

## MELTING AT HIGH PRESSURES

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Usp. Fiz. Nauk 96, 467-496 (November, 1968)

MELTING occupies a special position in the general system of phase transitions as a universal physical phenomenon that can be observed for virtually any substance. In this respect, melting can be compared with boiling, which is just as universal. Even more essential is still another special feature of melting, for which there exists no analog, namely, the fact that melting represents a result of competition between two condensed and yet fundamentally different states of matter: liquid and solid. Obviously, this phenomenon cannot be disregarded and has been the subject of painstaking studies by many investigators, which have resulted in accumulating a large number of experimental findings and empirical generalizations concerning melting and crystallization (see, e.g., [1]). Despite its abundance, however, the accumulated experimental material has not yet adequately contributed to developing some acceptable theory of melting that could unify the known facts and predict some new aspects of this phenomenon. Aside from the known difficulties of a rigorous statistical approach to the problem of phase transition in general, such a situation is chiefly attributable to the lack of sufficiently suitable models of molten state that could qualitatively reflect reality faithfully [2-4]. It is perfectly obvious that under these conditions research into the effect of pressure on the melting temperatures is of major interest and may lead to the discovery of new and possibly unexpected effects.

The present review is an attempt to expound and, to some extent, critically generalize the experimental material on the melting of substances at high pressures.

## 1. ELEMENTARY INFORMATION ON MELTING

Melting, like crystallization, occurs at strictly defined temperatures and is accompanied by abrupt changes in volume and entropy. It is worth noting that the melting process is distinguished kinetically by a major feature, namely, by the fact that when a crystal is heated from the surface, its superheating above the melting point is virtually impossible and in these conditions melting always commences at the surface of the crystal. The decisive role of the surface is here indubitable and it essentially lies in reducing to zero the activation energy for the formation of a surface nucleus (thin liquid film) [2,5].

This feature of melting, when considered outside its relation to kinetic conditions, has prompted many investigators to assume that a solid at its melting point is absolutely unstable [6].

First of all, it must be observed that any substance not in internal equilibrium cannot be in equilibrium with any other substance. However, observations of the coexistence of the liquid and crystal at the melting point leave no doubt that this coexistence is of an equilibrium nature. Further, there exist proofs that if a crystal is

heated from the inside, so that its surface is colder than its interior, superheating can be accomplished [7,8]. Similar results can be obtained during melting under pressure at a constant temperature [8].

Thus, melting represents a typical first-order phase transition with metastable states existing on both sides of the transition point, and the transition point itself is determined by the equality of the corresponding thermodynamic potentials. Like other first-order phase transitions, it is governed by the Clausius-Clapeyron equation

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}, \quad (1)$$

where T and P are the melting temperature and pressure,  $\Delta V$  and  $\Delta S$  are the changes in volume and entropy due to melting. The entropy of the liquid phase is always greater\* than the entropy of the crystal and hence the change in entropy upon melting is always positive:

$$\Delta S_{\text{melt}} > 0. \quad (2)$$

The change in volume upon melting may be either positive or negative and hence, as follows from (1) and (2), the slope of the melting curve  $dT/dP$  also may differ in sign and is entirely determined by the sign of the change in volume.

To provide an idea of the order of magnitude of the changes in volume and entropy upon melting, Table I

Table I

Element	Crystal structure	$\Delta V/V$	$\Delta S$ , cal/mol-deg	$dT/dP$ , deg/kg-cm <sup>-2</sup>
Lithium	Body-centered cubic	0.0165	1.59	0.0032
Sodium	" "	0.025	1.68	0.0084
Potassium	" "	0.0255	1.65	0.0166
Rubidium	" "	0.025	1.79	0.0183
Cesium	" "	0.026	1.69	0.0252
Aluminum	Face-centered cubic	0.060	2.74	0.0054
Copper	" "	0.0415	2.30	0.0032
Silver	" "	0.038	2.19	0.0044
Gold	" "	0.051	2.21	0.0058
Lead	" "	0.035	1.90	0.0081
Magnesium	Hexagonal closed-packed	0.041	2.31	0.0062
Zinc	" "	0.042	2.55	0.0036
Cadmium	" "	0.040	2.44	0.0052
Indium	Tetragonal face-centered	0.020	1.82	0.0042
Tin	Tetragonal body-centered	0.028	3.41	0.0031
Antimony	Rhombohedral	-0.0095	5.25	-0.00078
Bismuth	" "	-0.0335	4.78	-0.0035
Germanium	Cubic diamond	-0.05	6.28	-0.0026
Gallium	Rhombic	-0.032	4.41	-0.0020
Argon	Face-centered cubic	-0.144	3.35	0.0255
Krypton	" "	0.151	3.36	0.0322
Xenon	" "	0.151	3.40	0.0398

\*One of the exceptions to this rule is associated with the ordering of nuclear spins in liquid He<sup>3</sup> at extremely low temperatures [9,10].

Table II

Element	Solid State			Liquid state		
	Temperature, °K	Coordination Number	Interatomic distance, Å	Temperature, °K	Mean coordination Number	Mean Interatomic distance, Å
Lithium		8	3.03	453.7	9.5	3.15
Sodium		8	3.72	373	9.0	3.82
Potassium		8	4.50	338	9.0	4.64
Rubidium	100*	8	4.87	313	9.5	4.97
Cesium	100	8	5.24	303	9.0	5.31
Aluminum		12	2.86	973	10.6	2.96
Copper		12	2.55	1373	11.5	2.56
Silver		12	2.88	1323	11.0	2.86
Gold		12	2.88	1350	11.0	2.85
Lead		12	3.49	623	11.7	3.38
Magnesium		6+6	3.19-3.20	933	10.0	3.35
Zinc		6+6	2.66-2.50	733	10.8	2.94
Cadmium		6+6	2.97-3.29	623	8.3	3.06
Indium		4+8	3.24-3.37	433	8.5	3.30
Tin		4+2+4	3.02+3.17-3.76	505	8.2	3.26
Antimony		3+3	2.87-3.37	938	6.4	3.12
Bismuth		3+3	3.10-3.47	558	7.6	3.35
Germanium		4	2.44	1273	8.0	2.7
Gallium		1+2+2+2	2.44+2.71+ +2.74+2.80	293	11.0	2.77
Argon	40	12	3.83	86.3	8.2	3.9
Krypton	20.5	12	3.95	117	8.5	4.02
Xenon	88	12	4.40		~8.3	4.43

\*Temperature in this column is specified only whenever it markedly differs from room temperature.

presents the corresponding data for a number of elements. It also lists the initial slope of melting curves, calculated as the ratio  $\Delta V/\Delta S$  in accordance with Eq. (1).

Moreover, it is worthwhile to compare certain structural characteristics of solids and the corresponding liquids. To this end, Table II presents information on the number of nearest neighbors or the coordination number of atoms in solids and liquids, as well as on the shortest interatomic distances. It is worth recalling that the fundamental differences existing between the structures of liquids and crystals make this comparison highly arbitrary, if only because the very concept of the coordination number has a different meaning for crystals and for liquids<sup>[4]</sup>.

The principal source of information on liquid structure is the radial distribution function, which can be calculated from the data on the scattering of x rays and neutrons by the liquid. The radial distribution function  $g(r)$  determines the probability of finding a liquid particle at a distance between  $r$  and  $r + dr$  from another fixed particle, and is specified by the relation

$$dW(r) = g(r) \frac{4\pi r^2 dr}{V}$$

The function  $g(r)$  oscillates with damping about the value of unity and it usually displays two or three distinct maxima, pointing to the existence of short-range ordering and determining the mean distances from a given fixed particle to particles located in the first, second, etc. coordination spheres. The number of particles in the corresponding coordination spheres can be calculated with the aid of the integral

$$\int_{r_1}^{r_2} g(r) 4\pi r^2 \frac{N}{V} dr,$$

where  $r_1$  and  $r_2$  are the coordinates of the minima of the function  $g(r)$ .

In contrast with the above, the radial distribution function in crystals displays a pronounced discontinuous nature, so that the probability of finding atoms outside fixed positions is practically zero.

Nonetheless, we shall speak of the similarity of or, conversely, difference between the structures of liquids and crystals, but we shall construe thereby only the similarity of and difference between the mean coordination numbers and interatomic distances.

When Tables I and II are both simultaneously examined, interesting correlations between the liquid structure due to melting and the variations in thermodynamic properties can be perceived. On melting of substances with closely packed structures the coordination number in the liquid acquires a lower value than in the crystal, while interatomic distances do not change markedly. The volume jump then reaches 4–15% and is to a large extent determined by the coordination number in the liquid. On melting of substances with relatively loose structures, on the other hand, a distinct tendency toward a rise in coordination number and a decrease in volume change manifests itself. In cases where the coordination numbers increase significantly (which naturally is possible only for the originally highly loose structures), moreover, the sign of the volume jump may be reversed; then, in accordance with the rules of sphere packing, the interatomic distances also increase.

The material presented in the tables demonstrates that the changes in thermodynamic and structural properties during melting are to a sufficient degree individual and therefore we cannot assume the existence of some universal law, such as the law of corresponding states, that could apply equally to the melting of any substance.

However, laws of this kind may exist for individual groups of elements or compounds with a common nature of interaction and common crystallochemical features. Moreover, it is conceivable that, given extremely high pressures at which all substances acquire some one of the close-packed structures and the interaction between atoms will be determined only by the repelling part of the interaction potential, the melting phenomenon must display certain common basic features both as regards the shape of the melting curve and as regards the variation in various thermodynamic properties during melting. In all likelihood, it is the hope to discover these fundamental properties of melting that prompts the investigators to study the melting of substances under increasingly higher pressures. A major stimulus in this respect is also the striving to solve a number of geophysical and technological problems.

## 2. BASIC THEORIES OF THE BEHAVIOR OF THE MELTING CURVE AT HIGH PRESSURES

At present there still does not exist a universally accepted and rigorously substantiated theory of the behavior of the melting curve at high pressures. The existing fundamentally intuitive theories mostly reduce to ideas of unlimited rise in melting temperature with rise in pressures and of conservation of the thermodynamic characteristics of melting as a first-order phase transition under even the highest pressures. At the same time, the old hypothesis that the melting curve, like the boiling curve, terminates at the critical point still enjoys wide currency<sup>[19-22]</sup>.

Let us recall that, generally speaking, two types of critical points at which the first-order phase transition terminates may be considered<sup>[23]</sup>: 1) critical point of

the first type, analogous to the critical point on the boiling curve, above which there does not exist any continuity of properties of the system; 2) critical point of the second type, at which the first order phase transition switches to a second-order phase transition.

The impossibility of the critical point of the first type in melting is at present sufficiently obvious and can be substantiated by the arguments proposed in 1937 by L. D. Landau<sup>[23]</sup>. The absence of long-range order in liquids results in their complete isotropy, whereas crystals are always anisotropic. Hence, the transition from liquids to crystals entails the disappearance of a number of symmetry elements. But since a gradual disappearance of elements of symmetry is impossible, a gradual transition from liquid to crystal state also is impossible.

As for the possibility of existence of the critical point of the second type, here the situation is less clear. The melting theory of Lennard-Jones and Devonshire<sup>[24]</sup> predicts the existence of this point, but the shortcomings of this theory are so substantial that its predictions cannot be accepted as arguments.

L. D. Landau considered this question by his well-known method of expanding the thermodynamic potential in powers of a small parameter and arrived at the conclusion that the critical point of the second type cannot exist on the melting curve<sup>[23]</sup>. But this conclusion clearly is valid only to the extent that the assumption of the possibility of expansion of the thermodynamic potential in the neighborhood of the transition point is valid. Since  $\Delta V = 0$  and  $\Delta S = 0$  are necessary conditions for the existence of critical points of the first and second types, this problem can be logically resolved by considering the variations of  $\Delta V$  and  $\Delta S$  along the melting curve. The corresponding experimental material will be presented in the next chapter but, to anticipate the matter somewhat, it must be stated that the experimental situation is not favorable to the idea that  $\Delta V$  and  $\Delta S$  both turn to zero at some one final pressure. This conclusion was first most clearly formulated by P. Bridgman<sup>[25]</sup>.

It should be noted that, despite the mention of the existence of melting curves with a negative slope ( $dT/dP < 0$ ), we shall not consider these curves in our discussion. This is not accidental, since even P. Bridgman in his time established that substances with a negative slope of the melting curve—he had termed melting curves of this kind “anomalous”—undergo phase transition with rise in pressure, whereupon their melting curve acquires a positive slope<sup>[25]</sup>. Modern studies confirm this regularity (see later pages). It is not our aim to trace the entire history of this question and hence we shall not consider various hypotheses that are merely of historical interest. Practically the entire material concerning the various theories of melting curves can be found in Bridgman's reviews<sup>[25,26]</sup>. However, for reasons which will become clear later on, we shall dwell for the moment on Tammann's hypothesis of the temperature maximum on the melting curve<sup>[27]</sup>. Tammann based his arguments on his theory of the molecular structure of liquids. He assumed that, owing to their non-ordered structure, liquids under high pressures can occupy a smaller volume than solids. The experimentally established fact that liquids are more compressible than the corresponding solids was adduced in

favor of Tammann's argument. Tammann had succeeded in discovering a maximum on the melting curve of Glauber's salt  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , which further strengthened his conviction of the validity of his hypothesis. However, his opponents pointed out that Glauber's salt behaves as a two-component system and its “melting curve” actually represents the line of a three-phase equilibrium. In particular, Bridgman persisted in his idea of the unlimited rise of the melting curve with rise in pressure. Ultimately, Bridgman's elegant experimental studies enabled him to consolidate in science his theory of the behavior of the melting curve. Such had been the state of the question in the late 1930s.

It must be noted, however, that the technical level of experiment at that time did not make it possible to investigate substances with melting points exceeding  $200\text{--}250^\circ\text{C}$  and the maximum pressures then attainable in the laboratory were limited to  $30,000\text{ kg/cm}^2$ . Therefore, the variety of substances investigated had been very limited. In the postwar years, on the other hand, high-pressure technology has been making extremely rapid progress owing chiefly to such stimuli as the demand for artificial diamonds. Methods of creating pressures reaching as much as  $100,000\text{ kg/cm}^2$  have been developed, in a combination with temperatures of the order of  $2000^\circ\text{C}$ , on using plastic solids as the pressure-transmitting media<sup>[28]</sup>.

Special mention should be made of the development of methods for determining the melting points of transparent substances under conditions of shock compression<sup>[38]</sup>.

The possibilities of the old method—the creation of hydrostatic pressures by compressing gases or liquids—also have been markedly expanded, owing to the introduction of heaters inside high-pressure chambers, which made it possible to attain much higher temperatures. Such great methodological advances considerably broadened the stream of new information, including also new information on the melting of various substances under high pressures. One of the most interesting results of recent research into phase equilibria under high pressures was the discovery of temperature maxima on the melting curves of a large number of substances (see later). It is highly intriguing that these curves display the same regularity as the melting curves with negative slope. Beyond the maximum, i.e., in the region of pressures corresponding to a negative slope of the melting curve, solids undergo a phase transition whereupon the slope of the melting curve becomes positive. Thus the totality of the experimental data known at present makes it possible to divide the T-P diagrams of monocomponent systems into three types, as illustrated in Fig. 1.

It is noteworthy that monatomic substances such as

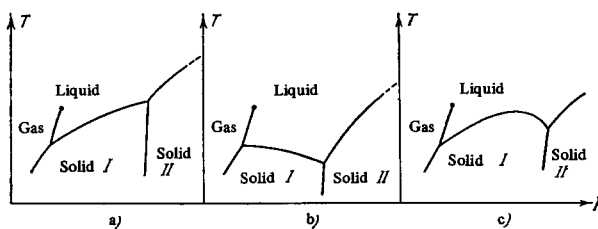


FIG. 1. Three types of phase diagrams of monocomponent systems

solidified noble gases, noble metals, etc. which already have a close-packed structure under normal conditions, in all likelihood can undergo a phase transition only at extremely high pressures. Clearly, transition of this kind will be conditioned by changes in the electronic structure of atoms, collectivization of electrons and nuclear transformations<sup>[5]</sup>. Hence, on confining attention to the pressure range of the order of  $10^4$ – $10^6$  kg/cm<sup>2</sup>, we cannot presuppose the absence of any transformations in these substances that might distort the ideal course of the melting curve. For this very reason, in our present attempt to elucidate the basic laws of melting, we shall consider only close-packed and similar substances whose melting curves, within the limits of experimental data, display a continuous rise with rise in pressure. Melting curves with a negative slope and with temperature maxima, which we shall term "anomalous," are considered separately.

### 3. MELTING OF SUBSTANCES WITH CLOSE-PACKED STRUCTURES

We have already pointed out above that the melting points of a substance with close-packed or similar structures rise with increase in pressure. The rate of this rise, or the magnitude of the derivative  $dT/dP$ , ranges within very broad limits. Some idea of the initial slopes of melting curves can be derived from Table I. On the whole, it may be noted that at atmospheric pressure the highest  $dT/dP$  is displayed by substances with a large molar volume and weak interatomic forces. Figures 2–3 present the melting curves of a number of elementary substances. It must be immediately noted that

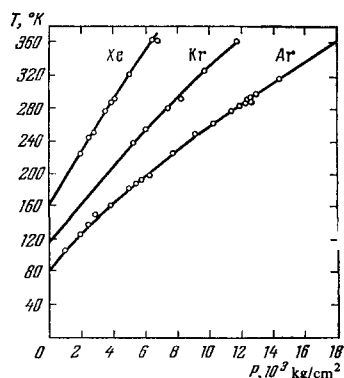


FIG. 2. Melting curves of Ar, Kr and Xe [29]

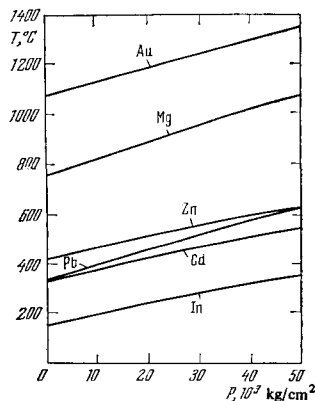


FIG. 3. Melting curves of metals [30, 31]

it is not our purpose to expound here the available numerical or graphic material on melting curves. This material and the pertinent bibliographical references can be found in recent reviews<sup>[33–35]</sup>.

It can be seen from Figs. 2–4 that the slope of the melting curves decreases with increase in pressure, i.e.,  $d^2T/dP^2 < 0$ . This points to a more rapid decrease in the volume jump than in the entropy jump along the melting curve.

It is interesting to note that the melting curves of many substances have at present been traced up to temperatures greatly exceeding the critical-point temperature. This can be readily ascertained by comparing the critical temperatures for Ar, Kr and Xe, which are 87.3, 119.8 and 165°K, respectively, with the melting curves of these substances shown in Fig. 3.

The information that can be extracted solely from knowing the P-T coordinates of melting is not very considerable, but nevertheless it warrants the conclusion that the general pattern of the melting curves remains unchanged up to the highest pressures corresponding to a nearly twofold compression of the substance (Fig. 4). Moreover, since melting, like any other first-order phase transition, is reflected by the continuity of some properties, it can be stated that this continuity persists throughout the experimentally investigated range of pressures. Nevertheless, it cannot as yet be confidently stated that the application of still higher pressures will not affect the nature of this phenomenon.

We shall now consider the variation in the volume jump  $\Delta V$  and entropy jump  $\Delta S$  along the melting curve. It must be emphasized that some caution must be applied when investigating the pressure dependence of  $\Delta V$  and  $\Delta S$  and, a fortiori, when extrapolating these variables beyond the limits of experimental pressures. The point is that the measurement of  $\Delta V$  along the melting curve is an intricate problem that is compounded by difficulties of a fundamental nature. The measurement errors are very large and in some cases may reach 30%<sup>[36]</sup>. By way of an example, Fig. 5 presents the temperature dependence of the volume discontinuity during the melting of mercury according to Bridgman's data and the more thorough measurements by V. S. Bogdanov<sup>[36]</sup>. It can be seen that the course of the two curves is markedly dissimilar, although their absolute values are similar. Even greater caution must be preserved when considering  $\Delta S$ , since this quantity, as a rule, is derived from known values of  $dT/dP$  and  $\Delta V$  instead of being directly measured.

In this connection, it seems reasonable to us, when examining the behavior of  $\Delta V$  and  $\Delta S$  along the melting curve, to confine attention only to the experimental results in which the variation in these quantities has been

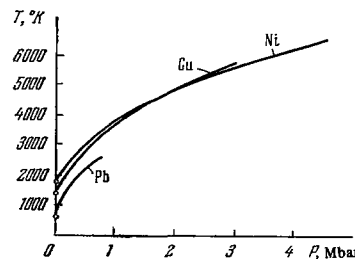


FIG. 4. Melting curves of Cu, Ni and Pb (derived from data on shock compression [32])

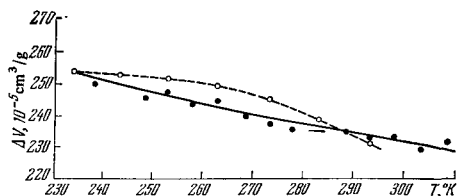


FIG. 5. Temperature dependence of volume discontinuity during the melting of mercury [36]. ●—Bridgman's data; ○—V. S. Bogdanov's data [36].

traced over a broad range of values. Figures 6–10 present the corresponding data in the coordinates  $(\Delta V_m/V_s) - P$  and  $(\Delta S/R) - P$ , where  $\Delta V_m$  is the volume discontinuity during melting,  $V_s$  is the current volume of the solid at the melting point, and  $R$  is the gas constant. On these plots the values of solid-phase volume at the melting point also are presented along the pressure axis in order to provide an idea of the degree of compression of the substance.

We note that when elucidating the common features of the variation in some quantity along the melting curves the isotopes of helium should perhaps not be considered by way of an example, since the behavior of these isotopes is largely determined by zero-point energy. Moreover, in view of the closeness of the melting points of helium to absolute zero at low pressures, the manifestation of Nernst's heat theorem is essential here and hence the entire behavior of thermal characteristics must differ from the ordinary. However, there is reason to hope that so far as volume properties are concerned the situation is more favorable.

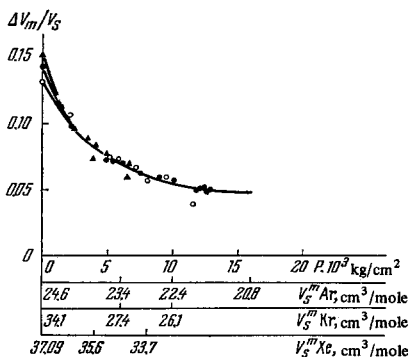


FIG. 6. Pressure dependence of relative volume discontinuity during melting of Ar, Kr and Xe [29].

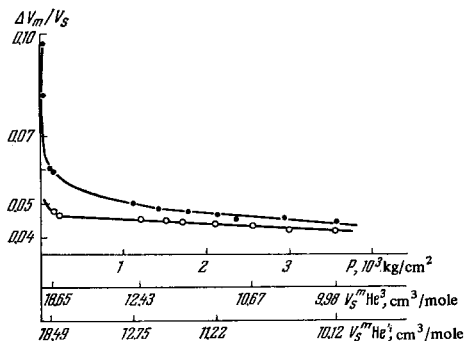


FIG. 7. Pressure dependence of relative volume discontinuity during melting of He<sup>3</sup> (○) and He<sup>4</sup> (●) [37].

Returning to our discussion of the plots in Figs. 6–10, we consider first the variation in  $\Delta V_m/V_s$ . It can be seen that  $\Delta V_m/V_s$  decreases very rapidly at low pressures. This effect is satisfactorily explained by the early observations of Bridgman [25], who established that the compressibility of liquids under low pressures greatly exceeds the compressibility of the corresponding solids. However, Bridgman also pointed out that already under pressures of the order of several thousand kg/cm<sup>2</sup> the compressibility of liquids comes markedly close to the compressibility of solids. Hence, it can be seen in Figs. 6–10 that as pressure increases the rate of variation in  $\Delta V_m/V_s$  diminishes appreciably, and it is highly probable that this ratio tends to a constant value. This is especially clearly exemplified by the helium isotopes and NaCl\*, whose behavior can be traced up to extremely high degrees of compression (Figs. 7 and 10).

So far as the variation in the entropy discontinuity is concerned, this discontinuity also rapidly diminishes under low pressures and in the case of Cu, Al and NaCl (cf. Figs. 8 and 10) it rapidly reaches a nearly constant value. For noble gases the results are not as definite, but the limiting degree of compression reached in their case is much smaller than for Cu, Al and NaCl. Nevertheless, even these substances too display some tendency toward saturation (cf. the curve of Ar in Fig. 9).

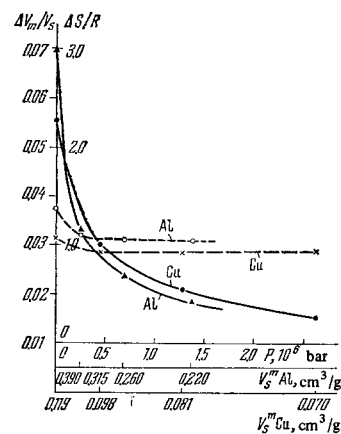


FIG. 8. Pressure dependence of relative volume discontinuity and entropy discontinuity during melting of Al and Cu. Derived from data on shock compression [32] ○ and ×— $\Delta S/R$ ; ● and ▲— $\Delta V_m/V_s$ .

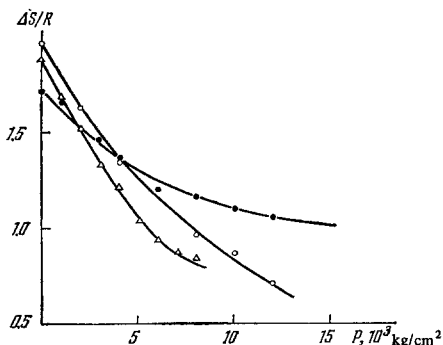


FIG. 9. Pressure dependence of entropy discontinuity during melting of Ar, Kr and Xe [29].

\* As is known, NaCl is not a substance with a close-packed structure, but we deemed it possible to use here the findings of [38], since they point to the absence of any perturbing effects on the melting curve at pressures of up to 10<sup>6</sup> kg/cm<sup>2</sup>.

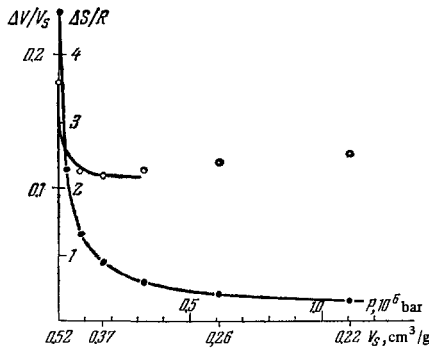


FIG. 10. Pressure dependence of relative volume discontinuity and entropy discontinuity during melting of NaCl. Derived from data on shock compression [38].

Thus, the available experimental material, though highly limited, demonstrates that the quantities  $\Delta V_m/V_s$  and  $\Delta S$  do not tend to zero. Moreover, the assumption that

$$\begin{aligned} \frac{\Delta V_m}{V_s} &\rightarrow \text{const}, \\ \Delta S &\rightarrow \text{const} \\ \text{as } p &\rightarrow \infty, \end{aligned} \quad (3)$$

becomes highly likely, and we have no choice but to conclude that, in the words of Bridgman penned many years ago<sup>[25]</sup>: "... We must recognize that the experimental data available at present point to a high probability that the melting curves of all substances rise without limit at a gradually decreasing rate until the pressure reaches a value at which phenomena of a completely new kind will arise..."

Here it is appropriate to consider the recent study by Ross and Alder<sup>[39]</sup>, which concisely presents the calculations of the melting curve of argon by the Monte Carlo method. As is known<sup>[40]</sup>, the Monte Carlo method can be used to directly calculate the configuration integral by means of numerical integration over a random ensemble of points, and hence the solution of the problem requires only specifying the function of intermolecular interaction. The results of these calculations are presented in Table III and in Figs. 11 and 12.

Figure 11, in which the experimental and theoretical isotherms at 108.15° K are compared, shows that the Monte Carlo method is in good agreement with experiment. As can be seen from the table, the calculations can be extrapolated to extremely high pressures and temperatures ( $\sim 4 \times 10^6$  bar and  $> 10^4$  K) and, in all likelihood, the behavior of real argon may differ from the behavior dictated by the calculations owing to the deviation of the interaction potential from additiveness at high temperatures and pressures<sup>[41]</sup>. Hence, in a certain sense, the described "machine" experiment is even of a greater value than a real experiment, since it allows tracing the "pure" line of the phenomenon.

Table III

$T_m, ^\circ\text{K}$	$P_m, \text{kbar}$	$V_s, \text{cm}^3/\text{mole}$
83.81	—	24.61 *
108.15	$1.01 \pm 0.08$	$24.49 \pm 0.12$
2440	$292 \pm 10$	$11.44 \pm 0.12$
12200	$3970 \pm 30$	$5.815 \pm 0.015$

\*Experimental result

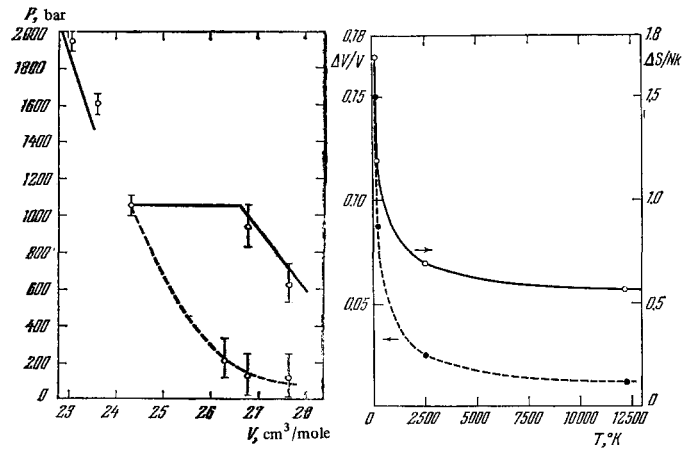


FIG. 11

FIG. 11. Comparison of experimental isotherm of argon with the isotherm calculated by the Monte Carlo method at 108.15° K [39]

FIG. 12

FIG. 12. Relative volume discontinuity and entropy discontinuity during melting of argon according to the Monte Carlo method [39]

The principal conclusions of the aforementioned study are presented in Fig. 12 which shows the temperature dependence of the melting entropy  $\Delta S/Nk$  and relative change in volume  $\Delta V_m/V_s$  during melting: it is distinctly seen that  $\Delta S$  and  $\Delta V_m/V_s$  tend to the asymptotic limit and hence the conclusions of this Monte Carlo study confirm the conclusions drawn from real experiments.

#### 4. THE SIMON EQUATION

In 1927 F. E. Simon<sup>[42]</sup>, while investigating the possibility of extrapolating melting curves to the high-pressure region, attempted to find some melting-curve parameters that could be linked to the physical properties of coexisting phases. He transformed the Clausius-Clapeyron equation to the form of

$$\frac{d \ln P}{d \ln T} = \frac{\Delta H}{P \Delta V}, \quad (4)$$

where  $\Delta H$  is the heat of melting and, on deriving in the right-hand part of Eq. (4) the dimensionless quantity  $\Delta H/P \Delta V$ , he investigated the behavior of that quantity along the melting curve. On studying the available data, Simon discovered that all melting curves presented in the coordinates  $\ln P - \ln T$  become straight lines at high pressures. Moreover, most of these straight lines were parallel to each other. Naturally, in the region of low pressures the linear relationship between  $\ln P$  and  $\ln T$  was upset. But as it turned out, for any substance it is possible to select a characteristic quantity  $a$  which, when introduced as an addend under the pressure logarithm, makes the relation of  $\ln(P + a)$  to  $\ln T$  linear regardless of pressure. This implies the following equation of the melting curve

$$\ln(P + a) = C \ln T + b, \quad (5)$$

or

$$\frac{P}{a} = \left(\frac{T}{T_0}\right)^C - 1,$$

where  $a$  and  $C$  are constants,  $T_0$  is the melting point at atmospheric pressure. When melting curves are inves-

tigated in a region close to the triple point, Eq. (5) must be rewritten as

$$\frac{P-P_0}{a} = \left(\frac{T}{T_0}\right)^C - 1, \quad (6)$$

where  $P_0$  and  $T_0$  are the coordinates of the triple point.

This equation and its modifications have been termed the Simon equation. It is perfectly obvious that relations (5) and (6) can be rewritten as follows:

$$\frac{d \ln(P+a)}{d \ln T} = \frac{\Delta H}{(P+a)\Delta V} = C. \quad (7)$$

Equation (7) implies a linear dependence of the ratio  $\Delta H/\Delta V$  on pressure<sup>[43,44]</sup>, and hence knowledge of the melting parameters ( $T$ ,  $P$ ,  $\Delta V$  and  $\Delta H$ ) even at a single point makes it possible to determine the constants in Eqs. (5) and (6) and to derive the melting equation for the substance investigated.

Simon interpreted the constant  $a$  as a quantity determined by the relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P, \quad (8)$$

where  $E$  is the intrinsic energy. The quantity  $(\partial E/\partial V)_T$  is often termed the intrinsic pressure. From Eq. (7) it is readily concluded that the melting pressure of a substance at absolute zero will be  $P = -a$ . On the other hand, relation (8) implies that at absolute zero the intrinsic pressure  $(\partial E/\partial V)_T = -P$ . Thus we indeed find that the quantity  $a$  can be characterized as "intrinsic" pressure which at absolute zero is identical in both liquids and solids. Simon found that the quantity  $a$  derivable from his equation satisfactorily correlates with the corresponding quantity of intrinsic pressure derived from the Van der Waals equation for liquids<sup>[45]</sup> (cf. Table IV).

Table V presents by way of an example the values of the constants in Simon's equation for certain substances.

As shown by experience of as much as 40 years, the Simon equation satisfies, as it were, the requirements which we can pose to an equation pretending to the name of the equation of the melting curve. It is equally suitable for interpolation and extrapolation. The example with  $\text{He}^4$  is highly instructive. Langer<sup>[46]</sup> found that at 77.3°K  $\text{He}^4$  does not solidify under a pressure of 14,140 ± 200 bar. Attempting to compare his finding with the data of other investigators, he extrapolated the results of<sup>[47,48]</sup> with the aid of the Simon equation and found that

Table IV

Substance	Derived from Van der Waals equation	Derived from Simon equation
H <sub>2</sub>	260	237
HD	345	318
D <sub>2</sub>	440	407

Table V

Substance	$a, 10^3 \text{ kg/cm}^2$	$c$	Substance	$a, 10^3 \text{ kg/cm}^2$	$c$
Ar	2.087	1.593	Au	110	2.08
Kr	2.345	1.617	Zn	61.2	2.4
Xe	2.576	1.589	In	36.5	2.3
Ag	79.6	2.39	Pb	32.9	2.405

at 77.3°K the melting pressure of helium is 14,135 and 14,285 bar. Surprising as it may seem, such an excellent agreement was obtained on extrapolating in one case from 3500 bar and in the other, from 5000 bar. Mention should also be made of the study by Babb<sup>[34]</sup> who calculated the parameters of the Simon equation for practically every substance whose melting coordinates are known in the published literature. The number of these substances proved to be fairly large (>200) and, as it was discovered, all the melting curves except the "anomalous" curves can be described with the aid of Eq. (5). However, there also exist indications that some melting curves deviate from the Simon equation. For example, Goodwin<sup>[49]</sup> states this with respect to hydrogen in a region close to the triple point.

## V. LAW OF CORRESPONDING STATES AND THE SIMON EQUATION

From Table V, which presents values of constants in the Simon equation, it can be seen that certain substances, e.g., noble gases, are characterized by nearly the same constant  $C$ .

We rewrite the Simon equation as

$$P^* = (T^*)^C - 1, \quad (9)$$

where

$$P^* = \frac{P}{a}, \quad T^* = \frac{T}{T_0}.$$

Then it is clear that the melting curves of all substances having the same constant  $C$  will be reflected by the same curve. Hence the Simon equation may be termed the law of corresponding states<sup>[45]</sup>.

On the other hand, it is known<sup>[50]</sup> that for substances of the noble gas type it can be assumed that the total interaction energy determining the system state represents the sum total of the pair-interaction energies

$$U_N(q_1, \dots, q_n) = \sum_{i \leq j \leq n} \Phi(|q_i - q_j|). \quad (10)$$

The intermolecular potential  $\Phi(r)$  in relation (10) may be written as the product of some energy constant  $\epsilon$  and the function of the dimensionless argument  $r/a_0$ :

$$\Phi(r) = \epsilon \varphi\left(\frac{r}{a_0}\right). \quad (11)$$

This is exemplified by the Lennard-Jones potential, written as

$$\Phi(r) = 4\epsilon \left\{ \left(\frac{a_0}{r}\right)^{12} - \left(\frac{a_0}{r}\right)^6 \right\}. \quad (12)$$

The quantities  $\epsilon$  and  $a_0$  may be used to introduce molecular units for volume  $a_0^3$ , temperature  $\epsilon/k$ , pressure  $\epsilon/a_0^3$  and energy  $\epsilon$ .

Introducing the dimensionless quantities

$$T^* = \frac{kT}{\epsilon}, \quad V^* = \frac{V}{a_0^3}, \quad P^* = \frac{a_0^3 P}{\epsilon}, \quad E^* = \frac{E}{\epsilon}, \quad (13)$$

we can be confident that for substances with the same kind of the potential  $\Phi(r)$  there exist the universal state functions

$$P^*(T^*, V^*), \quad E^*(T^*, V^*) \quad (14)$$

and hence the thermodynamic properties of this group of substances, expressed in molecular units, will prove to be identical. We shall not specially consider here the

influence of quantum effects on melting, but nonetheless let us note that relations (14) hold true only in the classical limit. In the quantum case the above equations of state are written as

$$P^*(T^*, V^*, \Lambda) \text{ and } E^*(T^*, V^*, \Lambda), \quad (15)$$

where  $\Lambda = h/a_0\sqrt{m\epsilon}$  is a dimensionless parameter characterizing the magnitude of quantum effects in the system and representing the ratio of the de Broglie wavelength of the system particles to a characteristic length  $a_0$  equal to the collision diameter. Moreover, the very form of the function (15) depends on the statistical law obeyed by the given system.

Figure 13 shows "adjusted" melting curves of noble gases. The values of the molecular units of pressure and temperature, calculated under the assumption that the potential (12) is valid, are given in Table VI<sup>[51]</sup>.

Figure 13 indeed demonstrates that the law of corresponding states holds true for Ar, Kr, and Xe in part for Ne. The adjusted melting curves of He<sup>3</sup> and He<sup>4</sup> deviate from the totality, showing that the behavior of these substances can no longer be explained from the classical standpoint.

It is patently obvious that the empirical parameters  $a$  and  $T_0$  of the equation and the molecular units of pressure and temperature must be proportional to each other, since both these parameters and these units can be used to construct the adjusted melting curve. Table VI confirms in general this conclusion. In this connection it would be an attractive goal to relate in some manner the dimensionless parameter  $C$  in Simon's equation to the dimensionless quantities characterizing the interaction potential. As we shall see later, a relationship of this kind apparently does exist.

VI. THE LINDEMANN EQUATION

The semiempirical Lindemann equation (cf. <sup>[52,53]</sup>) often represents the basis for investigating the melting of substances at high pressures <sup>[54,55]</sup>. Hence it would be worthwhile to consider here some questions regarding this equation.

In 1910 Lindemann<sup>[52]</sup> suggested that melting occurs when the neighboring atoms begin to collide, i.e., when the oscillation amplitude reaches one-half of the interatomic distance. The relation conventionally termed the Lindemann equation

$$\frac{m\theta^2V^{2/3}}{T_m} = C^2, \quad (16)$$

(where  $m$  is the mass of the atom,  $V$  is the volume,  $\theta$  is the Debye temperature, and  $C$  is the Lindemann constant, proportional to the oscillation amplitude) is readily derived from the well-known relation linking the total energy of a harmonic oscillator to the oscillation amplitude if the oscillator frequency is identified with the Debye frequency.

Table VI

Substance	$P_{mol}$ , kg/cm <sup>2</sup>	$T_{mol}$ , °K	$a$ , kg/cm <sup>3</sup>	$a/P_{mol}$	$T$ of triple point, °K	$T_{tr}/T_{mol}$
Ne	233.6	35.6	1037.53	4.44	24.56	0.690
Ar	410.9	119.49	2087	5.080	83.81	0.701
Kr	456.0	166.67	2345	5.143	115.743	0.694
Xe	455.3	225.3	2576	5.658	161.362	0.716

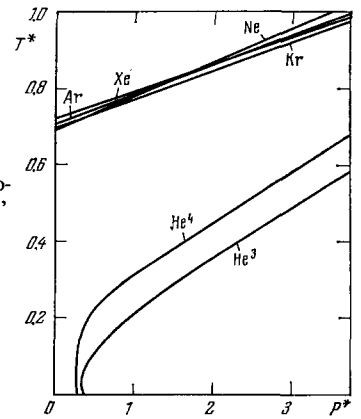


FIG. 13. Melting curves of noble gases, expressed in "adjusted" coordinates <sup>[51]</sup>.

As it turned out, the quantity  $C$  from Eq. (16) is indeed nearly constant for many substances and depends little on the nature of the interaction forces (Table VII).

However, the numerical value of the ratio of oscillation amplitude to interatomic distance at the melting point is much smaller than the value proposed by Lindemann. An analysis carried out by Pines<sup>[58]</sup> shows that at the melting point the mean square displacement of atoms from the equilibrium state amount to about one-eighth of the interatomic distance.

Gilvarry<sup>[59]</sup> (see also<sup>[2]</sup>) reformulated Eq. (16) in terms of the volumetric modulus of elasticity and the Poisson ratio. According to Gilvarry, Eq. (16) may be rewritten as

$$RT_m = \Omega k_m V_m, \quad (17)$$

where  $R$  is the gas constant,  $T_m$  is the melting temperature,  $k_m$  is the volumetric modulus of elasticity at the melting point,  $V_m$  is the volume of the solid at the melting point, and  $\Omega = (S_m C)^2$  (where  $S_m = f(\sigma)$ ,  $\sigma$  is the Poisson ratio,  $C$  is the Lindemann constant).

Gilvarry's calculations also show that the quantity  $C$  is nearly constant for substances with elementary structures.

Thus, the available material warrants, as it were, the claim that at the melting point the relative oscillation amplitude of atoms reaches some critical value. What is the physical meaning of this claim? Can we agree with those investigators who, following Lindemann, take Eq. (16) to be the melting criterion? Clearly, not. At any rate, vibration instability should correspond to the absolute stability limit of the crystal but not to the equilibrium point of the crystal-to-liquid transition. An excellent example confirming the absence of any direct relationship between melting and the oscillation amplitude is the behavior of He<sup>4</sup> along the melting curve<sup>[60]</sup>. The specific properties of helium cause its zero-point

Table VII

Parameters of Lindemmen equation	Cu *)	Ar *)	Au *)	Ar **)	Kr **)	D <sub>2</sub> **)
$T_m$ , °K	1356	1233	1336	84	116	18.7
$\theta_D$	315	215	170	69	58	102
$C$	134	140	142	139	152	130

\*After <sup>[56]</sup>  
 \*\*After <sup>[57]</sup>



energy to markedly exceed the thermal energy along the melting curve. As a corollary, the zero-point oscillation amplitude of helium atoms also exceeds the amplitude of the thermal oscillations. On the whole, the ratio  $\sqrt{u^2}/a$  (where  $\sqrt{u^2}$  is the mean square amplitude and  $a$  is the interatomic distance) is not constant along the melting curve and greatly exceeds the corresponding values inherent in other substances at the melting point (cf. Table VIII).

Recently Dugdale<sup>[57]</sup> verified yet again, on the basis of new measurements<sup>[61]</sup>, the applicability of the Lindemann relation to the melting of He<sup>4</sup>. Table IX presents the values of the parameter  $C$  from Eq. (16) for He<sup>4</sup> (hcp) at various volumes.

It can be seen from Table IX that the Lindemann parameter  $C$  changes markedly along the melting curve, gradually coming close to a value characteristic of "classical" substances (cf. Table VII).

The material cited above can only signify that generally speaking the oscillation amplitude does not correlate with melting and hence the Lindemann equation requires a new interpretation. It is not surprising, however, that in the classical sense there exists a universal relationship between the melting temperature and the oscillation amplitude, since both these quantities can be expressed in terms of interatomic forces. We are thus justified in regarding the Lindemann equation solely as a law of corresponding states. Lennard-Jones and Devonshire<sup>[24]</sup> and subsequently Domb<sup>[62]</sup> have outlined the paths for proving this assumption.

It is perfectly obvious that, given the validity of Eq. (16) over a broad range of pressures, on using a sufficiently satisfactory equation of state, a melting curve equation of the Simon type can be derived with a purely phenomenological interpretation of the constants entering in it. This has been accomplished by Salter<sup>[54]</sup> on the basis of the Gruneisen-Gilvarry equation of state<sup>[55]</sup> derived from the empirical Murnahan equation. These calculations definitely deserve attention and may be highly useful, but the validity of the extrapolation of the relations derived in<sup>[54]</sup> and<sup>[55]</sup> to the high-pressure region can never be guaranteed.

## VII. MELTING IN A SYSTEM OF SOLID SPHERES AND THE EQUATION OF THE MELTING CURVE

The function  $\Phi(r)$  of the interaction between particles in a system of solid spheres may be written as

$$\begin{aligned} \Phi(r) &= +\infty \text{ when } r < a, \\ \Phi(r) &= 0 \text{ when } r > a. \end{aligned} \quad (18)$$

In Fig. 14 this function is compared with the real function of molecular interaction. It can be seen that interaction in real substances markedly differs from interaction in the system considered. However, at high temperatures at which the kinetic energy of the particles greatly exceeds the energy corresponding to the minimum of the potential energy of the interaction, the properties of real molecular systems are largely determined solely by the repelling part of the potential. Hence, if the potential energy increases at a sufficiently fast rate with decrease in interatomic distances, solid

Table VIII

Molar volume, cm <sup>3</sup>	Melting Temperature T, °K	$\Theta$ , °K	$T_m/\Theta$	Zero-point energy, cal/mole	Thermal energy, cal/mole	Ratio $\sigma = \sqrt{u^2}/a$	Ratio $\sigma' *$
21.18	0	21	0.0	46.9	0	0.310	0
20.0	2.12	24	0.088	53.6	0.17	0.303	0.067
18	3.4	31.5	0.108	70.4	0.49	0.277	0.074
16	5.35	42.5	0.126	95.0	1.19	0.251	0.077
14	8.65	57.0	0.152	127.0	3.18	0.228	0.083
12.5	13.1	76.3	0.172	170.0	6.43	0.212	0.086
11.5	17.65	92.5	0.191	207.0	11.2	0.201	0.088
10.5	23.55	114	0.207	255.0	17.8	0.190	0.089

\* $\sigma'$  is the ratio of the amplitude of thermal oscillations to the interatomic distance.

Table IX

$V_m$	$T_m$ , °K	$\Theta(V_m)$	$T_m/\Theta$	$C$
11.0	20.3	123	0.165	121
11.6	17.0	109	0.156	119
13.1	11.05	82	0.135	117
14.4	7.85	66	0.119	113
18.3	3.47	38.5	0.091	115
20	2.15	28.5	0.073	105

spheres can represent a satisfactory simulacrum of certain properties of real systems in the presence of high densities and temperatures. It is practically obvious that in the presence of high densities when  $a^3/V \sim 1$ , the system of solid spheres can exist in two fundamentally different states:

- 1) The "crystalline" state with long-range order such that the sphere centers are statistically located at the nodes of a periodic spatial lattice.
- 2) The non-ordered "gas-dense" or liquid-like state such that the statistical spatial correlation of the spheres exists only over a distance of the order of several sphere diameters.

It is interesting to note that for solid spheres in liquid-like state the radial distribution function highly resembles the corresponding function in real monatomic liquids<sup>[63]</sup>.

Despite the obviousness of these two states of the system investigated at high densities, the nature of the transition between these states could not be determined for a long period of time<sup>[64]</sup>. This problem was finally resolved as a result of the "machine" experiments conducted by the Monte Carlo method<sup>[65]</sup> as well as by means of direct integration of the classical equations of motion<sup>[66]</sup>. The results of the "machine" experiments

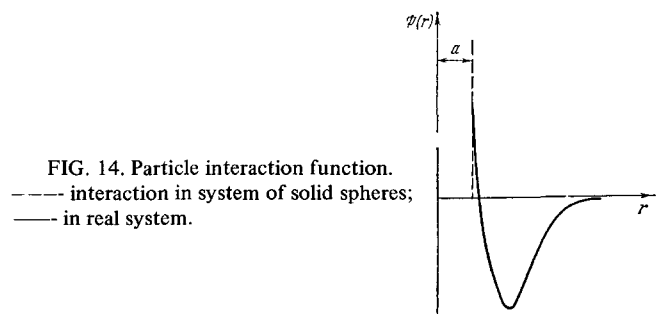
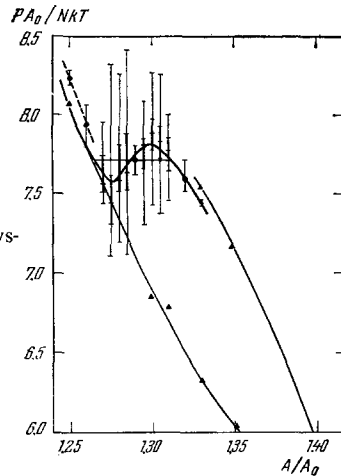


FIG. 14. Particle interaction function.

--- interaction in system of solid spheres;  
— in real system.

FIG. 15. Phase transition in system of solid disks [67].



made it possible to establish that the transition between liquid-like and crystalline states of the solid spheres represents a first-order phase transition. A proof of this is the occurrence of discontinuities in the corresponding isotherms characterizing the relation  $P(V)_T$ , with distinct regions of "superheated" and "supercooled" states. However, in view of the small number of particles used in the experiments described ( $N \leq 500$ ), alternating jumps of the system from one state to the other were observed instead of the coexistence of both phases in the transition region; such a coexistence was obtained by Alder et al. [67] in their investigation of a two-dimensional system consisting of 870 solid disks. Since the number of particles needed to form a sector of any one phase of a given size is much smaller in the two-dimensional case than in the three-dimensional, the investigated system of 870 solid disks was much more effective than the system of 500 solid spheres. Figure 15 shows an isotherm of the system of solid disks, in the coordinates  $PA_0/NkT$  and  $A/A_0$ , where  $A_0$  is the area of the system in the state of closest packing. Two segments of the isotherms, corresponding to different phases and linked by a Van der Waals loop can be seen. The pressure in the coexistence region is calculated with the aid of the known rule of "equal areas." Clearly, as the dimensions of the system increase the Van der Waals loop will get flattened into a straight line. In view of the specific features of the equation of state of this system, the jump  $\Delta A/A_0$  in area during melting is independent of temperature and amounts to 0.046. The corresponding change in entropy  $\Delta S/Nk$  during melting also is constant and equal to 0.36. The equation of the melting curve is

$$\frac{PA_0}{NkT} = 7.72. \quad (19)$$

Similarly, for the melting of solid spheres we can write

$$\frac{PV_0}{NkT} = \text{const.} \quad (20)$$

A marked feature of the considered systems is that the relative instability of each phase occurs in the presence of a rigorously specific and temperature-independent ratio of the overall size of the phase to the size proper of the particles.

By way of an example, let us point out that phase co-

existence in the solid disk system is observed when  $1.312 \geq A/A_0 \geq 1.266$ . Clearly, it is these numbers, too, that determine the corresponding boundaries of relative stability of the ordered and non-ordered states. Here also mention should be made that a most important feature of the mechanism of the melting of solid particle systems is collective motion, which in the two-dimensional case reduces to sliding between series of particles.

It is worthwhile to compare the results of the study of melting in model and real systems. During melting in a system of solid particles the following relations apply:

$$\left. \begin{aligned} V_l &= mV_0, & V_s &= nV_0, \\ \frac{\Delta V_m}{V_s} &= \frac{m-n}{n} = \text{const.}, \\ \Delta S &= \text{const.} \end{aligned} \right\} \text{ for } \infty \gg p \gg 0 \quad (21)$$

( $m$  and  $n$  are constants).

In real systems it is highly probable that

$$\left. \begin{aligned} \frac{\Delta V_m}{V_s} &\rightarrow \text{const.}, \\ \Delta S &\rightarrow \text{const.} \end{aligned} \right\} \text{ as } p \rightarrow \infty.$$

It is conceivable that if the real particles had solid nuclei, the analogy between melting in the system of solid particles and melting in real systems under extremely high pressures would be complete.

Assuming an identical melting mechanism in both real systems and solid-particle systems, it is possible with the aid of Eq. (20) to gain an idea of the limiting form of the equation of the melting curve of a real system [4,69].

And indeed, we rewrite Eq. (20) as follows:

$$\frac{PV_{\text{eff}}}{kT} = \text{const.}, \quad (22)$$

where  $V_{\text{eff}}$  is the effective temperature-dependent volume of the real-system particle.

Clearly,  $V_{\text{eff}}$  can be derived from the condition

$$\Phi(r_{\text{eff}}) = \frac{1}{2} kT, \quad (23)$$

where  $\Phi(r)$  is the interaction potential. Taking the following type of potential

$$\Phi(r) \sim \frac{1}{r^n}, \quad (24)$$

for the interaction function in the system, i.e. allowing only for power-law repulsion, we have

$$V_{\text{eff}} \sim T^{-3/n}. \quad (25)$$

It follows from (22) and (25) that

$$P \sim T^{1+(3/n)}. \quad (26)$$

Clearly a term characterizing the potential pressure of the system must be introduced into Eq. (26). Then Eq. (26) will resemble the Simon equation

\*Recently Kraut and Kennedy [70] proposed an empirical formula relating the melting temperature to the solid-phase volume:

$$\frac{T_m}{T_0} = 1 + m \frac{\Delta V}{V_0},$$

where  $\Delta V/V_0 = (V_0 - V)/V_0$  is the relative volume compression;  $T_0$  is the melting temperature for the volume;  $m$  is a constant. Then, following the assumption that  $V/V_{\text{eff}} = \text{const}$  at the melting point, the Kraut-Kennedy relation should reflect the temperature dependence of the effective volume of particles. In this connection, it seems highly unlikely that the relation cited above has universal validity.

$$P = bT^{1+(3/n)} + P_{\text{pot}}^* \quad (27)$$

and, as we expected, the exponent in the Simon equation is naturally related to the dimensionless parameter  $n$  characterizing the interaction potential. Note that the quantity  $1 + (3/n)$  is numerically too small, since for noble gases, in which interaction can be described by a power-law potential with  $n = 10-12$ , the required value of  $C \sim 1.5-1.6$  is not reached. Clearly, if the forces of attraction are properly allowed for, the exponent would have been more correct, since here it is presented as a quantity inversely proportional to the slope of the potential.

It is readily shown on the basis of (21) that the relations

$$\frac{\Delta V_m}{V_s} = \text{const and } \Delta S = \text{const} \quad (28)$$

apply at the limit of the purely repelling forces at any pressure. Naturally, for a real system we are justified in disregarding the forces of attraction only at extremely high temperatures and hence relations (28) may be regarded as asymptotic for systems with attraction. This conclusion completely tallies with our earlier empirical conclusions (cf. (3)).

### VIII. "ANOMALOUS" MELTING CURVES

There exist substances whose volume diminishes upon melting. This may be exemplified by water, bismuth, gallium and a number of other elements and compounds (cf. also Table I). The slope of the melting curves of these substances, as implied by the Clausius-Clapeyron equation (1), is negative. Figures 16-18 present examples of the phase diagrams of substances of this kind. As shown by experiments<sup>[25]</sup>, the compressibility of the liquid phase of these substances continues to exceed the compressibility of the corresponding solids. Hence the absolute value of the volume jump on melting increases with rise in pressure. A consequence of this is the progressive increase in the absolute value of the slope  $dT/dP$  of the melting curve. This is clearly seen in Fig. 16, which presents the phase diagram of bismuth. Thus, the "anomalous" melting curves, like their rising counterparts, are concave with respect to the pressure axis. In this case, however, this signifies an increasingly rapid fall in melting temperature with pressure. On this basis, Bridgman<sup>[25]</sup> assumed that the "anomalous" melting curves are an indicator of the approaching instability of the crystalline phase. Bridgman's conclusion is corroborated by aforementioned

\*The equality of thermodynamic potential for a first-order phase transition implies

$$P = -\frac{\Delta F}{\Delta V} = -\frac{\Delta E}{\Delta V} + \frac{\Delta S}{\Delta V} T,$$

where  $F$  is the free energy, and  $E$  is the intrinsic energy. Assuming that the thermal parts of intrinsic energy are identical for the liquid and the solid, we denote  $\Delta E/\Delta V = P_{\text{pot}}$ , where  $P_{\text{pot}}$  is the pressure associated with potential energy. Clearly,  $P_{\text{pot}}$  can be represented by the sum  $P_{\text{pot}} = P_{\text{pot}}^0 + P_{\text{pot}}(T)$ , where  $P_{\text{pot}}^0$  is the potential pressure at absolute zero while  $P_{\text{pot}}(T)$  is the potential pressure that depends on melting temperature owing to change in volume. Then the melting pressure will be written as  $P = -P_{\text{pot}}^0 - P_{\text{pot}}(T) + \frac{\Delta S}{\Delta V} T$ , and hence, for a more rigorous derivation of the Simon equation, it remains to be proved that  $P_{\text{pot}}(T) \sim T^m$ ,  $\Delta S/\Delta V \sim T^{m-1}$  ( $m$  is a quantity characterizing the interaction potential).

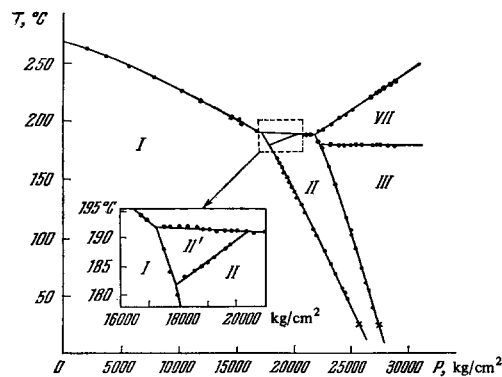


FIG. 16. Phase diagram of bismuth [71]

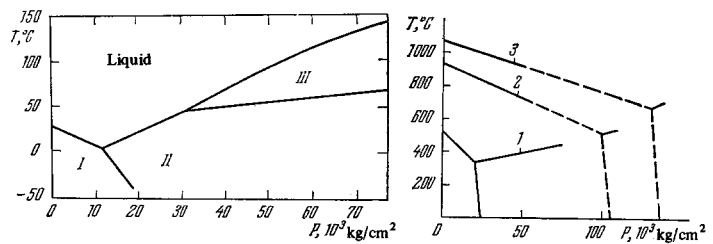


FIG. 17. Phase diagram of gallium [72]. FIG. 18. Phase diagram of InSb

observations indicating that substances with "anomalous" melting curves sooner or later get rearranged into more dense phases whose melting curves are characterized by a positive slope.

The material presented in Tables I and II is sufficient to conclude that "anomalous" substances display, as a rule, a loose crystalline structures with low coordination numbers whose stability is determined by rigid oriented bonds. Hence there exists the fundamental possibility of forming from particles of a given size a more dense ordered or non-ordered structure. Properly speaking, this possibility comes true during the melting of "anomalous" substances and, as we pointed out above, the structure of melts of these substances (cf. Table II) is characterized by higher coordination numbers compared with solids and hence also by a more compact arrangement of the particles. This results in a corresponding behavior of thermodynamic properties: decrease in volume during melting and an anomalously high value of melting entropy (cf. Table I). It must be emphasized that the equations of Simon (5) and Lindemann (16) are not satisfied for substances with "anomalous" melting curves.

It should also be noted that the presence of a loose-packed structure is not a sufficient sign of "anomalous" behavior. As an example, consider the melting of  $\text{In}_2\text{Te}_3$ . The crystalline structure of this substance represents a defective structure of the sphalerite  $\text{ZnS}$  type, containing  $1/3$  vacancies in the cation sublattice. Nevertheless, during its melting  $\text{In}_2\text{Te}_3$  increases in volume<sup>[74]</sup> and its melting curve should have a positive slope.

Now consider the aforementioned melting curves with temperature maxima. This question is of special interest in connection with Tammann's hypothesis but, as we were able to ascertain, this hypothesis lacks any real foundations and, obviously, the existence of these maxima can be explained without coming into contradic-

tion with the general conclusions drawn in the preceding sections.

In 1959 Bundy<sup>[75]</sup>, while investigating the melting curve of rubidium, discovered that under pressures of  $>40,000 \text{ kg/cm}^2$  the originally positive slope of the melting curve became negative. Bundy's astonishment was so great that he placed a question mark on the plot of the melting curve of rubidium. Now that G. C. Kennedy et al. have published their studies<sup>[76,77]</sup> we can state that the question mark on Bundy's plot was quite logical. As it turned out, Bundy's findings were erroneous, but nevertheless, as shown in<sup>[76,77]</sup>, the melting curve of rubidium does have a maximum, though at much higher pressures. In 1959, however, Bundy's study had acted as a major stimulus to research. In 1962 maxima on the melting curves of cesium and tellurium were discovered practically at the same time<sup>[78,79]</sup>. This was followed by a large series of studies reporting on the presence of maxima on the melting curves of barium<sup>[80]</sup>, europium<sup>[81]</sup>, antimony<sup>[82]</sup>, sulfur<sup>[83]</sup>, selenium<sup>[84]</sup>, the tellurides of antimony, bismuth and lead<sup>[85,86]</sup>, nitrate and nitrite of potassium<sup>[87,88]</sup>, sodium chlorate<sup>[89]</sup>, and lithium chromate<sup>[90]</sup>. Figures 19, 20 and 21 present examples of phase diagrams of substances with maxima on their melting curves.

The results of the studies cited above demonstrate that the maxima on the melting curves represent a sufficiently widespread phenomenon inherent in a broad variety of substances. Again, as in the preceding case, we can state that one of the most characteristic features of the phase diagrams with maxima on melting curves is the presence of a phase transition, such that the maximum is necessarily followed by the triple point: crystal I—crystal II—liquid (cf. Figs. 19–21), whereupon the melting curve again acquires a positive slope.

What are the physical causes conditioning the presence of the maximum?

The Clausius-Clapeyron equation (1) implies that  $\Delta V = 0$  at the maximum point of the melting curve.

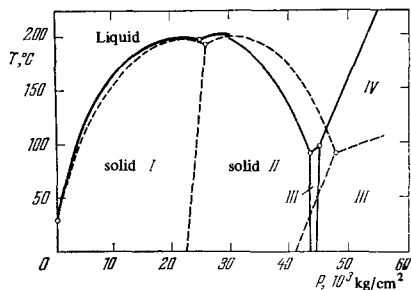


FIG. 19. Phase diagram of cesium. ---- [78]; — [91]; — - [92]

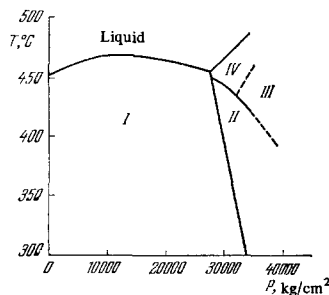


FIG. 20. Phase diagram of tellurium [93]

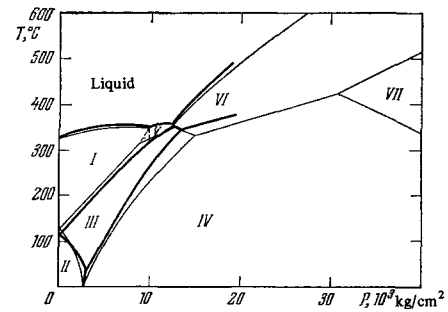


FIG. 21. Phase diagram of potassium nitrate. — after [87]; — after unpublished data of S. M. Stishov, N. A. Tikhomirova, and E. Yu. Tonkov.

Direct measurements of the volume discontinuity along the melting curve, performed for potassium nitrate<sup>[94]</sup> and cesium<sup>[95]</sup>, confirm this conclusion (Figs. 22 and 23). On the other hand, we already ascertained that in the normal case, i.e., for continuously rising melting curves,  $\Delta V$  does not tend to zero. We are thus forced to assume that the occurrence of maxima is associated with volume anomalies that may take place in the liquid or solid. To avoid contradictions with the laws of thermodynamics, however, it can only be concluded that the temperature maxima on the melting curve arise owing to an anomalous decrease in the volume of the liquid along that curve.

To clarify this statement, it is worthwhile to consider the phase diagram of cerium (Fig. 24), which is, moreover, of interest in itself. As shown by numerous studies<sup>[96–99]</sup>, the phase transition in solid cerium discovered by Bridgman<sup>[25]</sup> at high pressures is apparently associated with an electronic transition and is accompanied only by a decrease in the cell parameter of the original face-centered cubic structure. On moving along the curve of equilibrium between  $\alpha$  and  $\gamma$  phases, a decrease in the volume and entropy discontinuities is observed and, in all likelihood, these discontinuities disappear entirely at pressures and temperatures exceeding  $18,000 \text{ kg/cm}^2$  and  $300^\circ\text{C}$ . Thus the experimental situation points to the existence of a critical point on the curve of the  $\gamma\text{-Ce} - \alpha\text{-Ce}$  equilibrium and, since the phases  $\alpha$  and  $\gamma$  have the same symmetry, this critical point must pertain to the first of the types considered above. It is conceivable that here, as in the case of the critical point on the boiling curve, anomalies of com-

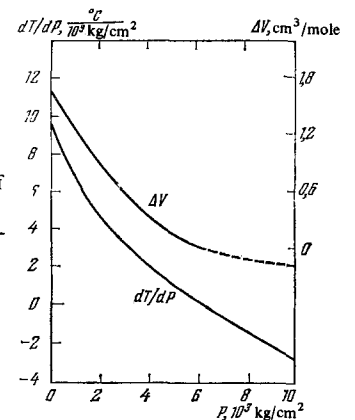


FIG. 22. Pressure dependence of molar volume discontinuity during melting and of the slope of the melting curve for  $\text{KNO}_3$  [94]

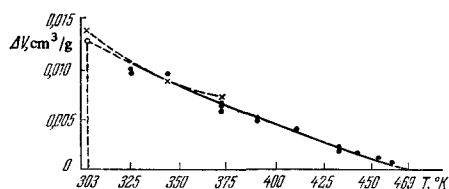


FIG. 23. Unit volume discontinuity during melting of cesium as a function of temperature [95].

compressibility and other properties, extending far beyond the critical point, should be expected. Considering now the melting curve of cerium, we see that it displays a minimum and that the continuation of the equilibrium curve of phase transition intersects the melting curve of cerium precisely in the region of the minimum. Thus in this case the relationship between the anomaly on the melting curve and the anomalous behavior of one of the phases coexisting along that curve is obvious.

No less obvious is that the analogous process occurring in a liquid would lead to a maximum on the melting curve. Useful information can be extracted from an examination of Fig. 1 and Tables I and II. It can be ascertained that during the melting of "normal" substances the structure of the liquid is, in a certain sense, similar to the structure of the corresponding solid at least so far as interatomic distances and—up to a point—coordination numbers are concerned. Properly speaking, this fact is the basis of the quasicrystalline models of liquids. But for substances with a negative slope of the melting curve a correspondence of this kind does not apply and the structure of the liquid displays sharply different characteristics. Since a melting curve having a maximum contains both an ascending branch (with  $dT/dP > 0$ ) and a descending branch (with  $dT/dP < 0$ ), the foregoing considerations warrant the assumption that a change in the liquid structure occurs in the region of the maximum, resulting in the additional compression of the liquid phase which, in its turn, results in reversing the polarity of  $\Delta V$ .

The phase diagram of cesium (Fig. 19) is a convenient object for demonstrating this assumption. At atmospheric pressure and normal temperature cesium has a body-centered cubic structure. On investigating the compressibility of cesium Bridgman<sup>[100]</sup> discovered two phase transitions at 23,000 and 45,000 kg/cm<sup>2</sup>, accompanied by a decrease in volume by 1.5 and 11%, respectively. Bardeen<sup>[101]</sup> suggested that the phase transition in cesium at 23,000 kg/cm<sup>2</sup> is associated with the rearrangement of this element into a face-centered structure. As for the transition under 45,000 kg/cm<sup>2</sup>, E. Fermi advanced the hypothesis that this pertains to the transition of an electron from the state 6s to the state 5d, which ensues in a corresponding change in volume. Fermi's hypothesis was corroborated by the calculations of Sternheimer<sup>[102]</sup>. Subsequently both these theories were experimentally proved.

Hall et al.<sup>[103]</sup> discovered with the aid of x-ray structural analysis that at 23,000 kg/cm<sup>2</sup> the bcc lattice of Cs indeed is converted to a fcc lattice and at 45,000 kg/cm<sup>2</sup> the parameter of the face-centered cell of the structure of cesium abruptly decreases, thus demonstrating an abrupt decrease in atomic dimensions. The same study by Hall et al. also reported on the dis-

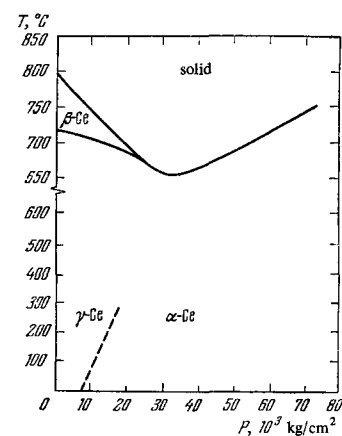


FIG. 24. Phase diagram of cerium [99]

covery of yet another phase of cesium, whose structure has not as yet been identified.

On again considering the question of the maxima, we note that the melting curve of Cs-II (cf. Fig. 19) represents a unique phenomenon in the sense that, except for a narrow region, it displays a negative slope. Hence, the volume of Cs-II diminishes during melting. But, as we know, Cs-II has the most close-packed structure of all the possible structures of this element, and hence it cannot be expected that the liquid can form a more compact structure given the same atomic dimensions. Thus we are forced to assume that in liquid cesium there occurs an electronic transition analogous to the transition occurring in the solid cesium. A situation of this kind can also be expected for other substances with maxima on their melting curves. Naturally, we do not mean that the transformations in various liquids are of an electronic nature—that is a very rare phenomenon in the presence of moderately high pressures. In liquids with a complex structure there exists a sufficient number of possibilities for manifesting excess compressibility and, so far as the final result is concerned, it does not matter whether the additional decrease in volume was due to electron transition or to a change in the nature of the packing. For example, in the case of tellurium, the chain structure of the solid phase is to some extent inherited by the liquid<sup>[104]</sup>. In liquid tellurium, as in solid tellurium, each atom has two nearest neighbors at a distance of  $\sim 2.9$  Å. Clearly, liquid tellurium can at least be transformed to a pure coordination liquid with a corresponding volume effect.

The question of the dimensions of the P-T regions in which transformations occur in various liquids is of great interest. This question can be more concretely formulated as follows: Does there exist a mechanism of additional compression throughout the region of existence of a given liquid such that its entire compression curve can be termed anomalous, or does this mechanism manifest itself only in individual segments of that curve pertaining to narrow regions of pressures and temperatures? This problem has been investigated for liquid cesium and liquid tellurium<sup>[91,92,105]</sup>. As it turned out, these two substances behave in a completely different manner each. In liquid tellurium<sup>[105]</sup> measurements of electrical resistance revealed anomalous sectors separating the region of existence of tellurium into individual fields with different activation energies of conductivity,

with the anomaly sectors being extremely narrow and occupying not more than 1000–1500 kg/cm<sup>2</sup> in pressure and about 15° C in temperature. In liquid cesium<sup>[91,92]</sup> on the other hand, it was not possible to isolate any singularities pointing to localized transformation. Using certain indirect data, Stishov et al.<sup>[92]</sup> concluded that transformation in liquid cesium occupies an extremely broad range of pressures which extends from 10,000 to ~25,000 kg/cm<sup>2</sup>. It appears that here the decisive factor is the nature of the interaction forces, and while in liquid tellurium, which still has rigid covalent bonds, the transformations resemble to some extent phase transitions, in cesium-like substances the transformations may get "blurred" over a broad range of pressures. Recently Rapoport<sup>[106]</sup> attempted to describe a "cesium type" transformations on the basis of a two-liquid model, utilizing the theory of regular solutions.

In conclusion, it is important to point out that, in all likelihood, the temperature maxima on the melting curves are a specific manifestation of distinctive processes in liquids, associated with the regrouping of the component particles of liquids. In view of the fact of a close structural correspondence between liquids and their corresponding solids, it is conceivable that these transformations in liquids represent to some extent a reflection of phase transitions in solids.

Generally speaking, a complete agreement between the coordinates of the corresponding transformations in liquids and solids cannot be expected. Hence transformations in liquids may occur both at lower and at higher pressures than transitions in solid phases. Moreover, then the transformations in liquids cause a rapid decrease in the slope of the melting curves but, as is readily inferred, the occurrence of a maximum is possible only when the transformation in the liquid phase occurs ahead of the transformation in the solid phase.

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