PHYSICAL REVIEW A VOLUME 2, NUMBER 4 OCTOBER 1970

Thermodynamics of Binary Systems near the Liquid-Gas Critical Point

W. F. Saam
Institut Max von Laue-Paul Langevin, Grenoble, France
(Received 26 January 1970)

The liquid-gas critical line in binary mixtures is discussed in terms of a theory based on the assumption that the phase transition may be described in terms of a single ordering field and an effective critical temperature. The theory, an application of a theory of Fisher to a case not considered by him, makes a number of predictions, among them that the specific heat at constant pressure and the isothermal compressibility, both at constant concentration, are weakly singular at the critical line. Azeotropic critical points, as well as points where either the critical pressure or critical temperature shows an extremum, are special cases in which the transition differs from that at a general point on the critical line. The theory is consistent with the few available experimental results.

I. INTRODUCTION

In recent years there have been striking advances in both the static and dynamic theories of pure systems in the vicinity of their critical points. Our understanding of transitions in impure systems is considerably less advanced. Fisher[1] has proposed a phenomenological theory dealing with the static critical properties of special types of impure systems. The predictions of this theory have been confirmed by a number of calculations on model systems, but have yet to be firmly tested experimentally,[2] primarily for the reason that rather detailed knowledge of somewhat inaccessible thermodynamic quantities is required. The available data are, however, consistent with Fisher's predictions. In this paper, we apply Fisher's theory to a case more general than that considered by him and work out in some detail the consequences for the liquid-gas phase transition in binary mixtures. A number of predictions capable of rather straightforward experimental check are derived. We predict that the isothermal compressibility and the specific heat at constant pressure should exhibit weak divergences at a general point on the critical line of a binary mixture. These results have been derived for a simple-model system by Helfand and Stillinger[3] and have been suggested to be generally true by Rowlinson.[4] A divergent compressibility also exists in models discussed by Widom and Wheeler.[5] The adiabatic compressibility and the specific heat at constant density are predicted to be nonsingular along any finite segment of the critical line, in agreement with general arguments.[6] However, at a point where the critical pressure shows an extremum, the theory predicts a weak divergence in the adiabatic compressibility. Conversely, when the critical temperature shows an extremum, the specific heat at constant density should be weakly singular.[7]

The theory also provides a natural description of an azeotropic point. In this case we find that the impurity concentration plays a rather inert role, as in the case discussed by Fisher, and that both the specific heat at constant density[7] and the adiabatic compressibility remain finite.

The basic assumption underlying the theory is that the essentials of the transition may be described in terms of a single effective critical field μ^* together with a single effective critical temperature T^*, both assumed to be regular functions of the temperature T and the chemical potentials μ_1 and μ_2 of the two components. In the limit of zero concentration x, $T^* \to T$ and $\mu^* \to \mu_2$. Specifically, it is assumed that the free energy in the binary system may be written as the sum of a regular term plus the free-energy function of the pure system with arguments T^* and μ^*. The singularities of physical quantities in the binary system are thus related to those in the one component system.

Our treatment will differ from Fisher's in that we will assume, in general, that the introduction of the impurity, especially in sizable quantities, does alter the ordering field; all quantities in Eq. (3) below will be assumed in general to be nonzero on the critical line. If the theory is to be valid for all values of x for which there is a critical point, alteration of the ordering field with x is mandatory; in some systems the critical line extends from $x=0$ to $x=1$.

In Sec. II, we present the basic formalism, including discussions of the notion of an order parameter and of the way in which the experimental approach to the critical point is described theoretically. In Sec. III, we discuss critical correlations (static spacially uniform limit) near a general point on the critical line. Special points where the critical pressure or critical temperature show extrema, as well as azeotropic critical points, are given separate treatment in Sec. IV. Section V is devoted to additional comments.

II. BASIC FORMULATION

Following Fisher, we commence with the basic assumption that the free energy (here, the pressure) may be written in the form

$$F(T, \mu_1, \mu_2) = F_0[T^*(T, \mu_1, \mu_2), \mu^*(T, \mu_1, \mu_2)] + g(T, \mu_1, \mu_2) . \tag{1}$$

F_0 is the critical part of the free-energy function at zero impurity concentration, g is a regular background term, and T^* and μ^* are, respectively, the effective critical temperature and the effective critical field, both assumed to be regular functions of their arguments. The critical points (i.e., line) in this formalism are given by the solution to the equations

$$T^*(T_c, \mu_1, \mu_{2c}) = T_c^0, \quad \mu^*(T_c, \mu_1, \mu_{2c}) = \mu_c^0, \tag{2}$$

as a function of the impurity chemical potential μ_1. The particle number densities n_1 (the impurity) and n_2 and the entropy density s are given by

$$\begin{aligned} n_i &= \frac{\partial F}{\partial \mu_i} = \frac{\partial F_0}{\partial T^*} T_i + \frac{\partial F_0}{\partial \mu^*} w_i + \frac{\partial g}{\partial \mu_i} , \qquad i = 1, 2 \\ s &= \frac{\partial F}{\partial T} = \frac{\partial F_0}{\partial T^*} T_T + \frac{\partial F_0}{\partial \mu^*} w_T + \frac{\partial g}{\partial T} , \end{aligned} \tag{3}$$

where we have introduced the notations

$$\begin{aligned} \left(\frac{\partial T^*}{\partial T}, \frac{\partial T^*}{\partial \mu_1}, \frac{\partial T^*}{\partial \mu_2} \right) &\equiv (T_T, T_1, T_2), \\ \left(\frac{\partial \mu^*}{\partial T}, \frac{\partial \mu^*}{\partial \mu_1}, \frac{\partial \mu^*}{\partial \mu_2} \right) &\equiv (w_T, w_1, w_2). \end{aligned} \tag{4}$$

It is seen that all three densities in (3) contain both the nonanalytic behavior of the entropy and that of the order parameter in the pure system. In general, then, in contrast to the case studied by Fisher, there will be no unique order parameter; n_1, n_2, or s or any linear combination thereof exhibits coexistence curves as a function of T^* when $\mu^* = \mu_c^0$. However, we do not know how, from an experimental point of view, to hold μ^* constant, while the coefficients in (3) are unknown. In an experiment, the approach to the critical point will be along some curve in μ^*- T^* space, a curve which will not in general follow the critical isochore. We now consider the problem of determining this curve in the cases where the critical point is approached at constant concentration and either constant pressure or density. To proceed we first need a model for the critical thermodynamics of the pure system as the critical point is approached in a rather general direction in the (μ, T) plane denoting by μ the critical field. A parametric model which compares quite well with experiment has recently been proposed by Schofield.[8] The two parameters in his model are r, a quantity which gives a measure of the distance from the critical point in $\mu - T$ space and θ, which measures the distance along a contour of constant r. The critical parts of the order parameter and of the entropy are written in terms of these variables as

$$\delta \hat{\sigma}_{\mathrm{cr}}^0 = r^\beta g \theta , \quad \delta s_{\mathrm{cr}}^0 = r^{1-\alpha} s(\theta) , \tag{5}$$

while the analogous quantities for the critical field, temperature, and pressure are

$$\begin{aligned} \delta T &= r(1 - b^2\theta^2) = T - T_c^0, \\ \delta \mu &= r^{\beta\delta} a\theta (1 - \theta^2) = \mu - \mu_c^0, \\ \delta P &= r^{\beta(\delta+1)} P(\theta) = F_0(\mu, T) . \end{aligned} \tag{6}$$

$\theta = 0$ represents the critical isochore, $\theta = \pm 1$ represents the two sides of the coexistence curve, and $\theta = \pm b$ represents the two parts of the critical isotherm for $\delta\mu \gtrless 0$. g, a, and b are constants.

Let us now apply Schofield's theory. To lowest order the deviations of μ^* and T^* from their critical values are

$$\begin{aligned} \delta T^* &= T_T^c \delta T + T_1^c \delta\mu_1 + T_2^c \delta\mu_2 , \\ \delta \mu^* &= w_T^c \delta T + w_1^c \delta\mu_1 + w_2^c \delta\mu_2 . \end{aligned} \tag{7}$$

These may be solved to yield equations of the form

$$\begin{aligned} \delta\mu_1 &= a_1 \delta T^* + b_1 \delta\mu^* + c_1 \delta T , \\ \delta\mu_2 &= a_2 \delta T^* + b_2 \delta\mu^* + c_2 \delta T . \end{aligned} \tag{8}$$

The condition that $x = n_1/(n_1 + n_2)$ be constant is

$$(n_1^c w_2^c - n_2^c w_1^c) \frac{\partial F_0}{\partial \mu^*} + (n_1^c T_2^c - n_2^c T_1^c) \frac{\partial F_0}{\partial T^*} + c_1' \delta\mu_1 + c_2' \delta\mu_2 + c_3' \delta T = 0 , \tag{9}$$

in which the superscript c indicates that the quantity is evaluated at the critical point in question. Putting Eqs. (5), (6), and (8) in (9), we find

$$(n_1^c w_2^c - n_2^c w_1^c) g\theta^* r^{*\beta} + (n_1^c T_2^c - n_2^c T_1^c)\, s(\theta^*) r^{*(1-\alpha)} + c_1 r^* (1 - b^2\theta^{*2}) + c_2 a r^{*\beta\delta} \theta^* (1 - \theta^{*2}) + c_3 \delta T = 0 , \tag{10}$$

where the asterisks indicate quantities in the solution. In a similar fashion, we find the conditions for constant n and constant P to be, respectively,

$$(w_1^c+w_2^c)g\theta^* r^{*\beta}+(T_1^c+T_2^c)s(\theta^*)r^{*(1-\alpha)}$$
$$+d_1 r^*(1-b^2\theta^{*2})+d_2 a r^{*\beta\delta}\theta^*(1-\theta^{*2})+d_3\delta T=0, \tag{11}$$

$$e_1\delta T+e_2 r^*(1-b^2\theta^{*2})+e_3 r^{*\beta\delta}\theta^*(1-\theta^{*2})$$
$$+r^{*\beta(\delta+1)}p(\theta)=0. \tag{12}$$

The various constants appearing in Eqs. (10)–(12) are combinations of s_c, n_{ic}, and derivatives of T^*, μ^*, and g^* evaluated at the critical point.

Suppose now that the critical point is approached at constant P and x. Since $\beta<1-\alpha<1<\beta\delta<\beta(\delta+1)$, it is clear that (10) and (12) can only be solved if, to leading order,

$$\theta^*\to(r^*)^{1-\alpha-\beta}+\cdots\quad \delta T\to r^*+\cdots, \tag{13}$$

[Note that $s(0)\neq 0$, $p(0)\neq 0$.] Thus, near the critical point

$$\delta T\sim\delta T^*,\quad \delta\mu^*\sim(\delta T)^{\beta\delta+1-\alpha-\beta}=(\delta T)^{\gamma+1-\alpha}, \tag{14}$$

for P and x constant. The system is thus forced to approach the critical point near the critical isochore of F_0. It has of course been assumed in the above that the various constants in (10) and (12) are such that $\delta T=T-T_c>0$ corresponds to $\delta T^*>0$. The case $\delta T<0$ may be worked out similarly. Here $\mu^*=0$ and the new variable replacing $r^{*\beta}\theta^*$ is an average of $\partial F_0/\partial\mu^*$ over the two phases of the system. All three quantities n, x, and s will exhibit coexistence curves with the usual temperature dependence $|\delta T|^\beta$. The results for constant n and x are only slightly different. A little inspection convinces us that in this case

$$\theta^*\to(r^*)^{1-\alpha-\beta}+\cdots,\quad \delta T\to(r^*)^{1-\alpha}\sim(\delta T^*)^{1-\alpha},$$
$$\theta\mu^*\to(\delta T)^{(\delta+1-\alpha)/(1-\alpha)}, \tag{15}$$

for n and x constant and for $T>T_c$. The result for $T<T_c$ is the analog of the previous one. n, x, and s have coexistence curves with temperature dependence $|\delta T|^{\beta/(1-\alpha)}$ in leading order. The result $|\delta T|\sim|\delta T^*|^{1-\alpha}$ is the same as that found by Fisher for his more restricted model. We note in passing that the result Eq. (14) is quite different from that at constant P and $x=0$ owing to the fact that the restriction $x=\text{const}$ is, for $x\neq 0$, a restriction on the "order parameter" $\partial F_0/\partial\mu^*$. The restrictions n, $x=\text{const}$ have only a slightly different effect; thus the result of Eq. (15). The approach to $x=0$ in our model is quite similar to that in Fisher's model and will not be dealt with here.

When either (14) or (15) hold, we have several additional relations from Schofield's model which will be of use; these are

$$\frac{\partial^2 F_0}{\partial\mu^{*2}}\sim(\delta T^*)^{-\gamma},\quad \frac{\partial^2 F_0}{\partial T^{*2}}\sim(\delta T^*)^{-\alpha},$$
$$\frac{\partial^2 F_0}{\partial T^{*2}}-\left(\frac{\partial^2 F_0}{\partial\mu^*\partial T^*}\right)^2\bigg/\frac{\partial^2 F_0}{\partial\mu^{*2}}\sim(\delta T^*)^{-\alpha}, \tag{16}$$
$$\frac{\partial^2 F_0}{\partial T^*\partial\mu^*}\sim(\delta T^*)^{+(\beta-1)}.$$

III. CRITICAL CORRELATIONS

We now turn to the calculation of critical correlations. The general liquid-gas critical point will be treated first; special critical points require special attention and will be discussed in Sec. IV. Correlations may be calculated in a straightforward manner from Eq. (3). We will not go through the algebra in great detail; we will, for the most part, just present the results for the quantities of greatest interest experimentally, and, for those, only the divergent parts near the critical line.

First let us consider the compressibility at constant temperature and concentration. We have

$$\left(\frac{\partial n}{\partial P}\right)_{T,x}=\frac{1}{n}\frac{\langle nn\rangle\langle xx\rangle-\langle nx\rangle^2}{\langle xx\rangle}$$
$$=n\frac{\langle n_1n_1\rangle\langle n_2n_2\rangle-\langle n_1n_2\rangle^2}{n_2^2\langle n_1n_1\rangle-2n_1n_2\langle n_1n_2\rangle+n_1^2\langle n_2n_2\rangle}, \tag{17}$$

where, for convenience, we have introduced the correlation function notation[9]

$$\langle ab\rangle=\beta\int d^3r\,d^3r'[\langle a^{\text{op}}(r)b^{\text{op}}(r')\rangle-\langle a^{\text{op}}\rangle\langle b^{\text{op}}\rangle]. \tag{18}$$

Now, each of the correlation functions in (17) contains, as we see from (3), the three singular quantities $\partial^2F_0/\partial\mu^{*2}$, $\partial^2F_0/\partial\mu^*\partial T^*$, and $\partial^2F_0/\partial T^{*2}$. Calculating the coefficients of these terms, we find

$$\langle n_1n_1\rangle\langle n_2n_2\rangle-\langle n_1n_2\rangle^2=(T_1w_2-T_2w_1)^2$$
$$\times\left[\frac{\partial^2F_0}{\partial\mu^{*2}}\frac{\partial^2F_0}{\partial T^{*2}}-\left(\frac{\partial^2F_0}{\partial\mu^*\partial T^*}\right)^2\right]+O\left(\frac{\partial^2F_0}{\partial\mu^{*2}}\right), \tag{19}$$

$$n^4\langle xx\rangle=n_2^2\langle n_1n_1\rangle-2n_1n_2\langle n_1n_2\rangle+n_1^2\langle n_2n_2\rangle$$
$$=\frac{\partial^2F_0}{\partial\mu^{*2}}(n_2w_1-n_1w_2)^2+2\frac{\partial^2F_0}{\partial\mu^*\partial T^*}(n_2w_1-n_1w_2)$$
$$\times(n_2T_1-n_1T_2)+\frac{\partial^2F_0}{\partial T^{*2}}(n_2T_1-n_1T_2)^2$$
$$+\text{(nondivergent terms)}. \tag{20}$$

Combining (17), (19), and (20), we obtain

$$\left(\frac{\partial n}{\partial P}\right)^{\mathrm{cr}}_{T,x}=\frac{nC^0_{\hat{\sigma}}(T^*,\mu^*)}{T}\,\frac{(T_1w_2-T_2w_1)^2}{(n_2w_1-n_1w_2)^2} \tag{21}$$

for the singular part (denoted by the superscript cr) of $(\partial n/\partial P)_{T,x}$. Here

$$C^0_{\hat{\sigma}}=T\left[\frac{\partial^2F_0}{\partial T^{*2}}-\left(\frac{\partial^2F_0}{\partial T^*\partial\mu^*}\right)^2\Big/\frac{\partial^2F_0}{\partial\mu^{*2}}\right] \tag{22}$$

is the specific heat at constant order parameter in the pure system. Note the reduction in the degree of the singularity in (22) which resulted from holding x constant; $(\partial n/\partial P)_{T,\tilde{Z}}=\langle nn\rangle/n$ has a term proportional to $\partial^2F_0/\partial\mu^{*2}$ (here $\tilde{Z}=\mu_1-\mu_2$), the isothermal compressibility in the pure system. This sort of reduction will be a common feature in all of our calculations, and may be thought of as resulting from a restriction of the freedom of motion of the variable in question. Similarly, we may calculate the critical part of the specific heat at constant x and P, finding

$$\begin{aligned}C^{\mathrm{cr}}_{P,x}=&\left[C^0_{\hat{\sigma}}(T^*,\mu^*)/(n_2w_1-n_1w_2)^2\right]\\&\times[\{T_T(n_1w_2-n_2w_1)+w_T(n_2T_1-n_1T_2)\}\\&-(s/n)(T_1w_2-T_2w_1)]^2.\end{aligned} \tag{23}$$

Combining (14)–(16) with (21) and (23) we find[10]

$$\begin{aligned}\left(\frac{\partial n}{\partial P}\right)^{\mathrm{cr}}_{T,x}&\sim|\delta T|^{-\alpha},\quad P,x\ \mathrm{const}\\&\sim|\delta T|^{-\alpha/(1-\alpha)},\quad n,x\ \mathrm{const}\end{aligned} \tag{24}$$

$$\begin{aligned}C^{\mathrm{cr}}_{P,x}&\sim|\delta T|^{-\alpha},\quad P,x\ \mathrm{const}\\&\sim|\delta T|^{-\alpha/(1-\alpha)},\quad n,x\ \mathrm{const}.\end{aligned} \tag{25}$$

It is also instructive to calculate $C_{n,x}$ and $(\partial n/\partial P)_{\sigma,x}$ in the present model. We have, for example,

$$\frac{C_{n,x}}{Tn}=\left(\frac{\partial\sigma}{\partial T}\right)_{n,x}=n\frac{[\langle\sigma\sigma\rangle-\langle\sigma x\rangle^2/\langle xx\rangle][\langle nn\rangle-\langle nx\rangle^2/\langle xx\rangle]-[\langle\sigma n\rangle-\langle\sigma x\rangle\langle nx\rangle/\langle xx\rangle]^2}{[\langle nn\rangle-\langle nx\rangle^2/\langle xx\rangle]}, \tag{26}$$

in which σ is the entropy per particle (not to be confused with $\hat{\sigma}$, a symbol for an order parameter). Calculation shows that each of the terms in square brackets in (26) has as its only singular part a term proportional to $C^0_{\hat{\sigma}}(T^*,\mu^*)$. Compare, for example, (17) and (23). The coefficients turn out to be such that the terms proportional to $(C^0_{\hat{\sigma}})^2$ in the numerator of (26) exactly cancel, leaving a term proportional to $C^0_{\hat{\sigma}}$. Thus, the numerator and denominator of (26) have the same singular behavior. We find a precisely similar result for $(\partial n/\partial P)_{\sigma,x}$, so that we may write for a general point on the critical line

$$C_{n,x}\to\mathrm{const}<\infty\quad\mathrm{and}\quad\left(\frac{\partial n}{\partial P}\right)_{\sigma,x}\to\mathrm{const}<\infty. \tag{27}$$

These results are, indeed, required by rather general thermodynamic arguments.[6] We now turn to the problem of comparing theory with experiment. The lack of precise data prevents us from doing much in this area,[11] but we can check two things. Experiment[12] shows that for a general critical point the quantities

$$\left(\frac{\partial n}{\partial x}\right)_{P,T}=\frac{\langle nx\rangle}{\langle xx\rangle}\quad\mathrm{and}\quad\left(\frac{\partial P}{\partial T}\right)_{x,n}=-\left(\frac{\partial n}{\partial T}\right)_{P,x}\Big/\left(\frac{\partial n}{\partial P}\right)_{T,x} \tag{28}$$

approach constants. The numerators and denominators of both expressions in (28) diverge in our model, but in each case, the numerator and denominator have the same type of divergence. Straightforward algebra yields

$$\left(\frac{\partial n}{\partial x}\right)^{\mathrm{cr}}_{P,T}=n^2\frac{w_1+w_2}{n_2w_1-n_1w_2}, \tag{29}$$

$$\left(\frac{\partial P}{\partial T}\right)_{x,n}=-\frac{[T_T(n_1w_2-n_2w_1)+w_T(n_2T_1-n_1T_2)-\sigma(T_1w_2-T_2w_1)]}{T_1w_2-T_2w_1} \tag{30}$$

at a general point on the critical line. Many of the conclusions of this section are invalid at special points on the critical line. These points require special attention, and we now turn to an examination of them.

IV. SPECIAL POINTS

A. Extremum in P_c

Let us first consider the changes in the above results at a point where P_c has an extremal value.

By varying Eqs. (2) and using the Dibbs-Dunhem relation (F_0 is constant on the critical line)

$$\delta P_c = s_c \delta T_c + n_{1c}\,\delta\mu_1 + n_{2c}\delta\mu_{2c}, \tag{31}$$

one easily finds that the condition that P_c be extremal is

$$T_T^c(n_1w_2 - n_2w_1)^c + w_T^c(n_2T_1 - n_1T_2)^c - s_c(T_1w_2 - T_2w_1)^c = 0. \tag{32}$$

From (23), we see that when (32) holds, $C_{P,x}$ ceases to be singular. From (21) we see that the singularity in $(\partial n/\partial P)_{T,x}$ remains. Since

$$\frac{C_{P,x}}{Tn^2} = \langle\sigma\sigma\rangle - \frac{\langle\sigma x\rangle^2}{\langle xx\rangle}, \tag{33}$$

and since one may show that

$$\begin{aligned}\frac{\langle xx\rangle}{n}\left(\frac{\partial n}{\partial T}\right)_{P,x} &= \langle\sigma n\rangle\langle xx\rangle - \langle\sigma x\rangle\langle nx\rangle \\ &= \frac{C_\sigma^0}{Tn^3}\frac{\partial^2 F_0}{\partial\mu^{*2}}(T_1w_2 - T_2w_1)[T_T(n_1w_2 - n_2w_1) \\ &\quad + w_T(n_2T_1 - n_1T_2) - s(T_1w_2 - T_2w_1)] + O\left(\frac{\partial^2F_0}{\partial\mu^{*2}}\right).\end{aligned} \tag{34}$$

it is clear upon comparing Eqs. (23), (26), and (32)–(34) that $C_{n,x}$ also remains finite. However, since

$$\left(\frac{\partial n}{\partial P}\right)_{\sigma,x} = \left(\frac{\partial n}{\partial P}\right)_{T,x}\frac{C_{n,x}}{C_{P,x}} \tag{35}$$

$(\partial n/\partial P)_{\sigma,x}$ becomes singular, with the same singularity as $(\partial n/\partial P)_{T,x}$. The result (15) remains unchanged so that we may write, for a critical point where P_c exhibits an extremum,

$$\begin{aligned}&C_{n,x} < C_{P,x} \to \text{const} < \infty, \\ &\left(\frac{\partial n}{\partial P}\right)_{\sigma,x} \sim \left(\frac{\partial n}{\partial P}\right)_{T,x} \to |\delta T|^{-\alpha/(1-\alpha)},\end{aligned} \tag{36}$$

for n and x constant. Combining (20) and (28) with the above gives $(\partial P/\partial T)_{n,x} \sim |\delta T|^{\alpha/(1-\alpha)}$, n and x are constants. Extrema in P_c are quite common.[4]

B. Extremum in T_c

It is easy to show by varying Eqs. (2) that T_c shows an extremum when

$$(T_1w_2 - T_2w_1)^c = 0. \tag{37}$$

The situation in this case is complimentary to that considered in Sec. IV A. From (21) and (37) we see that $(\partial n/\partial P)_{T,x}$ loses its singularity and $(\partial n/\partial P)_{T,x}$ remains finite. From (23), $C_{P,x}$ retains its singularity, and thus from (35), $C_{n,x}$ becomes singular.[7] Result (15) is again unchanged, so that we summarize by writing

$$\begin{aligned}&C_{n,x} \sim C_{P,x} \to |\delta T|^{-\alpha/(1-\alpha)}, \\ &\left(\frac{\partial n}{\partial P}\right)_{\sigma,x} < \left(\frac{\partial n}{\partial P}\right)_{T,x} \to \text{const} < \infty,\end{aligned} \tag{38}$$

for n and x constant. Combining (20) and (28) with the above gives the result that $(\partial P/\partial T)_{n,x}$ approaches a nonzero constant. Extrema in T_c are also quite common.[4]

C. Azeotropic Points

We next consider an azeotropic point as described in our model. Such a point is one at which the transition is rather like that in a pure system; both phases have the same concentration below the transition. From (9) we see that x will cease to be an order parameter when

$$n_2^c w_1^c - n_1^c w_2^c = 0 \tag{39}$$

holds at the critical point in question. We thus take (39) to be the defining characteristic of an azeotropic point. It might be thought that we should also require $n_2^cT_1^c - n_1^cT_2^c$ to be zero, thus removing all critical behavior in x. However, this latter condition combined with (31) gives (37), and hence requires that T_c have an extremum at an azeotropic point.[13] This phenomenon is not observed experimentally.[14]

Let us now examine some of the consequences of (39). First, note that (39) reduces x to the status of an inert impurity variable, essentially the case treated by Fisher except for the fact the relation between the chemical potentials appearing in F_0 and x is somewhat more complicated. This slight complication is of no real consequence; the predictions of our model of an azeotropic critical transition are in essence the same as those of Fisher, the order parameter now being the density n. When the transition is approached at constant n and x [condition (15) is not altered],

$$\begin{aligned}\langle xx\rangle &\to \frac{(n_2^cT_1^c - n_1^cT_2^c)^2}{(n^c)^2}\frac{\partial^2F_0}{\partial T^{*2}} \sim |\delta T|^{-\alpha/(1-\alpha)}, \\ \langle nn\rangle &\to (w_1^c + w_2^c)^2\frac{\partial^2F_0}{\partial\mu^{*2}} \sim |\delta T|^{-\gamma/(1-\alpha)}, \\ \langle nx\rangle &\to \frac{w_1^c + w_2^c}{n^c}(T_1^cn_2^c - T_2^cn_1^c)\frac{\partial^2F_0}{\partial\mu^*\partial T^*} \\ &\sim |\delta T|^{(\beta-1)/(1-\alpha)}.\end{aligned} \tag{40}$$

In addition, one finds after some calculation that

$$C_{P,x} \to |\delta T|^{-\gamma/(1-\alpha)}, \quad C_{n,x} \to \text{const} < \infty,$$

$$\left(\frac{\partial n}{\partial P}\right)_{T,x} \to |\delta T|^{-\gamma/(1-\alpha)}, \quad \left(\frac{\partial n}{\partial P}\right)_{\sigma,x} \to \text{const} < \infty . \tag{41}$$

Finally, let us note from (40) that

$$\left(\frac{\partial n}{\partial x}\right)_{P,T} = \frac{\langle nx\rangle}{\langle xx\rangle} \sim |\delta T|^{\beta/(1-\alpha)-1} , \tag{42}$$

a divergence in this quantity is observed experimentally.[4] There exists an experiment in apparent disagreement with our prediction that $C_{n,x}$ remain finite at an azeotropic critical point. Voronel *et al.*[15] have observed what appears to be a logarithmic singularity in $C_{n,x}$ at the azeotropic point of a carbon-dioxide–ethane mixture. However, in this mixture there is a minimum in T_c extremely close to the azeotropic critical point. Since we expect $C_{n,x}$ to be weakly singular at this minimum, we would expect the maximum in $C_{n,x}$ at the azeotropic critical point to be quite large. Further experimental work is needed to clarify this point.

V. FURTHER COMMENTS

A thorough study of the critical line of a system, such as HCl-Me_2O (see Ref. 4), in which the critical line extends from $x=0$ to $x=1$ and which contains an intermediate azeotropic point, as well as extrema in P_c and T_c, would be a most exacting test of the ideas presented here. In this connection it should be pointed out that correction terms to our results might make it necessary to go rather close to a given critical point before the limiting critical behavior could be observed.

It is instructive to look once again at the assumption involved in the theory. The theory, an extension of the ideas of Fisher, has been based on the assumption that the transition in the binary system may be described in terms of a free energy F, one term of which is the free energy $F_0(\mu^*, T^*)$ of the pure system, but its conclusions are really slightly more general. The predictions of the model would be changed in no essential way if $F_0(\mu^*, T^*)$ were replaced by $f(\mu_1, \mu_2, T)F_0(\mu^*, T^*)$, f being a regular function of its arguments. In fact, it seems that if one is to be able to describe the liquid-gas critical line in binary systems in terms at all naturally analogous to those used for one-component systems, one is forced to use a model in essence the same as that considered here.

ACKNOWLEDGMENT

The author wishes to thank Professor R. B. Griffiths for a valuable discussion concerning the work presented here.

---

[1] M. E. Fisher, Phys. Rev. 176, 257 (1968).

[2] Evidence consistent with the theory, as applied to the λ transition in He^3-He^4 solutions, has been presented by F. Gasparini and M. R. Moldover, Phys. Rev. Letters 23, 749 (1969), and by T. Alvesalo, P. Berglund, S. Islander, G. R. Pickett, and W. Zimmermann, Jr., *ibid.* 22, 1281 (1969).

[3] E. Helfand and F. H. Stillinger, Jr., J. Chem. Phys. 49, 1232 (1968).

[4] An excellent discussion of the experimental data on the liquid-gas transition in binary solutions is given by J. S. Rowlinson, in *Liquids and Liquid Mixtures*, 2nd ed. (Butterworths, London, 1969), Chap. 6.

[5] B. Widom, J. Chem. Phys. 46, 3324 (1967); J. C. Wheeler and B. Widom, J. Am. Chem. Soc. 90, 3064 (1968); here one must make the correspondence, mentioned by the authors, between ternary and binary systems.

[6] J. C. Wheeler and R. B. Griffiths, Phys. Rev. 170, 249 (1968).

[7] That $C_{n,x}$ might remain finite at an azeotropic critical point but diverge where the critical temperature shows an extremum has been suggested by R. B. Griffiths and J. C. Wheeler (private communication from R. B. Griffiths). (*Footnote added in proof*: See R. B. Griffiths and J. C. Wheeler, report prior to publication, 1970).

[8] P. Schofield, Phys. Rev. Letters 22, 606 (1969); see also P. Schofield, J. D. Lister, and T. Ho, *ibid.* 23, 1098 (1969).

[9] For a clear discussion of the relation between thermodynamic derivatives and correlation functions see L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963). Note that the operator for x is $n^2 x^{\text{op}} = n_2 n_1^{\text{op}} - n_1 n_2^{\text{op}}$.

[10] For the case $\alpha = 0$ (logarithmic singularity), $(\delta T^*) \sim (\delta T)^{1/(1-\alpha)}$ is replaced by $\delta T^* \sim \delta T/\ln \delta T$ as in Ref. 1.

[11] Many of the relevant experiments were in fact done around the year 1900. See Ref. 4 for an extensive bibliography.

[12] See Ref. 4, Sec. 6.3.

[13] This assumes, of course, that there are no additional nonanalyticities needed to describe an azeotropic critical point.

[14] The discussion and figures of Ref. 4 are somewhat misleading on this point. See J. P. Kuenen, Phil. Mag. 44, 174 (1897); F. Caubet, Z. Physik. Chem. (Leipzig) 49, 101 (1904); also useful is J. Zernike, *Chemical Phase Theory* (Kluwer, Antwerp, 1956).

[15] A. V. Voronel, V. G. Gorbunova, and N. G. Shmakov Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 9, 333 (1969) [Soviet Phys. JETP Letters 9, 195 (1969)].