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NEGATIVE PARTIAL MOLAR VOLUME OF SOLVENT IN DILUTE CRITICAL PHASES OF A BINARY SOLUTION

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It is known that in dilute solutions the partial molar volume of the solvent v_1^* is usually close to the molar volume of the pure solvent and becomes comparable with it in the limit when $N_2 = 0$; this limit, naturally, does not depend on the path along which the molar fraction N_2 of the dissolved substance vanishes:

$$\lim_{N_2 \to 0} v_1 = v_1^0$$

$$N_2 \to 0.$$

(1)

We shall show that this general statement is incorrect at least in one case. Indeed, let us write down the general expression for the partial molar volume

$$\bar{v}_1 = v + N_2 \frac{(\partial p / \partial N_2)_{v,T}}{(\partial p / \partial v)_{T,N_2}}.$$

(2)

Al all finite $(\partial p/\partial v)_{T,N_2}$ and $(\partial p/\partial N_2)_{v,T}$ this expression yields (1) in the limit as $N_2 \to 0$, but in the case when one of these derivatives has a singularity, further investigation is necessary [2]. We know that at the critical point of the pure substance $(\partial p/\partial v)_T = 0$. This means that the limit of v_1 as $N_2 \to 0$ can differ from $v_{1,cr}^0$ in different manners, depending on the path along which the critical point of the pure solvent is approached. Two of us (L. A. M. and E. S. S.) obtained p-v-T-N data for binary dilute solutions of carbon dioxide (solute) in sulfur hexafluoride (solvent). From these data we calculated the partial molar volumes of the solvent for the initial section of the critical liquid-vapor equilibrium curve, i.e., for dilute critical phases [3]. The partial molar volume of the solvent for these phases was not only not close to the molar volume of the pure solvent but, varying along the critical curve, it was not comparable with the molar volume even in the limit, at the critical point of the pure solvent.

In the dilute critical phase, the partial molar volume of sulfur hexafluoride is so far from the molar volume of the pure sulfur hexafluoride, that it even has a negative value [3]. According to Eq. (1), of course, the partial molar volume of the solvent in

dilute solutions should always be positive. The figure shows the dependence of the partial molar volume, obtained from the data of [3], on the concentration of the dilute solution along the critical curve. It is seen clearly that v_1 has an almost constant negative value that differs strongly from $v^0_{1,cr}$, namely $v_1 = -240$ cm^3/mole.
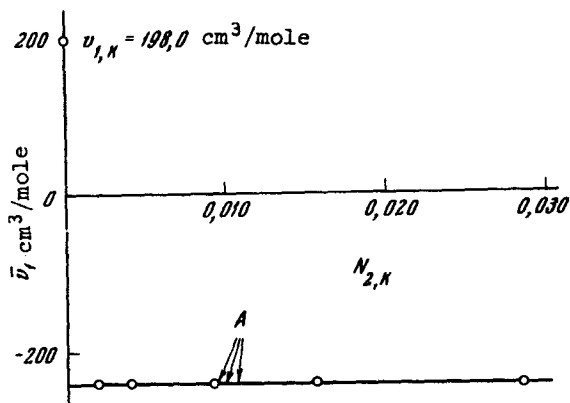
Partial molar volume of SF$_6$ in the dilute critical phase of a binary solution (CO$_2$ in SF$_6$). A - point of injection of solvent (SF$_6$) in the critical phase.

Such a behavior of this quantity agrees with the notion of the approximately linear relation between the compressibility of the solution and the concentration N_2 along the critical point, advanced in [4,5]:

$$\left(\frac{\partial p}{\partial v}\right)_{T,N_2,K} = A N_{2,K}.$$

(3)

Since relation (3) and the statements associated with it concerning the character of the singularities of $(\partial p/\partial v)_{T,N_2}$ and $(\partial p/\partial N_2)_{v,T}$ seem to us to be very important, it would be desirable to confirm the foregoing results of the calculations (see the figure) by an independent experiment.

The idea of the experiment can be understood from the equation (see [6])

$$(\partial p/\partial n_1)_{T,V,n_2} = -v_1 (\partial p/\partial V)_{T,n_1,n_2}.$$

(4)

The derivative $(\partial p/\partial V)_{T,n_1,n_2}$ is always negative, and therefore the signs of $(\partial p/\partial n_1)_{T,V,n_2}$ and v_1 always coincide.

The authors measured the change in pressure upon addition of a small amount of the solvent SF$_6$ to the dilute critical phase (with the temperature and the total volume constant). We used in this case the setup described earlier [7].

The points of injection are designated in the figure by arrows.

A decrease in pressure was observed (exceeding the measurement error [3]), this being incontestable evidence of the negative value of the partial molar volume of SF$_6$ in dilute critical phases. The main purpose of the experiments was to obtain such a qualitative confirmation (see the figure). But the experimentally measured pressures are furthermore in a sufficient quantitative agreement with those calculated from (4). The right side of (4) was

The system SF_6 - CO_2

Critical phase				SF_6 added,	Change in pressure,
$N_2 \times 10^3$	p_{cr}, kg/cm^2	T, °C	Weight of phase, g	g	kg/cm^2 $\times 10^2$
10.70	38.708	45.180	12.2749	0.8713	-2.7
10.00	38.699*	45.223*	12.2733	0.2875	-1.2
9.76	38.680	45.218	12.2300	0.9895	-2.4

* $p = p_{cr} + 0.015$ kg/cm^2, $T = T_{cr} + 0.013$°C.
Total volume of system 16.670 cm^3.

also calculated from the data given in [3].

We see thus that it is necessary to excercise great caution in extrapolating the ordinary thermodynamic relations for solutions into the region of the critical point. It can apparently also be regarded as firmly established that $(\partial p/\partial N_2)_{T,v}$ is finite and $(\partial p/\partial v)_{T,N_2}$ is proportional along the critical curve of the solution to the impurity concentration (Eq. (3)), at least to concentrations ~0.1%.

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* By definition, $(\partial V/\partial n_1)_{p,T,n_2} = v_1$ (we are considering a binary solution), where V is the total volume of the solution, p the pressure, T the temperature, n the number of moles, 1 the solvent, and 2 the solute. See [1] concerning the partial molar quantities.

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