METHOD OF CALCULATING THE HEAT CAPACITY OF A BINARY MIXTURE NEAR THE CRITICAL LINE

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The behavior of the heat capacity at constant volume is analyzed for solutions of NaCl in water near the liquid–gas critical line using the pseudospinodal hypothesis.

The pseudospinodal hypothesis has been used successfully in recent years [1-12] to obtain the equation of state and to calculate the thermophysical properties of pure materials near the critical point in terms of the thermodynamic variables (T, ρ).

According to this hypothesis, the heat capacity at constant volume of a pure material near the critical point is given by the equation

$$\frac{\rho C_v}{T}=\frac{P_c}{T_c^2}\left[A_{s0}\left(\frac{T-T_s(\rho)}{T_s(\rho)}\right)^{-\alpha}+A_{s1}|\Delta\rho|^2 Z_{0c}^{2\beta}\left(\frac{T-T_s(\rho)}{T_s(\rho)}\right)^{\gamma-2}\right], \tag{1}$$

where the pseudospinodal curve $T_s(\rho)$ has the asymptotic form

$$T_s(\rho)=T_c\cdot[1-Z_{0s}|\Delta\rho|^{1/\beta}]. \tag{2}$$

It is not difficult to see that (1) and (2) completely describe the anomalous behavior of C_v near the critical point (along the critical isochore, the critical isotherm, and also along the phase equilibrium curve) in terms of the power laws predicted by the scaling theory of critical phenomena [13]. The addition of the second term in (1), which was given in [14], makes it possible to predict the correct behavior of the caloric properties and also gives a qualitatively correct description of the structural features of the thermodynamic surface [7]. When $\rho = \rho_c$, $T_s(\rho_c) = T_c$, (1) reduces to the usual power law of the scaling theory and describes the behavior of C_v for pure materials on the critical isochore. The introduction of the pseudospinodal function of the density $T_s(\rho)$ in (1) generalizes the power law of the scaling theory (describing the behavior of the thermodynamic properties on the critical isochore ($\rho = \rho_c$) to noncritical densities ($\rho \neq \rho_c$). This fundamental concept of the pseudospinodal hypothesis is used in the present paper to develop a method of calculating the heat capacity at constant volume of binary mixtures near the critical line in terms of the thermodynamic variables T, ρ, x, and the method satisfies all of the requirements of the isomorphism hypothesis [15, 16].

The concept of the "pseudospinodal curve" was introduced in an attempt to extrapolate the thermodynamic properties of materials obtained in the stable phase to the metastable region. Hence the pseudospinodal is a certain curve in the metastable phase, just as the true physical spinodal. The pseudospinodal may not coincide with the physical spinodal and this often occurs in practice. In some cases the pseudospinodal $T_s(\rho)$ is obtained from a best fit to the experimental data obtained in the stable phase, i.e., it is considered to be a regular function. In this case too the pseudospinodal may not coincide with the true spinodal. But in those cases when we are interested in describing thermodynamic properties such as C_p, K_T, and the coefficient of volume expansion α, which all diverge on the physical spinodal, $T_s(\rho)$ coincides with the true spinodal and can be determined in advance from the experimental (T–ρ) data on the spinodal [5, 6]. In other cases, when the quantity of interest is C_v, or other thermodynamic properties which do not diverge on the spinodal, as is the case in the present paper, $T_s(\rho)$ is taken to be adjustable and is determined from experimental data in the stable phase. Obviously in this case the pseudospinodal does not coincide with the true spinodal and turns out to be a convenient mathematical recipe for calculating the thermodynamic properties of materials in the critical region in terms of the physical variables (T, ρ).

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TABLE 1. Values of the Constants of Eqs. (11) and (13) for Solutions of NaCl in Water

A^*	B^*	C	A	T_1, K^{-1}	T_2, K^{-1}	T_3, K^{-1}	T_{k1}, K	T_{k2}, K	α	β
0,00311	0,00222	0,00102	22,003	—0,02924	0,06956	—0,04657	647,067	2005,281	0,1085	0,325

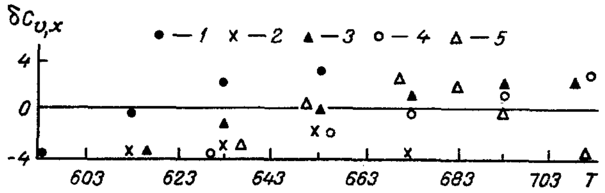

Fig. 1. Deviations $\delta C_{v,x} = (C_{v,x}^{expt} - C_{v,x}^{cal})/C_{v,x}^{expt} \cdot 100\%$ between the experimental values of the heat capacity at constant volume of NaCl—water solutions along the saturation line and the values calculated from (11) for different concentrations: 1) x = 0.0031 molar fraction; 2) 0.0160; 3) 0.0331; 4) 0.0716; 5) 0.0964 T, °K.

According to the isomorphic equation of state of a binary mixture near the critical line [16], the heat capacity at constant volume along the critical isochore ($\rho = \rho_c(x)$) is given by the equation

$$\frac{C_{v,x}}{T} = A_{s0}\tau^{-\alpha}(x) F_s''(\varphi) + B\tau(x) + C, \tag{3}$$

where A_{s0}, B, C are adjustable parameters; $F_s''(\phi)$ is related to the universal function $F_s(\phi)$ whose asymptotic properties are known [16]; $\tau(x) = (T - T_c(x))/T_c(x)$. According to [16], the function $F_s(\phi)$ has known asymptotic properties which follow from the isomorphism hypothesis, and has the form

$$F_s(\varphi) = \left(\frac{\varphi}{1+\varphi}\right)^{\frac{2-\alpha}{1-\alpha}}, \tag{4}$$

here $\phi = \tau^{\alpha}(x)\xi$ is a dimensionless variable determining the nature of the renormalization. For dilute solutions ξ has the form

$$\xi = \frac{T_c^3 \rho_c}{A} \frac{R}{x} \left(\frac{dT_c}{dx}\right)^{-2}, \tag{5}$$

where A is an adjustable parameter.

In [17] (3) was verified numerically for solutions of NaCl in water along the critical isochore. Using the fundamental principle of the pseudospinodal hypothesis, i.e., the extension of (3) to noncritical isochores $\rho \neq \rho_c(x)$ by introducing the pseudospinodal function $T_s(\rho, x)$, we obtain

$$\frac{C_{v,x}}{T} = (A_{s0}\tau_s^{-\alpha}(x) + A_{s1}|\Delta\rho|^2 Z_{0co}^{2\beta}\tau_s^{\gamma-2}(x)) F_s''(\varphi) + B\tau_s(x) + C, \tag{6}$$

where

$$\tau_s(x) = \frac{T - T_s(\rho,\ x)}{T_s(\rho,\ x)}; \quad \Delta\rho = \frac{\rho - \rho_c(x)}{\rho_c(x)};$$

$T_s(\rho, x)$ is the pseudospinodal curve, which in the asymptotic approximation, in analogy with (2), has the form

$$T_s(\rho,\ x) = T_c(x)[1 - Z_{0s}|\Delta\rho|^{1/\beta}]. \tag{7}$$

The amplitude Z_{0s} for mixtures can be represented in the first approximation as a linear interpolation between the values $Z_{0s}^{(i)}$ of the pure components:

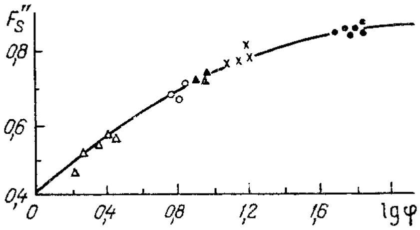

Fig. 2. Universal scaling function $F_s''(\varphi)$ for the heat capacity. solid curve: calculated from (4); the notation is the same as in Fig. 1.

$$Z_{0s} = Z_{0s}^{(1)} + (1-x)(Z_{0s}^{(1)} - Z_{0s}^{(2)}). \tag{8}$$

Similarly the amplitude of the coexistence curve of the binary mixture is represented as

$$Z_{0co} = Z_{0co}^{(1)} + (1-x)(Z_{0co}^{(1)} - Z_{0co}^{(2)}), \tag{9}$$

where $Z_{0co}^{(i)}$ are the amplitudes of the coexistence curves of the pure components.

Obviously $T_s(\rho_c(x)) = T_c(x)$ at $\rho = \rho_c(x)$, and equation (6) reduces to (3). In this case the universal function $F_s''(\phi)$ determining the behavior of the singular part of (6) has the asymptotic properties of [16], and hence satisfies all of the requirements of the isomorphism hypothesis. On the phase equilibrium line

$$T_{cco}(\rho, x) = T_c(x)[1 - Z_{0co}|\Delta\rho|^{1/\beta}], \tag{10}$$

and equation (6) takes the form

$$\frac{C_{v,x}}{T} = [A_{s0}(Z_{sco} - 1)^{-\alpha} + A_{s1}(Z_{sco} - 1)^{\gamma-2}]\,\tau^{-\alpha}(x)\,F_s'' + B(Z_{sco} - 1)\,\tau(x) + C, \tag{11}$$

where $Z_{sco} = Z_{0s}/Z_{0co}$.

This relation was verified numerically using the experimental values of the heat capacity at constant volume for solutions of NaCl in water on the saturation line. Measurements were performed on the calorimetric device of [18] using the continuous heating method for the concentrations 0.0031; 0.0159; 0.0331; 0.0715 and 0.0963 molar fraction of NaCl in the temperature interval 373-723°K. The solutions were prepared by gravimetric determination from chemically pure salts with a purity of 99.8% and twice-distilled water with a specific electric conductivity of $10^{-6}\ \Omega^{-1}\cdot$cm at 293°K. The mass of the solution was determined by weighing on the VLA-200M scale with a weighing error of 0.2 mg. The density was found by dividing the mass of the solution by the volume of the calorimeter at the temperature corresponding to the boundary curve, and the error was 0.1-0.15%. The temperature was measured with the platinum thermometer PTS-10 with an error of 0.01°K. About 90 values of $C_{v,x}$, ρ, T were obtained for each concentration studied. The error in the measurements of the heat capacity was 2.5% in the high temperature region. The critical temperature and density for the concentrations 0.0331 and 0.0159 molar fraction of NaCl were determined from the maximum of $C_{v,x}$ in the one-phase state on the boundary curve; published critical parameters were used for the other concentrations.

In fitting the obtained values of $C_{v,x}$ by equation (11), the adjustable parameters were taken to be A*, B*, C, and A, where $A^* = A_{s0}(Z_{sco} - 1)^{-\alpha} + S_{s1}(Z_{sco} - 1)^{\gamma-2}$; $B^* = B(Z_{sco} - 1)$. Values of the parameters A*, B*, C, and A were determined by minimizing the quadratic functional

$$S(A^*, B^*, C, A) = \sum_{i=1}^{N} W_i \left[\left(\frac{C_{v,x}}{T} \right)_i^{\text{expt}} - A^* \tau_i^{-\alpha}(x)\,F_{is}''(\varphi) - B^* \tau_i(x) - C \right]^2, \tag{12}$$

where W_i is the statistical weight of the i-th experimental point and was determined according to the method of [19]. Because the parameter A appears nonlinearly in (12), the functional was minimized using the estimation method developed in [20]. The derivative dT_c/dx is necessary for the calculations and was determined by differentiating the relation

$$\frac{1}{T_c(x)} = \frac{1-x}{T_{c1}} + \frac{x}{T_{c2}} + x(1-x)[T_1 + (1-2x)T_2 + (1-2x)^2 \cdot T_3], \tag{13}$$

where T_1, T_2, and T_3 are adjustable parameters which were obtained by a least-squares fit of the critical temperatures $T_c(x)$ (published and obtained here) for different concentrations. Since the values of the critical temperature of the second component (NaCl) available in the literature are not consistent (in certain cases the disagreement reaches 100%), in determining the constants of (13) the parameter T_{c2} was taken to be adjustable and lying between 2000 and 4000°K, where the limits of this interval were determined from data on the critical parameters of NaCl available in the literature. An equation of the form (13) was given in [21] and verified for a series of mixtures.

In the minimization of (12), the critical indices α, β, γ, and also the critical parameters of the first component (water) T_{c1}, ρ_{c1} were held fixed [22]. Values of the other coefficients of (12) and (13) are presented in Table 1. Figure 1 shows the deviations between the calculated values of $C_{v,x}$ and the experimental values obtained here. The mean-square error in the calculated heat capacities is about 2%. The maximum relative error $\delta C_{v,x}$ does not exceed 4%. Figure 2 shows the behavior of the universal scaling function for the heat capacity $F_s''(\phi)$. It is evident from Fig. 2 that nearly all of the experimental points at different concentrations are close to the theoretical curve calculated from (4).

Equation (6) can be used to calculate $C_{v,x}$ for binary mixtures over a wide region around the critical line along noncritical isochores, in the one-phase region.

NOTATION

T_c, P_c, ρ_c, critical temperature, pressure, and density; α, β, γ, critical indices; C_v, heat capacity at cnstant volume; T, temperature; ρ, density; $Z_{0co} = B_s^{-1/\beta}$; B_s, amplitude of the pseudospinodal curve; $Z_{0co} = B_{co}^{-1/\beta}$; B_{co}, amplitude of the coexistence curve; x, concentration of the solution; R, universal gas constant; T_{c1}, critical temperature of the first component of the mixture (water); T_{c2}, critical temperature of the second component of the mixture (NaCl).

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MACROKINETIC EQUATIONS FOR A PHASE TRANSITION OF THE FIRST SORT

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Differential equations are derived for phase transition kinetics. Analytic solutions are obtained for linear dependence of new phase growth rate on the degree of completion of the phase transition.

A phase transition of the first sort in solutions or alloys involves the simultaneous stages of new phase nucleus formation and growth [1-3]. Let I(t) be the frequency of nucleus formation per unit volume at time t, while v(t, τ) is the volume of the growing center at the actual time τ. In analogy to [2], but for systems in which only a definite fraction of the material α^* can transform to the new phase (as is characteristic, for example, of polymer systems where $\alpha^* = 0.1$-0.9), one can write the following integral equation:

$$\alpha(\tau)=\frac{\rho_A}{\rho_k}\int_0^\tau v(t,\ \tau)\, I(t)\,[\alpha^*-\alpha(t)]\,dt,\quad 0\leqslant\alpha\leqslant\alpha^*, \tag{1}$$

where

$$v(t,\ \tau)=\beta\left[\int_t^\tau G(\eta)\,d\eta\right]^n;\quad t\leqslant\eta\leqslant\tau. \tag{2}$$

Introducing the degree of completion $X = \alpha/\alpha^*$, we write Eqs. (1), (2) in the form

$$X(\tau)=a\int_0^\tau [l(t,\ \tau)]^n\, I(t)\,[1-X(t)]\,dt; \tag{3}$$

$$l(t,\ \tau)=\int_t^\tau G(\eta)\,d\eta;\quad a=\rho_A\beta/\rho_k. \tag{4}$$

When the quantities I and G are variable, integral equation (3) is nonlinear, and its solution is extremely difficult. For constant I and G analytical solutions of Eq. (3) have been obtained [2-4], but they describe only the free growth stage up to values of X = 0.1-0.3, after which the solutions lose physical meaning.

For this reason, despite the fact that the formulation of Eqs. (3), (4) is the most physically correct and formal, at present other approaches are used to describe phase transition kinetics [1-9].

In the present study integral equations (3), (4) will be transformed to a differential equation convenient for practical applications. We write Eqs. (3), (4) in the form

$$X(\tau)=a\int_0^{l(\tau)} [l(\tau)-l(t)]^n\,\frac{I(t)}{G(t)}\,[1-X(t)]\,dl(t); \tag{5}$$

$$l(\tau)=\int_0^\tau G(\eta)\,d\eta;\quad l(t)=\int_0^t G(\eta)\,d\eta. \tag{6}$$

In accordance with [10] the integral in Eq. (5) can be replaced by a multiple integral

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