CHANGE OF PHASE UNDER PRESSURE.

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

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Introduction.

This paper is the first of a projected series of papers dealing with the various problems offered by the phenomena of change of phase under pressure. At high pressures we are concerned with phase changes of only two types, from the fluid to the solid (or crystalline) phase, and from one solid phase to another, since at high pressures the gaseous phase no longer has an independent existence. It is the first of these changes, that from the liquid to the solid, that is to be the special subject of this paper. The problem presented by the change from liquid to solid involves for its complete solution a description of the molecular arrangement of the liquid and the crystal and of the nature of the forces that produce crystallization. Hitherto one narrow aspect of this problem has received almost exclusive attention, the question as to the general shape of the melting curve. Evidently an answer to this question would go far in pointing the way to the essential difference between a liquid and a crystal. Two answers to this question have been regarded as most probably correct; the first is that the liquid-solid curve ends in a critical point, and the second, directly opposed to the first, is that the melting curve passes through a maximum temperature, so that if pressure is raised sufficiently high at constant temperature we may first freeze the liquid to the solid and then melt it again to the liquid. The more particular object of this paper is to settle definitely, with the help of new data, this long discussed question as to the shape of the melting curve.

The data hitherto available have covered a pressure range of about 3,000 kgm. These data are mainly due to Tammann, who measured the relation between pressure and melting temperature over this pressure range, and also measured for some of his substances, with considerably less accuracy, the difference of volume between solid and liquid along the melting curve. The data presented here cover a pressure range up to 12,000–13,000 kgm. per sq. cm., and a temperature range from 0° to 200°. Over this entire range the relation between melting temperature and pressure has been measured, and the difference of volume between solid and liquid has also been determined. These two kinds of data are necessary and sufficient from a thermodynamic point of view to settle the point at issue. Eleven substances have been experimented on, including simple and complicated organic compounds and three elements. These all indicate the same answer to the question in hand.

For the immediate purposes of this first paper those substances were selected which had only one known modification of the solid, in order not to complicate the study by the entrance of a second solid phase. But four of the substances studied have been found to have new solid modifications at high pressures. It may be, therefore, that polymorphism at high pressures is a common instead of an exceptional phenomenon. The data given in this paper include data that will be used later in the discussion of the relation between different solid modifications. And similarly, some of the data to be presented in future papers may be expected to have a bearing on the narrower question to be discussed here.

Summary of Previous Work and Present State of the Problem.

It is proposed to quote here only those papers bearing on the question at issue, the true character of the melting curve. This will omit a few papers giving measurements only, and also much of the earlier work, which was occupied with experimental proof of the validity of the formulas deduced by thermodynamics, at a time when complete confidence apparently was not felt in thermodynamic arguments. Most of the early speculators on the true nature of the melting curve seem to have been guided mostly by analogy with the then recently established critical point between liquid and vapor, and assumed the existence of a similar critical point between liquid and solid. Poynting[1] was one of the earliest of these. He predicted by analogy between water and its vapor that there were two critical points between water and ice; one at − 120° and 16,000 atmos., the other at + 14° and some high negative pressure. Practically no experimental evidence was given. Planck[2] thought that there was a critical point, and deduced some thermodynamic relations which must hold if such a point exists. Peddie[3] also gave thermodynamic relations for a critical point if it exists, and quoted observations of Bunsen on paraffine suggesting the possible existence of such a point. Amagat[4] then contributed some actual observations up to 1,100 atmos. on the solidification of CCl_4, and stated that the appearance was as if a second liquefaction took place at a higher pressure than that required to produce solidification. In his opinion a critical point seemed likely. Two papers by Damien[5] with new experimental data gave the subject new impetus from the experimental side. His results reached to 200 atmos. and he claimed to have found for several organic substances, not a critical point, but a maximum melting temperature. At temperatures below the maximum the continually increasing application of pressure first freezes the body to a solid and then melts it again. This seems to have been the first suggestion in the literature of such a phenomenon. Barus[6] in 1892 published investigations up to 2,000 atmos. on a number of organic liquids, but his results did not become known until later. He found no evidence of a maximum up to 2,000 atmos., but there was a certain cyclic character in the transformation solid-liquid which reminded him of the unstable part of the isotherms of James Thomson. He seems to have been of the opinion that at high enough pressures there is a critical point. Amagat[7] then published data on water, obtained with the same apparatus as for CCl_4, up to 1,000 atmos. He was of the opinion, although his results do not suggest it particularly strongly, that at high enough pressures there might be an inversion point beyond which ice is more dense than water, so that at high pressures the melting point of ice would be raised by pressure instead of lowered; that is, a minimum point, the reverse of Damien's maximum. Demerliac[8] in two papers next subjected Damien's results to further experimental scrutiny up to 300 kgm. Demerliac's results are usually quoted as supporting Damien's theory, but only because of a misunderstanding. Demerliac found that for the lower pressures of his range his results could be very accurately represented by a formula which predicts a maximum, but that at the higher pressures the results no longer fitted the formula, the temperature tending to approach more and more closely to a limiting value. Demerliac's opinion, therefore, was that the melting curve tends to approach a horizontal asymptote. He nearly reached the asymptote for several substances. The years 1898–99 marked great activity in this field, several of the results appearing without knowledge of the others. Heydweiller[9] published results showing that there could not by any possibility be a maximum at pressures as low as Damien supposed, and was of the opinion that there must be a critical point at high enough pressures. He chose substances to investigate that might be expected to be near their critical points, but he could find no critical phenomena up to pressures estimated to be between 1,000 and 3,000 atmos. At the same time he observed effects of another kind on menthol which he thought were indicative of a critical point. Mack[10] published results up to 2,100 atmos. on several organic substances, and could find evidence of neither a critical point nor of a maximum. His melting curves were nearly linear. Hulett[11]), inspired by Ostwald who was of the opinion that there was a critical point, investigated liquid crystals up to 300 kgm. It seemed natural to suppose that liquid crystals might be near the critical point, but he found on the contrary that the difference between liquid crystal and the liquid became more strongly accentuated at increasing pressure. If there were a critical point, it could exist only at negative pressures. About this time Tammann[12] began to publish his experiments and theory, and he has since then almost monopolized the field. His results cover a range of 3,000 kgm., higher than had been reached hitherto. One of his first services was to explain the remarkable discrepancies between previous experimental results by calling attention to the effect of dissolved impurities. Damien provides a particularly striking example of this; his medium of compression was air, which is dissolved more and more at high pressures. The cycles found by Barus are also similarly explained by the action of impurities. Tammann's theory is well known, and will be described again only briefly. It is, in part, that all substances show a maximum melting point, but this maximum is very much higher than supposed by Damien. Tammann himself was never able to reach it, but supposed that it might be in the neighborhood of 10,000 kgm. for a number of substances. In support of this theory, Tammann shows that we must consider all the thermodynamic elements of the phenomena of melting, the change of volume and the latent heat, as well as the melting curve itself. His data show that the change of volume decreases along the melting curve, while the latent heat increases or remains nearly constant. Now at a critical point the change of volume and the latent heat must vanish together, but at a maximum the change of volume vanishes, while the latent heat remains finite. The data are unquestionably more favorable to the second than to the first of these alternatives, and this constitutes the evidence for a maximum. Still the evidence, even from Tammann's own data, is by no means conclusive, and there have been at least two upholders since then of the idea of a critical point. Weimarn[13] in 1910 argued from the behavior of colloids to the probable existence of a critical point. His argument is briefly as follows. At any pressure, no matter how high, the temperature may be raised so high that the dispersive forces due to the intense molecular agitation overcomes the orienting forces, so that the substance can exist only in the form of very finely disperse crystals. When the crystals become molecular in dimensions we have achieved continuous passage between the two states, or have reached the critical point. Van Laar[14] also, from an entirely different point of view, has deduced a theory demanding a critical point. This has been described in greater detail elsewhere; briefly, the difference between a liquid and a solid consists in an association of the molecules in the solid, which produces a second loop in the isotherm of James Thomson, with the possibility of a critical point. For substances which contract on freezing, this theory demands that there shall always be a critical point solid-liquid, but never a maximum. Because of an error in one of the figures of the original article, the author stated in a previous summary of van Laar's theory that under some conditions a maximum might occur. In 1911 the author published two experimental papers bearing on this subject,[15] over a pressure range considerably higher than previously reached. The evidence of the first paper, on mercury to 12,000 kgm., was against the existence of Tammann's maximum, but left open the question of a critical point. The second paper, on water to 20,000 kgm., did not give so valuable evidence because of the many abnormalities of water. However, all the evidence suggests that these abnormalities disappear at high pressures. If water can be regarded as really normal at high pressures, then the evidence of water is that there is neither critical point nor maximum, but that the melting curve continues rising indefinitely. Van Laar[16] has since this published a short paper in which he regards the evidence of the mercury as on the whole favorable to his theory, but apparently regards water as too abnormal to make its evidence of much value.

APPARATUS AND EXPERIMENTAL METHOD.

Apparatus.—The apparatus is in essentials the same as that used in previous work[15] and needs only brief description. Some slight changes have been necessitated by the higher temperature reached here, 200° instead of 80°. The apparatus finally used consists of an upper and a lower cylinder, connected by a heavy piece of tubing. The upper cylinder contains the moving piston, actuated by a hydraulic press, by which pressure is produced. The motion of the piston, measured with a micrometer, may be combined with the cross section to give the change of volume of the substance under investigation in the lower cylinder. The upper cylinder also contains the coil of manganin wire, from the change in the resistance of which the pressure is determined. The upper cylinder contains one feature not found in the previously used apparatus. The compressibility of some of the substances was so high that a single stroke of the piston would not have given the maximum pressure desired. The difficulty was avoided by starting the experiment with initial pressure. To accomplish this, a very minute by-pass was provided at the upper end of the cylinder connecting the interior of the cylinder with an auxiliary pressure pump. The by-pass connects with the interior of the cylinder only when the piston is withdrawn to the extreme position. In this position, pressure was raised to the desired amount, 2,000 or 3,000 kgm., by the auxiliary pump acting through the by-pass, and then the auxiliary pump cut off by advancing the piston slightly beyond the by-pass. It is necessary that the by-pass be very small indeed, otherwise the rubber packing on the moving piston gets blown into it as the piston moves by. A sufficiently minute hole was made by drilling and tapping a hole through the side of the cylinder, and then screwing into the hole a tightly fitting screw, across the threads of which a lateral scratch had been made. The upper cylinder, together with the lower part of the hydraulic press, was placed in a thermostat maintained at about 35°. In this way all temperature corrections of the manganin coil were avoided. A temperature as high as 35° was necessary because the conduction of heat along the connecting tube from the lower cylinder sufficed (when the lower cylinder was as high as 200°) to keep the upper thermostat at nearly 35°.

The lower cylinder contained the substance to be investigated. It was held suspended in another thermostat by the connecting tube, led through a water-tight stuffing box in the bottom of the upper thermostat. The temperature of the lower thermostat was systematically run to 200°. For the higher temperatures, "Crisco," a substitute for lard by the Proctor and Gamble Co., was chosen for the bath liquid, because of its comparative freedom from odor. The temperature regulation was by means of an ordinary mercury contact device. This worked well for the few hours occupied by a single run, but at the higher temperatures trouble might arise if longer runs were necessary, because of a slow drift of temperature due to the very gradual distillation of mercury from the temperature regulator. The difficulty can be largely avoided by carefully designing the mercury bulb. The substance to be investigated, if it was such as not to be attacked by the kerosene which transmitted the pressure, was placed in an open cup, or if it were attacked by the kerosene, it was placed in a steel bulb with a mercury seal, of exactly the same design as was used in investigating the thermal properties of twelve liquids.[17]

The dimensions of the various parts of the apparatus were as follows. The upper cylinder: length 8 inches, outside diameter 4½ inches, inside diameter 17/32 of an inch, length of stroke of piston 3½ inches. The connecting pipe: length 16½ inches, outside diameter 1½ inches, inside diameter 1/16 of an inch. The connections at the end of this tube were especially heavy, the minimum outside diameter at places where the pressure was entirely internal was ¾ of an inch. The lower cylinder had the dimensions: length 10½ inches, outside diameter 4½ inches, inside diameter 11/16 of an inch, depth of interior cavity 9 inches. All parts of the apparatus were made of the Halcomb Steel Co.'s electric furnace chrome-vanadium steel, which has proved itself the best yet found for the purpose.

The apparatus in the form just described was not the form first used. In the first form there were three pressure cylinders and two connecting pipes. In the one cylinder the pressure was produced by the moving piston, in the second was placed the manganin coil with which pressure was measured, and in the third was the liquid under investigation. There was only one thermostat, around the third cylinder. Conduction of heat to the second cylinder was avoided by a water jacket with running water around the connecting tube. The temperature fluctuations in the second cylinder were not large and could be readily corrected for. The fatal weakness in this original apparatus was in the connecting pipes. The connections were of a type in which the end of the tube was turned down to 5/16 of an inch and threaded with a 32 thread, bringing the minimum outside diameter of points where there is only internal pressure to about ¼ of an inch (the inside diameter was 1/16 of an inch). The result was that the tubes were invariably torn apart at the connections, sometimes at pressures as low as 7,000 kgm. The high temperature has a perceptible weakening effect on the tubing, since the same type of connection had been previously used to 12,000 kgm. in the work on mercury at 20°. Various other types of connection were tried with this first form of apparatus, but none with permanent success. Finally, after six explosions, the attempt to use this form of apparatus was entirely given up, since for one thing, the labor of drilling each new piece of tubing with a hole 1/16 of an inch in diameter and 16 inches long is considerable. However, the data obtained at the lower pressures with this apparatus are perfectly reliable, and form an important part of the data of this paper.

To prevent rupture of the connections, a piece of apparatus much like that finally used was constructed, but which had no connections, everything being made out of one piece of steel. This necessitated drilling a hole 1/8 of an inch in diameter through a piece of steel 30 inches long and 5 inches in diameter, turning the steel to 1½ inches over the middle third, and to the dimensions given above for the cylinders at the two ends, hardening in oil, seasoning by subjecting to 17,000 kgm. at 200°, and finally machining to the final size after the preliminary stretching. Some measurements had already been made with this apparatus when a flaw developed in the steel which made the whole apparatus valueless. The flaw developed rapidly into a crack through which the kerosene could be forced in a stream.

The risk of flaws in the steel, as exemplified by this accident, is one which is apparently unavoidable in work at very high pressures. Several pieces of Krupp's best chrome nickel steel have previously developed flaws under high pressure, but it was a great surprise to find a flaw in this apparently perfectly homogeneous product of the electric furnace. That the flaw was very small is shown by the fact that the steel had withstood the first application of 17,000 kgm. at 200°.

Rather than run the risk and lose the time of making another piece of apparatus, an attempt was then made to design a form of connection which should not have the weakness of the other, and the attempt was entirely successful. The packing is a thin ring of lead confined between two Bessemer rings. The lead gives the initial tightness, and at the high pressures the soft Bessemer rings become sufficiently deformed to give tightness. The connection has not leaked or broken once in several months of use.

Besides the two forms of apparatus described above for high pressure a third form was used to find points at approximately atmospheric pressure. The necessity of this was not contemplated in the original plan of the work, but an examination of the existing data showed rather large discrepancies in the values for the change of volume (ΔV) on melting at atmospheric pressure, so that a redetermination of these data became necessary. The chief possibility of error in previous work, apart from impurity, seems to have been the formation of unfilled cracks, and uncompensated capillary effects. To avoid this, these determinations were made at a slight pressure, about 60 kgm., and then extrapolation made from 60 to 1 kgm. The change of ΔV with pressure is so small that this can be done without danger. The readings with this apparatus may also be used to give by extrapolation an approximate value of the freezing temperature at atmospheric pressure, but the extrapolation is sometimes uncertain, and the freezing point determined in this way is not so good as that directly measured. However, the freezing point so found may be of some value, and it is given in those cases where it was not determined by direct measurement.

The apparatus for the low pressure measurements is in essentials the same as that used for high pressures. First there is a cylinder of known cross section in which there is a moving piston. This piston was actuated by a screw instead of by a hydraulic press, and the connection between the screw and the piston was a positive one, so that the piston could be either advanced or withdrawn. The position of the piston was measured as usual with a micrometer. To avoid error from the distortion of the piston or the wearing away of the packing, the piston was made hollow, and a rod was led through the piston and through the packing to the washer retaining the packing at the inner end. The position of the free end of this rod evidently gives directly the position of the upper surface of the liquid in the cylinder. This cylinder connects with a pressure gauge (a Geneva Bourdon gauge was accurate enough) and a second cylinder, containing the substance to be investigated, which was placed in a thermostat. The procedure in making measurements was to vary the temperature at constant pressure, instead of to vary the pressure at constant temperature as in the high pressure measurements. The data give the means of plotting volume against temperature, from which the discontinuity of volume at the freezing temperature may be found graphically. Because of the low pressures used with this apparatus, it was possible to enclose the liquid under investigation in a glass bulb with a mercury seal, instead of a steel bulb, as was necessary at the higher pressures. In this way somewhat greater purity was ensured. The use of the glass also allowed examining the liquid after the experiment, to be sure that none of the transmitting fluid had found its way to it. In no case had this happened. To further ensure purity, no glass bulb was used more than once. The bulbs were filled by boiling the liquid into them under reduced pressure, in the same way as for the steel bulbs. The liquid transmitting pressure in this low pressure experiment was a mixture of water and glycerine, instead of kerosene, which was used at the high pressures. Corrections for the thermal expansion of the glycerine and water on passing from one clyinder to the other were determined and applied in the same way as for the kerosene at high pressures.

Procedure.—This was in most respects like that used either in the work on ice[18] or on twelve liquids[17]. A brief summary will suffice. The purified liquid was boiled into the bulb under reduced pressure to exclude all air, and its quantity determined by weighing. The apparatus was then assembled, the upper thermostat adjusted to 35°, the zero of the manganin coil determined, initial pressure of 1,000–2,000 kgm. applied through the by-pass, the by-pass shut off by pushing in the piston, and then the lower thermostat adjusted to the desired temperature. Pressure was now increased beyond the freezing point sufficiently far to ensure complete freezing, and then the pressure decreased, and readings made of the position of the piston for about 700 kgm. on each side of the melting point. Ordinarily four points were found above the melting point and three below it, with two determinations of the equilibrium pressure, one from above and one from below, with the liquid about two thirds melted. The results were plotted on a large scale, and the change of volume calculated from the discontinuity at the melting point. The temperature was then changed and the next point found in a similar manner. Ordinarily the points were obtained with increasing pressure and temperature. During one experiment on a single substance the apparatus was left with the pressure continuously at least as high as the initial value. This might be for three or four days. The procedure in finding the point at approximately atmospheric pressure has been indicated, the temperature being varied a few degrees at a time at constant pressure, instead of the pressure being varied at constant temperature.

Corrections.—Several corrections were to be applied, but these have been so carefully described in previous papers that a mere enumeration will suffice; a correction for slight variations in temperature of the manganin coil (in the final form of apparatus there was no such correction), a correction for the distortion by pressure of the cylinder containing the moving piston, a correction for the thermal expansion of the transmitting fluid on passing from one cylinder to the other,* a correction necessary only with the first form of apparatus for slight variations of temperature of the cylinder containing the manganin coil, and finally corrections not peculiar to this particular work, such as corrections for the lack of uniformity of the bridge wire, or corrections for the thermometers, which were mercury thermometers, calibrated at the Reichsanstalt or at the Bureau des Poids et Mesures.

Accuracy.—The accuracy of the melting curves, *i. e.*, the curves showing the relation between melting temperature and pressure, was limited only by the accuracy with which pressure could be determined with the manganin coil. This was as good as .1 per cent. at the higher pressures. The coil was calibrated several times during the course of the experiment by determining with it the freezing pressure of mercury at 0°, the coil being at 35°. There was no change in the coil of so much as 0.1 per cent. during the experiment. The freezing pressure of mercury at 0° was taken as 7,640 kgm., and the relation between pressure and change of resistance was assumed to be linear. (For further particulars on this matter see Proc. Amer. Acad., vol. 47, No. 11, Dec., 1911.)

The accuracy of the values for ΔV is not so high as that for the equi-

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* This is the most important correction, and may be as high as 6 per cent.; it was entirely overlooked by Tammann.

librium pressures, chiefly because it is seldom possible to entirely eliminate a slight rounding of the corner at the discontinuity of the curve of volume against pressure. This source of error has also been always present in all previous determinations of ΔV at atmospheric pressure. All the indications are that the special form of apparatus used here avoids this effect at atmospheric pressure more successfully than has yet been accomplished. Of course the error varies greatly with the nature of the substance. Several substances were tried and discarded because they could not be obtained sufficiently pure. Some of the substances show no perceptible rounding of the corners. The order of accuracy can be judged for each separate liquid from an examination of the curves in detail.

The general accuracy of the results is further vouched for by the fact that we have here three independent pieces of data, obtained with different pieces of apparatus at different times; the first with the original high pressure apparatus up to 7,000–10,000 kgm., the second at nearly atmospheric pressure with the low pressure apparatus, and the third with the final high pressure apparatus up to 12,000–13,000 kgm. The inconsistency between the three sets of data is not greater than the discrepancies between readings with the same apparatus.

In addition to the directly measured quantities p, t and ΔV, there are tabulated the latent heat of the change of state and the difference of internal energy between solid and liquid. The latent heat, ΔH, was computed from Clapeyron's equation,

$$\Delta H = \frac{\tau \Delta V}{\frac{d\tau}{dp}}.$$

The computation involves, therefore, the slope of the melting curve. Now the slope of an experimental curve is known with somewhat less accuracy than the points of the curve themselves. To avoid as much as possible error in finding the derivative, two independent methods were used; first the derivative was obtained directly graphically from a large scale drawing, and secondly the melting curve was approximated to by two straight lines, the difference curve drawn, the slope of the difference curve found graphically, and combined with the slope of the straight lines to give the slope of the original melting curve. The two methods agreed very well, usually better than 0.5 per cent., so that we may feel confident that there is no large error in computing the derivatives from the actual melting curves. But aside from the error usually met in finding a derivative, there is here a special source of error operative only at the low pressures. The curvature of the melting curve decreases rapidly as pressure increases, so that to find the initial curvature as accurately as the curvature at high pressures, a large number of observations would be necessary at the lowest pressures. But the form of apparatus used made it impossible to obtain points at much less than 1,200 kgm. This was due to the sticking of the piston and has been alluded to elsewhere. To avoid it, especially constructed apparatus would be necessary. As a result, the slope at atmospheric pressure of all the curves, and hence the latent heat, is much more in doubt than at any higher pressure. The agreement between the latent heat at atmospheric pressure, computed in this way, and that found by other experimenters by direct experiment, is not very good. In those cases in which reliable direct measurements of the latent heat exist, they have been accepted, and the most probable value of the initial slope computed backward from the accepted value of the latent heat. But unfortunately, the latent heat has been directly measured for only a few of the substances used here. For the other substances it must be borne in mind that the initial latent heat listed here may be subject to correction. The numerical details are given under the separate substances.

The change of internal energy differs from the latent heat only by the external work ($p\Delta V$) during change of state. This involves only quantities directly measured, so the errors in the change of energy are the same as those in the latent heat. In particular, the latent heat and the change of energy are practically the same at atmospheric pressure.

In order to avoid the troublesome work of changing units, and to permit the direct substitution of the values given here in Clapeyron's equation, the latent heat and the change of internal energy are given here in mechanical units, kgm. m. per gm. instead of the familiar gm. cal. per gm. To change kgm. m. to gm. cal. multiply by 2.3442.

Materials.—It is of the utmost importance that the materials be as pure as possible; erroneous results by other experimenters have been obtained because of this, as for example when Tammann announced two solid modifications of carbon dioxide, but later found the effect was due to impurity. The materials to be used were selected by running through a catalogue of chemicals and choosing those which were not prohibitively expensive, which it was known could be obtained fairly pure, which had freezing points within the desired range, and for which only one solid modification was known. These were then subjected to further purification, either by fractional distillation or by crystallization from the melt, or in those cases that were practicable, by both methods. The details of the purification by distillation do not require comment. The purification by crystallization was performed with more care than is perhaps usual. The substance to be purified was placed in the melted condition in a closed glass vessel, within a larger glass vessel, which dipped into a bath kept at constant temperature by a thermostat. The thermostat was then adjusted to a temperature a few tenths of a degree, or perhaps as much as 1.5° (depending on the purity of the substance) below the freezing point of the pure substance. After temperature equilibrium had been attained and the substance was in a slightly subcooled condition, it was inoculated with a minute crystal, and crystallization allowed to take place. Transfer of heat from the bath to the substance took place across an air space, and was therefore slow. Crystallization might continue in some cases for a couple of days. The remaining liquid was then drained off by inverting the glass vessel. The draining occupied several hours. During the draining the temperature of the thermostat was raised a few tenths of a degree in order to melt off more perfectly any layer of impurity clinging to the crystals. The advantages of the method are the very slow crystallization, and the fact that one can be perfectly sure that there is not enough impurity present to depress the freezing point as much as the depression artificially maintained by the thermostat.

No special analysis is necessary to show the amount of purity finally attained, because the conditions of the experiment themselves impose one of the sharpest tests that could be applied. If the substance is perfectly pure it will all freeze sharply at one temperature, but if it is impure, the impurity will remain in the liquid as crystallization progresses, becoming more and more concentrated, so that the freezing temperature will drop as freezing proceeds. Or if the freezing takes place at constant temperature, as here, the freezing pressure will increase as the liquid approaches complete solidification. This will be shown by a rounding of the upper corner (where melting begins) of the curve of volume against pressure. It has been already stated that in only a few cases was it possible to entirely get rid of the rounding, but it was never allowed to become large enough to raise doubt; if it did the liquid was discarded, or further purified. It was very seldom that the rounding was perceptible more than 200 kgm. beyond the freezing point, and the curve from which extrapolation was made was usually run 700 kgm. beyond the point.

One other effect of impurity is to greatly slow the reaction, so that it may be necessary to wait hours for equilibrium. The reason for this is evident. As the liquid crystallizes the pure substance separates, leaving an excess of impurity in the neighborhood of the freshly formed crystal. Further freezing cannot now continue until the excess of impurity has been removed by diffusion into other parts of the liquid. But at high pressures the diffusion takes place very slowly because of the greatly increased viscosity. One striking example of this was found while working on monochloracetic acid. After setting up the apparatus the acid was found to become gradually impure by attacking the steel envelope. Three points at high pressure were determined. The progressive gain of impurity was shown not only by the much greater rounding of the corners at the last reading (which was at lower pressure than the first two), but by the exasperating slowness of the reaction. The impurity of this one substance finally became so great that it was not worth while to attempt any more readings.

The slowness of the reaction furnishes, therefore, a further rough test of the purity of the substance. Thus Tammann mentions that he was troubled by the slowness of freezing of a number of his substances, while no such trouble was found here. The presumption is that Tammann's materials were impure. An example is the case of sodium. Tammann found a very slow reaction, while in the present work the reaction ran as rapidly and as cleanly as one would expect from a metal, as rapidly as for mercury, for example.

In some cases actual experiment showed that the commercial materials were pure enough. Examples are phosphorus and sodium. The details of the purification are to be found under the data for the separate liquids.

Unsuccessful attempts were made to purify acetophenone and para-xylol. Two crystallizations of acetophenone did not raise the freezing point more than 0.5°, from 19.1° to 19.6°, although the pure substance melts at 20.5°. Two distillations of para-xylol failed to give a liquid that approximated to a constant boiling point. An attempt was also made to purify acetone. This was Kahlbaum's best, "from bisulfite," and would have been judged to be perfectly pure from the constancy of the boiling point, but the freezing under about 10,000 kgm. was spaced over a wide pressure interval. Monochloracetic acid was also tried and discarded because it collected impurities from the pressure apparatus, not because it could not be sufficiently purified initially.

Depression of Freezing Point under Pressure.—One question of interest in this connection is as to the variation of the depression of the freezing point by impurity with pressure. It admits of simple thermodynamic treatment as follows.

We shall find it easy to deduce this relation by considering first the equilibrium between pure liquid and pure solid, both being at the same temperature, but the hydrostatic pressure on one being different from that on the other. Let us suppose that the liquid (1) and the solid (2) are in equilibrium under normal conditions at p and t. The temperature of both phases is now raised by Δt, and the pressure on the liquid kept at its original value. We require to find the increment of pressure (Δp) on the solid, so that the liquid at p and $t + \Delta t$ may be in equilibrium with the solid at $p + \Delta p$ and $t + \Delta t$. The relation may be found by an obvious thermodynamic cycle to be

$$\frac{\Delta t}{\Delta p} = \frac{-v_2 t}{\Delta H},$$

where ΔH is the latent heat of transformation. Δt and Δp are, therefore, of opposite sign.

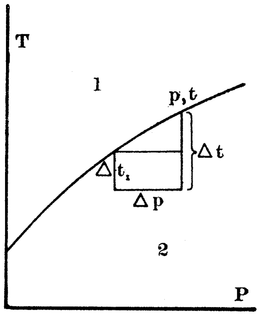

Fig. 1.

Diagram for the depression of the freezing point by impurities.

We now apply this formula to determine the depression of the freezing point. Given pure (1) and (2) in equilibrium at p and t, and impure (1) in equilibrium with pure (2) at p and $t - \Delta t$. We require to find Δt. The direct contact between pure (2) and impure (1) may be separated by an intermediate step. Impure (1) at p and $t - \Delta t$ shall be in equilibrium with pure (1) at $p - \Delta p$ and $t - \Delta t$, and the pure (1) at $p - \Delta p$ and $t - \Delta t$ shall be in equilibrium with pure (2) at p and $t - \Delta t$. Under these conditions we shall evidently also have impure (1) at p and $t - \Delta t$ in equilibrium with pure (2) at p and $t - \Delta t$. The decrement of pressure is evidently the osmotic pressure of the dissolved impurity. Now the formula deduced above gives a relation between Δt_1 and Δp (see Fig. 1). We have, therefore, the two equations

$$\frac{\Delta t_1}{\Delta p} = \frac{v_2 t}{\Delta H},$$

and

$$\Delta t_1 = \Delta t - \Delta p \frac{d\tau}{dp}.$$

Whence

$$\frac{\Delta t}{\Delta p} = \frac{v_2 t}{\Delta H} + \frac{d\tau}{dp} = \frac{v_1 t}{\Delta H},$$

and finally,

$$\Delta t = \frac{v_1 t}{\Delta H} \Delta p.$$

This gives the depression of the freezing point in terms of the osmotic pressure of the dissolved impurity. Now Δp does not change much with increasing pressure, since for impurities of slight concentration it is equal to the pressure that would be exerted by the impurity in the form of a gas occupying the same volume. ΔH changes only slightly on the melting curve, as will be shown later. v_1 decreases and t increases as pressure increases; the two partly neutralize each other. We need expect, therefore, that the depression of the freezing point due to a given quantity of dissolved impurity will not change markedly on the freezing curve, what change there is probably being in the direction of an increase.

(*To be continued in following number, p. 153.*)