crystallization zone was measured with a microthermocouple. Then the thermocouple was frozen into the strip and the temperature distribution of the solid phase during crystallization was recorded. Measurement of the phase-transition temperature is necessary, due to the presence of supercooling, which differs for various crystallization rates.

The results are given in the table.

We note that Eq. (6) can be used to determine supercooling, and this is of considerable interest.

NOTATION

u is the extraction rate; T_m is the melt temperature; T_0 is the phase-transition temperature; ϑ_1 is the liquid phase temperature; ϑ_2 is the solid phase temperature, X is the interface coordinate; K is the thermal conductivity coefficient; a^2 is the thermal diffusivity coefficient; L is the specific heat of fusion; ρ is the density; X_{calc} is the calculated value of the interface coordinate; X_{meas} is the measured value of the interface coordinate.

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RETARDATION OF PHASE TRANSITION NEAR THE CRITICAL POINT

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The nonequilibrium-thermodynamics method is used to examine the kinetics of the liquid-vapor phase transition of a pure substance. It is shown that there is a sharp increase in the pressure-relaxation time in an isothermic system near the critical point.

For a phase transition of the first kind to take place at a finite rate it is necessary to change the conditions for phase equilibrium, for example, to change the pressure while we hold the temperature constant or to maintain a certain temperature difference between phases. However, this situation is often not apparent because heat transfer and hydrodynamic or diffusion processes associated with phase transition predominate.

It has long been known [1] that at low temperatures the relationship between the evaporation rate and the pressure difference $p_s - p$ is given by

$$i = \alpha (2\pi\, mkT)^{-\frac{1}{2}} (p_s - p). \qquad (1)$$

In this case, the evaporation rate is low because of low vapor density, and heat transfer is not a limiting factor. Retardation of phase transition near the critical point is due to some other factor. Here the evaporation rate drops because the difference between coexisting phases becomes negligible.

S. L. Rivkin et al. [2, 3] observed the protracted change (up to 8–10 hours) in water pressure in a two-phase region under isothermal conditions when $T_{cr} - T \simeq 1$–$2°$ C. If we do not expect equilibrium to be established, the condensation lines on the p- and v-diagrams will be inclined. The authors of [3] note that this slope is not caused by impurities.

Consider a one-component isolated system consisting of two isotropic coexisting phases. In the general case, we consider that the phase temperatures and pressures differ and are not equal to their values in an equilibrium system. We assume that internal equilibrium in the phases is established much more rapidly than equilibrium between phases, i.e., a quasi-steady state exists for the discontinuous system. We apply the fundamental equation of thermodynamics to each phase:

$$TdS = dU + pdV - \mu\, dM. \qquad (2)$$

With (2) and the conditions that the mass, volume, and internal energy of the entire system be constant, we find the rate of increase in entropy by a direct method:

$$\dot S = \left(\frac{1}{T''} - \frac{1}{T'}\right)\dot U'' - \left(\frac{\mu''}{T''} - \frac{\mu'}{T'}\right)\dot M''.$$

Therefore, the mass and energy flows have the form

$$J_1 \equiv \dot M'' = -L_{11}\left(\frac{\mu''}{T''} - \frac{\mu'}{T'}\right) + L_{12}\left(\frac{1}{T''} - \frac{1}{T'}\right), \qquad (3)$$

$$J_2 \equiv \dot{\tilde{U}}'' = -L_{21}\left(\frac{\mu''}{T''} - \frac{\mu'}{T'}\right) + \\ + L_{22}\left(\frac{1}{T''} - \frac{1}{T'}\right). \qquad (4)$$

The flows are referred to a unit area of phase interface. We assume that flow is positive when it is directed toward the second (high-temperature) phase. As is usual $L_{12} = L_{21}$.

When the phase pressures are not equal even at equilibrium, the following situations can occur: a) small drops of liquid surrounded by vapor, or vapor bubbles in the liquid; b) a solid phase, subjected to additional compression, but freely miscible with the gas or liquid phase. We ignore related cases and assume that $p' = p'' = p$. Then $\tilde{U}'' = U'' + pV'' = H''$.

We consider several examples of the way in which relationships (3) and (4) can be used, assuming that the deviations from equilibrium are minor and that $|\Delta T|/T \ll 1$, $|\Delta p|/p \ll 1$. To be specific, we consider a liquid-vapor system.

1) $T' = T'' = T \neq T_s$, $p = p_s$;

$$J_1 = -\frac{L_{11}}{T}(\mu'' - \mu'), \; J_2 = -\frac{L_{21}}{T}(\mu'' - \mu').$$

We have

$$\frac{J_2}{J_1} = \frac{L_{21}}{L_{11}} = Q^* \simeq h'' = l + h'. \qquad (5)$$

Allowing for the fact that $\mu''(T_s, p_s) = \mu'(T_s, p_s)$, we can represent the difference in chemical potentials as

$$\mu''(T, p_s) - \mu'(T, p_s) \simeq \frac{\partial \mu''}{\partial T}\Delta T - \\ - \frac{\partial \mu'}{\partial T}\Delta T = -\frac{l}{T}\Delta T.$$

For the mass flow we have

$$J_1 = \frac{L_{11}}{T^2} l \Delta T. \qquad (6)$$

For a given deviation in temperature from the equilibrium value, the mass flow of the evaporating molecules is proportional to the heat of phase transition and to the term L_{11}/T^2.

2) $T' = T'' = T_s$, $p \neq p_s$. As in the preceding case, we expand μ about the equilibrium point in powers of Δp and limit ourselves to the first degree in the expansion; we then obtain

$$J_1 = -\frac{L_{11}}{T}(v_s'' - v_s')\Delta p. \qquad (7)$$

Here the mass flow for given Δp is proportional to the difference in specific volumes of the phases and to L_{11}/T.

3) $T' = T'' = T \neq T_s$, $p \neq p_s$. This case is a combination of the two preceding ones:

$$J_1 = \frac{L_{11}}{T}\left[l\frac{\Delta T}{T} - (v_s'' - v_s')\Delta p\right]. \qquad (8)$$

When there is no mass flow it is necessary that

$$\frac{\Delta p}{\Delta T} = \frac{l}{T(v_s'' - v_s')}. \qquad (9)$$

This is the well-known Clapeyron-Clausius equation and applies to the phase-equilibrium line.

4) $T' \neq T'' = T_s$, $p = p_s$.

$$J_1 = -L_{11}\left(\frac{\mu_s''}{T_s} - \frac{\mu'}{T'}\right) + L_{12}\left(\frac{1}{T_s} - \frac{1}{T'}\right). \qquad (10)$$

If we substitute $L_{12} = L_{11}(l + h')$ into (10) and expand μ' in series, we obtain expression (6) after minor changes.

In all of the cases considered, the mass flow corresponds to system "conductivity," which decreases as the critical point is approached and becomes zero when $v_s' = v_s'' = v_k$, $l = 0$. Therefore, the time required to restore phase equilibrium for comparable experimental conditions must increase greatly near the critical point.

We now construct the kinetic equation for pressure relaxation in a liquid-vapor system. Isothermic conditions will be used (this was done in Rivkin's experiments).

A small change in the specific vapor volume dv'' results from a pressure change $dp = (\partial p/\partial v)_T dv''$. This means that

$$\dot{p} = -\gamma''\frac{\dot{v}''}{v''}. \qquad (11)$$

Making use of the condition that the system mass

$$\frac{\dot{v}''}{v''} = \frac{\dot{V}''}{V''} - \frac{\dot{M}''}{M''} = -\left(1 - \frac{v'}{v''}\right)\frac{\dot{M}''}{M''}$$

be constant, we substitute expression (7) for the mass flow into (11) and assume that $v' \simeq v_s'$, $v'' \simeq v_s''$; then

$$\dot{p} = (p - p_s)\frac{L_{11}\gamma''(v_s'' - v_s')^2}{TV''} \equiv (p - p_s)\psi. \qquad (12)$$

Integrating (12) for the conditions $p = p_0$, when $t = 0$ and $p = p_s$ and as $t \to \infty$, we obtain a relaxation equation of the usual form:

$$p - p_s = (p_0 - p_s)\exp[-\psi t]. \qquad (13)$$

The relaxation time

$$\tau = \psi^{-1} = \frac{TV''}{L_{11}\gamma''(v_s'' - v_s')^2} \qquad (14)$$

depends upon the difference in specific volumes of the phases and on the elasticity coefficient γ''. As $T \to T_{cr}$ the relaxation time increases extremely rapidly because both terms approach zero. Thus, the observations of Rivkin et al can be explained qualitatively within the framework of ordinary thermodynamic concepts.

Quantitative estimates of τ are complicated by the fact that the kinetic coefficient L_{11} is unknown. However, for relative estimates over a small interval of temperatures and pressures we can let $L_{11} = \text{const}$. For water, the required experimental data near the critical point are given in [4, 3]. We choose three values for the temperature: $T_1 = 365°$ C, $T_2 = 372°$ C, and $T_3 = 373°$ C ($T_{cr} = 374.15°$ C). From (14) we obtain $\tau_3/\tau_2 = 2.8$, $\tau_3/\tau_1 = 27$, without allowing for differences in the volume of the vapor phase. From [3], we have $\tau_3 \simeq 1.5$ hr; therefore, $\tau_1 \simeq 3$ min. The last quantity is less than the time required to verify that the temperature is constant and to measure the pressure with a piston manometer.

In this type of experiment it is quite important that the substance be pure. Impurities not only change the slope of the condensation line but, near the critical point, they will also result in a slow drop in pressure to the equilibrium value with a different and probably much greater relaxation time than for the pure substance. This is due to very strong retardation in the diffusion impurity molecule near the critical point [5, 6].

At low pressures, where (1) is valid, we can find L_{11} and estimate the relaxation time (14). Allowing for the fact that $i = J_1/m$ and equating the flows in (1) and (7), we obtain

$$L_{11} = \alpha \left(\frac{mT}{2\pi k} \right)^{1/2} \rho''. \tag{15}$$

For water at 100° C we have $\tau = 1.25 \cdot 10^{-2}$ sec for $\alpha = 0.5$ and $V'' = 100\ \text{cm}^3$.

NOTATION

i is the molecular evaporation rate; p is the pressure; α is the condensation coefficient; m is the mass of a molecule; k is the Boltzmann constant; M is the mass of the substance; V is the volume; v is the specific volume; ρ is the density; T is the temperature; U is the internal energy; μ is the chemical potential per unit mass; J_1 and J_2 are the mass and energy flows; $\tilde{U}'' = U'' + [(p''/T'' - p'/T')/(1/T'' - 1/T')]V''$; H is the enthalpy; $h = H/M$; $l = h'' - h'$ is the specific heat of the phase transition; $\Delta T = T - T_s$; $\Delta p = p - p_s$; $\gamma = -v(\partial p/\partial v)_T$ is the reciprocal of iosthermic compressibility (the elasticity coefficient); t is the time; τ is the relaxation time. Quantities with one prime pertain to a liquid and those with double primes to a vapor. Quantities with the subscript s refer to the saturation line. Differentiation with respect to time is denoted by a dot.

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HEAT TRANSFER IN LIQUID HELIUM IN THE PULSED MODE

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It is shown that for pulsed thermal loads on the boundary between a solid and liquid helium most of the heat transfer takes place to the liquid helium; consequently, such transfer mainly depends on the helium temperature. The phenomena accompanying this process are discussed.

When studying phenomena occurring in metals and semiconductors due to low-duration current pulses, we encounter a number of cases in which the Joule heat liberated determines the kinetics of the processes observed, particularly at liquid-helium temperatures. However, an analysis of thermal balance for the pulsed mode with large specific heat loads for precisely this temperature range was previously lacking in the literature. Given such a state for film superconductors on a dielectric backing, the solution to the problem essentially reduces to determining the effective heat transfer in the steady-state mode by using average values for the corresponding quantities. Calculations of such a type also lead to the conclusion that it is not necessary to allow for heat transfer directly from the film to the helium since the thermal conductivity of helium is much lower than that of the backings used [1].

In several articles [2, 3], only non-steady-state processes in a backing are considered, and heat transfer to helium is allowed for by means of parameters characteristic of the steady-state mode at low thermal loads.