predicted that not more than one crystalline form will be found. We have just seen that CCl_4 has at least three solid forms and benzol two. Even granting the validity of Tammann's ideas as to the reason for different allotropic forms, it must seem to have been a trifle too venturesome to predict that because a liquid is not associated at atmospheric pressure it may not become so at high pressures.

Law of Corresponding States.—The data have bearing on one other question which may be mentioned because it has been a good deal discussed lately. The quantum hypothesis applied to solids leads us to expect a law of corresponding states analogous to that predicted by van der Waals' equation for liquids. The argument as usually given applies only to monatomic solids, but the assumption of a law of corresponding states has been applied with some success to solids known to be not monatomic. Lindemann,[81] for example, has deduced the melting point of a number of salts on this hypothesis. The question suggests itself, therefore: do the substances studied here obey the law of corresponding states? The question can be readily answered, for in this case the melting curves and the change of volume curves of different substances should be corresponding curves.

The question may be put to a simple numerical test as follows. If the curves are corresponding, then zero pressure must be a corresponding pressure on all the curves, and the temperatures and changes of volume at zero pressure must also be corresponding. But the change of volume at zero pressure is practically the same as at atmospheric pressure. The changes of volume at atmospheric pressure, therefore, are corresponding. Similarly, the freezing temperatures at atmospheric pressure are corresponding. Therefore the coördinates of the point at which the change of volume has become reduced to half its initial value must be corresponding coördinates. This means that the temperatures at the normal freezing point and at the point at which the change of volume has become one half of its initial value are corresponding temperatures. The ratio of the absolute value of these temperatures should be a constant for all substances if the law of corresponding states holds. Table XIII. shows the results. It will be seen that the ratio of the two temperatures is not constant, and that therefore the law of corresponding states does not hold for these substances. The ratio is nearly the same for sodium and potassium, but this one would expect, quite apart from any law of corresponding states, from the close chemical similarity of the two elements. This suggests the same result that some writers on the quantum hypothesis have already reached from other grounds; namely, that although the law of corresponding states may hold for solids, it does not hold for liquids, and therefore does not hold for the transition curve solid-liquid.

TABLE XIII.

Law of Corresponding States.

Substance.	ΔV_0.	T_0, **Abs. temp. of normal mpt.**	T, **Abs. temp. at which** $\Delta V = \frac{1}{2}\Delta V_0$.	$\frac{T}{T_0}$.
Potassium	.0268	335.6	409	1.218
Sodium	.02785	370.7	451.6	1.218
Anilin	.0854	267	427	1.60
Diphenylamine	.0956	326	467	1.44
Nitrobenzol	.0813	278.7	454	1.64
Benzol	.1316	278.5	375	1.35
Carbon tetrachloride	.0258	251	363	1.45
Orthokresol	.0839	304	355	1.17
Phosphorus	.0193	317	509	1.61

SUMMARY.

The melting curves and the change of volume curves have been found for eleven substances between 0° and 200° and up to 12,000 kgm. Four of the substances have been found to have new allotropic forms of the solid: CCl_4 two new forms, o-kresol one new form, benzol one new form, and phosphorus two new forms, one of which transforms itself into yellow phosphorus reversibly under the proper conditions, while the other is a form (grayish-black) stable under atmospheric conditions, obtained from yellow phosphorus irreversibly at 200° and 12,000 kgm.

The results have been used in discussing the most probable shape of the melting curve. There is no evidence for either a critical point or a maximum melting point, the two hypotheses which have been hitherto considered most probable. The results suggest strongly, so far as such a conclusion can be suggested by results over a limited range, that the melting curve continues to rise indefinitely to higher pressures and temperatures.

Acknowledgment.—It is a pleasure to acknowledge assistance in purchasing the chemicals used in this investigation from a generous grant from the Bache Fund of the National Academy of Sciences.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

REFERENCES.

1. J. H. Poynting, Phil. Mag., 12, 32 and 232 (1881).
2. M. Planck, Wied. Ann., 15, 446 (1882).
3. W. Peddie, Proc. Roy. Soc. Edin., 13, 155 (1885).
4. E. H. Amagat, C. R., 105, 165 (1887).
5. B. C. Damien, C. R., 108, 1159 (1889), and C. R., 112, 785 (1891).
6. C. Barus, Bull. U. S. Geol. Sur., No. 96 (1892).
7. E. H. Amagat, C. R., 117, 507 (1894).
8. R. Demerliac, C. R., 122, 1117 (1896), and C. R., 124, 75 (1897).
9. A. Heydweiller, Wied. Ann., 64, 725 (1898).
10. E. Mack, C. R., 127, 361 (1898).
11. G. A. Hulett, Zs. f. phys. Chem., 28, 629 (1899).
12. G. Tammann, The following is only a partial reference to Tammann's papers. Wied. Ann., 62, 280 (1897); 66, 473 (1898); 68, 553 and 629 (1899). Ann. Phys., 2, 1 (1900); 3, 161 (1900); and his book "Kristallisieren und Schmelzen," E. Barth, Leipzig.
13. P. P. von Weimarn, Zs. Chem. u. Ind. Koll., 6, 307 (1910).
14. J. J. van Laar, Arch. Néerl. (3A), 1, 51 (1911).
15. P. W. Bridgman, these Proceedings, 47, 347 (1911), and 47, 441 (1912).
16. J. J. van Laar, Chem. Zentralbl., 2, 1798 (1912).
17. P. W. Bridgman, Proc. Amer. Acad., 49, 1 (1913).
18. P. W. Bridgman, Proc. Amer. Acad., 47, 441 (1912).
19. E. B. Hagen, Wied. Ann., 19, 436 (1883).
20. W. Holt and W. E. Sims, Trans. Chem. Soc., 65, 432 (1894).
21. N. S. Kurnakow and N. A. Puschin, Zs. anorg. Chem., 30, 109 (1902).
22. G. Tammann, "Kristallisieren und Schmelzen," p. 248. (In the future reference to Tammann's book will be abbreviated by "K. S.")
23. M. Toepler, Wied. Ann., 53, 343 (1894).
24. A. Joannis, Ann. Chim. et Phys. (6), 12, 358 (1887).
25. G. Tammann, "K. S.," p. 247.
26. G. Tammann, Zs. phys. Chem., 72, 609 (1910).
27. G. Tammann, "K. S.," p. 245.
28. G. Tammann, "K. S.," p. 245.
29. P. Villard and R. Jarry, C. R. 120, 1413 (1895).
30. G. Tammann, "K. S.," p. 294.
31. G. Tammann, Zs. f. phys. Chem., 80, 737 (1912).
32. G. Tammann, "K. S.," p. 282.
33. P. W. Bridgman, Proc. Amer. Acad., 49, 18 (1913).
34. Niescher (1909), quoted in the Collection of Constants of the Soc. Franc. de Phys.
35. E. Lucius, Ber. Chem. Ges., 5, 154 (1872).

36. G. Tammann, "K. S.," p. 228.
37. De Forcrand, C. R., 136, 945 (1903).
38. G. Tammann, "K. S.," p. 282.
39. L. Meyer, Zs. phys. Chem., 72, 225 (1910).
40. G. Tammann, "K. S.," p. 227.
41. O. Pettersson and O. Widman, Vet. Akad. Förh. Stock., 36, 75 (1879).
42. G. Tammann, "K. S.," p. 227.
43. A. Heydweiller, Ann. Phys., 64, 725 (1898).
44. J. M. Stillman and R. E. Swain, Zs. phys. Chem., 29, 705 (1899).
45. H. Block, Zs. phys. Chem., 87, 385 (1912).
46. A. Battelli and M. Martinetti, Att. Lin. Rend., 1, 621 (1884).
47. A. Bogojawlensky, quoted by Tammann, "K. S.," p. 238.
48. G. Tammann, "K. S.," p. 236.
49. G. Tammann, Zs. phys. Chem., 75, 75 (1910).
50. R. Demerliac, Jour. de Phys. (3), 7, 591 (1898).
51. J. Ferche, Ann. Phys., 44, 265 (1891).
52. Br. Lachowicz, Ber. Chem. Ges., 21, 2206 (1888).
53. S. W. Pickering, Proc. Roy. Soc., 49, 11 (1891).
54. O. Pettersson and O. Widman, Jour. prak. Chem., 24, 163 (1881).
55. W. Fischer, Wied. Ann., 28, 400 (1886).
56. A. Bogojawlensky, quoted by Tammann, "K. S.," p. 213.
57. G. Tammann," K. S.," p. 207.
58. E. H. Amagat, C. R., 105, 165 (1887).
59. G. Tammann, "K. S.," p. 222.
60. G. Tammann, Wied. Ann., 66, 490 (1898).
61. G. Tammann, Ber. Chem. Ges., 44, 3624 (1911).
62. S. Bugarszky, Zs. phys. Chem., 71, 705 (1910).
63. G. Tammann, "K. S.," p. 222.
64. G. Tammann, "K. S.," p. 268.
65. Béhal and Valeur, quoted in the Collection of Constants of the Soc. Franc. de Phys., p. 265.
66. G. A. Hulett, Zs. phys. Chem., 28, 629 (1899).
67. C. C. Person, C. R., 23, 163, 336 (1846).
68. G. Pisati and G. De Frenchis, Gazz. Chim. Ital., 4, 497 (1874).
69. S. Lussana, Nuov. Cim., 5, 153 (1903).
70. O. Pettersson, Jour. Prak. Chem., 24, 296 (1881).
71. G. Tammann, "K. S.," p. 250.
72. A. Hess, Phys. Zs., 6, 185 (1905).
73. H. Kopp, Lieb. Ann., 93, 129 (1885).
74. B. C. Damien, Jour de Phys., 10, 394 (1881).
75. A. Leduc, quoted by Tammann, "K. S.," p. 250.
76. G. Tammann, "K. S.," p. 250.
77. G. Tammann, "K. S.," p. 87.
78. P. W. Bridgman, Proc. Amer. Acad., 47, 437 (1911).
79. P. W. Bridgman, Proc. Amer. Acad., 49, 86 (1913).
80. G. Tammann, Ber. Chem. Ges., 44, 3618 (1911).
81. F. A. Lindemann, Phys. Zs., 11, 609 (1910).