VERTICAL DISTRIBUTION OF THE SUBSTANCE IN A BINARY MIXTURE NEAR THE CRITICAL EVAPORATION STATE

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Based on the thermodynamic theory of critical states, the content and the density distribution in a binary mixture along the height of the system are analyzed, assuming isothermal conditions with positive temperature gradients beyond the critical evaporation point.

Near the critical state of a binary liquid–vapor system one observes a considerable gravitational effect. Under the influence of the gravity field there occurs in an isothermal binary mixture a noticeable redistribution of content and density along the height of the system [1, 2, 3]. The present phenomenological theories of the gravitational effect deal with the distribution of a substance along the height of a system at the critical temperature [4, 5, 6]. Since an experimental study is conducted at temperatures not exactly equal to the critical temperature, as a rule, it becomes necessary to consider the content and the density of an isothermal binary mixture along the height of the system at temperatures which differ from the critical temperature by some small increment $T-T^{cr}$. We will consider here only the case where $T > T^{cr}$.

We use the equation of balance for a binary system in the gravity field, which has been derived by different authors in different ways [6, 7]:

$$G_{XX}dx = -\left[M_2 - M_1 - P\left(\frac{\partial V}{\partial X}\right)_{p,T}\right] g_0 dZ. \tag{1}$$

Equation (1) can be easily transformed with the aid of the relation

$$V = \frac{M_1(1-X) + M_2 X}{P}$$

into an expression more convenient in certain cases:

$$G_{XX}dX = -V\left(\frac{\partial P}{\partial X}\right)_{p,T} g_0 dZ. \tag{2}$$

The critical state of a binary mixture is characterized by a vanishing of both the second and the third derivative of the thermodynamic potential with respect to the molar fraction, while the stability condition for this state with regard to diffusion requires the respective fourth derivative to be positive [8], i.e.,

$$G_{XX}^{cr} = 0, \quad G_{XXX}^{cr} = 0, \quad G_{XXXX}^{cr} > 0. \tag{3}$$

Assuming the thermodynamic functions in Eq. (2) to be analytic and resolving them into series with respect to small deviations in the independent variables p, T, X from their critical values, we obtain

$$\begin{gathered} G_{XX} = \frac{1}{2} G_{XXXX}^{cr}(X - X^{\text{кр}})^2 + G_{XXT}^{cr}(T - T^{cr}) + G_{XXp}^{cr}(p - p^{cr}) \\ + \frac{1}{6} G_{XXXXX}^{cr}(X - X^{cr})^3 + G_{XXXT}^{cr}(X - X^{cr})(T - T^{cr}) + G_{XXXp}^{cr}(X - X^{cr})(p - p^{cr}) + \ldots, \end{gathered} \tag{4}$$

$$V\left(\frac{\partial P}{\partial X}\right)_{p,T} = V^{cr}\left(\frac{\partial P}{\partial X}\right)_{p,T}^{cr} + \left[\frac{\partial}{\partial X}\left(V\frac{\partial P}{\partial X}\right)\right]_{p,T}^{cr}(X - X^{cr}) + \ldots \tag{5}$$

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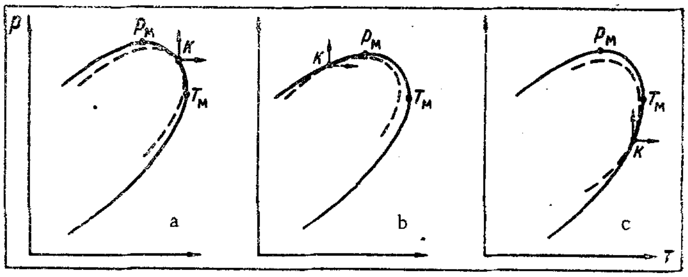

Fig. 1. Possible locations of the critical point K on the tip portion of the p–T coexistence diagram for a binary mixture; p_M and T_M are the maximum pressure and the maximum temperature respectively at which a two-phase equilibrium is possible in a solution with some given concentration. The spinodal curve for such a solution is indicated by a dashed line.

In order to examine the signs of the coefficients in the first three terms of series (4), which determine the behavior of a solution in the immediate vicinity of the critical state, we will use the p–T diagram for a binary mixture. There are three possible locations of the critical point on this diagram (Fig. 1).

In the first case (Fig. 1a) the critical point lies between the maximum-pressure point P_M and the maximum-temperature point T_M on the binodal curve. Here a temperature rise at the critical pressure and composition or a pressure rise at the critical temperature and composition (such processes are indicated on the diagram by arrows) shifts the system from the critical state into the region of single-phase stable states where $G_{XX} > 0$. This means, as can be seen in expression (4), that both derivatives G^{cr}_{XXT} and G^{cr}_{XXp} are positive when the critical point is located in this range. In the second case (Fig. 1b) the critical point K lies to the left of point p_M. Here a temperature rise at the critical pressure and composition shifts the system from the critical state into the region of unstable states (inside the spinodal curve) defined where $G_{XX} < 0$. Consequently, the derivative $G^{cr}_{XXT} < 0$ while the derivative G^{cr}_{XXp} remains positive when the critical point is located in this range.

In the third case (Fig. 1c) the critical point K lies below point T_M. Here $G^{cr}_{XXp} < 0$ while $G^{cr}_{XXT} > 0$.

To study the behavior of binary mixtures near the critical liquid–vapor state, one usually pours such a mixture into a hermetic chamber so that the average density and composition are close to critical, i.e., that $\bar{P} \approx P^{cr}$ and $\bar{X} \approx X^{cr}$. Then the meniscus separating the liquid from the gaseous phase will disappear when the critical temperature is reached inside the chamber. At temperatures somewhat above the critical point one should expect the two conditions $X = X^{cr}$ and $P = P^{cr}$ to be simultaneously satisfied at the level where the meniscus vanishes.

At this level the temperature-dependent change in pressure is $(\partial p/\partial T)^{cr}_{V,X}(T - T^{cr})$. The departure of the pressure from its critical value at any height may, taking into account the hydrostatic pressure component, be expressed as follows:

$$p - p^{cr} = \left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X} (T - T^{cr}) - P^{cr} g_0 (Z - Z^{cr}), \tag{6}$$

where $Z - Z^{cr}$ is the height above the level where $X = X^{cr}$ and $P = P^{cr}$. Inserting (6) into expression (4), we obtain

$$\begin{aligned} G_{XX} = {} & \left[G^{cr}_{XXT} + G^{cr}_{XXp} \left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X}\right] (T - T^{cr}) + \frac{1}{2} G^{cr}_{XXXX} (X - X^{cr})^2 \\ & + \frac{1}{6} G^{cr}_{XXXXX} (X - X^{cr})^3 + \left[G^{cr}_{XXXT} + G^{cr}_{XXXp} \left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X}\right] (X - X^{cr}) (T - T^{cr}) \\ & - G^{cr}_{XXp} P^{cr} g_0 (Z - Z^{cr}) - G^{cr}_{XXXp} P^{cr} g_0 (X - X^{cr}) (Z - Z^{cr}). \end{aligned} \tag{7}$$

The derivative $(\partial p/\partial T)^{cr}_{V,X}$ is positive. In the first case (Fig. 1a), when the critical point lies between p_M and T_M, both terms in the coefficient of $(T - T^{cr})$ in (7) are positive. In the second and in the third case (p–T diagrams in Fig. 1b, c) these terms have opposite signs. We will prove that the expression by which $(T - T^{cr})$ in (7) is multiplied remains always positive, regardless of the signs of its component

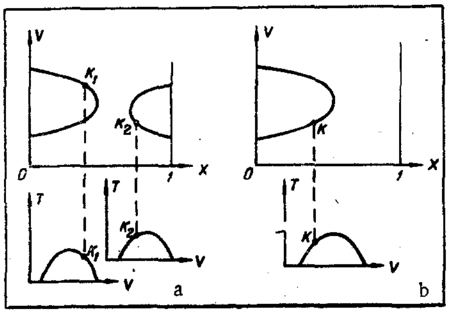

Fig. 2. V–X and V–T sections of the T–V–X coexistence surface of a binary mixture: a) for a solution the $T^{cr} = f(X)$ curve of which has a minimum; b) for a solution the $T^{cr} = f(X)$ curve of which does not have a minimum T^{cr}.

terms, i.e., regardless of the location of the critical point on the binodal surface of a binary mixture. For this purpose, using the van der Waals' relation [7]

$$\left(\frac{dp}{dT}\right)^{cr}_{X,\mathrm{bin}} = -\frac{G^{cr}_{XXT}}{G^{cr}_{XXp}}, \tag{8}$$

we transform the coefficient of $(T - T^{cr})$ into the following expression:

$$G^{cr}_{XXT} + G^{cr}_{XXp}\left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X} = \left[\left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X} - \left(\frac{dp}{dT}\right)^{cr}_{X,\mathrm{bin}}\right] G^{cr}_{XXp}. \tag{8'}$$

On the other hand, we have

$$\left(\frac{dp}{dT}\right)^{cr}_{X,\mathrm{bin}} = \left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X} + \left(\frac{\partial p}{\partial V}\right)^{cr}_{T,X}\left(\frac{dV}{dT}\right)^{cr}_{X,\mathrm{bin}}. \tag{9}$$

Inserting (9) into (8) yields

$$G^{cr}_{XXT} + G^{cr}_{XXp}\left(\frac{\partial p}{\partial T}\right)^{cr}_{V,X} = \left(-\frac{\partial p}{\partial V}\right)^{cr}_{T,X}\left(\frac{dV}{dT}\right)^{cr}_{X,\mathrm{bin}} G^{cr}_{XXp}. \tag{10}$$

The first factor on the right-hand side of (10) is always positive. The other two factors, although they change signs depending on the location of the critical point, have always both the same sign. This becomes evident, if one considers the V–X and the V–T sections through the same critical point on the binodal surface of a binary mixture (Fig. 2). The situation in Fig. 2a represents the most general case, namely an azeotropic mixture the binodal surface of which, in V, T, X coordinates, is saddle-shaped. For such mixtures, within the range of concentrations between that corresponding to the termination of the azeotropic curve on the critical curve and that corresponding to the minimum critical temperature, the critical point K_1 is located on the upper half of the V–X section of the binodal surface and the derivative G^{cr}_{XXp} is negative [7]. At the same time, point K_1 lies also on the right-hand half of the V–T section of the binodal surface, i.e., the derivative $(dV/dT)^{cr}_{X,\mathrm{bin}}$ is also negative. In the other cases (point K_2 in Figs. 2a and point K in Fig. 2b) the critical point is located on the lower half of the V–X section of the binodal surface with both positive derivatives G^{cr}_{XXp} [7] and $(dV/dT)^{cr}_{X,\mathrm{bin}}$. Thus, the coefficient of $(T - T^{cr})$ in (7) is always positive.

Disregarding in (7) the last term, which is of a high-order of smallness, and inserting (7) as well as (5) into (2) will yield, after a change to the dimensionless variables:

$$x = \frac{X - X^{cr}}{X^{cr}}, \quad t = \frac{T - T^{cr}}{T^{cr}}, \quad p' = \frac{p - p^{cr}}{p^{cr}}, \quad v = \frac{V - V^{cr}}{V^{cr}},$$

$$\rho = \frac{P - P^{cr}}{P^{cr}}, \quad h = \frac{P^{cr} g_0 (Z - Z^{cr})}{p^{cr}}, \quad g = \frac{G}{p^{cr}V^{cr}},$$

a linear nonhomogeneous differential equation which relates a change in the composition of a binary mixture to the height in the system – at small temperature excursions from the critical point:

$$\frac{dh}{dx} - \frac{D}{C}h + \frac{A}{C}t + \frac{B}{C}x^2 + \frac{CF - AL}{C^2}tx + \frac{CE - BL}{C^2}x^3 = 0, \tag{11}$$

where the following symbols are used for dimensionless coefficients:

$$A = g^{cr}_{xxt} + g^{cr}_{xxp'}\left(\frac{\partial p'}{\partial t}\right)^{cr}_{v,x}, \quad B = \frac{g^{cr}_{xxxx}}{2}, \quad C = \left(\frac{\partial \rho}{\partial x}\right)^{cr}_{p',t}, \quad D = g^{cr}_{xxp'},$$

$$E = \frac{g^{cr}_{xxxxx}}{6}, \quad F = g^{cr}_{xxxt} + g^{cr}_{xxxp'}\left(\frac{\partial p'}{\partial t}\right)^{cr}_{v,x}, \quad L = \left[\frac{\partial}{\partial x}\left(v\frac{\partial \rho}{\partial x}\right)\right]^{cr}_{p',t}.$$

The solution to Eq. (11) with the condition $x = 0$ at $h = 0$ is

$$h = \frac{CE - BL}{CD} x^3 + \frac{C}{D}\left[\frac{B}{C} + \frac{3(CE - BL)}{CD}\right]\left(x^2 + \frac{2C}{D}x\right)$$

$$+ \frac{CF - AL}{CD} tx + \frac{C}{D}\left[\left(\frac{A}{C} + \frac{CF - AL}{CD}\right)t + \frac{2BC}{D^2} + \frac{6(CE - BL)C}{D^3}\right]\left[1 - \exp\left(\frac{D}{C}x\right)\right]. \tag{12}$$

In the physically meaningful extreme case $|(D/C)x| \ll 1$ the solution becomes

$$h + \frac{B}{3C}x^3 + \frac{A}{C}tx + \frac{A(D - L) + CF}{2C^2}tx^2 + \left(\frac{E}{4C} - \frac{BL}{4C^2} + \frac{BD}{12C^2}\right)x^4 = 0. \tag{13}$$

The solution to this equation, $x(h, t)$, is found by successive approximations and, as a result, we obtain a formula for the departure of the composition from the critical one:

$$x = x_0 - \frac{2[A(D - L) + CF]tx_0^2 + [B(D - L) + CE]x_0^4}{4C(At + Bx_0^2)}, \tag{14}$$

with the zeroth approximation $x_0(h, t)$ representing the solution to the cubic equation

$$\frac{B}{3}x_0^3 + Atx_0 + Ch = 0. \tag{15}$$

The second term in (14) represents a small correction found from (13) in the next approximation.

Solving (15) for the extreme case $[(A/B)t]^3 \gg [(3C/2B)h]^2$, which corresponds to small changes along the height of the system at relatively large temperature excursions, and inserting the found solution into (14) yields

$$x(h, t) = -\frac{Ch}{At}\left[1 + \left(D - L + \frac{CF}{A}\right)\frac{h}{2At}\right], \tag{16}$$

which means that in the immediate vicinity of level $h = 0$ the composition seems to vary linearly with height.

At small temperature excursions and at relatively small deviations along the height, which corresponds to the inequality $[(A/B)t]^3 \ll [(3C/2B)h]^2$, the composition varies with height according to the relation:

$$x(h, t) = -\left(\frac{3Ch}{B}\right)^{1/3}\left[1 + \frac{At}{B\left(\frac{3Ch}{B}\right)^{2/3}}\right] - \frac{B(D - L) + CE}{4BC}\left(\frac{3Ch}{B}\right)^{2/3}\left[1 + \frac{A(D - L) + CF}{B(D - L) + CE} \cdot \frac{t}{\left(\frac{3Ch}{B}\right)^{2/3}}\right], \tag{17}$$

where the first term represents the solution to the zeroth approximation (15) and the last term represents a small correction.

It is to be noted that for mixtures having a minimum on the $T^{cr} = f(X)$ curve the quantity $C = (\partial p / \partial x)^{cr}_{p',t}$ may be either positive or negative [7]. This means, according to (16) and (17), that the concentration of the mixture can either decrease or increase, depending on the location of the $x = 0$ point on the critical curve for the given mixture.

Inserting solution (17) into the original inequality $|(D/C)x| \ll 1$ and considering that the change in composition as a function of temperature is determined essentially by the first term in (17), we arrive at the criterion

$$|h| - \frac{At}{|D|} \ll \frac{BC^2}{3|D|^3}, \tag{18}$$

for the range of heights within which the composition of a mixture as a function of the height is described by Eq. (13) and by the respective solutions (16) and (17) to this equation.

Reverting to dimensional quantities and taking note of the relation $V = [(M_2 - M_1)X - M_1]/P$, we can now transform the right-hand side of inequality (18) into

$$\frac{G^{cr}_{XXXX}\left[M_2 - M_1 - P^{cr}\left(\frac{\partial V}{\partial X}\right)^{cr}_{p,T}\right]^2}{6\rho^{cr}(P^{cr})^2\left|\left(\frac{\partial^2 V}{\partial X^2}\right)^{cr}_{p,T}\right|^3}. \tag{19}$$

Expression (19) represents a large quantity, since the derivative $\partial^2V/\partial X^2$ is small. The situation may change when the critical phase is diluted, or near the azeotropic point on the critical curve. In both cases the quantities $(\partial V/\partial X)^{cr}_{p,T}$ and $(\partial^2V/\partial X^2)^{cr}_{p,T}$ increase infinitely [7].

It can be proved, by differentiating the identity $(\partial G/\partial X)_{p,T} \equiv (\partial \Psi/\partial X)_{V,T}$ with respect to the composition X (where Ψ denotes the free energy per mole of a solution), that during dilution as well as near the azeotropic point G^{cr}_{XXXX} increases as $(\partial V/\partial X)^4$.

During dilution $(\partial V/\partial X)^{cr} \sim (X^{cr})^{-1}$ [9]. Differentiating the thermodynamic equation $\partial V/\partial X = -(\partial p/\partial X)(\partial p/\partial V)^{-1}$ with respect to the composition, with the behavior of $(\partial p/\partial X)^{cr}_{V,T}$ at the limit taken into account, will yield the following relation:

$$\frac{\partial^2 V}{\partial X^2} \sim \left(\frac{\partial V}{\partial X}\right)^2 \sim (X^{cr})^{-2}.$$

Inserting these values into (19), we will then find that during dilution of the critical phase the range of heights defined by (18) becomes finite.

The situation is different at the point where the azeotropic curve terminates into the critical curve for a solution. At this point, approximately, $\partial^2V/\partial X^2 \sim (\partial V/\partial X)^3$ [7], i.e., expression (19) tends toward zero as $(\partial V/\partial X)^{-3}$ does. This means that in solutions having a composition close to that of an azeotropic mixture the composition varies along the height according to relation (17) only within a narrow range of heights, this range tending toward zero as the special point on the critical curve for a given solution is approached.

In order to find the density distribution over the height of an isothermal binary mixture near the $x = 0$, $\rho = 0$ level at small positive temperature excursions, we will use the resolution:

$$\rho = \left(\frac{\partial \rho}{\partial x}\right)^{cr}_{p',t} x + \left(\frac{\partial \rho}{\partial p'}\right)^{cr}_{t,x} p' + \left(\frac{\partial \rho}{\partial t}\right)^{cr}_{p',x} t. \tag{20}$$

During critical evaporation of binary mixtures the derivative $(\partial \rho/\partial p')^{cr}_{t,x}$ is generally a finite quantity. Using the obvious relation $(\partial \rho/\partial t)_{p',x} = -(\partial \rho/\partial p')_{t,x}(\partial p'/\partial t)_{\rho,x}$ and replacing p' in (20) with expression (6), after a prior conversion to dimensionless form, we obtain after some simplications:

$$\rho = \left(\frac{\partial \rho}{\partial x}\right)^{cr}_{p',t} x - \left(\frac{\partial \rho}{\partial p'}\right)^{cr}_{t,x} h. \tag{21}$$

The density distribution in a binary mixture within the range of heights defined by (18) can be found by inserting solutions (16) and (17) into (21).

Thus, in binary mixtures at near-critical states there exists a distinct content and density distribution over the height of the system. The character of content and density deviations from critical appears to be the same as the character of density deviations in single-component systems. At small distances above level $h = 0$ and when the temperature excursions from the critical point are relatively large, the composition and the density vary as linear functions of the height. At considerable heights and when the temperature excursions are small, the composition and the density of binary mixtures vary as cubic functions of the height.

The results obtained so far are useful in analyzing another interesting problem. It is well known that the vertical distribution of density in a solution at constant temperature can be expressed as [6]:

$$\frac{dP}{dZ} = -\frac{Pg_0}{\left(\frac{dp}{dP}\right)_{T,\mathrm{grav}}}, \tag{22}$$

where the derivative $(dp/dP)_{T,\mathrm{grav}}$ is taken along the gravitational curve.

One of the authors here has stated earlier that $(dp/dP)_{T,\mathrm{grav}}$ along the critical curve for a binary mixture is not equal to zero [6]. It can be proved rigorously that this derivative will tend toward zero as the critical state of the mixture is approached. Indeed, it follows from the isothermal conditions that

$$\frac{dP}{dZ} = \left(\frac{\partial P}{\partial X}\right)_{p,T} \frac{dX}{dZ} + \left(\frac{\partial P}{\partial p}\right)_{T,X} \frac{dp}{dZ}. \tag{23}$$

Comparing (23) with (22) and using expression (2), we obtain

$$\frac{P}{\left(\frac{dp}{dP}\right)_{T,\mathrm{grav}}} = \frac{V\left(\frac{\partial P}{\partial X}\right)_{p,T}}{G_{XX}} + \left(\frac{\partial P}{\partial p}\right)_{T,X} P.$$

On the critical curve for a mixture $G_{XX}^{cr} = 0$ and the derivatives $(\partial P/\partial X)_{p,T}^{cr}$, $(\partial P/\partial p)_{T,X}^{cr}$ are generally finite, from which we have that $(dp/dP)_{T,\mathrm{grav}}^{cr} = 0$. We observe here an analogy to single-component systems. In the latter case the gravitational curve coincides with the isotherm and, therefore, the partial derivative $(\partial p/\partial P)_T$, which vanishes at the critical point, becomes also the derivative taken along the gravitational curve.

NOTATION

G	is the thermodynamic potential per mole of mixture;
X	is the molar fraction of the second component in a mixture;
G_{XX}	is the second derivative of the thermodynamic potential with respect to the molar fraction of the second component;
G_{XX}^{cr}	is the value of this derivative at the critical point of a mixture;
M_1, M_2	are the molecular weight of the first and the second component, respectively;
P	is the density;
V	is the molar volume;
p	is the pressure;
T	is the absolute temperature;
g_0	is the acceleration due to gravity;
Z	is the vertical coordinate;
$(dp/dT)_{X,\mathrm{bin}}$	is the derivative of pressure with respect to temperature, taken along the binodal curve;
x, t, p', v, ρ	are the relative deviations of the composition, temperature, pressure, molar volume, and density from their respective critical values;
h	is the dimensionless height above the critical density and composition level;
g	is the dimensionless thermodynamic potential per mole;
$(dp/dP)_{T,\mathrm{grav}}$	is the derivative of pressure with respect to density, taken along the gravitational curve.

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