SOVIET PHYSICS JETP VOLUME 21, NUMBER 5 NOVEMBER, 1965

HYDROSTATIC EFFECT AT THE CRITICAL POINT OF A BINARY MIXTURE

A. V. VORONEL' and M. Sh. GITERMAN

Submitted to JETP editor December 9, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **48**, 1433-1436 (May, 1965)

The influence of gravity on the distribution of concentration with height is considered for binary systems near the critical point. The d mixture concentration gradient along the height of the container is proportional to this height taken to the power $\frac{1}{3}$ (for example, for an He^3—He^4 mixture near the liquid—liquid critical point, it should reach ~ 7% at a height of ~ 10 cm). There are grounds for assuming that in a liquid—vapor system this effect is considerably greater. The possibility of separating mixtures by means of the hydrostatic effect is considered.

A density gradient along the height of a vessel (the hydrostatic effect[1]) appears near the critical point of a pure substance, owing to the unlimited rise in the compressibility, and this effect exerts a considerable influence on all the measured properties of the substance in the critical state. In binary mixtures, the critical phenomena appear in two cases: along the liquid—vapor critical equilibrium curve of the solution (this curve is limited in the p—T—c space by the critical points of the pure components) and along the critical curve of separation of the solution into two liquid phases (this curve may have a break at a change in the aggregate state, or it may continue without limit[2,3]). In both cases, the compressibility of the substance remains finite and the systems are characterized in the same way by zero values of the first two derivatives of the chemical potential of each of the components with respect to the concentration:

$$(\mu_1')^{\mathrm{cr}} = (\mu_1'')^{\mathrm{cr}} = 0; \qquad (\mu_1''')^{\mathrm{cr}} > 0 \tag{1}$$

(here and below, the primes denote the derivatives with respect to c_1 at constant values of p, T).

We shall consider the effect of the force of gravity on such a system. The condition of equilibrium for each of the components of the mixture in the gravitational field has the following form for a system at constant temperature ($dT = 0$):

$$d\mu_1 = v_1 dp + M_1 g dh + \mu_1' dc_1 = 0, \tag{2}$$

where M_1 and v_1 are the molecular weight and the molar volume of one component and h is the height of the liquid layer.

Equation (2), together with the condition of equilibrium of a two-component system (Gibbs-Duhem rule)

$$c_1\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T} + c_2\left(\frac{\partial\mu_2}{\partial c_1}\right)_{p,T} = 0 \tag{3}$$

leads, after elementary transformations, to a general formula for the dependence of the solution concentration on height:[4]

$$-\mu_1' dc_1 = \left(M_1 - v_1\frac{M_1c_1 + M_2c_2}{v_1c_1 + v_2c_2}\right) g dh. \tag{4}$$

In the usually considered case of ideal solutions, we have $\mu_1 \sim \ln c_1$ and Eq. (4) reduces to the barometric formula with the Archimedean correction.[2]

Near the critical state, the solution is probably far from ideal and its equation of state can, following condition (1), be written in the form

$$\mu_1' = \tfrac{1}{2}B(c_1 - c_1^{\mathrm{cr}})^2 + \ldots \tag{5}$$

Here, $B = (\mu_1''')^{\mathrm{cr}}$ is the main quantity which governs the properties of the system in the region of the critical point.

Substituting Eq. (5) into Eq. (4), integrating, and retaining only the first non-zero terms with $c_1 - c_1^{\mathrm{cr}}$, we obtain

$$c_1 - c_1^{\mathrm{cr}} = \left[\frac{6g}{B}\left(M_1 - v_1\frac{M_{\mathrm{cr}}}{v_{\mathrm{cr}}}\right)(h - h_0)\right]^{1/3};$$

$$M_{\mathrm{cr}} = M_1c_1^{\mathrm{cr}} + M_2c_2^{\mathrm{cr}}, \quad v_{\mathrm{cr}} = v_1c_1^{\mathrm{cr}} + v_2c_2^{\mathrm{cr}},$$

$$c_2^{\mathrm{cr}} = 1 - c_1^{\mathrm{cr}}, \tag{6}$$

where the constant h_0 determines the level at which the critical conditions are realized.1) Al-

---

1)In the present work, as in[1], we use the assumption that the thermodynamic quantities near the critical point can be expanded in series consisting of small departures of the parameters from the critical values. The singularity, detected at the critical point of a pure substance, is such[5] that it does not affect the expansions used in[1] but alters only the numerical values of the coefficients. We may expect that in the analogous case considered here the assumption of the possibility of expanding in series gives the correct result.

lowance for the further terms in the expansion of Eq. (6) gives a small correction, proportional to $(h - h_0)^{4/3}/B^{4/3}$.

Bearing in mind that the experimentally measured quantity is usually not the concentration of the mixture but its density, and assuming, in the first approximation, that the molar volumes of the components of the mixture are additive

$$v = v_1 c_1 + v_2 c_2,$$

we may rewrite Eq. (6) for the molar volume in the form

$$v - v_{\mathrm{cr}} = (v_1 - v_2)\left[\frac{6g}{B}\left(M_1 - v_1\frac{M_{\mathrm{cr}}}{v_{\mathrm{cr}}}\right)(h - h_0)\right]^{1/3}. \quad (7)$$

Thus a considerable hydrostatic effect should be observed in a binary system, in spite of its finite compressibility.

We shall consider some conclusions which follow from relationships (6), (7).

1. Due to the presence of the hydrostatic effect, there is some distortion in the form of the experimentally observed curve for coexistence near the critical point in the coordinates $T-c_1$. In the same way as in [1], the magnitude of the flattening Δc_1 of the "hump" of the $T(c_1)$ curve is found to be

$$\Delta c_1 = \frac{3}{2}\left[\frac{6gH}{B}\left(M_1 - v_1\frac{M_{\mathrm{cr}}}{v_{\mathrm{cr}}}\right)\right]^{1/3}. \quad (8)$$

Kohler and Rice[6] observed this flattening for the system triethylamine—water at the liquid—liquid critical point. The value of Δc_1 (at the vessel height H of about 10 cm and the critical concentration given by ~ 0.930 molar fraction of water) was found to be close to 0.03.

The formulas of Krichevskiĭ and Khazanova[7] make it possible to estimate the value of B for a solution from the data on the specific-heat discontinuity $\Delta C_{p,c_1}$ and from the form of the boundary curve $T(c_1)$ near the critical point. Using the results of the experimental studies (cf. [8,9]) of the triethylamine—water mixture, we obtain $B = (2 - 5) \times 10^4$ J·mole^{-1}·(mol. fraction)^3. Then we find from Eq. (8) that $\Delta c_1 = 0.025 - 0.03$.

Thus, the hydrostatic effect explains quite satisfactorily the flat part of the $T(c_1)$ curve, obtained by many workers, without using any additional assumptions of the type employed in Mayer's theory.[10] 2)

A similar explanation is obtained for the results of Zavalin et al.,[12] which show the presence of a strong hydrostatic density effect at the liquid—vapor critical point of the hexane—octane system [$B \approx 5$ J.mole^{-1}·(mol. fraction)^3 at $c_{\mathrm{cr}} \approx 0.5$] and the benzene—propyl alcohol system [$B \approx 15$ J·mole^{-1}·(mol. fraction)^3 at $c_{\mathrm{cr}} \approx 0.5$]. We note that the value of the quantity B for the liquid—vapor system is 3—4 orders of magnitude lower than the corresponding values for the liquid—liquid system.

2. We may expect the hydrostatic effect to be detected in an investigation of a He^3—He^4 mixture near the critical stratification point ($T = 0.84$°K; $c_1 = 0.63$ He^3). We shall estimate the possible reduction in the concentration of He^3 in the mixture at a vessel height of 10 cm. Using the values of $\Delta C_{p,c_1}$ taken from [13] and the form of the $T(c_1)$ curve taken from [14], we obtain $B = 50—90$ J·mole^{-1}·(mol. fraction)^3. Then $\Delta c_1 = 0.06—0.075$, i.e., the effect is quite considerable. It is possible that the observation of this effect will yield information on the problem of the relative positions of the λ-curve and the phase-stratification curve near the critical point of the mixture.

3. We note that the appearance of a concentration gradient of components along the vessel height represents a separation effect. For the case of the He^3—He^4 system considered above, we obtain, at a column height of 10 cm and taking the upper half of the mixture enriched in He^3, a separation coefficient $\alpha \approx 1.05$ near the critical concentration. Separating the fractions and then varying temperature and pressure in such a way as to remain on the critical curve, we can make the process of separation repetitive and continuous. Thus we can approach the critical points of the pure components along the critical liquid—vapor curve, i.e., we can separate the mixture completely.

From the law of corresponding states (cf. [15]), the quantity B is very unlikely to be proportional to a combination of the critical parameters with the right dimensions:

$$B \sim \mu_1^{\mathrm{cr}} / c_{1,\mathrm{cr}}^3. \quad (9)$$

Then the separation coefficient (at each step we remove half the mixture) would almost cease to depend on the concentration, in accordance with Eq. (6), and would become constant over the whole critical curve, except for the regions close to $c_1 = 0$ and $c_1 = 1$, where $\alpha - 1$ should tend to zero.

Unfortunately, the values of B are known only for the liquid-liquid case, which does not provide the same opportunities for separation. (For

---

2)Rice[11] denies the influence of the hydrostatic effect on the form of the curve representing coexistence in a binary mixture on the basis of the erroneous application of the formulas for ideal solutions to a system near the critical state. This has lead to the lowering of the values of the characteristic inhomogeneity parameter $c^{-1}dc/dh$ by four orders of magnitude.

He^{-3}—He^{-4}, the critical concentration, for example, is practically independent of pressure.[16]). However, we have seen above that in the liquid—vapor system this quantity is in all cases not greater than that for the liquid—liquid system and this means that the hydrostatic effect will not be less in the liquid—vapor system. This is confirmed by direct measurements.[12]

Thus, a 50% mixture of He^3 and He^4 could be definitely separated completely in 15 steps. Conversely, from the separation of the mixture we can estimate parameters in Eq. (6). There are grounds for assuming that the real separation coefficient (i.e., $\alpha - 1$) is several times larger than the coefficient calculated in Sec. 2 above.

Finally, we note that the effect may be increased greatly by centrifuging (then instead of g in Eq. (6) we have the acceleration $\omega^2 r$). Usually, centrifuging is inefficient in isotope separation because the back diffusion impedes the separation. However, at the critical point not only is the effect amplified, but the diffusion also stops. In fact, as shown by Krichevskiĭ and Tsekhanskaya,[17] at the critical point of a binary system the diffusion decreases sharply due to the condition $(\mu_1')^{cr} = 0$ and consequently there will be practically no diffusion equalization of the concentration, which would impede the separation.

This method should be particularly effective in the separation of heavy isotopes with similar critical parameters and high initial concentrations in the original mixture (Ar, Xe, Hg, etc.,).

In conclusion, the authors have much pleasure in thanking I. R. Krichevskiĭ for valuable discussions and N. S. Rudenko for his interest in this work.

---

[1] A. V. Voronel' and M. Sh. Giterman, JETP **39**, 1162 (1960), Soviet Phys. JETP **12**, 809 (1961).

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Gostekhizdat, 1951.

[3] J. S. Rowlinson, Liquids and Liquid Mixtures, Butterworths Sci. Publ., 1959.

[4] E. A. Guggenheim, Modern Thermodynamics (Russ. Transl., GNTIKhL, 1941).

[5] Azbel', Voronel', and Giterman, JETP **46**, 673 (1964), Soviet Phys. JETP **19**, 457 (1964).

[6] F. Kohler and O. K. Rice, J. Chem. Phys. **26**, 1614 (1957).

[7] I. R. Krichevskiĭ and N. E. Khazanova, ZhFKh **29**, 1087 (1955).

[8] Krichevskiĭ, Khazanova, and Linshitz, DAN SSSR **100**, 737 (1955).

[9] É. V. Matizen, Dissertatsiya (Dissertation), Institute for Physics Problems, Academy of Sciences, U.S.S.R., 1957.

[10] J. E. Mayer and Maria G. Mayer, Statistical Mechanics (Russ. Transl. IIL 1952).

[11] O. K. Rice, J. Chem. Phys. **23**, 164 (1955).

[12] Zavalin, Shimanskaya, and Shimanskiĭ, Ukr. fiz. zh. **9**, 491 (1964).

[13] de Bruyn, Ouboter, Taconis, Le Pair, and Beenakker, Physica **26**, 853 (1960).

[14] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 901 (1960).

[15] A. V. Voronel', JETP **40**, 1516 (1961), Soviet Phys. JETP **13**, 1062 (1961).

[16] K. N. Zinov'eva, JETP **44**, 1837 (1963), Soviet Phys. JETP **17**, 1235 (1963).

[17] I. R. Krichevskiĭ and Yu. V. Tsekhanskaya, ZhFKh **30**, 2315 (1956).

Translated by A. Tybulewicz
209