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;
- \( \varphi_1 \) is the liquid phase temperature;
- \( \varphi_2 \) is the solid phase temperature;
- \( X \) is the interface coordinate;
- \( K \) is the thermal conductivity coefficient;
- \( \alpha_2 \) is the thermal diffusivity coefficient;
- \( L \) is the specific heat of fusion;
- \( \rho \) is the density;
- \( X_{\text{calc}} \) is the calculated value of the interface coordinate;
- \( X_{\text{meas}} \) is the measured value of the interface coordinate.

**REFERENCES**


15 July 1966

Ioffe Physicotechnie Institute
AS USSR, Leningrad

**RETARDATION OF PHASE TRANSITION NEAR THE CRITICAL POINT**

V. P. Skripov


UDC 536.763

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 isothermal 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

\[
i = a \left( \frac{2\pi mkT}{\varphi} \right)^{\frac{1}{2}} (p_s - p).
\]  

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 \( T_{cr} \) = 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 quasisteady state exists for the discontinuous system. We apply the fundamental equation of thermodynamics to each phase:

\[
TdS = dU + pdV - \mu dM.
\]  

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

\[
J_1 = \dot{M} = -L_{11} \left( \frac{\mu^*}{T^*} - \frac{\mu'}{T'} \right) + \\
+ L_{12} \left( \frac{1}{T^*} - \frac{1}{T'} \right),
\]
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 \( U'' = U'' + pV'' = H'' \).

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) \( T' = T'' = T \neq T_S, p = p_S \):

\[
J_1 = -L_{11} \left( \frac{\mu'}{T} - \frac{\mu''}{T} \right) \Delta T.
\]

We have

\[
\frac{J_2}{J_1} = \frac{L_{21}}{L_{11}} = Q^s = h^* = I + h'.
\]

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

\[
\mu''(T, p_S) - \mu'(T, p_S) = \frac{\partial \mu''}{\partial T} \Delta T - \frac{\partial \mu'}{\partial T} \Delta T = -\frac{l}{T} \Delta T.
\]

For the mass flow we have

\[
J_1 = \frac{L_{11}}{T^2} l \Delta T.
\]

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) \( T' = T'' = T \neq T_S, p \neq p_S \). As in the preceding case, we expand \( \mu \) about the equilibrium point in powers of \( \Delta p \) and limit ourselves to the first degree in the expansion; we then obtain

\[
J_1 = -L_{11} \left( \frac{\mu'}{T} - \frac{\mu''}{T} \right) (\psi' - \psi') \Delta p.
\]

3) \( T' = T'' = T \neq T_S, p \neq p_S \). This case is a combination of the two preceding ones:

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

When there is no mass flow it is necessary that

\[
\frac{\Delta p}{\Delta T} = \frac{l}{T(\psi' - \psi')},
\]

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

4) \( T' = T'' = T_S, p = p_S \):

\[
J_1 = -L_{11} \left( \frac{\mu'}{T_S} - \frac{\mu''}{T_S} \right) + L_{21} \left( \frac{1}{T_S} - \frac{1}{T'} \right).
\]

If we substitute \( L_{12} = L_{11}(l + h') \) into (10) and expand \( \mu' \) 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 \( \psi_S = \psi''_S = \psi_k, l = 0 \). 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

\[
\dot{p} = -\frac{\psi''}{\psi'^{2}} \cdot \frac{v''}{v'^{2}}.
\]

Making use of the condition that the system mass be constant, we substitute expression (7) for the mass flow into (11) and assume that \( v'' = v''_S, v'' \approx v''_S \); then

\[
\dot{p} = (p - p_S) \frac{L_{11} \psi''(v'' - v'_S)^2}{T v''} = (p - p_S) \psi(1 - \psi'/\psi') \cdot \frac{M''}{M'}.
\]

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:

\[
(p - p_S) = (p_0 - p_S) \exp \left[-\psi(t)\right].
\]

The relaxation time

\[
\tau = \psi^{-1} = \frac{T v''}{L_{11} \psi''(v'' - v'_S)^2}
\]

depends upon the difference in specific volumes of the phases and on the elasticity coefficient \( \psi'' \). As \( T \to T_C \) 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 \( \tau \) are complicated by the fact that the kinetic coefficient \( L_{11} \) is unknown. How-