

*THERMODYNAMIC PROPERTIES OF DILUTE SOLUTIONS IN THE VICINITY OF THE
CRITICAL POINT OF THE SOLVENT*

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The classical theory of critical phenomena is extended to dilute solutions. The compositions of the coexisting phases, equations for boundary and critical curves (the latter is a straight line for small concentrations of the solute) are found. It is found that the equations satisfactorily describe the experimental data. For the V-N projection of the critical curve, a correction for the irregular free energy component is important. It is shown that a number of thermodynamic properties of the solutions have at the critical point of the solvent a singularity due to loss of continuity with respect to the set of variables. The values of these properties of the pure substance also possess a similar singularity). The partial molar volume of the solvent, for example, with the solute concentration approaching zero, may not only differ from the molar volume of the solvent but may be negative or even infinite.

INTRODUCTION

A phenomenological description of the thermodynamic properties of solutions of non-electrolytes^[1-3] is actually based on the assumption that a number of properties of the solutions (for example, the molar volume V) are analytic functions of the concentration (the molar fraction N of the dissolved substance). Actually, putting

$$V = V_1^0 + a_1N + a_2N^2 + a_3N^3 + \dots, \quad (1)$$

we obtain the well known equations for the partial molar volumes¹⁾ of the components in the dilute solution^[1-3]

$$\bar{V}_1 = V - N(\partial V / \partial N)_{P,T} = V_1^0 + aN^2,$$

$$\bar{V}_2 = V + (1 - N)\partial V / \partial N = \bar{V}_2 - 2aN + (a - 3b/2)N^2, \quad (2)$$

where V_1^0 is the molar volume of the solvent, V_2 is the value of V_2 at $N = 0$, and $a = -\alpha_2$, $b = -3\alpha_2$ are functions of the pressure and the temperature; the index 1 denotes the solvent and 2 the solute.

It follows from (2) that when $N \rightarrow 0$ the partial molar volume of the solvent becomes equal to the molar volume of the pure solvent, and the $V_1(N)$ curve has a horizontal tangent.

Closely related with relations (2) is the concentration dependence of the chemical potential in dilute solutions, since

$$\mu = \mu_1^0 + RT \ln f_1, \quad f_1 = f_1^0 N_1 \gamma_1, \quad RT \ln \gamma_1 = \int_0^P (\bar{V}_1 - V_1^0) dP, \quad (3)$$

where f are the volatilities (f_1^0 —of the pure solvent)²⁾,

¹⁾The partial molar volume is the increment of the volume of the system, referred to one mole of the added component $\bar{V}_i = \partial \tilde{V} / \partial n_i$, where \tilde{V} is the total volume of the system and n_i is the number of moles of the i -th component.

²⁾Volatility is a convenient form of representing the values of the chemical potential. In a solution, by definition, $\mu_1 = \mu_2^0 + RT \ln f_1$, where μ_1^0 is the chemical potential of the pure solvent (in the standard state, an idealized gas). If the gas phase is an ideal gas, then f_1 equals the partial pressure, and f_1^0 is equal to the pressure of the saturated vapor P_1^0 , when $\gamma_1 = 1$, Eq (3) reduces to Raoult's law $P_1 = P_1^0 N_1$.

γ is the activity coefficient, and $N_1 = 1 - N$. Integrating we obtain, with allowance for (2), for a dilute solution

$$RT \ln \gamma_1 = \bar{a}N^2, \quad \bar{a} = \int_0^P a dP,$$

$$\mu_1 = \mu_1^0 + RT \ln f_1^0 N_1 + \bar{a}N^2 = \mu_1^0 + RT \ln N_1 + \bar{a}N^2. \quad (4)$$

As $N \rightarrow 0$, we get $\gamma \rightarrow 1$, i.e., we obtain Raoult's law (and analogously Henry's law).

It can be shown, however, that the expansion (1) is not valid near the critical point of the solvent^[3]. Accordingly it can be shown that the laws of dilute solutions (2) and (4) will likewise not be satisfied. This was recently demonstrated experimentally^[4]. Moreover, certain unusual properties of solutions were observed^[5-7]. Thus, it turned out that in the system SF_6 - CO_2 , when the concentration of the CO_2 is decreased and the critical point of SF_6 is approached along the critical curve of the solutions, the limiting value of the partial molar volume of the solvent (SF_6) does not equal the molar volume of the solvent (198 cm^3 /mole), but assumes an entirely different value, and is furthermore negative (-230 cm^3 /mole). On moving towards the critical point along the critical isotherm—isochores, a different value of \bar{V}_1 was obtained experimentally (-40 cm^3 /mole), likewise different from the molar volume of the solvent. It was also found that the partial molar volume of the solute increases without limit.

We shall show that the observed phenomena can be attributed to the fact that certain thermodynamic quantities have a singularity at the critical point: their value depends on the direction of motion towards the critical point. We shall also show that this result follows from the classical theory of critical phenomena (for example^[8]), if the latter is extended to solutions (i.e., if the concentration dependence of the pressure is taken into account).

**EQUATION OF STATE OF A SOLUTION NEAR THE
CRITICAL POINT OF THE SOLVENT**

We supplement the usual expansion of $P(V, T)$ in the vicinity of the critical point with first terms con-

taining the concentration. To be sure, following the discovery by Voronel' (for pure substance $CV \sim \ln(T - T_c)^{[9]}$) it became clear that the classical expansion^[10] must be supplemented, since the free energy F has an irregular component^[11] (in dimensionless variables):

$$F = F_0 + \delta F, \quad \delta F = at^2 \ln \varphi(t, v), \quad \varphi = (t + bv^2)^2 + cv^4 \quad (5)$$

(according to I. M. Lifshitz, $\varphi = b't + c'v^2$). It can be shown, however, that the additional terms that follow from (5) do not influence the behavior of the quantities that become infinite at the critical point in accordance with a power law, namely C_P and $(\partial V/\partial T)_P$.³⁾ On the other hand, the derivative $(\partial V/\partial N)_{P,T}$, which determines the value of the partial molar volumes, behaves in the vicinity of the critical point in analogy with $\partial V/\partial T$. Therefore, assuming that F_0 is analytic, we supplement the equation of^[10] with first terms of the expansion in N :

$$\Delta P = AN + A'\Delta T - (BN + B'\Delta T)\Delta V - C\Delta V^3, \quad (6)$$

or in dimensionless form

$$p = aN + \mu t - (\beta N + \beta' t)v - \gamma v^3, \quad (7)$$

where

$$\Delta P = P - P_{c1}, \quad \Delta T = T - T_{c1}, \quad \Delta V = V - V_{c1}, \\ p = \Delta P/P_{c1}, \quad t = \Delta T/T_{c1}, \quad v = \Delta V/V_{c1},$$

and the coefficients are the values of the corresponding derivatives of P , V , T , and N at the critical point of the solvent; when $N \rightarrow 0$ we have

$$A = \left(\frac{\partial P}{\partial N} \right)_{v, c1}, \quad A' = \left(\frac{\partial P}{\partial T} \right)_{v, c1}, \quad B = - \left(\frac{\partial^2 P}{\partial N \partial V} \right)_{c1}, \\ B' = - \left(\frac{\partial^2 P}{\partial T \partial V} \right)_{c1}, \quad C = - \frac{1}{6} \frac{\partial^3 P}{\partial V^3}, \quad \alpha = \frac{A}{P_{c1}}, \quad \mu = \left(\frac{T_{c1}}{P_{c1}} \right) A', \\ \beta = \frac{BV_{c1}}{P_{c1}}, \quad \beta' = \frac{B'V_{c1}T_{c1}}{P_{c1}}, \quad \gamma = \frac{CV_{c1}^3}{P_{c1}}.$$

The constants μ , β' , γ for the pure solvents are presently known; they are universal (within the accuracy of the law of corresponding states) and amounts to $\mu = 6-8$ ^[12], $\beta' = 4.5$ ^[7], and $\gamma = 0.2$ ^[13]. The constants α and β have individual values for each binary system. It can be stated that they are finite; using the Van der Waals equation and putting $a = a_1(1 - N)^2 + 2a_{12}N(1 - N) + a_2N^2$, $a_{12} \approx \sqrt{a_1a_2}$ (nonpolar gases), and $b \approx b_1(1 - N) + b_2N$, we can obtain the qualitative estimates

$$\alpha = \frac{1}{P_{c1}} \left(\frac{\partial P}{\partial N} \right)_{v, c1} = 2 \left(\frac{V_{c2}}{V_{c1}} - 1 \right) - 6 \left(\frac{V_{c2}}{V_{c1}} \sqrt{\frac{P_{c2}}{P_{c1}}} - 1 \right) \\ \beta = - \frac{V_{c1}}{P_{c1}} \left(\frac{\partial^2 P}{\partial N \partial V} \right) = 6 \left(\frac{V_{c2}}{V_{c1}} - 1 \right) - 12 \left(\frac{V_{c2}}{V_{c1}} \sqrt{\frac{P_{c2}}{P_{c1}}} - 1 \right), \quad (8)$$

where the indices 1 and 2 denote the critical constants of the solvent and of the solutes.

Apparently relations (8) give the correct sign and order of magnitude of the corresponding quantities. Thus, for the SF_6 - CO_2 system ($V_{c1} = 198$ cm³/mole, $P_{c1} = 38.3$ kg/cm² for the first component and $V_{c2} = 99$ cm³/mole, $P_{c2} = 73$ kg/cm² for the second) we get $\alpha = 0.86$ and $\beta = 0.72$, giving $A = 33$ and $B = 0.12$,

³⁾For this reason, the conclusions of [10] concerning the properties of gases in the supercritical region remain valid.

whereas the experimental values are 63 kg/cm² and 0.27 kg/cm⁵mole⁻¹ respectively^[7]. If $A > 0$ and $B > 0$ ⁴⁾, then when the concentration is increased the isotherms of the solution are analogous to the isotherms of the pure substance with increasing temperature (Fig. 1a). If $A < 0$, then addition of the second component lowers the pressure in the system (Fig. 1b). If $B < 0$, then addition of the second substance has the same effect as a lowering of the temperature: when $T > T_{c1}$ and when N is sufficiently large, the layer becomes stratified into two phases, and when $T = T_{c1}$ the stratification occurs following an arbitrary small addition N , and the boundary of the two-phase region of the solution is tangent to the boundary liquid-vapor curve of the pure substance (Fig. 1b). If $A = 0$, then it is necessary to consider expansion terms containing N^2 ; this case (azeotrope at the critical point) calls for a separate analysis.

The aforementioned analogy between the action of addition of the solute and the change of the temperature can be formulated also quantitatively. The equation of state of the solution (6) can be transformed, by shifting the origin, into the equation of state of the pure substance. Let $P_{c'} = P_{c1} + \lambda P N$, $T_{c'} = T_{c1} + \lambda T N$; determining λ from (6) we get

$$P_{c'} = P_{c1} + (A - A'B/B')N = P_{c1}[1 + (\alpha - \mu\beta/\beta')N], \\ T_{c'} = T_{c1} - (B/B')N = T_{c1}(1 - N\beta/\beta'). \quad (9)$$

Putting $\Delta P' = P - P_{c'}$, $\Delta T' = T - T_{c'}$, $p' = \Delta P'/P_{c'}$, $t' = \Delta T'/T_{c'}$.

we obtain for the solution in place of (6)

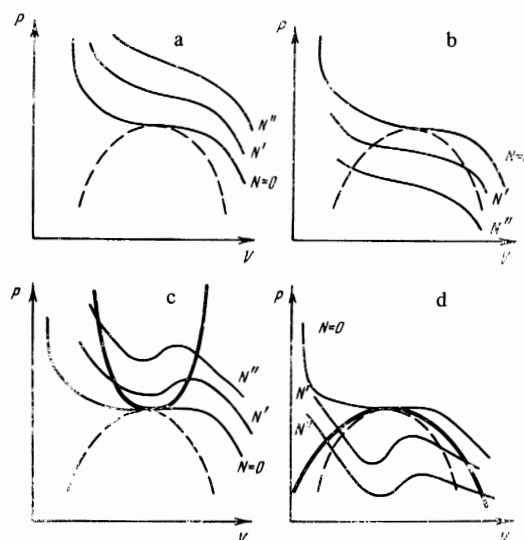


FIG. 1. P-V isotherms of dilute solutions near the critical point of the solvent, $N'' > N'$ at $T = T_{c1}$: a- $A > 0$, $B > 0$; b- $A < 0$, $B > 0$; c- $A > 0$, $B < 0$; d- $A < 0$, $B < 0$. Dashed curve—boundary curve of the pure substance, thick line—boundary curve for the solution.

⁴⁾According to (8), no limitations are imposed on the signs of A and B , and the possibility of $A > 0$ and $A < 0$ is subject to no doubt. Apparently, the best known cases are those when the signs of A and B are equal (Fig. 1); this is possibly connected with the fact that when P_{c1} and P_{c2} are close, then, in accordance with (8), α and β should be proportional. The case $A > 0$ and $B < 0$ corresponds apparently to the equilibrium gas-gas of the helium type.

$$\Delta P' = A'\Delta T' - B'\Delta V\Delta T' - C\Delta V^3, \quad p' = \mu t - \beta'vt - \gamma v^3, \quad (10)$$

i.e., the equation of state of the pure substance.

Thus, P'_C and T'_C are pseudocritical parameters of the solution regarded as a homogeneous substance. In coordinates P/P'_C and V/V'_C , in our approximation, in accordance with (10), we obtain the same set of isotherms for the pure substance and for the solution (Fig. 2). However, the limits of the two-phase region will not coincide, since the conditions for the stratification are different, and the negative value of $(\partial P/\partial V)_P$ (i.e., the absence of extrema on the isotherms of Fig. 1) still does not ensure stability of the two-component system. Accordingly, the critical temperature of the solution T_C can be higher than the pseudocritical temperature. Actually, using the results of the sections that follow, we get

$$T_C = T'_C + NA^2/RT_{c1}B', \quad P_C = P'_C + NA'A^2/RT_{c1}B'.$$

Thus, the larger the concentration of the solute, the more the critical temperature and the pressure of the solution differ from the pseudocritical parameters, and the more the critical isotherm of the solution differs from the pseudocritical isotherm with horizontal inflection (Fig. 2). We note in addition that the parameters (9) differ also from the customarily employed pseudocritical parameters of mixtures, which are assumed to be additive^[14], so that

$$P_{ca} = P_{c1} + (P_{c2} - P_{c1})N, \quad T_{ca} = T_{c1} + (T_{c2} - T_{c1})N.$$

There may also be a difference in the signs of $\partial P'_C/\partial N$ and $\partial P_{ca}/\partial N$. For example, for the SF_6 - CO_2 system the pressure P_{ca} increases with concentration while P'_C decreases.

It now can be easily shown that, for example when $B > 0$, addition of the solute changes the isotherm in the same manner as a rise in temperature: when N increases T'_C decreases, and consequently the relative temperature T/T'_C increases and $\Delta T' = (B'\Delta T + BN)/B'$. In our approximation, $V'_C = V_{c1}$. To find the dependence of V'_C on the concentration, it is necessary to supplement (6) with terms containing N^2 and ΔTN .

COMPOSITION OF COEXISTING PHASES AND BOUNDARY CURVE

When the chemical potentials are expressed in terms of the volatilities ($\mu = \mu^0 + RT \ln f$), the equilibrium condition takes the form $RT \ln f_g = RT \ln f_l$, where f_g and f_l are the volatilities of the gas and of the liquid.

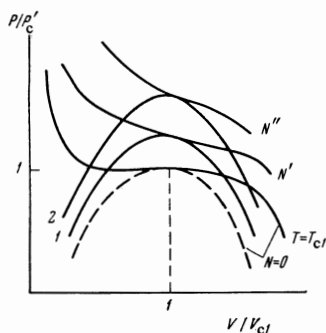


FIG. 2. P-V isotherms of dilute solutions in pseudo-reduced coordinates. 1 and 2—boundary curves for $N'' > N'$; dashed—the same for the solvent ($N = 0$).

Since the independent variables in the equation of state (6) are T and V , we shall use for the calculation of the volatilities the relation (161) from the book of Krichevskii^[1], which can be written in the form⁵⁾

$$RT \ln f_i = RT \ln \frac{N_i RT}{V} + PV - RT - \int_0^V \left(\bar{P}_i - \frac{RT}{V} \right) dV, \\ \bar{P}_i = P + \sum N_c \left(\frac{\partial P}{\partial N_i} \right)_{VT}.$$

The compositions of the coexisting phases are not equal, $N_g \neq N_l$ (Fig. 3). Therefore $\bar{P}_i(N_g) \neq \bar{P}_i(N_l)$, i.e., the integrand expressions for the volatilities in the gas and liquid phases in general do not coincide, and to perform the calculations we need either an equation of state that is valid up to $V = \infty$, or to perform the calculation relative to a certain state that is sufficiently remote from the critical point, for which the dependence of the volatility on the composition is given by relations (3)–(4). However, in the approximation (6) the quantities P_1 and P_2 do not depend on the composition (with $P_1 = P_1^0$, where P_1^0 is the pressure of the pure solvent). Accordingly, the integrands for both phases coincide. This yields the balance equations and the separation coefficient α :

$$RT \ln \alpha = \int_1^{V_g} \left(\frac{\partial P}{\partial N} \right)_{V,T} dV \approx A(V_g - V_l), \quad \alpha = \frac{N_g}{N_l} \frac{1 - N_l}{1 - N_g}. \quad (11)$$

Calculating N_g/N_l in this manner for small N (confining ourselves to the first two terms of the expansion in $V_g - V_l$), using the balance equation (or the equality $P_g = P_l$), we get $\Delta V_g \approx -\Delta V_l$. The equation of the coexistence curve of the liquid and gas phases is

$$C\Delta V^2 + B'(T - T_{c1}) + N(B - A^2/RT) = 0, \\ \Delta V = \pm \sqrt{-B'(T - T_{c1})}, \quad (12)$$

where T_C is the critical temperature of the mixture:

$$T_C = T_{c1} + N[(A^2/RT) - B]/B' = T_{c1} + \lambda_{Tc}N. \quad (13)$$

By changing variables, it is possible to obtain the equation of the boundary curve in coordinates P and V :

$$A'C\Delta V^2 + B'(P - P_C) + NB'A^2\Delta V/RT = 0. \quad (14)$$

Thus, the T - V and P - V projections of the coexistence curves (binodals) are quadratic parabolas, just as for the pure substance near the critical point, and are described by analogous equations. On the other hand, the form of the V - N projection of the binodal depends on the sign of λ_{Tc} (see Eqs. (13) and (20)). If $\lambda_{Tc} < 0$ (addition of the solute lowers the critical temperature of the solution), then the heterogeneous region exists only when $T < T_{c1}$ (Fig. 3b); Eq. (12) can be reduced to the form

$$\Delta V = \pm r \sqrt{N_c - N}, \quad (15)$$

where $N_c = (T_{c1} - T)/\lambda_{Tc}$ is the critical concentration, $r = \sqrt{B'\lambda_{Tc}/C}$. With decreasing $T_{c1} - T$, the

⁵⁾We note that the \bar{P}_i have certain properties of partial molar quantities, for example, $\bar{P}_1 N_1 + \bar{P}_2 N_2 = P$. For a solution obeying the Bartlett law, $\bar{P}_1 = P_1^0$ and $\bar{P}_2 = P_2^0$ in the entire range of concentrations, and for an infinitely dilute solution $\bar{P}_1 = P_1^0$ and $\bar{P}_2 = K$, where K is the Henry constant at $V = \text{const}$. Equation (6) can be written in the form $P = P_1^0 N_1 + KN$, i.e., the laws of dilute solutions are satisfied in the approximation (6) when $V = \text{const}$.

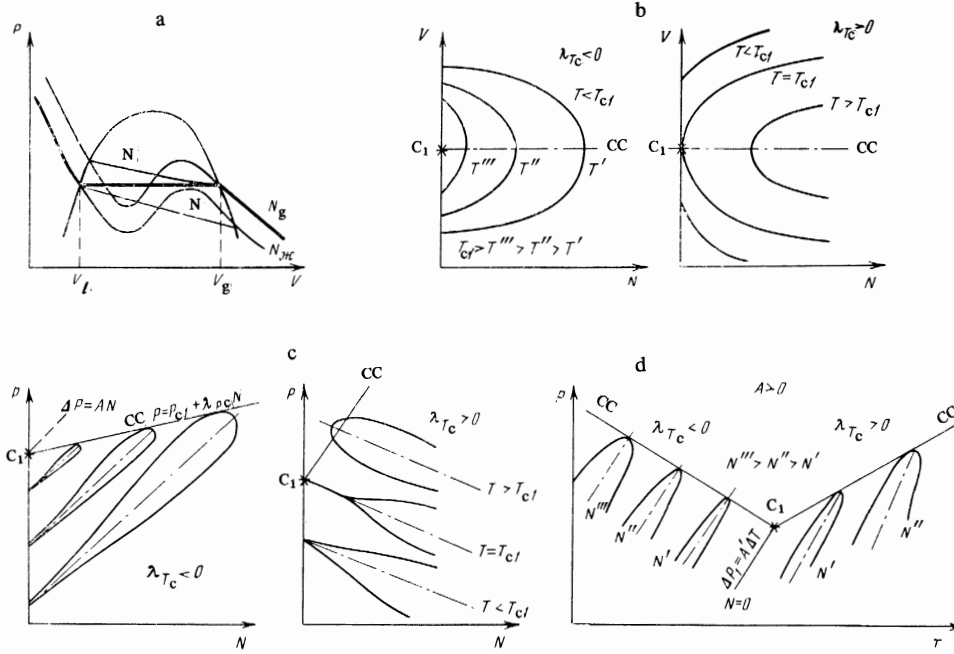


FIG. 3. Theoretical coexistence curves of the liquid and solid phases of a solution (binodals) in coordinates P-V (a), V-N (b), P-N (c), and P-T (d). CC—critical point, C₁—critical point of solvent, N—nodes.

binodal becomes flatter and gradually contracts to a point, with

$$(\partial V / \partial N)_{N \rightarrow 0} \sim (\Delta T + |\lambda_{Tc}|N)^{-1/2} \rightarrow \infty.$$

If $\lambda_{Tc} > 0$, then the heterogeneous region exists also when $T > T_{c1}$ in this case $\Delta V = \pm r \sqrt{N - N_c}$. When $T = T_{c1}$ we have

$$\Delta V = \pm r N^{1/2}. \tag{16}$$

We note that the relation (16), the existence of which was already indicated by Kortevg ([15], page 156) can be realized only when $\lambda_{Tc} > 0$.

In the coordinates P and N, the binodal is described by the equation

$$P = P_1^0 + AN \mp NA^2 \Delta V / RT = P_{c1} + A' \Delta T + AN \mp N(A^2 / RT) \sqrt{B'(T_{c1} - T + \lambda_{Tc}N)} / C. \tag{17}$$

When $\lambda_{Tc} < 0$, the last term is proportional to $N \sqrt{N_c - N}$, and corresponds to ‘balloons’ with axes parallel to the critical isochore $P = P_1^0 + AN$ (Fig. 3c); when $T \rightarrow T_{c1}$ the difference between the slopes of the branches of the liquid (upper branch) and the gas (lower branch), proportional to $\sqrt{N_c}$, decreases; when $\Delta T \rightarrow 0$ we get $N_c \rightarrow 0$, i.e., the ‘balloon’ contracts to a point. When $\lambda_{Tc} > 0$ (Fig. 3c), interest attaches to the case $T = T_{c1}$, when

$$P = P_1^0 + AN \mp (A^2 / RT) r N^{3/2}, \quad N_g = N \pm (A^2 / RT) N^{3/2}$$

and the liquid and gas branches have a common tangent; when $N \rightarrow 0$ the separation coefficient $\alpha = 1 + (A/RT)N^{1/2} \rightarrow 1$, i.e., the enrichment coefficient ($\alpha - 1$) vanishes. This is the consequence of Eq. (11) and of the equality of the volumes of the gas and liquid phases.

In coordinates P and T we obtain

$$P - P_c = A'(T - T_c) - N \Delta V A^2 / RT = A'(T - T_c) \mp N(A^2 / RT) \sqrt{B'(T - T_c)} / C. \tag{18}$$

Thus, in the classical approximation (6), the P' - T binodals represent parabolas with axis parallel to the

critical isochore of the pure substance. The parabolas become narrower with decreasing molar fraction of the dissolved substance, and in the limit as $N \rightarrow 0$ they contract to the straight line $\Delta P = A' \Delta T$ (Fig. 3d). Since $\Delta V_g > 0$ and $\Delta V_l < 0$, the pressure of the liquid P_l exceeds the pressure of the gas P_g , and the upper branch of the parabola always corresponds to the liquid. Accordingly, the nodes (the lines joining the points of equal compositions) on the P-V diagram will have the form shown in Fig. 3a.

It is interesting to note that, for the SF₆-CO₂ system, Eqs. (17) and (18) at $A = 63.5$, $B = 3.4 \times 10^{-3}$, $C = 0.7 \times 10^{-6}$, $B' = 0.27$, and $A' = 0.85$ [7] practically describe quantitatively the binodals in coordinates P and T (data of [7]) and coordinates P and N (data of [16]), see Figs. 4a and 4b. On the other hand, in the

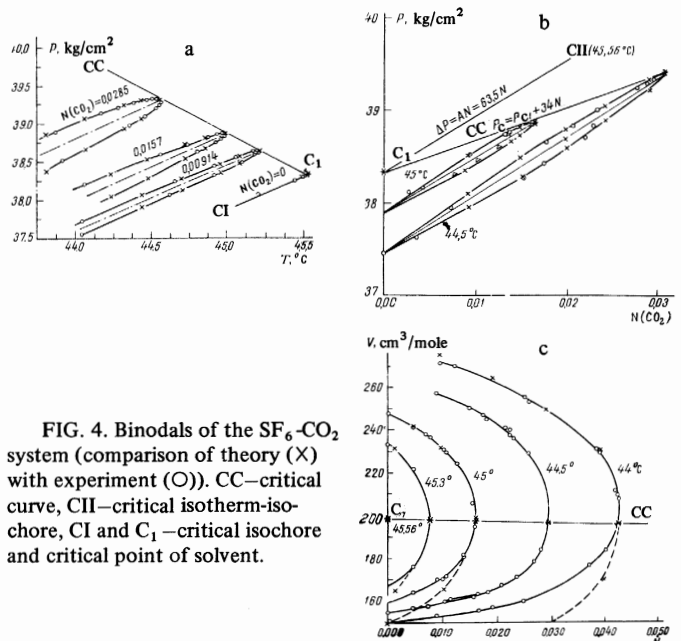


FIG. 4. Binodals of the SF₆-CO₂ system (comparison of theory (X) with experiment (O)). CC—critical curve, CII—critical isotherm-isochore, CI and C₁—critical isochore and critical point of solvent.

case of the V-N binodals (data of^[16]) and V-T binodals for SF₆^[7] only the initial section is described (Fig. 4c), since the binodals are asymmetrical, and for their accurate description it is necessary to take into account the terms tv^2 , Nv^2 , v^4 , etc.

PARAMETERS OF CRITICAL CURVE

The initial section of the critical curve of solutions (liquid-vapor critical points) are characterized by a linear relation between the parameters P, V, T, and N:

$$\begin{aligned} T_c &= T_{c1} + \lambda_{Tc}N, & P_c &= P_{c1} + \lambda_{Pc}N, \\ V_c &= V_{c1} + \lambda_{Vc}N, \end{aligned} \quad (19)$$

We have actually already determined the derivative λ_{Tc} : it follows from (13) that

$$\lambda_{Tc} = dT_c/dN = [(A^2/RT_{c1}) - B]/B' = T_{c1}(a^2z_c - \beta)/\beta', \quad (20)$$

where $z_c = P_{c1}V_{c1}/RT_{c1}$. The same result can be obtained by transforming the equation proposed by Van der Waals (^[15], page 202, formula (9)) for dT_c/dN . Equation (20) is confirmed also by the fact that from (6) and (20) we get the expression obtained in^[6] for $(\partial P/\partial V)_T$ on the critical curve.

We obtain the second coefficient from (6), putting $\Delta P = \lambda_{Pc}N$. We get

$$\lambda_{Pc} = (dP/dN)_c = A + A'\lambda_{Tc} = P_{c1}\{\alpha + [\mu(a^2z_c - \beta)/\beta']\}. \quad (21)$$

From (20) and (21) it follows that along the critical curve

$$\left(\frac{dP}{dT}\right)_c = A' + \frac{A}{\lambda_{Tc}}, \quad \frac{T_{c1}}{P_{c1}}\left(\frac{dP}{dT}\right)_c = \mu + \frac{\alpha\beta'}{a^2z_c - \beta}. \quad (22)$$

the second term determines the angle between the critical curve and the critical isochore.

In approximation (6), $\lambda_{Vc} = (d, D/tN)_c = 0$; for a more accurate determination of λ_{Vc} , equation (6) should be supplemented with quadratic terms relative to N and T. We get

$$\lambda_{Vc} = -1/2(D + E\lambda_{Tc} + 2F\lambda_{Tc}^2)/(Q + A^2/RT_{c1}), \quad (23)$$

where

$$D = (\partial^2 P/\partial N^2)_{T, v, c1}, \quad E = (\partial^2 P/\partial N\partial T)_{c1}, \quad F = (\partial^2 P/\partial T^2)_{v, c1}$$

are the derivatives corresponding to the regular component of the free energy, and Q is the correction for the irregular addition to the free energy.

Let us compare (20)–(23) with experiment^[7]. From Fig. 20 of^[7] we get $\Delta T_c = 34$ N, $\Delta P_c = 34$ N, and $\Delta V_c = -130$ N, i.e., $\lambda_{Tc} = -34.5$, $\lambda_{Pc} = 34$, and $\lambda_{Vc} = -130$. Further, putting $A = 63.5$ kg/cm², $A' = 0.85$ ($\mu = 6.2$), $B = 0.27$ kg/cm⁵mole, and $B' = 3.4 \times 10^{-3}$ kg/cm⁵deg-mole ($\beta' = 4.5$), we get from (20) and (21), in good agreement with experiment, $\lambda_{Tc} = 34.5$ and $\lambda_{Pc} = 34.1$. We estimate λ_{Vc} in the Van der Waals approximation, assuming $F = Q = 0$ and

$$\begin{aligned} \omega = \frac{D}{P_c} &= P_{c1}\left(\frac{\partial^2 P}{\partial N^2}\right)_{v, N=0} = 2\left(\frac{V_{c2}}{V_{c1}} - 1\right)^2 - 6\left(\frac{V_{c2}}{V_{c1}}\sqrt{\frac{P_{c2}}{P_{c1}}} - 1\right)^2, \\ &\approx \frac{T_{c1}}{P_{c1}}F = \frac{T_{c1}}{P_{c1}}\frac{\partial^2 P}{\partial N\partial T} = 2\left(\frac{V_{c2}}{V_{c1}} - 1\right). \end{aligned}$$

We get $\omega = -0.4$ and $\kappa = 1$; putting $\lambda_{Tc} = -34$, we get $\lambda_{Vc} = -100$, which is close to the experimental value.

If the irregular part of the free energy is described by Eq. (5), and the function $\varphi(t, v, N)$, as proposed by

Giterman and Voronel', is homogeneous with respect to $t + bv^2$ and N:

$$\varphi(t, v, N) = (t + bv^2)^2 + (b_2t + b_3v^2)N + b_4N^2,$$

then the correction Q amounts to

$$Q = 2a\lambda_{Tc}^2(2b_1\lambda_{Tc} + b_3)/(\lambda_{Tc}^2 + b_2\lambda_{Tc} + b_4).$$

An analogous result is obtained when the function $\varphi(t, v)$ proposed by I. M. Lifshitz is used. If the first factor is homogeneous with respect to t and N, namely

$$\delta F = (a_1t^2 + a_2tN + a_3N^2) \ln \varphi,$$

then

$$Q = 2(a_1\lambda_{Tc}^2 + a_2\lambda_{Tc} + a_3)(2b_1\lambda_{Tc} + b_3)/(\lambda_{Tc}^2 + b_2\lambda_{Tc} + b_4).$$

Apparently the study of the V-N projection of the critical curve can yield valuable information both concerning the values of the derivatives D, E, and F and concerning the irregular component of the free energy.

We note simultaneously that the vanishing of the first two derivatives of the chemical potential with respect to the concentration, and the critical-curve equations (19)–(23) that follow from this condition, are ensured by the "classical" (regular) component of the free energy⁶⁾.

It should be noted, however, that a calculation of the change of the volatility along the critical curve in accordance with the equations for $\ln f_1$, if \bar{P}_2 is determined from (6) and (19)–(21), yields $RT \ln f_2 \sim N$. We note further that the relation $RT \ln f_2 \sim N^m$, where $m < 1$, which was obtained in^[4], is possibly due to the influence of the irregular part of the free energy δF .

PARTIAL MOLAR VOLUME OF SOLVENT

We use the relation^[1]

$$\bar{V}_1 = V - N\left(\frac{\partial V}{\partial N}\right)_{P,T} = V + N\frac{(\partial P/\partial N)_{T,V}}{(\partial P/\partial V)_{T,N}}. \quad (24)$$

Calculating the derivative from (6), we get

$$\bar{V}_1 = V - N\frac{A + B\Delta V}{B'\Delta T + BN + 3C\Delta V^2}. \quad (25)$$

It is seen from (25) that the value of \bar{V}_1 at the critical point of the solvent has not been determined, and it is necessary to specify the path of the motion towards this point.

If we move along the line

$$\Delta T = \lambda_{Tc}N, \quad \Delta V = \lambda_{Vc}N, \quad (26)$$

then

$$\lim_{N \rightarrow 0} \bar{V}_1 = V_1^0 - A/(B + \lambda_{Tc}B') = V_1^0 + \delta\bar{V}_1, \quad (27)$$

i.e., the limiting value of the partial molar volume of the solvent at the critical point differs in the general case from the volume of the pure solvent, and depends on the direction of motion towards the critical point

⁶⁾ Along the critical curve we have

$$\left(\frac{\partial \mu_2}{\partial N}\right)_{P,T,c} = \frac{RT}{N_c} + \frac{(\partial P/\partial N)_{v,T,c}}{(\partial P/\partial V)_{T,N,c}} - \frac{v}{N_c} \left(\frac{\partial^2 P}{\partial N^2}\right)_{v,T}$$

Calculation in accordance with (6) and (20) yields $(\partial P/\partial N)_{T,N,c} = -(B + B'\lambda_{Tc})N = -NA^2/RT_c$ and $(\partial^2 P/\partial N^2)_V = 0$, hence $(\partial \mu_2/\partial N)_{P,T,c} = 0$.

λ_T . In the particular case of motion along the critical curve of the solutions ($\lambda_T = \lambda_{T_C}$), we get $\delta\bar{V}_1 = A/(B + \lambda_{T_C}B') = -RT_{C1}/A$. For the SF₆-CO₂ system, according to the data of [7], we have $A = 63.5$, $B = 0.27$, and $B' = 3.4 \times 10^{-3}$, and we get $\lambda_{T_C} = -34$ whence $\delta\bar{V}_1 = -430$ cm³/mole, in agreement with the results of [5,7]. In the other particular case, that of motion along the critical isotherm-isochores ($\lambda_T = 0$), we get $\delta\bar{V}_1 = -A/B = -240$ cm³/mole. However, all the values $-\infty < \delta\bar{V}_1 < +\infty$ are possible. Indeed, when $\Delta V = 0$ along the line of pseudocritical temperatures of the mixture, $\lambda_T = -B/B'$ and $\delta\bar{V}_1 = \pm\infty$ ⁷⁾. To the contrary, when $\lambda_T \rightarrow \infty$ we have $\delta\bar{V}_1 \rightarrow 0$. Thus, the partial molar volume of the solvent at the critical point has a singularity connected with the loss of continuity with respect to the set of variables, and due to the dependence of $(\partial P/\partial V)_T$ on the direction. It is interesting that this singularity is brought about by the regular component of the free energy.

One must not think that the limiting value of \bar{V}_1 is reached by a jumpwise equal to $\delta\bar{V}_1$ directly at the critical point (discontinuity of the first kind). It is easy to show that \bar{V}_1 has a value close to the limit in a relatively wide interval of values of N , ΔT , and ΔV . For example, for the already mentioned SF₆-CO₂ system, along the critical curve, at the values of A , B , λ_T indicated above and $C \approx 10^{-6}$, relation (25) takes the form⁸⁾

$$\bar{V}_1 = V - N \frac{63.5 - 0.27\Delta V}{0.27 + 3.4 \cdot 10^{-3}\Delta T + 2 \cdot 10^{-6}\Delta V^2}. \quad (25a)$$

Putting $N = 0.08$, i.e., at a considerable concentration of the solute, we get $\Delta V = -10$ cm³ and the correction in the numerator of (25a) is only 4%.⁹⁾ The correction in the denominator ($2 \times 10^{-6} \Delta V^2 = 2 \times 10^{-4}$) plays an even smaller role. Thus, $\delta\bar{V}_1 = -430$ cm³ \approx const on a considerable section of the critical curve. The length of the section $\delta\bar{V}_1 = \text{const}$ is even larger in the case of motion on the critical isotherm-isochores here $\delta\bar{V}_1 = \text{const}$ in the entire region for which the expansion (6) is valid.

When moving towards the critical point of the solvent along curves with a power-law dependence, $\Delta T = \lambda' N^{\mu'}$ and $\Delta V = \lambda'' N^{\mu''}$, where $\mu' < 1$ and $\mu'' < 0.5$, the paradox disappears and $\delta\bar{V}_1 = 0$. For example, in the case of motion along the critical isotherm-isobar ($\Delta T = \Delta T = 0$), we get $\bar{V}_1 = V_{C1} + aN^{1/3} \rightarrow V_{C1}$.

This case is best investigated more conveniently by solving (6) or (7) with respect to the volume. We get

$$v = (Q + \sqrt{Q^2 + R^3})^{1/3} + (Q - \sqrt{Q^2 + R^3})^{1/3}; \quad (28)$$

$$Q = (\alpha N + \mu t - p) / 2\gamma, \quad R = (\beta N + \beta' t) / 3\gamma.$$

Along the critical isotherm-isobar, at small N , Eq. (28) can be expanded in powers of $N^{1/3}$:

⁷⁾ However, the largest possible negative value in the stable region is reached (if $A > 0$) on the critical curve, since in the approximation (6) at the critical phase we have $\partial\mu_2/\partial N \approx [RT_{C1} + A(V_1 - V)] / N = (RT_{C1} + A\delta\bar{V}_1) / N$, and when $|\delta\bar{V}_1| > |\delta\bar{V}_1|_c$ we get $\partial\mu_2/\partial N < 0$, i.e., the state is labile.

⁸⁾ According to the data of Makarevich, $\Delta T = -1.5 \times 10^{-4} \Delta V^2$, along the boundary curve, hence $C = 1.5 \times 10^{-4}$ and $B = 5 \times 10^{-7}$. According to the law of corresponding states $C = 10^{-6}$.

⁹⁾ Since the numerator of (25a) is $(\partial P/\partial N)_{V,T}$, it is not surprising that no dependence of $(\partial P/\partial N)_{V,T}$ on the composition was observed in [7].

$$v = (V - V_{C1}) / V_{C1} = \rho_1 N^{1/3} - \rho_2 N^{2/3} + \rho_4 N^{1/3} + \rho_5 N^{2/3} + \dots, \quad (29)$$

where $\rho_1 = (\alpha/\gamma)^{1/3}$, $\rho_2 = (\beta/3\gamma)(\alpha/\gamma)^{-1/3}$, etc.

It is interesting that (29) has no term with N in the first power; this term appears if we use in place of (6) the more complete expansion, which contains v^2 .

From (24) and (29) we get the partial molar volume:

$$\bar{V}_1 = V_{C1}(1 + {}^2/3\rho_1 N^{1/3} - {}^1/3\rho_2 N^{2/3} + \dots). \quad (30)$$

It follows from (30) that, in motion towards the critical point along the isotherm-isobar, the limiting value of the partial molar volume of the solvent at $N = 0$ coincides with its molar volume, and $\delta\bar{V}_1 = 0$. However, the equations of dilute solutions (1)–(2) are not satisfied; the tangent is not horizontal, but is to the contrary vertical: $\partial\bar{V}_1/\partial N \sim N^{-2/3} \rightarrow \infty$ (Fig. 5).

PARTIAL MOLAR VOLUME OF SOLUTE

At small values of N it follows from (2) that $\bar{V}_2 = V + \partial V/\partial N$; accordingly, along the lines (26) we have

$$\bar{V}_2 = V - A / (B + \lambda_T B') N. \quad (31)$$

Thus, when $N \rightarrow 0$ the volume \bar{V}_2 increases like $1/N$, but with a variable coefficient that depends on the direction of $\lambda_T = dT/dN$.

Along the isotherm-isobar we get

$$\bar{V}_2 = V_{C1}(1 + {}^1/3\rho_1 N^{-2/3} - {}^2/3\rho_2 N^{-1/3} \dots), \quad (32)$$

i.e., in this case \bar{V}_2 (together with $\partial V/\partial N$) increases without limit, but this time like $N^{-2/3}$. In other words, the derivative $\partial V/\partial N$ and the partial molar volume of the dissolved substance $\bar{V}_2 \approx V + \partial V/\partial N$ also have a singularity at the critical point of the solvent, in that they depend on the direction of motion towards critical point and they increase without limit.

TRANSITION TO THE SUPERCRITICAL REGION

Equations (1) and (2) characterize the volume as functions of the concentration at constant temperature and pressure. We shall therefore consider the concentration dependence of the volume along the isotherms-isobars (28).

It can be concluded that at any finite deviation from the critical point of the first component (provided the state does not lie on the isochore $p = \mu t$), we can always find from (28) a sufficiently small concentration

$$N \ll |(p - \mu t) / \alpha| \quad \text{or} \quad N \ll \beta' t / \beta, \quad (33)$$

at which the expression (28) for the volume can be ex-

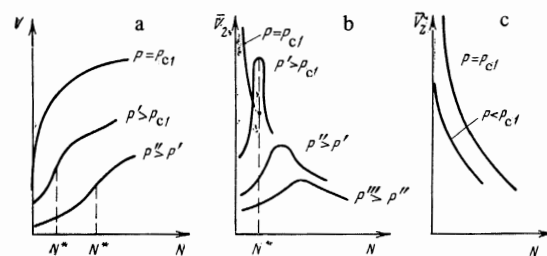


FIG. 5. Dependence of the molar volume (a) and of the partial molar volume (b,c) of the dissolved substance on its molar fraction $T = T_{C1}$. Case b— $\Delta P > 0$, c— $\Delta P < 0$.

panded in the series (1). Accordingly, Eqs. (2) and (4) will be satisfied, i.e., we arrive at the usual laws governing dilute solutions of non-electrolytes. It is easy to see that the region of dilute solutions, defined by (33), contracts to a point when $p, t \rightarrow 0$, and conversely broadens gradually with increasing distance from the critical point of the solvent.

The situation is similar also with the region of infinitely dilute solutions, which is characterized by satisfaction of the laws of Raoult and Henry: when $p, t \rightarrow 0$ it contracts to 0; for example, at $Q = 0.05$ the laws are satisfied at $N < 10^{-4}$ as against $N < 10^{-2}$ under ordinary conditions.

The transition from $\bar{V}_2 \rightarrow \infty$ (i.e., $\partial V/\partial V \rightarrow \infty$) to finite values is analogous to the variation of $(\partial V/\partial T)_P$ of gases in the supercritical region¹⁰⁾. In the latter case, the continuous transition from $\partial V/\partial T \rightarrow \infty$ to smooth curves far from the region of the critical point makes it geometrically necessary that the intermediate curves $(\partial V/\partial T)_P = f(T, P)$ have maxima that decrease with increasing distance from the critical point^[10]. Analogous maxima should be possessed also by the curves $\bar{V}_2 = f(T, P, N)$ (and the curves $V = \psi(T, P, N)$ should have an appropriate inflection) in Fig. 5. Calculation shows that the maximum is reached at $\Delta V^* = (B'\Delta T + BN)B/AC$ and a molar fraction $N^* = (\Delta P - A/\Delta T)/A$, and is equal to

$$(\Delta \bar{V}_2)_{max} = B / \Delta V^* \approx A / (B'\Delta T + BN) \approx A^2 / [(AB' - A'B)\Delta T + \Delta P]. \quad (34)$$

The maximum is realized, of course, only when $0 \leq N^* \leq 1$ (in particular, when $A > 0$ if $P > P_{C1}$ and $\Delta P > 0$ (Fig. 5)). Experiment^[17] confirms the presence of maxima of \bar{V}_2 . In the system ethane ($P_C = 49$ atm) + CO₂ ($P_C = 73$ atm), investigated by N. E. Khazanova and E. E. Sominskaya at pressures up to 73 atm^[18], maxima of \bar{V}_2 were observed near the critical point of the solvent (ethane) ($P > P_{C1}$), and were not observed near the critical point of CO₂ ($P < P_{C1}$). Since in this system $A > 0$ at both ends of the P-N diagram (the P(N) curves have maxima at $V = \text{const}$), these results agree with the foregoing conclusions (as do also the observed decrease of the maxima and their shift towards larger N with increasing P).

BEHAVIOR OF $(\partial V/\partial T)_T$, OF THE PARTIAL ENTHALPY AND PARTIAL ENTROPY, AND OF THE CHEMICAL POTENTIAL

The singularity of the partial molar volumes and of $\partial V/\partial N$ is due to the fact that these quantities are connected with $(\partial P/\partial V)_T$, the value of which depends on the direction of motion towards critical point. But the connection between $(\partial P/\partial V)_T$ and $(\partial V/\partial T)_P$ is similar:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \left|\left(\frac{\partial P}{\partial T}\right)_T = \frac{A' - B'\Delta V}{B'\Delta T + BN + 3C\Delta V^2} \quad (35)$$

Since the correction $B'\Delta V$ is relatively small, it

follows that $(\partial V/\partial T)_P \approx (A'/A)(\partial V/\partial N)_P$, and its value depends on the pressure in the same manner as the value of $(\partial V/\partial N)_P, T$. A similar conclusion can be drawn also with respect to C_P , and also with respect to the partial molar enthalpy $h_1 = h - N\partial h/\partial N$, since

$$(\partial h/\partial N)_{P, T} = (\partial e/\partial N)_{V, T} + T(\partial P/\partial T)_V(\partial V/\partial N)_{P, T}$$

(where e is the molar energy). Accordingly, just as for the volume V_1 , we get $\lim \bar{h}_1 = h_1^0 + \delta h_1$, where $\delta h_1 = A'T\delta V_1$, as $N \rightarrow 0$ (see (27)). A similar singularity is possessed also by the partial molar entropy: $\lim s_1 = s_1^0 + \delta s_1$ as $N \rightarrow 0$, where $\delta s_1 = A'\delta V_1$. Since $\delta h_1 = T\delta S_1$, the chemical potential $\mu_1 = \bar{h}_1 - T\bar{s}_1$ does not have a similar singularity; this is seen also from the fact that $(\partial \Phi/\partial N)_{P, T} = (\partial F/\partial N)_{V, T}$. However, the relation (4) is not satisfied for $\mu(N)$. Assuming that Eq. (6) is valid starting with a certain pressure $P_a < P_{C1}$, we get

$$\mu_1 = \mu_1^0 + RT \ln f_1^0 N_1 + AN\Delta V - (2BN + B'\Delta T)\Delta V^2/2 - 3/4 C\Delta V^4 + \dots, \\ \mu_2 = \mu_2^0 + RT \ln K(P, T)N - A\Delta V + B\Delta V^2 - \dots,$$

where ΔV is determined by relation (28). On the critical isothermisobar ($\Delta T = \Delta P = 0$), the dependence of μ on the composition will be

$$\mu_1 = \mu_1^0 + RT \ln f_1^0 N_1 + lN^{1/2} + \dots, \quad l = A^{1/2}/4C^{1/2}; \\ \mu_2 = \mu_2^0 + RT \ln KN - mN^{1/2} + \dots, \quad m = A^{1/2}/C^{1/2}.$$

When $N \rightarrow 0$ we get $(\partial \ln f_1/\partial N)_{P, T, C1} \propto N^{1/3} \rightarrow 0$, $(\partial(f_2/N)/\partial N) \propto N^{-2/3} \rightarrow \infty$.

The derivatives $\mu(P, T, N)$ have the following singularity: when $N \rightarrow 0$, the limiting value of $(\partial \mu_1/\partial P)_T = \bar{V}_1$ depends on the direction in accordance with (27), and all the derivatives $\mu_2(P, T, N)$ increase without limit, the coefficient and the order of magnitude of the growth being dependent on the direction.

ON THE SINGULARITIES OF CERTAIN THERMODYNAMIC PROPERTIES OF PURE SUBSTANCES

We shall show that certain thermodynamic properties of a pure substance, like the properties of solutions, also depend on the direction of motion towards the critical point (particularly if they are connected with $\partial P/\partial V$):

$$(\partial V/\partial T)_P \approx A' / (B'\Delta T + 3C\Delta V^2),$$

$$C_P \approx C_V + TA' / (B'\Delta T + 3C\Delta V^2).$$

It is easy to see that along the critical isochore $\partial V/\partial T = A'/B\Delta T$; along the boundary curve, when $\Delta V = \sqrt{-B\Delta T/C}$ ^[8], we get $\partial V/\partial T = -A/2B\Delta T$. Finally, along the critical isobar, when $\Delta V = (A'\Delta T/C)^{1/3} + \dots$ ^[10], we find that $\partial V/\partial T$ already increases like $\Delta T^{-2/3}$ on approaching the critical point. The variation of C_P is similar^[11].

The limiting value of the quantity $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$, which is the temperature analog of the partial molar volume of the solute (see (2)), depends to an equal degree on the direction of motion to the critical point.

¹⁰⁾We must emphasize the symmetry of Eq. (6) with respect to ΔT and N . Accordingly, a similar behavior is exhibited by $\partial V/\partial T$ and $\partial V/\partial N$, by the form of the boundary curves in coordinates V-T and V-N, by the effect of the temperature and of the molar fraction on the two-phase equilibrium, etc.

¹¹⁾The remark that, in particular, $v \sim \sqrt{t}$ for states on the equilibrium curve, and therefore $C_P \sim 1/t$ ([⁸], p. 324), can be regarded as an indication that C_P depends on the path to the critical point.

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