BROAD PHASE TRANSITIONS OF THE FIRST KIND

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A study is made of the external factors broadening phase transitions under experimental conditions. The behavior of the isotherms and isochores of the specific heat C_V in the interval of the transition is shown.

In the compilation of tables of the thermophysical properties of substances, one of the most important regions of the phase diagram is the region of the liquid—gas transition. The parameters of the transition are generally established experimentally using various methods and for varying degrees of purity of the investigated substances. This complicates the problem of analyzing and comparing results and selecting the most reliable. Moreover, it has been shown in a number of experimental studies in recent years that in general phase transitions do not occur at a point for a given isoline of the thermodynamic surface, but in a certain finite interval of the state parameters (temperature, pressure, etc.). These transitions have been termed broad phase transitions [1]. Their existence is usually connected with fluctuational considerations and the finite dimensions of the experimentally investigated systems [2]. However, the relative fluctuations $\Delta f/f \sim N^{-1/2} \sim 10^{-11}$ (where N is the number of particles), which is several orders of magnitude less than the typical errors of thermophysical measurements, so that the finite range of transition parameters observed in experiment cannot be determined exclusively by these fluctuational reasons [3]. An experimentally measured phase transition must already be blurred on account of the indeterminacy of the state of a thermodynamic system with a real thermostat, the Hamiltonian of which

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + U(q) + u(q, \, q'),\tag{1}$$

even on the assumption that there are no other external incluences, contains the potential energy of interaction between the particles of the system and the thermostat u(q, q'). The set of permissible values of the coordinates of the particles of the thermostat q' means, in 6n-dimensional phase space, that the notion of a phase trajectory has to be replaced by a phase tube, the characteristic "dimensions" of which provide a measure of the indeterminacy of the thermodynamic state under experimental conditions compared with the classical system with an ideal thermostat (thermostat consists of particles of the same sort as the investigated system, exchange of particles between the system and the thermostat is forbidden). If, further, it is remembered that in practice a certain amount of impurities will always be present in the sample and that it is not always possible to avoid the influence of external fields, then one may expect that a point phase transition can occur in experiment only if the algebraic sum of all the external factors adds up to zero.

We allow for the effect of broadening factors by writing the thermodynamic potential of phase α in the form:

$$\Phi = U - TS + PV + \Lambda^\alpha \Pi^\alpha + \sum_i x_i^\alpha \mu_i^\alpha + \sum_j F_j E_j,\tag{2}$$

where U is the internal energy; T, temperature; S, entropy; P, pressure; V, volume; Λ, specific phase—surface interaction energy; Π, specific contact surface; x_i^α, molar fraction of component i in phase α; $\mu_i^\alpha = (\partial G/\partial n_i^\alpha)_{T,P}$; n_i^α, number of moles of component i in phase α; G = U − TS + PV, Gibb's energy; E_j, potential of the external field; F_j, force associated with the field. For simplicity let us assume that the net effect of impurities and external fields equals zero, and, for definiteness, let us consider an arbitrary cylindrical vessel of height H, radius R, and meniscus height h. Then, from

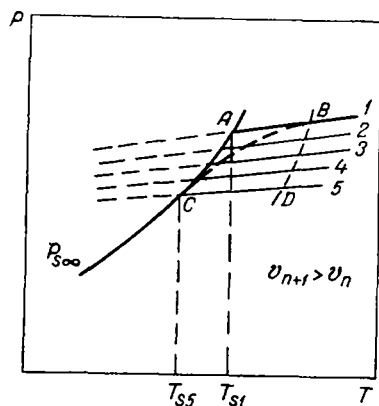$$\Phi'' - \Phi' = T\Delta S + \Delta H + \Lambda'' \Pi'' - \Lambda' \Pi' = 0\tag{3}$$
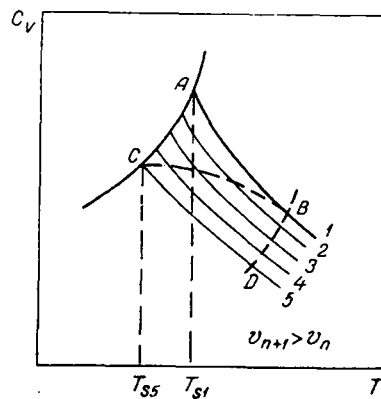
Fig. 1   Fig. 2

Fig. 1. P—T diagram near liquid—gas phase transition. The quasi-isochores of the gas are denoted by v_1, v_2, ..., v_5. AC is the phase equilibrium line; BD is the solution of Eq. (5).

Fig. 2. C_V—T diagram near liquid—gas phase transition. Notation as in Fig. 1.

for the case of small $\varepsilon = |(T_S/T_{S\infty}) - 1|$, where T_S and $T_{S\infty}$ are the temperatures of the phase transition for systems with real and ideal thermostats, we obtain the following expression for the temperature interval of the transition [3]:

$$T_s - T_{s\infty} = \frac{2\Delta H(H - 2h)}{RC_P\left(1 + \dfrac{\Delta H}{C_P T_{s\infty}}\right)}, \tag{4}$$

where ΔH is the heat of transition and C_P is the specific heat. This expression coincides with the particular case discussed in [4] of a sufficiently long capillary completely filled with liquid ($h = H$).

A somewhat different (but in principle equivalent) determination of the pressure interval of a transition was obtained previously [5] starting from the role of adsorption and capillary condensation of the investigated gas on the surface and in the micropores of the walls of the vessel:

$$P_s = P_{s\infty} \exp\left(-2\sigma V'/3DR^*T\right), \tag{5}$$

where σ is the surface tension; V', molar volume of the condensed phase; D, diameter of the molecules; R^*, gas constant. Expressions similar to (4) obtain when allowance is made for impurities and external (e.g., gravitational) fields.

Let us consider the influence of surface effects on, e.g., the behavior of the specific heat at constant volume C_V near a liquid—gas phase transition. Figure 1 shows how the quasi-isochores of the gas vary [5] for the case of point (BAC) and broadened (BC) transitions. We note that, according to [1], the gas—liquid phase transition point in this case should be taken to be the point of inflection of curve BC and not point A, i.e., we would obtain a degree of freedom for the transition parameters which is forbidden by the phase rule. The C_V vs T and C_V vs v diagrams of Figs. 2 and 3 show how this influence of surface effects is reflected on the behavior of the isochores and isotherms of C_V. A similar picture can be obtained for any other thermophysical properties. In this manner, relationships (4) and (5) can be used to estimate beforehand the systematic errors of measurement for a given concrete method so as to eliminate them in the relative comparison of results.

The most universal approach to the description of systems subjected to the aforementioned external influences is through the thermodynamic theory of perturbations, the applicability of which depends on the perturbation energy referred to a single particle being small compared with kT [6]. The role of small correction terms can be played in the simplest case by, e.g., the potential energy of the particles in an external field. Writing the expression for the free energy in the form
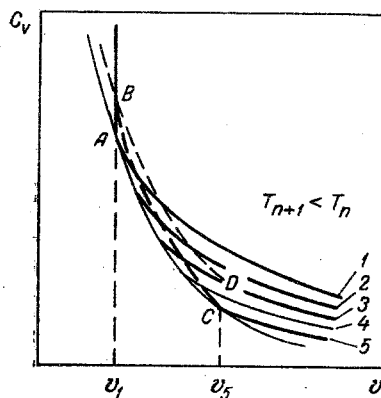
Fig. 3. C_V-v diagram near liquid—gas
phase transition. T_1, T_2, ..., T_5 denote
gas isotherms. Remaining notation as in
Fig. 1.

$$F = F_0 + \overline{V} - \frac{1}{2T}\ \overline{(V-\overline{V})^2},\tag{6}$$

where F_0 is the unperturbed free energy; V, perturbation energy; $\overline{V}$, perturbation energy averaged over the unperturbed free energy, i.e.,

$$F = F_0 + \int' \left(V - \frac{V^2}{2T}\right)\exp\left(\frac{F_0 - E_0(p,\ q)}{T}\right)d\Gamma + \frac{1}{2T}\left[\int'' V\exp\left(\frac{F_0 - E_0(p,\ q)}{T}\right)d\Gamma\right]^2,\tag{7}$$

and representing the total energy $E_0(p, q)$ as the sum of the potential and kinetic energy, we reduce the problem to the calculation of the corrections to the free energy from the interaction of the external perturbing fields with the basic intermolecular field.

In this manner, when utilizing the thermodynamic theory of perturbations, we require to reduce external influences to a certain effective external field and satisfy the conditions $V_{eff} \ll kT$.

The above discussion indicates that, for a correct comparison of the results of measurements performed in the vicinity of a phase transition and made almost always under different experimental conditions, a detailed analysis is desirable with a view to estimating the effect of phenomena distorting the experiment.

LITERATURE CITED

1. B. N. Rolov, Broad Phase Transitions [in Russian], Zinatne, Riga (1972).
2. M. Fisher, The Nature of the Critical State [Russian translation], Mir, Moscow (1968).
3. G. G. Kuleshov, "The problem of broad phase transitions," Izv. Akad. Nauk SSR, Ser. Fiz-Energ. Nauk, No. 3, 125-128 (1978).
4. I. G. Belousov and V. A. Pavlov, "Effect of boundary conditions on value of monophase thermodynamic potential," Preprint I. V. Kurchatov Institute of Atomic Energy, IAÉ-2287, Moscow (1973).
5. G. G. Kuleshov, "Influence of adsorption effects on PVT measurements in gas phase," Zh. Fiz. Khim., 46, No. 10, 2593-2595 (1972).
6. L. D. Landau and E. M. Livshits, Statistical Physics [in Russian], Nauka, Moscow (1964).