Equation of state and diffusion near the critical point

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The coefficients of the Landau equation of state are determined on the basis of the P-V-T-N data obtained. The diffusion coefficients as functions of V, T, and N are calculated by means of the Leontovich formula, which is derived under the assumption of constant mobility. Good agreement is obtained between these dependences and those obtained previously by direct measurements in the temperature range $(T\text{-}T_c)/T_c \gtrsim 10^{-3}$.

The present research is devoted to the measurement of P–V–T–N data of solutions of Ar in CO_2 with the purpose of explaining the dependence of the chemical potential of binary mixtures on the thermodynamic variables and a comparison of the resultant data with an experiment on mutual diffusion.[1]

The dependence of the gas pressure on the volume, temperature and concentration was measured in a variable-volume pressure gauge, provided with a piston to vary the volume and with windows for observation of the phase separation during change in the temperature of the system. The temperature was measured by a standard platinum resistance thermometer, the pressure by means of a loaded-piston manometer of the MP-60 type, and the volume change by the number of turns of a micrometer screw which moved the piston. The gas concentration was determined by a gravimetric method. Further details of the apparatus are given in[2]. The errors of measurement of the deviations from the critical values of the parameters are as follows:

$$\delta P=0.0025\ \text{bar}\quad \delta V=0{,}03\ \text{cm}^3/\text{mole}$$
$$\delta N=0.0002\,\text{mole fraction}\ \delta T=0{,}0002\,\text{K}.$$

The critical state of the mixture was established visually when the boundary of phase separation did not move upon following a several millidegree Kelvin change in the temperature of the system near the point of homogenization. Purification of the carbon dioxide was carried out by the method set forth in[3]. A mass-spectrometer analysis after cleaning showed that the amount of impurities in the CO_2 was less than 0.0007%. The critical temperature and pressure of the CO_2 used by us were T_c = 31.0128°C and P_c = 74.0408 bar, respectively. No determination of the critical specific volume was carried out; we took the value[3] V_c = 94.0171 cm^3/mole. Argon of grade "A" was used in the experiments; it had an impurity content of no more than 0.5 mol.%. Special purification of the argon was not attempted.

The volume dependence of the pressure was measured at constant temperatures in eight solutions of Ar in CO_2 with different concentrations (in molar fractions) in the range $0 \le N \lesssim 0.036$ (in all, about 650 points). The regions of change of temperature and volume were $0 \le |V-V_c|/V_c \lesssim 0.2$ and $10^{-3} \lesssim |T-T_c|/T_c \lesssim 10^{-2}$. The resultant P–V–T–N dependence was approximated by an equation of state in the form of the Landau expansion

$$\Delta P=AN+A_1\Delta T+BN\Delta V+B_1\Delta T\Delta V+C\Delta V^3+DN^2 +E\Delta T^2+EN\Delta T+G\Delta T\Delta V^2+G_1N\Delta V^2+H\Delta V^4, \tag{1}$$

where ΔP [bar], ΔT [°K], ΔV [cm^3/mole] are the deviations of pressure, temperature and volume from the critical values for the pure solvent, and N is the concentration in molar fractions. The terms with ΔV^2 and ΔV^4 were taken in order to describe the change in the critical volume upon increase of N, and also for the description of the nonsymmetry of the isotherms relative to the critical isochore of the mixture. The values of the coefficients in the expansion (1), obtained by the method of least squares with the Minsk-32 computer are

$$A=224\pm1,\ A_1=1{,}650\pm0{,}006,\ B=-3.97\pm0.03,$$
$$B_1=-0.0176\pm0{,}0002,\ C=-0.000048\pm0.000003,\ D=582\pm31;$$
$$F=0.0076\pm0.0015,\ E=1{,}67\pm0.18,\ G=0.00047\pm0{,}00002;$$
$$G_1=0{,}082\pm0{,}003,\ H=0{,}0000004\pm0{,}0000003.$$

The error in the approximation of the experimental data by the expansion (1) is δP = 0.09 bar.

The resultant equation of state was used to calculate the temperature, volume, and concentration dependence of the coefficients of mutual diffusion according to the Leontovich formula[4]

$$\frac{D}{bRT}=N(1-N)\frac{1}{RT}\left(\frac{\partial\mu}{\partial N}\right)_{P,T}=\frac{\Delta V^2+\alpha\Delta T+(\beta-\gamma)N}{\Delta V^2+\alpha\Delta T+\beta N}, \tag{2}$$

where

$$\alpha=\frac{2(\partial^2P/\partial V\,\partial T)_c}{(\partial^3P/\partial V^3)_c}\qquad \beta=\frac{2(\partial^2P/\partial V\,\partial N)_c}{(\partial^3P/\partial V^3)_c}$$
$$\gamma=-\frac{2(\partial P/\partial N)_c^2}{[RT(\partial^3P/\partial V^3)_c]}.$$

The subscript c means that the value of the derivative is taken at the critical point of the pure solvent. This expression for the diffusion coefficient is obtained under the assumption that the free energy of the solutions can be expanded in powers of ΔV, ΔT and N, that the mobility of the molecules b has no singularity at the critical point, and that the linear relation between the flux of the diffusing component and the gradient of the chemical potential is valid.[4]

If we use the values of the coefficients in the expansion (1), then the functional dependence (2) gives a picture of the behavior of the coefficient of mutual diffusion, which is close to that actually observed[1]—see Figs. 1 and 2. The quantitative difference in the behavior of the diffusion coefficient determined directly and calculated from (2) on the basis of thermodynamic data can be appreciably reduced by taking the next terms of the expansion in (2) into account.

It should be emphasized, however, that improvement of the description of the experimental data by the function (2) in a certain region by taking into account the next terms of the expansion cannot give the correct behavior of the diffusion coefficient in the region close to

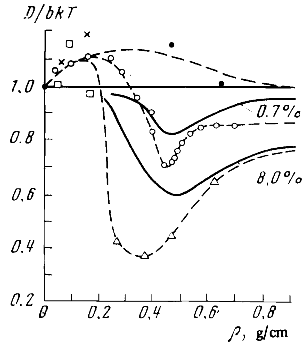

FIG. 1

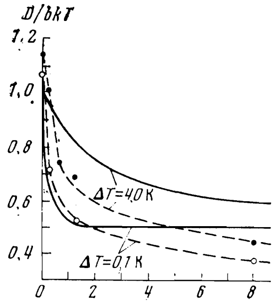

FIG. 2

FIG. 1. Comparison of the dependences of the coefficients of mutual diffusion of Ar and CO_2 at $T-T_c = 4°K$ on density and concentration, obtained from Eq. (2)—the continuous lines—and as determined from diffusion experiments [1]—dashed lines. The experimental points corresponds to the following: ●—0.02%; X—0.1%; O—0.7%; □—7.0%; the two left points of Δ on the lower curve correspond to 7.9% and the two on the right, 9.4%.

FIG. 2. Comparison of the dependences of the coefficients of mutual diffusion of Ar and CO_2 at $\rho = \rho_c$ on concentration and temperature, obtained from (2)—continuous curves—and determined from diffusion experiments—dashed curves. [1] The experimental points correspond to the following: ●—$(T-T_c) = 4.0°K$, ○—$(T-T_c) = 0.1°K$.

the critical point. The reason is that, in accord with the modern theory of second-order phase transitions and of critical phenomena,[5] the thermodynamic derivatives and the kinetic coefficients have a singularity at the critical point. Thus Eqs. (1) and (2), which are based on the series expansion, are generally inapplicable for the description of critical phenomena. If we do this in the present paper, then it holds only for the explanation of the approximate picture in a region far from the critical point. This is precisely the region where the singular behavior of the thermodynamic derivatives has little effect and where it is therefore possible to give a description of the behavior on the basis of the series expansion. In our case, we assume that Eq. (2) can serve as a description of the diffusion only at sufficient distances from T_c, when $(T-T_c)/T_c > 10^{-3}$.

It was found in[1] that the diffusion current of miscible components relative to the walls of the closed volume in which the diffusion is occurring, is accompanied by a flow of the gas as a whole, with some mean numerical velocity w. It was assumed that this gas flow is connected with a strong dependence of the specific volume of the mixture of gases on the concentration of the components and increases as one approaches the critical point of the solvent. For the case of diffusion in a capillary closed at one end, the total flow of the dissolved component, with account of the velocity w, is equal to[1]

$$j = -\frac{1}{V} D\left[1 - \frac{N}{V}\left(\frac{\partial V}{\partial N}\right)_{P,T}\right]\frac{\partial N}{\partial x} + \frac{N}{V}\int_x^l \frac{1}{V} D\left(\frac{\partial N}{\partial x}\right)^2 \frac{\partial^2 V}{\partial N^2} dx, \quad (3)$$

where x is the coordinate along the capillary, which is of length l.

For a sufficiently small gradient of the concentration, the term with the integral at the right is small in comparison with the first term and can be neglected.

It has been possible to estimate the term $(N/V)(\partial V/\partial N)_{P,T}$ in the present research on the basis of the experimental data. It turned out that it is positive and as one approaches the critical curve at low concentrations it rises almost to unity. Thus the decrease in the current, which equalizes the concentration, can be due not only to a decrease in the coefficient of mutual diffusion, but also to the counterflow of the gas as a whole.

Upon approach to the critical point of the pure solvent, because of the increase in $(\partial^2 V/\partial N^2)_{P,T}$, it is impossible to neglect the second term on the right side of (3). Just this fact leads to the result that the diffusion equation becomes nonlinear[4] when the two-component system approaches the critical point of steam generation of the pure solvent.

Thus, on the basis of our results, we can conclude that the Leontovich theory describes correctly the process of mutual diffusion in a certain region near the critical point of vapor production of the solvent, and that this diffusion, as also follows from this theory, is accompanied by strong flows of the gas solution as a whole.

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