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PHASE EQUILIBRIA AND METASTABLE STATES

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UDC 536.42

Agreement is remarked between the theory of homogeneous seed-formation and tests on the kinetics of the boiling and crystallization of fluids. The continuation of the two-phase equilibrium line into the domain where both phases are metastable is discussed. The application of thermodynamic similarity to describe the melting of substances is shown.

1. The phase equilibrium condition in a one-component system

$$\mu_\alpha(T,\ P)=\mu_\beta(T,\ P) \tag{1}$$

refers to a plane interface

$$\mu=u-Ts+Pv. \tag{2}$$

A part of the surface of the chemical potential μ which proceeds higher than the μ of the competing phase behind the line of intersection (1) corresponds to phase metastable states. Small amplitude perturbations in the metastable phase (density fluctuations, say) are resorbed if the spinodal is not reached, for which we have

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Branch of Physicotechnical Problems of Power, Ural Scientific Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 5, pp. 820-826, November, 1987. Original article submitted January 27, 1987.

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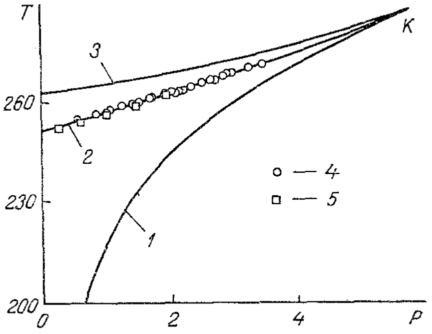

Fig. 1

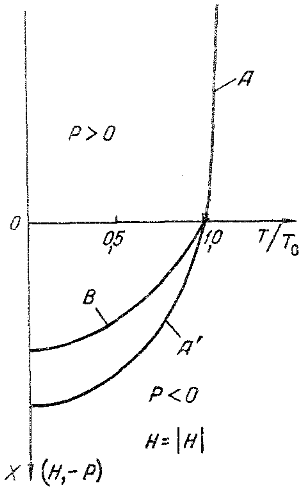

Fig. 2

Fig. 1. Superheating of liquid xenon, T, °K; P, MPa.

Fig. 2. Melting line AA' according to (6) and line of equilibrium superconductor-normal metal transition B according to (13), schematically.

$$(\partial P/\partial v)_T = 0. \tag{3}$$

However, local perturbations of a special kind and high amplitude result in instability. A spherical seed of radius r of the competing phase (β) is a form of these perturbations. The condition for its equilibrium with the medium has the form

$$\mu_\alpha(T,\ P_\alpha) = \mu_\beta(T,\ P_\beta),\ P_\beta = P_\alpha + \frac{2\sigma}{r^*}. \tag{4}$$

Taken into account in (4) is the additional pressure within a spherical volume of the phase β due to the surface tension σ on the interface with the phase α. For $r > r_*$ further growth of the phase β is specified thermodynamically.

In many cases the system contains numerous impurities and defects on which vital seeds of the new phase are formed for small supersaturation (heterogeneous nucleation). Great difficulties occur for poorly defined heterogeneous centers in physical theory and they result in unsatisfactory reproducibility in experiment. This raised doubts [1] in the possibility of observing the natural boundary of metastable states in a pure system. Such a boundary is associated with the kinetics of homogeneous nucleation when the seeds occur because of thermal fluctuations [1-3]. But at this time it has been clarified that the presence of a heterogeneous nucleation background does not, firstly, exist everywhere and, secondly, does not certainly hinder the isolation of a clear homogeneous nucleation signal [4, 5].

Good agreement has been established between theoretically expected heating and results of tests under quasistatic conditions as well as under impulsive thermal effects [4, 6, 7] for a large number of simple and molecular fluids. The stationary frequency of seed formation J = J(T, P) depends quite radically on fluid heating. The Gibbs number $G = W_*/k_bT$ is the quantity governing this dependence where

$$W_* = 16\pi\sigma^3 v_\beta^2/3\,(\Delta\mu)^2. \tag{5}$$

The phase chemical potentials for the compilation of Δμ are taken at the identical pressure (P_α). The expression (5) is valid not only for an overheated fluid but also for other kinds of metastability. We have approximately $d\ln J/dT = -dG/dT$, $d\ln J/dP = -dG/dP = 2\pi r_*^3/3k_bT$. The domain of overheated states is shown in Fig. 1 for liquid xenon in a broad range of pressures. It is located between the saturation line 1 and the spinodal 3. Test results on xenon heating by the method of continuous isobaric heating 4 and the method of a pressure drop to a given magnitude 5 are noted by points. In the former case $J = 10^{11}$ $\sec^{-1}\cdot m^{-3}$ and in the latter $J = 10^7$ $\sec^{-1}\cdot m^{-3}$. Although the effective seed-formation frequencies differ in the fourth order, the scale of the graph does not permit a clear display of the difference between the two series of tests. The theoretical curve 2 ($J = 10^{11}$ $\sec^{-1}\cdot m^{-3}$) passes through

TABLE 1. Quantities Characterizing Seed-Formation in Supercooled Liquid Metals $J(T_*) = 10^{11}$ $\sec^{-1}\cdot m^{-3}$

Substance	T_0, K	T_*, K	σ, mJ/m²	n_*	$\frac{d \lg J}{dT}$, K^{-1}
Gallium	257	158	40,4	170	0,39
Tin	505	383	59,0	270	0,39
Germanium	1211	915	241	160	0,15
Copper	1356	1079	200	480	0,19
Water	273	237	28,7	300	1,3

the array of points. For P = 0.5 MPa and $J = 10^7$ $\sec^{-1}\cdot m^{-3}$ an estimate by the preceding formulas yields $d\ln J/dT \approx 12$, i.e., a 1°K increase in temperature results in a five order increase in the stationary nucleation frequency. Consequently, the domain of spontaneous (homogeneous) effervescence has a sharp lower bound.

As tests with supercooled fluids show, application of the theory to the description of the kinetics of fluctuations seed formation during crystallization is possible [5]. For instance, for water and for tin the seed-formation frequency range studied includes 12-16 orders of variation of J. Presented in Table 1 are data for several metals; n_* is the number of atoms in the seed crystallite of critical size for supercooling $\Delta T = T_0 - T_*$, $J(T_*) = 10^{11}$ $\sec^{-1}\cdot m^{-3}$.

2. It is known from test that the saturated vapor pressure above a supercooled liquid P_ℓ is greater than the vapor pressure above a crystal P_s at the same temperature. The difference in the chemical potentials of a supercooled liquid and crystal $\Delta\mu(T) = \mu_\ell - \mu_s$ can be found in terms of the ratio between the pressures mentioned

$$\Delta\mu = RT \ln (P_l/P_s).$$

The quantity $\Delta\mu > 0$ characterizes the thermodynamic stimulus of the liquid-crystal phase transition, it enters into (5) for the work of critical seed formation. Presented here for water are values of P_ℓ/P_s (in parentheses) according to [8] for different supercoolings $\Delta T = T_{tr} - T$, K at the triple point ($T_{tr} = 273.16$°K, $P_{tr} = 609$ N/m²): 0 (1.000); 10 (1.102); 20 (1.215) 30 (1.340); 40 (1.474).

The following was important to us: although both coexisting phases, liquid and vapor, are metastable with respect to a crystal for $T < T_{tr}$, they can be in equilibrium with each other. This property is characteristic for phase transitions of the first kind. Not only metastable states of the separate phases are possible, but also metastable continuations of the phase equilibriums behind the triple point. Such a continuation into the negative pressure domain exists for the melting line, where the crystal and liquid are in a state of multilateral tension. Briggs obtained negative pressures of tens of MPa by the method of centrifuging; references are presented in [4].

Construction of the phase diagram with metastable continuation of the phase equilibrium line is useful when studying transformations into the solid phase (graphite—diamond, alloys on an iron base, aluminum and others). It is detected in tests with gallium droplets of 10-100 μm [5] and 10-30 nm [9] diameters that crystallization under high supercoolings occurs in the metastable β-phase. Its melting point at atmospheric pressure is 257°K, which is 47°K below the melting point of phase I. It is seen from the phase diagram of gallium [10] that the metastable section of the equilibrium line of crystalline β-phase-melt is 1.2 GPa in pressure.

Let us turn to the melting of simple substances. A good approximation for the melting line is the Simon equation [11]

$$1 + \frac{P}{P_0} = \left(\frac{T}{T_0}\right)^c. \qquad (6)$$

Here T_0 is the melting point at zero pressure, $P = -P_0$ is the pressure at which the continuation of the melting line arrives as T → 0°K. For substances melting as the volume increases ($\Delta v = v_\ell - v_s > 0$), $P_0 > 0$; for substances of the type of water $P_0 < 0$. If the origin of the pressure reference is moved to the point $\{T = 0,\ P = -P_0\}$, then we can write $\tilde{P} = \tilde{T}^c$ where $\tilde{P} = (P + P_0)/P_0$, $\tilde{T} = T/T_0$ instead of (6). Test shows that $c > 1$ and takes on different values for different substances. Substances with identical exponent c form a group of simi-

TABLE 2. Characteristic Quantities for Equilibrium Melting of Simple Substances

Substance	T_0, K	P_0, MPa	c	Δv, cm³/g-mole	$\Delta\tilde{v}$	$\Delta v/v_S$	$\Delta\tilde{s}_1$
Neon	24,6	104	1,60	2,03	1,03	0,156	0,62
Argon	83,8	211	1,59	3,50	1,06	0,142	0,63
Xenon	163,1	261	1,59	5,59	1,09	0,151	0,64
Nitrogen	63,2	161	1,78	2,50	0,77	0,084	0,60
Carbon tetrachloride	250,6	292	2,12	3,92	0,55	0,053	0,62
Sodium	370,8	1197	3,53	0,64	0,25	0,026	0,63
Potassium	335,7	427	4,44	1,17	0,18	0,025	0,62
Rubidium	311,9	395	3,74	1,45	0,22	0,027	0,61
Aluminum	933	7000	2,20	0,72	0,65	0,064	0,78
Cadmium	594	4500	2,40	0,44	0,40	0,033	0,56
Lead	600	3230	2,41	0,70	0,45	0,037	0,63
Copper	1358	13400	2,44	0,35	0,42	0,046	0,60

lar substances with respect to melting, and c can be called the thermodynamic similarity parameter. It is determined by the dimensionless slope of the melting line, $c = [T_1/(P_1 + P_0)][dP/dT]_{T_1}$. According to (6), the expression on the right side is independent of the location of the point $\{T_1, P_1\}$ on the curve. But if a similarity parameter is introduced without making the form of the equation specific

$$f(T/T_0,\ P/P_0,\ c) = 0, \tag{7}$$

then a compatible point should be selected for different substances. It is simplest to take it for $P \to 0$

$$c = \frac{T_0}{P_0}\left(\frac{dP}{dT}\right)_{T_0}. \tag{8}$$

To find $(dP/dT)_{T_0}$ it is sufficient to know the piece of the melting line abutting on atmospheric pressure, but additional information is required to estimate P_0. A direct path presumes extrapolation of the experimental data $P = p(T)$, referring to a large section of the melting line, to the low temperature domain.

By relying on (1) and (2), it is not difficult to express P_0 in terms of the ratio of asymptotic values of the jumps in the internal energy and volume during melting: $P_0 = (\Delta u/\Delta v)_{T=0}$. The quantity P_0 is close to the internal pressure in the condensed phase as $T \to 0$ [12]. Thermodynamically this means that as the temperature diminishes lowering of the internal stability of the liquid (and crystal) occurs on the melting line. The melting line approaches the spinodal [13. 14]. The spinodal of a liquid emerges from the critical point of liquid-vapor equilibrium. For a Van der Waals fluid we have $P_{sp}(T = 0) = -27P_c$. For a large number of substances for which the quantities P_0 differ by one or two orders of magnitude, a correlation is actually detected between P_0 and $27P_c$. This correlation can be utilized for a preliminary estimate of P_0 according to the critical pressure of the substance.

We obtain another useful correlation if we introduce a dimensionless volume $\tilde{v} = v/v_+$ by using the scale factor $v_+ = RT/(P + P_0)$. The dimensionless jump in the volume during melting $\Delta\tilde{v} = \Delta v(P + P_0)/RT$ correlates with the logarithm of the ratio between Δv and the volume of the crystalline phase v_S [15, 16]. For mono- and diatomic substances we have at the point $P = 0$

$$\Delta\tilde{v} = 0{,}480 \ln(\Delta v/v_s) + 1{,}955. \tag{9}$$

This correlation can be used to find the P_0 of substances studied slightly by means of values of Δv, v_S at one point of the melting line.

The empirical equation (6) should be compared with the Clapeyron–Clausius equation

$$dP/dT = \Delta s/\Delta v. \tag{10}$$

If the reduced jump in the entropy $\Delta\tilde{s} = \Delta s/R$ is introduced in addition to the volume jump $\Delta\tilde{v}$ then according to (10) the parameter c equals the ratio between the jumps $\Delta\tilde{s}$ and $\Delta\tilde{v}$:

$$c = \Delta\tilde{s}/\Delta\tilde{v}. \tag{11}$$

In the Simon approximation the ratio mentioned does not change during motion along the melting line. This assures integrability of (10). Returning to the determination of $\Delta\tilde{v}$ we note that the proportionality between $\Delta\tilde{v}$ and $\Delta\tilde{s}$ is obtained when using a shifted pressure scale $P' = P + P_0$. This indicates the fundamentality of the introduction of the asymptotic value $P_0 = -P(T \to 0)$ in the description of the melting line.

The relationship (11) taken at the point $P = 0$ corresponds to the definition (8) which is not related to the form of (7). If the model of an "ideal" condensed system with a phase transition of the melting type is introduced under the condition $\Delta u = 0$ (an analog is a system of solid spheres) [17], and $\Delta\tilde{s} = \Delta\tilde{s}_{id} + \Delta s_1$ is represented, where $\Delta\tilde{s}_{id} = \Delta\tilde{v}$, then we obtain $c = 1 + \Delta\tilde{s}_1/\Delta\tilde{v}$ for (11). It is very important that simple substances have an approximately identical "nonideal" part of the entropy jump $\Delta\tilde{s}_1 \approx 0.62$. Therefore, a simple approximate relationship

$$c = 1 + 0{,}62/\Delta\tilde{v}, \tag{12}$$

exists that permits finding the similarity parameter c by means of the value of $\Delta\tilde{v}$ at $P = 0$ (and at atmospheric pressure in practice). The quantities used above in the discussion of melting are presented in Table 2 for a number of substances. For polyatomic molecules the characteristic value of the "nonideal" part of the entropy jump is higher than for monoatomic (and analogous) molecules by approximately two units [15, 16], $\Delta\tilde{s}_1 \approx 2.60$.

3. Other equations besides (6) exist for melting [18, 19], but the power-law temperature dependence of the pressure can be taken as the fundamental approximation. In contrast to this for the liquid-vapor equilibrium line, resulting in the dependence $P = f(T)$ is the exponential factor $\ln P = A - (B/T) + \ldots$.

An equation of the type (6) has a broader range of application than was discussed above. It can be used to describe other phase transitions of the first kind also. The binodal in two-component stratified fluid systems is shifted as the external pressure changes. For a fixed concentration ω the derivative dP/dT is determined by the generalized Clapeyron–Clausius equation [20]. For many solutions with an upper critical temperature, the dependence $P = f(T, \omega)$ is approximated well for $\omega = \text{const}$ by (6). For instance, processing the data [21] for the methanol–cyclohexane system yields the following values of the parameters: $T_0 = 312.5°K$, $P_0 = 109$ MPa, $c = 8.32$. M. Z. Faizullin conducted a study of the dependence $P = f(T, \omega)$ for a number of alcane–perfluoroalcane solutions at the suggestion of the author and detected the applicability of the Simon equation. The authors of [22] arrived at the same deduction for methanol–heptane and methanol–octane solutions.

The phase transition of a metal into the superconducting state [23] is another example of a power-law dependence of the form (6) when the magnetic field intensity H is the thermodynamic force instead of the pressure. For superconductors of the first kind the relationship between the intensity H destroying superconductivity and the temperature is expressed approximately by the Goerter equation

$$1 - \frac{H}{H_0} = \left(\frac{T}{T_0}\right)^c \quad T \leqslant T_0. \tag{13}$$

It is completely analogous to the Simon equation if it is taken into account that P and H are in the expression for the work of the system with opposite signs; T_0 is the critical phase equilibrium temperature, and H_0 is the threshold field for $T = 0$ and $c \approx 2$.

Letting X denote the intensive thermodynamic parameter (thermodynamic force) $X = -P, H$ Eqs. (6) and (13) can be represented thus:

$$1 - \frac{X}{X_0} = \left(\frac{T}{T_0}\right)^c. \tag{14}$$

Shown schematically in Fig. 2 are the melting line A with the continuation A' into the domain of metastable phase states and the line B of the equilibrium superconductor-normal conductor transition. The essential distinction between cases B and A is that there is a phase equilibrium transformation point ($T = T_0$, $H = 0$) of the critical liquid–vapor equilibrium point type for the superconductor. An analogous point is not detected for the melting line up to pressures exceeding P_0 by an order. Another distinction is the superposition of the domain of metastable states (A') on the domain of stable phase coexistence (B) in the generalized phase diagram T/T_0, X.

The superconductor-normal conductor phase transition is more unified for different metals as compared with the melting. This is related to the fact that the jump in magnetization per unit volume ΔM which is the analog of the jump in volume for melting is defined in a universal manner $\Delta M \simeq 1/4\pi H$. If the exponent c in (13) is determined on different sections, shifting towards the low temperatures, then it is detected that $c \to 2$ as $T \to 0$. If c is found from the minimum of the deviation of H from experimental values on the whole phase equilibrium line $H = H(T, c)$, then values of the exponent between 1.6 and 2.1 are found for different metals. This range of c is considerably narrower than for the melting of simple substances (see Table 2) and the quantity c itself characterizes a group of thermodynamically similar metals with respect to the transition into the superconducting state. The parameter c can be determined by the relationship $c = -[T/(H_0 - H)](dH/dT)$ for a given reduced temperature T/T_0, for $T/T_0 = 0.8$, say, without connecting this definition to a specific form of the equation $f(H/H_0, T/T_0, c) = 0$. In order to obtain (13) from the Clapeyron–Clausius equation $dH/dT = \Delta s/\Delta M$ a proportionality must be assumed between the reduced entropy jumps $\Delta\tilde{s} = \Delta s/R$ and the magnetization $\Delta\tilde{M} = \Delta M(H_0 - H)/RT$: $\Delta\tilde{s} = c\Delta\tilde{M}$. The entropy jump $\Delta s = (c/4\pi)(T/T_0)^{c-1} \cdot (HH_0/T_0)$ has a maximum in the band $(0, T_0)$, vanishes for $T = 0$, $H = H_0$ and for $T = T_0$, $H = 0$. That the derivative dX/dT vanishes as $T \to 0$ is contained in the generalized Simon equation (14) if $c > 1$. Since (14) should be in agreement with the Clapeyron–Clausius equation, then the asymptotic $\Delta s \to 0$, $T \to 0$ hence already follows. The asymptotic mentioned is in agreement with the Nernst theorem and is an important corollary of (14).

Therefore, the power-law function (14) turns out to be a suitable approximation for the temperature dependence of the thermodynamic force X for certain phase transitions of the first kind in condensed systems of different nature. The presence of the quantity $X_0(P_0, H_0)$ that characterizes the internal field in the specimen as $T \to 0$ is essential in (14). The low-temperature part of the phase equilibrium line ($T < T_0$) can refer to the metastable states of co-existing phases, as takes place in the melting case.

NOTATION

p, pressure, Pa; v, molar volume; T, temperature, °K; s, entropy, J/kg·mole; σ, surface tension, J/m^2; μ, chemical potential; u, internal energy, J/kg·mole; W_*, work of critical seed formation, J; n_*, number of molecules therein; r_*, critical seed radius, m; k_b, Boltzmann constant; R, universal gas constant; $G = W_*/k_bT$, Gibbs number; J, frequency of seed-formation, $sec^{-1} \cdot m^{-3}$; P_c, pressure at the critical point; P_{sp}, pressure at the spinodal; $\Delta\tilde{v}$, $\Delta\tilde{s}$, reduced (dimensionless) jumps in the volume and entropy during melting; T_0, equilibrium melting temperature at p = 0; c, thermodynamic similarity parameter; $-P_0$, asymptotic pressure ($T \to 0$) on the phase transition line; ω, molar fraction of the component in solution; H, magnetic field intensity, A/m; M, magnetization; and α, β, ℓ, s, subscripts to denote the phases.

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MASS TRANSPORT IN A NONUNIFORM ISOTHERMAL MIXTURE OF REAL GASES

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UDC 533.15

A method of describing mass transport in a nonuniform isothermal mixture of real gases is given. The computed results are compared with experimental data.

It has been reliably established that for isothermal diffusion in gas mixtures in the absence of external forces, there is a loss of mechanical equilibrium [1, 2]. Therefore, even in a nonuniform mixture of ideal gases, the process of mass transport is composed of two physically distinct components. The first is due to the random migration of molecules in a mixture that is nonuniform in composition (self diffusion [2]), while the second component is due to pressure nonuniformities, which are practically unavoidable, and which lead to the transport of all of the components of the mixture in a given volume element as a whole (convective transport). The existence of two physically distinct transport mechanisms whose contributions to the total mass transport process can be of the same order of magnitude [2] means that both components must be taken into account in a theory of mass transport.

The usual method of taking into account the convective component of mass transport is to impose certain conditions on the fluxes, which are characteristic of the device in which the diffusion is observed. An example of a restriction of this kind is the assumption that the mean velocity is equal to zero in the diffusion of ideal gases in a two-bulb device [3]. When restrictions are introduced, mass transport can be described sufficiently accurately in the particular device under consideration. For example, in the two-bulb device the above restriction allows one to describe the quasistationary stage of the mass transport and to obtain a unique characteristic of the process – the coefficient of mutual diffusion [3].

However, there are at least two reasons why an approach of this kind cannot be considered completely satisfactory. The first is that if we want to describe diffusion in a device with a different geometric shape or with different conditions on the boundary of the device, the applicability of the restrictions must be re-examined because the characteristics of the process (such as the coefficient of mutual diffusion) are partly determined by these restrictions [2] and the same characteristics cannot be used to describe diffusion in a different device unless exactly the same restrictions are introduced. Here it should also be noted that the nature of the restrictions can change significantly when we go from ideal gases to real gases. For example, in the diffusion of real gases in a two-bulb device, the average velocity will not be zero even in the quasistationary case since the number densities of different real gases are not equal at equal pressure.

The second reason is that the introduction of restrictions reduces the description of a complicated mass transport process to a form natural for only one of the components. For example, the convective component is automatically included in the flux given by Fick's first law of diffusion. Such a reduction of two physically different processes into a single description leads to doubts about its validity (especially for real gases) and to difficulties in the interpretation of the experimental data [4].

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0022-0841/87/5305-1322 $12.50