CHANGE OF PHASE UNDER PRESSURE.[1]

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

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THERMODYNAMIC SPECIFICATIONS OF THE MELTING CURVE.

The equation of the melting curve in terms of the characteristic equations of solid and liquid may be found as follows. In the following the subscript (1) will refer to the liquid, and (2) to the solid. It is to be noticed, however, that the analysis applies to any two different phases, whatever their nature. The same equations will be used again in discussing polymorphic transformations of solids.

We know that along the melting curve the thermodynamic potential Z, $(= E - tS + pv)$, is the same for the two phases, that is $Z_1 = Z_2$. If now, we know a single point on the melting curve, $(p_0 t_0)$, we can determine the equation of the curve. For we have

$$\left(\frac{\partial Z}{\partial p}\right)_\tau = v$$

and

$$\left(\frac{\partial Z}{\partial \tau}\right)_p = -S.$$

Hence if we know Z at A (see Fig. 21), we find Z at C by integrating $(\partial Z/\partial \tau)_p$ from A to B, and $(\partial Z/\partial p)_\tau$ from B to C.

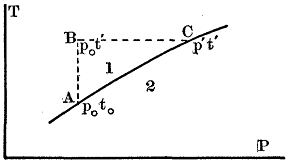

Fig. 21.

The paths followed in the integration for finding the difference of thermodynamic potential between liquid and solid.

Hence along AB,

$$Z(p_0 t') = Z_0 + \int_{\tau_0}^{\tau'} \left(\frac{\partial Z}{\partial \tau}\right)_p d\tau.$$

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[1] Concluded from preceding number.

But

$$\left(\frac{\partial Z}{\partial \tau}\right)_p = -S = -\left[S_0 + \int\left(\frac{\partial S}{\partial \tau}\right)_p d\tau\right] = -\left[S_0 + C_p \log\frac{\tau}{\tau_0}\right].$$

This assumes that C_p is constant over the range in question. The equations are seen to give a good approximation, for variations of the first order in C_p produce variations of only the second order in Z. Substituting the values above and integrating gives:

$$Z(p_0\tau') = Z_0 - (S_0 - C_p)(\tau' - \tau_0) - C_p\tau' \log\frac{\tau'}{\tau_0}.$$

Similarly along BC we have

$$Z(p'\tau') = Z(p_0\tau') + \int_{p_0}^{p'}\left(\frac{\partial Z}{\partial p}\right)_\tau dp.$$

If now we abbreviate the thermal expansion, $(\partial v/\partial \tau)_p$, by β, and the compressibility, considered as positive, by α ($\alpha = -(\partial v/\partial p)_\tau$), we shall have,

$$\int_{p_0}^{p'}\left(\frac{\partial Z}{\partial p}\right)_\tau dp = \int_{p_0}^{p'} v dp = \int_{p_0}^{p'}[v_0 + \beta(\tau' - \tau_0) - \alpha(p - p_0)]dp$$

$$= (p' - p_0)\left[v_0 + \beta(\tau' - \tau_0) - \frac{\alpha}{2}(p' - p_0)\right],$$

and finally,

$$Z(p'\tau') = Z(p_0\tau_0) + (p' - p_0)\left[v_0 + \beta(\tau' - \tau_0) - \frac{\alpha}{2}(p' - p_0)\right]$$
$$- (S_0 - C_p)(\tau' - \tau_0) - C_p\tau' \log\frac{\tau'}{\tau_0}.$$

If now we insert the subscripts (1) and (2) to indicate liquid and solid, and put

$$Z_1(p'\tau') = Z_2(p'\tau'),$$

we have an equation for the melting curve. If we furthermore abbreviated $(\partial v_1/\partial \tau)_p - (\partial v_2/\partial \tau)_p$ by $\Delta\beta$, etc., the equation of the melting curve takes the form:

$$(p - p_0)[\Delta v + \Delta\beta(\tau - \tau_0) - \tfrac{1}{2}\Delta\alpha(p - p_0)] - (\Delta S_0 - \Delta C_p)(\tau - \tau_0)$$
$$- \Delta C_p \tau \log\frac{\tau}{\tau_0} = 0.$$

This equation holds only over a pressure range within which α, β, and C_p may be regarded as constant; this condition is not satisfied over the pressure range of this paper. In fact, it is the variations in $\Delta\alpha$, $\Delta\beta$, and ΔC_p that are of chief importance in determining the shape of the curve over any extended pressure range. This is suggested by what occurs in one simple case. If we assume that $\Delta C_p = 0$, the curve crosses the pressure axis twice, rising to a maximum temperature at some intervening pressure. But we have seen that this maximum temperature does not occur in nature. One important reason for this is that $\Delta\alpha$ does not remain constant, but liquid and solid approach each other in compressibility with rising pressure. In view of the large effect of the variations in $\Delta\alpha$, $\Delta\beta$, and ΔC_p along the melting curve, we will postpone discussion of the form of the curve determined by the above equation until we treat of polymorphic solids, because for solids we expect that these coefficients are more nearly constant than for liquids. The important problem before us at present is to determine as far as we can, the way in which $\Delta\alpha$, etc., vary along the melting curve. We shall indicate first what sort of data are needed for a determination of these quantities, and then get as much information as we can from the data at hand.

Although the equation of the melting curve does not hold over any extended pressure range, it does indicate the initial trend of things, and by differentiation can give us accurately the values of the first and second derivatives at the origin. The differentiation gives

$$\frac{d\tau}{dp} = \frac{\Delta v_0 + \Delta\beta_0(\tau - \tau_0) - \Delta\alpha_0(p - p_0)}{\Delta S_0 + \Delta C_{p0}\log(\tau/\tau_0) - \Delta\beta_0(p - p_0)}.$$

This evidently reduces to Clapeyron's equation, as it should, when $t - t_0$ and $p - p_0$ vanish, since

$$\Delta S_0 = \frac{\Delta H_0}{\tau}.$$

For the second derivative we get:

$$\frac{d^2\tau}{dp^2} = -\frac{1}{\Delta v}\frac{d\tau}{dp}\left[\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\Delta\beta\frac{d\tau}{dp} + \Delta\alpha\right]. \tag{1}$$

We see, therefore, that the curvature of the melting curve gives us one relation between the differences of compressibility, thermal expansion, and specific heat of solid and liquid. The melting curve we have seen to be always concave downwards, or $d^2\tau/dp^2 < 0$. This means, whether the curve rises like most curves, or falls like the ice curve, that

$$\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\Delta\beta\frac{d\tau}{dp} + \Delta\alpha > 0.$$

If the curve should happen to be concave upwards, this would mean either an unusually small value of $\Delta\alpha$, or ΔC_p, or an unusually large value for $\Delta\beta$.

If the curve is to be accurately a straight line, with constant values of $\Delta\alpha$, $\Delta\beta$, and ΔC_p, then we must have the conditions satisfied: $\Delta C_p = 0$, and

$$\Delta\alpha = -2\Delta\beta\,\frac{d\tau}{dp}.$$

In addition to the information given by $d^2\tau/dp^2$, we may also obtain relations between $\Delta\alpha$, $\Delta\beta$, and ΔC_p from the curves for ΔV and ΔH. These relations may be easily deduced, and are

$$\frac{d\Delta H}{dp} = \frac{d\tau}{dp}\Delta C_p + \Delta v - \tau\Delta\beta, \qquad \text{(II)}$$

$$\frac{d\Delta V}{dp} = \frac{d\tau}{dp}\Delta\beta - \Delta\alpha. \qquad \text{(III)}$$

The quantities ΔV, $d\Delta H/dp$, and $d\Delta V/dp$ which enter these relations are to be determined from the curves already given. At first sight it appears that we now have three relations to determine $\Delta\alpha$, $\Delta\beta$ and ΔC_p, but as a matter of fact these relations are not independent. To see this, it is sufficient to observe that $\Delta\alpha$, $\Delta\beta$, and ΔC_p may all three be eliminated from I., II. and III., leaving the value of $d^2\tau/dp^2$ found by formal differentiation of Clapeyron's equation. Two of the relations are independent, however, so that we need only one more independent relation. The new relation must be experimental; we have exhausted the thermodynamic possibilities. At high pressures it might be possible to measure $\Delta\alpha$ or $\Delta\beta$ directly, but a direct measurement of ΔC_p would be much more difficult. Theoretically the measurements are already at hand to give $\Delta\alpha$; this could be determined from the difference of slopes of the isothermals above and below the melting point. But unfortunately very few of the curves are accurate enough to give useful information on this point. The difference of slope is small in any event, and the effect of a very minute quantity of impurity, producing a slightly premature melting, is sufficient in most cases to completely mask the effect sought. To find $\Delta\alpha$ directly, new experiments would be necessary. Perhaps the simplest way to do this would be to determine the isothermals of the solid at several temperatures considerably below the melting curve, and then extrapolate to the melting curve. This could be done without inaccuracy, because the variation of compressibility with temperature is small. Or a somewhat similar procedure would give $\Delta\beta$. However, two of the substances experimented upon give regular enough curves so that the directly determined values of $\Delta\alpha$ seem to have some significance. These quantities will be given later. Also we know from other experiments in a number of cases the values of $\Delta\beta$ or ΔC_p at atmospheric pressure. As complete a list as possible is given of these in the following.

Apparently the best we can do with this problem in general at high pressures is to try to get some idea of the magnitude of the quantities involved by approximations that seem reasonable. There are certain experimental inequalities that can help us. We have in the first place, the fact already mentioned, that universally $d^2\tau/dp^2 < 0$. We also have a nearly universal fact, for all the liquids so far worked with, that

$$\Delta v - \frac{d\Delta H}{dp} > 0$$

if $\Delta v > 0$. This condition may be readily proved to be equivalent in all cases to the condition

$$\frac{d}{d\tau}\left(\frac{\Delta H}{\tau}\right) < 0.$$

That is, the latent heat increases more slowly than the absolute temperature. This condition, if $d\tau/dp > 0$, is equivalent to

$$\frac{1}{\tau}\Delta C_p \frac{d\tau}{ap} - \Delta\beta < 0.$$

There are only two or three exceptional cases at isolated points for the eighteen liquids given above where $d\Delta H/d\tau$ has a very small positive value; the exceptions may be due to experimental error.

A third experimental inequality, with no exceptions, is that $d\Delta v/dp < 0$; that is, the change of volume decreases along the melting curve if positive, and increases in absolute value if negative. This inequality is equivalent to

$$\Delta\alpha > \frac{d\tau}{dp}\Delta\beta.$$

That is, along the melting curve the controlling factor in the change of volume is the difference of compressibility between the two phases, which is in general numerically greater and of opposite sign from the difference of thermal expansion along the melting line.

There is another universal feature of all the curves, namely that the Δv curve is concave upwards, or $d^2\Delta v/dp^2 > 0$. This condition, which is equivalent to

$$-\left(\frac{\partial\Delta\alpha}{\partial p}\right)_\tau + \left(\frac{d\tau}{dp}\right)^2\left(\frac{\partial\Delta\beta}{\partial\tau}\right)_p + \Delta\beta\,\frac{d^2\tau}{dp^2} > 0,$$

is of no immediate help to us here, because it gives the variations, instead of the actual values of $\Delta\alpha$ and $\Delta\beta$ along the curves.

In view of our inability at present to give precise values to $\Delta\alpha$, $\Delta\beta$, and ΔC_p, it becomes of interest to inquire if we cannot with the help of these inequalities find at least the order of magnitude of the several quantities. In general, we expect that $\Delta\alpha$, $\Delta\beta$, and ΔC_p are all positive, or that the compressibility, thermal expansion, and specific heat of the liquid are greater than the corresponding quantities for the solid. So far as I know, at atmospheric pressure, $\Delta\alpha$ is universally positive, even for water where the liquid occupies less bulk than the solid. $\Delta\beta$ is almost always positive; the only exception I know is for water, and even here $\Delta\beta$ becomes positive at higher pressures. And the only authentic example I know of a negative value for ΔC_p is that of sodium, recently measured by Griffiths.[34] We will assume in the following that these quantities are in general positive.

We rewrite the inequalities obtained so far

$$\Delta\alpha - \frac{d\tau}{dp}\Delta\beta > 0,$$

$$\frac{d\tau}{dp}\Delta\beta - \frac{1}{\tau}\Delta C_p\left(\frac{d\tau}{dp}\right)^2 > 0,$$

$$\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\frac{d\tau}{dp}\Delta\beta + \Delta\alpha > 0.$$

The terms entering these inequalities seem to be in general of the same order of magnitude, so that the inequalities usually can give us genuine information. As an average, for these experiments, $\Delta\alpha$ is of the order of 0.00001, $d\tau/dp$ of the order of 0.015, and τ of the order of 350°. This means that $\Delta\beta$ is of the order of 0.0006, and ΔC_p of the order of 10, or 0.2 cal. That is, $\Delta\alpha$, $\Delta\beta$ and ΔC_p are of the same orders as the compressibility, expansion, and specific heat of the liquid alone.

The inequalities may be represented graphically, as shown in Fig. 22. The three quantities are arranged in descending order of magnitude, as shown. The experimental fact that $d^2\tau/dp^2 < 0$ is equivalent to the condition that the difference A to B is greater than the difference B to C.

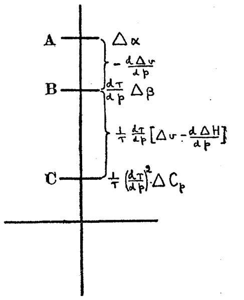

Fig. 22.

Graphical representation of the relative magnitudes of the thermodynamic quantities determining the freezing curve. These relative magnitudes are determined by experiment.

The diagram makes clear what must happen in those exceptional cases when $\Delta\alpha$, $\Delta\beta$ and ΔC_p are not all positive. If $\Delta\alpha < 0$, solid more compressible than liquid, then we must also have $\Delta\beta < 0$, and $\Delta C_p < 0$. That is, $\Delta\alpha$ cannot be exceptional without all three being exceptional. Now if $\Delta\beta < 0$, we must also have $\Delta C_p < 0$, but there is no necessary condition as to sign thereby imposed on $\Delta\alpha$. Finally, if $\Delta C_p < 0$, there is no necessary condition of sign thereby imposed either on $\Delta\alpha$ or $\Delta\beta$. We may therefore say, since the normal state of affairs is for $\Delta\alpha$, $\Delta\beta$ and ΔC_p all to be positive, that the probability of negative values is greatest for ΔC_p, intermediate for $\Delta\beta$, and least for $\Delta\alpha$.

Besides these inequalities, the equations we have written down give us numerically the distances between A and B, and between B and C. Suppose now that we assume a probable value for one of the three quantities, and then compute the other two with the help of the known differences A–B and B–C. It is obvious that we shall make the smallest percentage error in the other two if we assume ΔC_p, and the largest if we assume $\Delta\alpha$.

The numerical values that we give in the following will be computed in this way. We shall assume that $\Delta C_p = 0$, and then compute with the help of the above known differences the values of $\Delta\alpha$ and $\Delta\beta$. If, as is usually the case, ΔC_p is really positive, the values we find will be minimum values for $\Delta\alpha$ and $\Delta\beta$. The values for $\Delta\beta$ so found will not do much good, but the values for $\Delta\alpha$ will be somewhat better, and are perhaps worth giving. The values for all the eighteen liquids listed in this and previous papers will be computed in this way and tabulated.

In addition, where the results are available, the more accurate results will be given for atmospheric pressure. These accurate values at atmospheric pressure, combined with the rougher values at high pressures, will in some cases give us a better hold on the values under pressure. It should, however, be borne in mind that a direct experimental determination of either ΔC_p or $\Delta\beta$ is a matter of unusual difficulty, even at atmospheric pressure, because of the disturbing influence of premature melting due to very slight quantities of impurities. A striking example of the possibilities in this direction is shown in the discussion following under "sodium" of Griffiths' recent values. In particular, direct determinations of ΔC_p seem susceptible to error, as is shown by the very wide divergence of independent direct observations. In some cases, it is probable that the value of ΔC_p computed from the value of $\Delta\beta$ is better than the direct value. There seem to be practically no direct values of $\Delta\alpha$, either at atmospheric or higher pressures. In a few cases, I have, from my own data for determining ΔV at low pressures, been able to find a fairly good value for the difference of thermal expansion at atmospheric pressure, but in most cases the temperature range was not great enough to give satisfactory values for this.

DIFFERENCE OF COMPRESSIBILITY, EXPANSION AND SPECIFIC HEAT BETWEEN SOLID AND LIQUID.

In Table XI. are given these values of $\Delta\alpha$ at pressure intervals of 3,000 kgm. In addition, the values of $\Delta\beta$ at atmospheric pressure are listed. These values for $\Delta\beta$ should not be used without consulting the discussion, where the sources of information at atmospheric pressure are given and the most probable values indicated for each substance in detail.

TABLE XI.

Substance.	Difference of Compressibility (=$\Delta\alpha$).					Difference of Expansion (= $\Delta\beta$).	
	1	3,000	6,000	9,000	12,000	1	12,000
Potassium	$0.0_{5}47$	$0.0_{5}34$	$0.0_{5}27$	$0.0_{5}21$	$0.0_{5}16$	$0.0_{4}75$	?
Sodium	$0.0_{5}33$	$0.0_{5}18$	$0.0_{5}11$	$0.0_{6}8$	$0.0_{6}8$	$0.0_{4}89$	$0.0_{5}4$
Carbon dioxide		$0.0_{4}10$	$0.0_{5}9$	$0.0_{5}6$	$0.0_{5}35$		$0.0_{4}6$
Chloroform		$0.0_{5}37$	$0.0_{5}39$	$0.0_{5}30$	$0.0_{5}16$		$0.0_{4}4$
Anilin	$0.0_{5}82$	$0.0_{5}48$	$0.0_{5}36$	$0.0_{5}29$	$0.0_{5}30$	$0.0_{4}3$	$0.0_{4}8$
Nitrobenzol	$0.0_{4}11$	$0.0_{5}7$	$0.0_{5}32$	$0.0_{5}27$	$0.0_{5}24$[1]	$0.0_{3}11$	$0.0_{4}6$[1]
Diphenylamine	$0.0_{4}24$	$0.0_{5}7$	$0.0_{5}4$	$0.0_{5}3$[2]		$0.0_{3}28$	$0.0_{4}39$[2]
Benzol	$0.0_{4}50$	$0.0_{4}13$	$0.0_{5}6$	$0.0_{5}44$	$0.0_{5}38$[1]	$0.0_{3}48$	$0.0_{4}8$[1]
Carbon tetrachloride	$0.0_{4}12$	$0.0_{5}33$	$0.0_{5}33$	$0.0_{5}14$		$0.0_{3}12$	
O-Kresol { L– I..	$0.0_{4}19$	$0.0_{5}8$	$0.0_{5}36$	$0.0_{5}21$		$0.0_{4}41$	
L–II..			$0.0_{5}30$	$0.0_{5}27$	$0.0_{5}14$		$0.0_{5}4$
Phosphorus	$0.0_{5}43$	$0.0_{5}28$	$0.0_{5}14$			$0.0_{3}10$	
Bromoform	$0.0_{5}49$	$0.0_{5}38$	$0.0_{5}28$	$0.0_{5}19$	$0.0_{5}16$[1]	$0.0_{4}46$	$0.0_{4}54$[1]
Silicon tetrachloride		$0.0_{5}87$	$0.0_{5}37$	$0.0_{5}17$	$0.0_{5}12$[1]		$0.0_{4}21$[1]
Chlorobenzol	$0.0_{4}11$	$0.0_{5}58$	$0.0_{5}36$	$0.0_{5}26$	$0.0_{5}15$	$0.0_{4}13$	$0.0_{4}4$
Bromobenzol	$0.0_{4}13$	$0.0_{5}49$	$0.0_{5}34$	$0.0_{5}17$	$0.0_{5}10$	$0.0_{3}21$	$0.0_{4}4$
Benzophenone	$0.0_{4}29$	$0.0_{4}13$	$0.0_{5}7$	$0.0_{5}3$[2]		$0.0_{3}47$	
p-nitrophenol	$0.0_{4}20$	$0.0_{4}16$[4]	$0.0_{4}12$[5]			$0.0_{3}11$	
p-toluidine	$0.0_{4}31$	$0.0_{4}13$	$0.0_{5}9$	$0.0_{5}7$[2]		$0.0_{3}44$	$0.0_{3}18$[2]
Methyl oxalate	$0.0_{4}67$	$0.0_{5}99$	$0.0_{5}6$	$0.0_{5}7$		$0.0_{3}41$	$0.0_{3}19$[3]
Bismuth	$0.0_{7}57$					$0.0_{4}8$	

[1] 11,000 kgm. [2] 8,000 kgm. [3] 9,000 kgm. [4] 2,000 kgm. [5] 4,000 kgm.

If there is no discussion for any substance, the value of $\Delta\beta$ was computed, assuming $\Delta C_p = 0$. The Table also gives in most cases, for purposes of orientation, the values of $\Delta\beta$ at 12,000 kgm., computed on the assumption that $\Delta C_p = 0$.

Potassium.—There are two experimental values for $\Delta\beta$ at atmospheric pressure; $0.0_{4}84$ by Block,[18] and $0.0_{4}64$ by Hagen.[52] If we assume as an average value $0.0_{4}75$, we find $\Delta\alpha = 0.0_{5}47$, and $\Delta C_p = 0.046$ cal. (1.95 kgm. cm./gm.). The difference of the specific heats found in this way is considerably less than either of two direct values that we have; 0.15 cal. by Bernini,[53] and 0.08 cal. by Joannis.[54] The probability seems to be that 0.046 is nearer the truth; the value of Bernini seems improbably large, and doubt is cast on the value of Joannis by the fact that his value for the latent heat is without doubt too high, as is suggested by the recent work of Griffiths[51] on a similar substance, sodium, for which Joannis' value is certainly too high.

The value found for $\Delta\beta$, assuming $\Delta C_p = 0$, is undoubtedly not good, for it is negative ($= -0.0_{4}25$), but the value for $\Delta\alpha$ on this assumption

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52. E. B. Hagen, Wied. Ann., *19*, 436–474, 1883.
53. A. Bernini, Nuov. Cim. (5), *10*, 5–13, 1905.
54. A. Joannis, Ann. Chim. et Phys. (6), *12*, 358, 1887.

is 0.0_534. We see, as was proved above, that $\Delta\alpha$ is not very sensitive to the value of ΔC_p. In the table, the value for $\Delta\alpha$ is assumed 0.0_547 at atmospheric pressure, and at 12,000 kgm. the value given is on the assumption that $\Delta C_p = 0$. At intermediate pressures, the initial difference of the two values ($0.0_547 - 0.0_534$) is distributed proportionally to the pressure.

Sodium.—There are values for both ΔC_p and $\Delta\beta$ at atmospheric pressure. We have two values for ΔC_p, both negative; -0.07 cal. by Bernini,[53] and -0.06 by Griffiths.[51] Neither of these values are explicitly stated by the original authors, but have been estimated by me from curves plotted from their data giving C_p as a function of temperature above and below the melting point. In spite of the agreement of these values, careful examination of the data leaves the conviction that the agreement is accidental, and even leaves doubt as to whether the negative value for ΔC_p has been proved. The matter is of such importance that it will pay to dwell on it a little. In Fig. 23 are reproduced Griffiths' values for C_p above and below the melting point. It will be seen that the curve for C_p of the solid takes a sudden rise in the neighborhood of 70°. The question suggests itself whether this may not be due to a premature melting because of slight impurity. The amount of melting to account for this change of direction of the specific heat curve is very slight. If we suppose that the actual curve is really the dotted straight line, then the area between the dotted line and the curve through Griffiths' points represents the total heat set free in premature melting. This total heat is one fifth of a calorie which, combined with the latent heat, indicates that only two thirds per cent. of the total quantity of sodium need have melted prematurely to account for

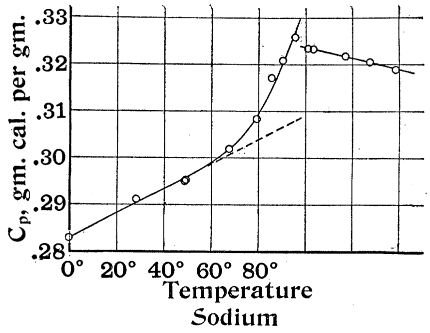

Fig. 23.

The recent values of Griffiths for the specific heat of solid and liquid sodium at atmospheric pressure. In the discussion it is pointed out that a very small quantity of impurity is sufficient to produce the deviation of the specific heat of the solid from linearity.

this. The total amount of impurity needed to produce this slight amount of melting is evidently much less than two thirds per cent., and may well be so small in amount as to resist most careful attempts to remove it. This consideration, of course, has been known for a long time to apply to determinations of differences of specific heat near the melting point, but this example of sodium shows in an unusually striking manner how very slight the amount of impurity need be in some cases to vitiate the result. It should be said that even if we assume the total variation of Griffiths' curve from linearity to be due to premature melting, the error so introduced into his value for the latent heat will be less than 1 per cent.

If we grant for the present the negative value for ΔC_p, and take the average of the two values, $-$ 0.065 cal. (= $-$ 2.78 kgm. cm.), we calculate $\Delta\beta = 0.0_{4}24$. Now the value of $\Delta\beta$ determined by direct experiment is $0.0_{4}83$ by Block,[18] and $0.0_{4}65$ by Hagen.[52] These values are both considerably higher than that found by using the negative value for ΔC_p, and make improbable the validity of the negative value. If we compute backwards with the average of the two experimental values for $\Delta\beta$ (= $0.0_{4}74$) we shall find a very small negative value for ΔC_p, $-$ 0.0004 cal./gm. But it is to be noticed that the same causes which make ΔC_p appear negative will make the experimental values for $\Delta\beta$ too small, and it is significant that the later, and presumably more accurate value for $\Delta\beta$ is the larger. It seems to me that the safest course at present is to assume $\Delta C_p = 0$. This is the assumption made in getting the values of the table. It gives $0.0_{4}89$ for $\Delta\beta$, close to Block's value, and $0.0_{5}33$ for $\Delta\alpha$.

As this paper was going to press, I have come upon a recent paper by Rengade (C. R., *156*, 1897–1899, 1913), in which he finds that the specific heat of the liquid is greater than that of the solid by 0.045 cal. and the melting point of the pure metal is 97°.90. Beyond stating that great precautions were taken to obtain the metal especially pure, no detail is given.

Diphenylamine.—The experimental value for $\Delta\beta$ by Block,[18] $0.0_{3}28$, agrees well with the value computed above, $0.0_{3}24$, assuming $\Delta C_p = 0$. There are, however, two direct determinations of ΔC_p; 0.043 cal. by Batteli,[28] and 0.134 by Bogojawlensky.[55] The values of $\Delta\beta$ computed with these values of ΔC_p are $0.0_{3}38$ and $0.0_{3}68$ respectively. Both of these are considerably higher than the experimental values. Apparently Batteli's value for ΔC_p is much more nearly right than Bogojawlensky's. $\Delta\alpha$ is not appreciably changed by using Block's value for $\Delta\beta$ instead of $0.0_{3}24$.

Benzol.—The experimental value of Block,[18] $0.0_{3}47$, agrees unusually well with that found assuming $\Delta C_p = 0$, $0.0_{3}46$. The presumption is that ΔC_p is small. There are three widely varying experimental values for

[55] Bogojawlensky, quoted by Tammann in "K. und S.," p. 45.

ΔC_p; 0.131 cal./gm. by Ferche,[56] 0.003 by Fischer,[57] and 0.078 by Bogojawlensky.[55] If we assume the intermediate value, we find $\Delta\beta = 0.0_{3}81$, which seems too much above the experimental value. Very recently, since the writing of most of this paper, Essex[58] has published data for the effect of pressure and temperature on the liquid and solid forms of benzol. His value for $\Delta\beta$ calculated by a linear extrapolation from his data for the solid at 1,500 and 2,500 kgm. is $0.0_{3}50$. There seems room for little doubt as to the approximate value of $\Delta\beta$ at atmospheric pressure.

Phosphorus.—There are three experimental values for $\Delta\beta$; $0.0_{3}10$ by Block,[18] $0.0_{3}10$ by Leduc,[59] and $0.0_{4}65$ by Kopp.[60] We shall assume the value $0.0_{3}10$. This is without doubt better than the value, which is 0, calculated assuming $\Delta C_p = 0$. If we assume $0.0_{3}10$ for $\Delta\beta$, we find $\Delta\alpha = 0.0_{5}43$, against $0.0_{5}14$, calculated from $\Delta C_p = 0$. This is an exceptional case where $\Delta\alpha$ is sensitive to the value assumed for ΔC_p. In the table, the values of $\Delta\alpha$ are adjusted at high pressures as they were in the case of Potassium. The value of ΔC_p calculated assuming $\Delta\beta = 0.0_{3}10$ is 0.027 cal./gm., which is in remarkably good agreement with the direct value, 0.026, found by Person.[61]

Monobrombenzol.—No direct experimental values are known for $\Delta\beta$ or ΔC_p, but this is the substance mentioned for which consistent experimental values of $\Delta\alpha$ were obtained over the pressure range. These values, at the pressure intervals of the above table, were $0.0_{4}11$, $0.0_{5}6$, $0.0_{5}3$, $0.0_{5}1$, $0.0_{6}5$, respectively. The agreement with the values computed assuming $\Delta C_p = 0$ is fairly good, and gives some confidence in the values for the other substances. It has been stated that the approximate values of the table are to be expected to be minimum values, but it will be noticed that the experimental values above are in most cases lower than the computed values. The reason for this is probably the unavoidable slight rounding of the corners of the freezing curve.

Benzophenone.—Block's[18] direct experimental value for $\Delta\beta$ is $0.0_{3}47$, against $0.0_{3}19$ assuming $\Delta C_p = 0$. There is no doubt that the direct value is better. The change in $\Delta\alpha$, however, is not so large; $0.0_{4}29$ using Block's value, and $0.0_{4}21$ assuming $\Delta C_p = 0$. The values at higher pressures are adjusted as in previous cases. Using $0.0_{3}47$ for $\Delta\beta$, we calculate $\Delta C_p = 0.075$ cal./gm., as compared with 0.096, the direct experimental value of Tammann.[62]

[56] J. Ferche, Wied. Ann., *44*, 265–287, 1891.

[57] W. Fischer, Wied. Ann., *28*, 400–432, 1886.

[58] H. Essex, Diss. Gött., 1914, Leopold Voss, Leipzig and Hamburg.

[59] A. Leduc, C. R., *113*, 259–261, 1891.

[60] H. Kopp, Trans. Roy. Soc., Vol. 155, 71–202, 1865.

[61] C. C. Person, Ann. Chim. et Phys. (3), *21*, 295–335, 1847.

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

Paratoluidine.—For $\Delta\beta$ there is the direct value $0.0_{3}30$ by Block,[18] $0.0_{3}22$ calculated assuming $\Delta C_p = 0$, and $0.0_{3}44$, a direct value of my own. The range of values of $\Delta\alpha$, letting $\Delta\beta$ vary from $0.0_{3}22$ to $0.0_{3}44$, is only from $0.0_{3}31$ to $0.0_{3}37$, showing again the comparative insensitiveness of $\Delta\alpha$. The value of ΔC_p, using the extreme value of $0.0_{3}44$, is 0.068 cal./gm. This is considerably lower than 0.146, the only experimental value there is, by Batteli.[28] This is apparently much too high, because if we compute back to $\Delta\beta$, assuming 0.146, we find $\Delta\beta = 0.0_{3}75$, which seems impossibly high. The value given in the table assumes $\Delta\beta = 0.0_{3}44$.

Methyl Oxalate.—For $\Delta\beta$ at atmospheric pressure there is the value of Block,[18] who gives 0.000236. I find 0.000405. It is evident that the same impurity which invalidated Block's value for the change of volume will also affect the difference of expansion, and in the same direction as the difference between Block's value and mine. I have, therefore, used my own value in the computations. The values at the higher pressures have been calculated on the assumption that $\Delta C_p = 0$. It is to be remarked that, using my initial value for $\Delta\beta$, the initial value for ΔC_p is negative ($-$ 15 kgm. cm.), an unusual and questionable result. This result depends on the large initial value for $d\Delta V/dp$ rather than on the value for $\Delta\beta$; it is quite probable that the initial value given above for $d\Delta V$ is really too large. There is a direct measurement of the difference of specific heats by Bruner,[34] who found that at the melting point the specific heat of the liquid was 1.41 kgm. m. greater than that of the solid. But Bruner's sample was unusually impure, as has been stated. In any event, this appears to be a substance for which the assumption that $\Delta C_p = 0$ is of more doubtful validity than usual.

Bismuth.—For this substance there are a number of data, none of which are very concordant, from which we may get some idea of $\Delta\alpha$, $\Delta\beta$ and ΔC_p at atmospheric pressure. For the specific heat of the solid there are the following values, shown in Table XII. A questionable extrapolation from all these values would indicate 0.0313 cal. as a probable value at the melting point. For the specific heat of the liquid there is only the value of Person,[42] 0.0363. The value of ΔC_p from these data is 0.0050 gm. cal. or 0.213 kgm. cm. per gm. For the thermal expansion there are two widely differing measurements. Vicentini and Omodei[43] find the average dilatation of the liquid between the melting point and 300° is $0.0_{3}120$, the liquid increasing regularly in volume between these limits. Their value for the average expansion of the solid, presumably from room temperature up to the melting point, is $0.0_{4}395$. Lüdeking,[47] on the other hand, finds that liquid bismuth has a maximum density at about 270°, just as water has above the freezing point. The freezing

TABLE XII.

C_p for Solid Bismuth.

Temperature.	C_p	Observer.
−186°	.0284	Giebe[63]
− 79°	.0296	"
18°	.0303	"
17°– 99°	.0304	Voigt[64]
22°–100°	.03035	Waterman[65]
0°	.03013	Lorenz[66]
50°	.03066	Lorenz[66]
75°	.03090	"
9°–102°	.02979	Bède[67]
15°– 98°	.03084	Regnault[68]
20°–100°	.0314	Schüz[69]

point he gives is about 260°. For the cubical expansion of the solid between 0° and 100° he gives 0.0_441. Lüdeking would make $\Delta\beta$ negative, therefore. His results seem open to considerable question, however, because he knew that there was some impurity of mercury, and because his melting point was 10° too low. If we assume that Vicentini and Omodei's value for $\Delta\beta$ is correct, and combine with the values that may be deduced from the above tables for $d\Delta V/dp$ $(-\ 0.0_78)$ and $d\Delta H/dp$, (− 0.0125 kgm. cm.) we shall find for ΔC_p, 0.17 cal., against 0.21, the experimental value of Person. If, however, we assume the negative value for $\Delta\beta$ given by Lüdeking, we find 0.35 for ΔC_p. Vicentini and Omodei's values seem more probably accurate. The calculated value for $\Delta\alpha$ at atmospheric pressure, using Vicentini and Omodei's value for $\Delta\beta$, is $-\ 0.0_757$. This means that the liquid, in spite of its smaller volume, is more compressible than the solid. If we combine this with the value for the compressibility given by Richards[70] for the solid at room temperature, 0.0_631 cm.^{3} per gm., we shall get some idea of the compressibility of liquid bismuth. At higher pressures, it turns out that bismuth is a substance for which the values of $\Delta\alpha$ are particularly sensitive to the values assumed for ΔC_p. If at atmospheric pressure we assume $\Delta C_p = 0$, we shall find for $\Delta\alpha$ 0.0_726 instead of 0.0_757. In view of this fact, it did not seem worth while to list the values of $\Delta\alpha$ at higher pressures assuming $\Delta C_p = 0$; one will find that on this assumption $\Delta\alpha$ becomes negative above 6,000 kgm., an improbable result.

Theorizing on the data of Table XI. can properly be left until more data are at hand. It will pay to emphasize, however, the fact that $\Delta\alpha$

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[63] E. Giebe, Verh. D. Phys. Ges.

[64] W. Voigt, Wied. Ann., Ann., *49*, 709–718, 1893.

[65] F. A. Waterman, PHYS. REV., Vol. 4, 161–190, 1896.

[66] L. Lorenz, Wied. Ann., *13*, 422–447, and 582–606, 1881.

[67] Bède, Mém. Acad. Roy. Belg., Vol. 27, 1855–56.

[68] V. Regnault, Ann. Chim. et Phys., 73, 1840.

[69] L. Schüz, Wied. Ann., *46*, 177–203, 1892.

[70] T. W. Richards, Pub. Carnegie Inst. Wash., May, 1907.

decreases very rapidly along the melting curve. We see that the equation written above for the melting curve in terms of $\Delta\alpha$ and $\Delta\beta$ cannot be expected to give even a rough approximation to the truth over so wide a pressure range as that here. It is also of interest to note that $\Delta\alpha$ approaches zero much more rapidly than does ΔV. This means that at high pressures the compressibility of liquid and solid are going to approach equality before the volumes reach equality. This seems to suggest that at high pressures a large part of the compressibility is afforded by the actual compression of the molecules, which would be expected to be the same for liquid and solid, while the outstanding difference of volume between liquid and solid is caused by the difference of structure. This observation comes to the same thing as a previous observation on mercury;[71] namely, that if the liquid should be compressed without freezing to the same volume as the solid, its compressibility would be less than that of the solid.

A comparison of the values of $\Delta\alpha$ and $\Delta\beta$ shows a state of affairs for the differences of compressibility and expansion similar to that previously found for the compressibility and expansion of liquids alone.[72] It was observed for liquids that the thermal expansion is decreased much less by pressure than the compressibility. An examination of the table and a comparison with the discussion of the numerical values shows that the decreases in the values of $\Delta\beta$ over the pressure range are much less than those for $\Delta\alpha$, in fact, for some of the substances the decrease is hardly noticeable.

A couple of other points in connection with the equation of the melting curve are worth especial comment. One is this; a complete thermodynamic knowledge of both liquid and solid separately is not enough to determine the location of the melting curve. It is well known that the behavior of a substance is completely determined thermodynamically if we can give the compressibility, thermal expansion, and specific heat at every point. Hence a complete thermodynamic description of solid and liquid separately determines the values of $\Delta\alpha$, $\Delta\beta$, and ΔC_p. But the equation of the melting curve contains one other quantity, ΔS, which cannot be found from the characteristic equation, but must be found by experiment. That is, we must find experimentally one point on the melting curve, and then the characteristic equation of solid and liquid will determine its course everywhere else. If, however, we knew the characteristic equation of the subcooled liquid down to $T = 0$, Nernst's equation would give a means of determining when $Z_1 = Z_2$.

The fact that the equation of the melting curve involves the thermo-

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[71] P. W. Bridgman, Proc. Amer. Acad., Vol. 47, 423, 1911.

[72] P. W. Bridgman, Proc. Amer. Acad., Vol. 49, 1–114, 1913.

dynamics of both liquid and solid has an important suggestion for the mechanism of melting. It means that melting is not determined by anything going on in the solid alone, or freezing by something in the liquid alone. For let us make the contrary hypothesis. We heat a solid at constant pressure, and let us suppose that when we arrive at a certain temperature the molecules of the solid become unstable and fall apart into the liquid. The contention is that this state of instability, whatever is the cause of it, cannot be determined by something taking place in the solid alone. For if we suppose for the moment that instability at the point under consideration is determined by the properties of the solid alone, we see, on heating the crystal again at a different pressure, that the new temperature of melting is determined by the properties of the liquid as well as those of the solid, and hence in general, the properties of both phases determine the melting point. Melting is not like the falling down of a row of dominoes. One possible explanation of this is that as a solid approaches the melting point, the molecules are in constant motion; some of them on the surface fall into the liquid, try it, and if the stability is greater there, the whole crystal follows; if the stability is less, they will ultimately recrystallize. This means that there may be something of the nature of balanced reactions at the melting point, the velocity of melting being equal to that of crystallization. A parallel case may make the nature of the reasoning here clearer. The angle of total internal reflection depends both on the index of refraction of the medium in which the reflection takes place, and on that of the surrounding medium. This means physically that the phenomena of reflection cannot be confined to the heavier medium, but some disturbance must penetrate into the lighter medium; that the light must try the second medium, as it were, and if it does not find it suitable, return to the first medium. This disturbance in the second medium is of course now known to exist, and may be accurately described.

One special application of these considerations is that we are not justified in putting as the criterion of melting that the total expansion of the solid from the absolute zero shall reach a certain value, as is frequently done. For example, Lindemann's[73] deductions, by the aid of the quantum hypothesis and this special assumption, of the natural frequency of the atoms at the melting points, can at best be only an approximation.

THE HYPOTHESIS OF SCHAMES.

Very recently, Schames[74] has published a new hypothesis as to the nature of the equilibrium solid-liquid. This hypothesis is that there

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73. F. A. Lindemann, Phys. ZS., *11*, 609–612, 1910.

74. L. Schames, Verh. D. Phys. Ges., *15*, 1017–1026, 1913, and *16*, 518–528, 1914.

are two critical points between solid and liquid, one at $p = 0$, $\tau = 0$, and the other at $p = \infty$, $\tau = \tau_k$. That is, these two critical points lie on the boundaries of the region that can be reached; continuous passage from solid to liquid is not possible because we cannot go around the critical points. The hypothesis of a critical point at infinite pressure is equivalent to saying that the melting curve rises to a horizontal asymptote. It was the opinion of Schames that the critical temperature corresponding to infinite pressure was the same as the critical temperature liquid-vapor. This seemed to him to be indicated by a very wide extra-

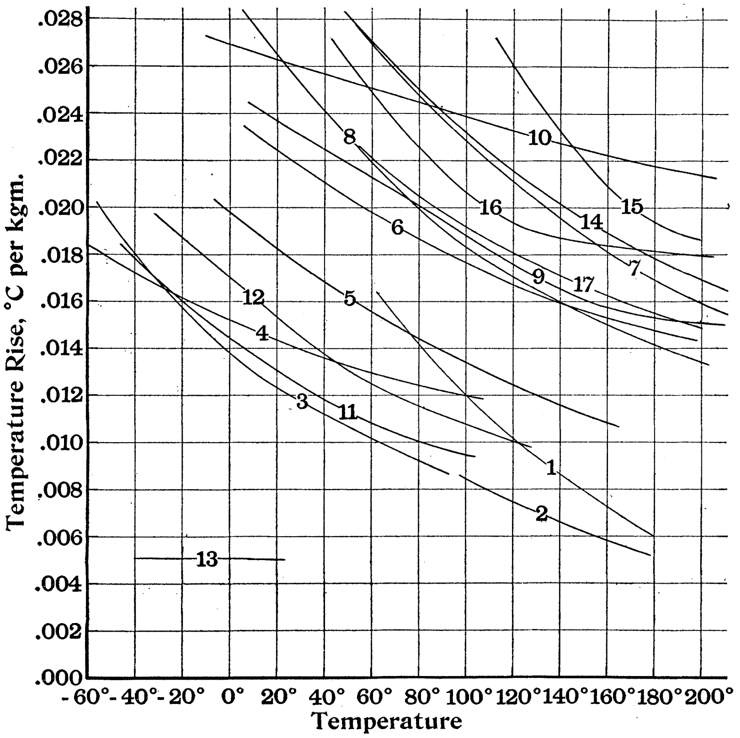

Fig. 24.

Collection in one diagram of the slope of the melting curves of most of the substances hitherto investigated in this series of papers, plotted against temperature. If the melting curve has a maximum temperature, the slope curve must cross the temperature axis vertically at a finite temperature; if it has a horizontal asymptote, it must cross the temperature axis at a finite angle at some finite temperature, or else it must become tangent to the axis at a finite temperature. The figures on the curves refer to the substances as follows: 1, potassium; 2, sodium; 3, carbon dioxide; 4, chloroform; 5, anilin; 6, nitrobenzol; 7, diphenylamine; 8, benzol; 9, bromoform; 10, silicon tetrachloride; 11, monochlorbenzol; 12, monobrombenzol; 13, mercury; 14, benzophenone; 15, paranitrophenol; 16, paratoluidin; 17, methyl oxalate.

polation from my data for water. This paper of Schames was published after the first of the present series of papers appeared, but was written before, so the data of the first paper were inaccessible to him. The fact, there stated, that the melting curve of CO_2 has been followed to above 100°, shows conclusively that the critical temperature, if it exists, cannot in general be the same as the critical temperature liquid-vapor. I have learned from private correspondence with Schames, however, that he does not regard this as an at all essential part of his theory; the essential point is the existence of the horizontal asymptote. It seems a matter of grave doubt, however, whether even this hypothesis is borne out by the data. In Fig. 24 the slope of the melting curve of a number of substances is plotted against temperature. If Schames's hypothesis is correct, these curves should tend to cross the temperature axis at a finite temperature. While one cannot say that the curves prove that this cannot be the case, it is nevertheless evident that such a state of affairs can be reached only by a very wide extrapolation, and that the curves, so far as known at present, offer no justification for supposing that there is such a critical temperature. The existence of curves like 16 shows that any extrapolation is hazardous, and in any event, it would seem to be the part of caution to be wary about extrapolating data from the comparatively low range of pressures open to direct experiment to " infinite " pressures. With out present conception of the structure of the atom, one may be prepared for entirely novel effects at pressures sufficiently high, even for the destruction of the atom itself.

THE EFFECT OF CHEMICAL CONSTITUTION.

There seem to be certain connections, not very definite, between the data of the melting curve and the chemical constitution. A number of these data are collected into Table XIII.: some substances are included here which will be more fully discussed in the next paper. In this table there are three groups of substances differing from each other only by the substitution of Br for Cl. These groups are CCl_4, CBr_4; $CHCl_3$, $CHBr_3$; and C_6H_5Cl, C_6H_5Br. We see that in every case replacing an atom of chlorine by a bromine has the effect of increasing $d\tau/dp$, Δv, and the melting point. There are two groups in the table in which an OH radical replaces a NH_2 radical, phenol, and anilin, and o-kresol and p-toluidine. The effect of the OH is to decrease both $d\tau/dp$ and Δv; the effect on the melting point is different in the two groups. Benzophenone differs from diphenylamine by the substitution of a NH group for a CO group. The heavier radical gives the larger $d\tau/dp$ and Δv. Similarly in the pair p-nitrophenol and o-kresol

Table XIII.

Chemical Relations.

Substance.	Formula.	Molecular Weight.	Melting Point.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$
Sodium	Na	23.05	97°.62	.02787	.00875
Phosphorus	P	31.0	44°.2	.01927	.0295
Potassium	K	39.10	62°.5	.02680	.0178
Carbon dioxide	CO_2	48.00	−56°.6	.14(?)	.0205
Benzol	C_6H_6	78.1	5°.43	.1317	.0286
Urethan	$CO\cdot NH_2\cdot OC_2H_5$	89.1	47°.90	.0599	.01105
Anilin	$C_6H_5NH_2$	93.1	− 6°.4	.0854	.0200
Phenol	C_6H_5OH	94.1	40°.87	.0567	.0140
p-toluidin	$C_6H_4\cdot CH_3\cdot NH_2$	107.1	43°.73	.1413	.0271
O-Kresol	$C_6H_4\cdot CH_3\cdot OH$	108.1	30°.8	.0838	.0177
Chlorobenzol	C_6H_5Cl	112.5	−45°.5	.072(?)	.0184
Methyl oxalate	$C_4H_6O_4$	118.0	54°.2	.1453	.0226
Chloroform	$CHCl_3$	119.4	−61 (?)	.065(?)	——
Nitrobenzol	$C_6H_5NO_2$	123.1	5°.6	.0814	.0219
p-nitrophenol	$C_6H_4\cdot NO_2\cdot OH$	139.1	114°	.0891	.0272
Carbon tetrachloride	$C\ Cl_4$	153.8	−22°.6	.0258	.0393
Bromobenzol	C_6H_5Br	157.0	−31°.1	.056?	.0191
Diphenylamine	$(C_6H_5)_2NH$	169.2	54°.0	.0958	.0257
Silicon tetrachloride	$Si\ Cl_4$	170.2	−67°.(?)	.052(?)	——
Benzophenone	$(C_6H_5)_2CO$	182.1	48°.11	.0904	.02845
Bismuth	Bi	208.5	271°.0	−.00345	−.00342
Bromoform	$CH\ Br_3$	252.9	7°.78	.0391	.0245
Carbon tetrabromide	$C\ Br_4$	331.8	92°		.062

in which a NO_2 replaces a CH_3, the heavier radical gives the larger $d\tau/dp$ and Δv. Nitrobenzol and anilin are another such group; the NO_2 of nitrobenzol replacing the NH_2 of anilin. In general, the effect of a heavier radical seems to be to increase both $d\tau/dp$ and Δv, with an irregular effect on the melting point. But in this respect the radicals H and OH are exceptional. The substitution of H for another radical may increase or decrease $d\tau/dp$ and Δv, and we have seen that OH decreases these quantities, although increasing the molecular weight. Other chemical similarities are not striking. In general, it seems that at present a discussion of the effects of chemical constitution is not very valuable, because the relations, if there are any, are not simple.

Summary.

The melting data for nine more substances have been obtained for the range from 0° to 200° and from atmospheric to 12,000 kgm. pressure. Bismuth has been investigated up to 270°. The evidence of these substances confirms the conclusion reached in the previous paper of this series; namely, that unless there is a reversal at high pressures of the effects

found up to 12,000 kgm., the melting curve continues to rise with pressure and temperature indefinitely, with neither a maximum, nor a critical point.

The equation of the melting curve is obtained in terms of the difference of compressibility, thermal expansion, and specific heat between solid and liquid. It is shown that in virtue of certain experimental inequalities, we may obtain a fairly good approximation to the difference of compressibility between solid and liquid by assuming the difference of specific heats is zero. These approximate values of the difference of compressibility are given as a function of pressure for all the substances whose melting curves have been obtained hitherto. It is found that the liquid and solid approach each other in compressibility more rapidly than they do in volume. A discussion is also given, where the data are available, of the most probable values of the differences of thermal expansion and specific heat at atmospheric pressure. A suggestion as to the mechanism of melting is found in the fact that the equation of the melting curve involves the properties of both liquid and solid. Certain uniform effects of chemical constitution are found, but at present the chemical clue does not seem especially helpful.

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