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The Melting Parameters of Nitrogen and Argon under Pressure, and the Nature of the Melting Curve

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New measurements have been made of the melting parameters (pressure-temperature coordinates of the melting curve and change of volume) of nitrogen and argon up to 5500 kg/cm^2, and the latent heat of melting has been calculated from them. The qualitative behavior of these parameters is exactly like those of all other normal substances (with rising melting curves) hitherto measured, so that there is no experimental basis for the expectation of a critical point between liquid and crystalline phases, or of a maximum or of an asymptotic temperature, but all the experimental evidence indicates only a rise of the melting curve to indefinitely high temperature and pressure.

THE question of the nature of the melting curve has been stimulated to fresh consideration recently by the measurements of Simon[1] of the melting curves of helium, hydrogen, neon, argon and nitrogen. These experiments contain an important and novel feature in that a domain of low temperature new for this type of experiment was entered; the pressure domain on the other hand was not as extensive as had been previously explored with respect to this class of phenomena.

The question at issue with regard to the character of the melting curve has at present apparently resolved itself into the question of which one of the following three possibilities corresponds to the facts: does the melting curve end in a critical point like the critical point between liquid and vapor at some finite pressure and temperature, so that continuous passage between liquid and solid (or crystalline) phase would be possible, or does it rise to a maximum temperature at some finite pressure, and from here fall again, so that a substance might be first frozen and then melted again by applying sufficient pressure at constant temperature (hypothesis of Tammann), or does it merely rise to indefinitely high temperatures and pressures, so that no matter how high the temperature a pressure could be found high enough to force crystallization? Obviously in the nature of the case the third possibility can never be proved by direct experiment, but can be indicated only by some plausible method of extrapolation. The first and second possibilities could, on the other hand, be established by reaching experimentally a critical point or a maximum temperature; this however has not been done, so that the existence of a critical point or maximum can at present also be made probable only by some method of extrapolation. The shape of the melting curve by itself gives no necessary information as to the existence of a critical point, for a curve with a form of equation indicating indefinite rise with temperature and pressure might well be terminated by a critical point. An example of this is Simon's own equation which he finds fits very well a large number of melting curves, $\log (p+a) = c \log \tau + b$. On such a curve a critical point can be indicated only by the extrapolation of some other datum, such as for example the difference of volume between the two phases or the latent heat, for both these quantities vanish at the critical point. Simon clearly recognized this. Since his personal opinion was that the curve ends in a critical point, he initiated measurements of the latent heat along the melting curve of helium, hoping to find the decrease that might point to a critical point. Most unfortunately, his experiments at Breslau had to be terminated before any satisfactory results could be obtained. The opinion of Simon, however, that there is a critical point, seems to be shared in a number of quarters, and in any event the opinion seems to be pretty widely spread that the question is still open. Thus in the thesis just published at Leiden of J. H. C. Lisman[2] on the melting curves of condensed

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[1] F. Simon, M. Ruhemann and W. A. M. Edwards, Zeits. f. physik. Chemie **B2**, 340 (1929); **6**, 62 (1929); **6**, 331 (1930).

[2] J. H. C. Lisman, *Smeltlijnen van gecondenseerde Gassen*, Thesis published by Eduard Ijdo, Leiden, 1934.

gases, in which there is a discussion of all previous results, the statement is made in conclusion that the grounds do not exist for a decision between a critical point and indefinite rise with pressure and temperature, although a maximum temperature may probably be ruled out.

My personal opinion on this subject, based on experiments made now 20 years ago on the melting of some 25 substances in the extreme temperature range from −38°C to +270°C and to pressures usually four times greater than the highest previously reached,[3] was that the experimental evidence unanimously agrees in giving no indication for the existence of a critical point or maximum, but indicates unequivocally that, unless there is some reversal at pressures at present beyond reach of trends nearly universal in the experimental domain, we must expect that the melting curve rises to indefinitely high temperatures and pressures. The only exceptions are the falling melting curves of the abnormal substances bismuth and gallium, and these evidently should not be given weight in drawing a general conclusion. The fact that this conclusion, which seemed to me to rest on such unexceptional experimental evidence, has not been generally accepted might be taken perhaps to indicate that there was some essential feature which I had overlooked. The suggestion therefore that the permanent gases in the low temperature region might give information qualitatively different in character from the information obtainable at higher temperatures from substances liquid under normal conditions challenged an experimental attack.

I have now succeeded in obtaining the complete melting parameters, that is, the pressure-temperature coordinates of the melting curve, the difference of volume between crystalline and amorphous phases, and the latent heat (this latter by calculation from Clapeyron's equation), of nitrogen and argon down to the temperature of boiling nitrogen (77° Abs.) and up to pressures of 5500 kg/cm², which was also approximately Simon's pressure range. That is, for these two substances I have completed Simon's data by measuring the difference of volume, thus obtaining the additional parameters necessary to indicate by extrapolation which of the three possibilities mentioned above is realized. Lower temperatures were not at my command, so that I could not examine Simon's other three gases.

There were experimental difficulties and modifications in previous technique necessary; no attempt will be made to describe these here, but they will be given in detail elsewhere, probably in *Proceedings of American Academy of Arts and Sciences*. Suffice it to say here that sharp melting curves were obtained, internal evidence of the purity of the gases and the satisfactory functioning of the apparatus. The detailed paper will also contain new data, not presented here, for the p–v–t relations of the amorphous phase in the new domain of temperature and pressure; it would seem that there are no previous measurements on nitrogen below 0°C, and no measurements at all at any temperature of the absolute volume of argon at pressures above 200 kg/cm², although there are measurements of my own on the *change* of volume of argon above 3000 kg/cm².

The melting parameters of nitrogen and argon are presented in Tables I and II. Some of the parameters at atmospheric pressure of nitrogen are bracketed in the table. The reason for this is

TABLE I. *Melting parameters of nitrogen.*

Pressure (kg/cm²)	Temp. Abs.	$d\tau/dp$	ΔV cm³/g	Latent heat kg cm/g	$p\Delta V$
1	63.14°	(.0209)	(.072)	(218)	0
1000	82.3	.0176	.058	271	58
2000	98.6	.0153	.047	302	94
3000	113.0	.0135	.040	334	120
4000	125.8	.0124	.033	335	132
5000	137.8	.0117	.029	342	145
6000	149.2	.0112	.026	346	156

TABLE II. *Melting parameters of argon.*

Pressure kg/cm²	Temp. Abs.	$d\tau/dp$	ΔV cm³/g	Latent heat kg cm/g	$p\Delta V$
1	83.9°	.0238	.0795	280	0
1000	106.3	.0211	.0555	280	55
2000	126.4	.0192	.0425	279	85
3000	144.9	.0178	.0340	277	102
4000	162.0	.0165	.0280	275	112
5000	178.0	.0155	.0240	276	120
6000	193.1	.0146	.0210	277	126

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[3] P. W. Bridgman, Phys. Rev. **3**, 126, 153 (1914); **6**, 1, 94 (1915).

that it is probable that the parameters at 1000 kg/cm^2 and higher refer to α-nitrogen (the modification stable below 35.5°K at atmospheric pressure) rather than to β-nitrogen, which melts at atmospheric pressure at 63.14°K. The point is not entirely certain, however, and cannot be settled until there are more accurate measurements of the density of the solid phases at atmospheric pressure. This matter is discussed at some length in the detailed paper.

As far as the pressure-temperature parameters alone are concerned my melting temperatures are distinctly higher than those of Simon at the same pressure; for argon the maximum discrepancy is about 2.5°, but for nitrogen the discrepancy is more serious, increasing steadily with increasing pressure to a maximum of about 6° at 5500 kg/cm^2. The direction of the discrepancy is such that it would be accounted for by impurity in Simon's material, but I think that the correct explanation is something else. Simon's method was the method of the plugging of a capillary, first used by Keesom.[4] Solidification is indicated by the failure of an increase of pressure at one end of the capillary to get transmitted to the other end. It is obvious that there must be shearing stresses in the plug of solid which stops the capillary, and it is known from thermodynamics that the melting point is depressed by a shearing stress by an amount proportional to the square of the stress. The shearing stresses would be expected to become larger at higher pressure, since it is general experience that viscosity may increase enormously under pressure. Simon's capillary was only 0.15 mm in diameter, so that there would seem to have been a possibility of fairly large shearing stresses. The point could be settled, if the experiments were repeated, by varying the size of the capillary.

The important data for the question at issue are contained in the ΔV and the latent heat columns of the tables. If there is a critical point, ΔV and latent heat must extrapolate in such a way as to indicate that they will vanish together at some finite temperature and pressure. For argon the latent heat is constant within experimental error over the entire range, and for nitrogen it rises to an approximately constant value; in neither case is there any justification for the supposition that the latent heat will ever vanish. ΔV decreases with rising pressure and temperature, but it is convex toward the pressure or temperature axis in such a way as to give no justification for the expectation that it will vanish at any finite temperature. If the behavior of ΔV were like that on the liquid-vapor curve it would be concave toward the pressure or temperature axis, and would plunge vertically into the axis at the critical point. As an incidental observation it may further be remarked that if ΔV vanishes at infinite pressure it vanishes less strongly than hyperbolically, as shown by the continuous increase of $p\Delta V$ over the entire range.

If there is a maximum temperature on the melting curve (hypothesis of Tammann), then $d\tau/dp$ plotted against temperature should be concave toward the temperature axis and should plunge vertically into it. Actually $d\tau/dp$ against temperature is convex toward the axis with no indication that it will ever cross. If there were an asymptotic temperature at infinite pressure, which is the hypothesis of Schames,[5] not previously mentioned, $d\tau/dp$ would cut the axis at some finite temperature.

In every one of these aspects just mentioned the behavior of nitrogen and argon is exactly like that of all other normal substances hitherto examined, that is, excepting bismuth and gallium, and the general conclusion must therefore be the same. Not one of the positive qualitative criteria demanded by either a critical point, a maximum temperature at finite pressure, or an asymptotic temperature at infinite pressure, is satisfied, but every qualitative feature points unequivocally toward the indefinite rise of the melting curve to continually higher temperatures and pressures.

The almost universal prevalence of these qualitative features appeals to me as something of great significance, which apparently has not yet been appraised at its full theoretical importance. The significance is increased now with the discovery of a new high pressure modification of bismuth,[6] and the certainty that beyond

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[4] W. H. Keeson, Communications from Leiden, No. 184b, 1926.

[5] L. Schames, Ann. d. Physik **38**, 830 (1912); **39**, 887 (1912).

[6] P. W. Bridgman, Phys. Rev. **45**, 844 (1934).

25,000 kg/cm² bismuth also has a rising melting curve.

It would of course have been gratifying if I could have extended these measurements to helium also and found its ΔV and latent heat along its melting curve, for Simon stresses the point that exploration of the melting curve of helium over a comparatively low range of pressure and temperature might be expected to give as much information about the essential character of the melting curve as an exploration over a much wider range for other substances. The reason given for this is that such an exploration for helium exceeds the critical temperature by a very much larger factor than is possible for other substances. Thus Simon explicitly comments on the fact that in following the melting curve of helium to 55° Abs. and 5500 kg/cm² he has exceeded the critical temperature by a factor of 8-fold, whereas previously the critical temperature had been exceeded at most by 20 percent in the case of CO_2. I believe, however, that examination will show that these considerations have less pertinence than at first appears. The implication, of course, is that in some way the critical parameters for the change from liquid to vapor are of importance for the phenomenon of freezing to the crystalline phase, and that something analogous to the law of corresponding states for liquid-vapor will carry over to amorphous-crystal, with some connection between the two sets of reduced parameters. Not only is there, so far as I know, no reason theoretically to expect any such connection, but I have previously shown on the basis of the experimental evidence that there can be no law of corresponding states for the freezing of different substances. Until some connection has been established therefore between liquid-vapor and amorphous-crystal phenomena, there would seem to me no reason to ascribe greater significance to the fact that Simon has been able to exceed the critical *temperature* of helium by a factor of 8 than to the fact that the critical *pressure* of CO_2, for example, had previously been exceeded by a factor of 165. It would seem to me on the contrary that any special effects to be shown by helium would be expected in the low temperature domain where degration and similar effects occur, and that having successfully got helium out of this domain into that of normal temperature phenomena, it would be expected to have exhausted its possibilities of giving unique information, and from here on to be of perhaps not much greater significance than other substances. The mere fact that it is possible to bring the melting curve of helium up into the region of normal temperature effects is in itself an argument for the significance of the universal traits of the melting curve discussed above.

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Erratum: A New Method for Measuring Elastic Moduli and the Variation with Temperature of the Principal Young's Modulus of Rocksalt Between 78°K and 273°K

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DR. S. L. QUIMBY of Columbia University, New York, has recently pointed out an error in Eq. (13) on page 716 of the above paper. This equation should read

$$f_i = n(G_i^{\frac{1}{2}}/2\rho_i l_i^{\frac{1}{2}})(1-\pi^2 n^2 \sigma_i^2 \theta_i / 2 l_i^2 A_i)$$

instead of

$$f_i = n(G_i^{\frac{1}{2}}/2\rho_i l_i^{\frac{1}{2}})(1-\pi^2 n^2 \sigma_i^2 \theta_i / 4 l_i^2 A_i).$$

However, the correct formula was used in computing the results compiled in the various tables in the paper.