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Magnification of singularities of the thermodynamic quantities near critical points in the presence of a chemical reaction

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A system with a chemical reaction behaves like a system with a smaller number of components which, in turn, results in growth of the critical indices.

I. INTRODUCTION

A great deal of progress has been made recently towards the understanding of critical phenomena. The universality theory describes the factors that determine a critical behavior and classifies different phase transitions, while the renormalization-group theory allows one to calculate critical indices for different cases.

The situation, however, becomes more complicated when one compares theoretical predictions with experiment. The theory predicts different critical indices depending on the thermodynamic path by which the critical point is approached. Theoretical calculations assume the constancy of some intensive variables, say, the pressure P or the chemical potential μ, while in practice it is impossible, for example, to ensure the constancy of μ (one has to vary the concentration during the course of the experiment). Similarly, P remains practically unchanged near the liquid-liquid (consolution) critical points because the experiment is carried out in the presence of saturated vapor. On the other hand, it is quite difficult to ensure constancy of P near the liquid-gas critical point where a fluid is highly compressible.

Moreover, there are different factors in real experiments perturbing the "ideal" behavior considered in a theory. All these factors influence differently the critical behavior. Impurities in fluids, for example, do not change the critical behavior of a fluid, and affect only the values of the critical indices, while in solids impurities are "frozen" and, in principle, they destroy a phase transition. A uniform magnetic field eliminates the ferromagnetic phase transition but does not destroy the phase transitions in antiferromagnetics, etc.

In order to compare theoretical calculations for an ideal system and experimental data obtained on the "real" objects, Fisher established[1] the theory of renormalization of critical indices in the case when an ideal system is perturbed homogeneously by some influence which, in turn, is subject to "constraints." A typical example is impurities x added to a pure single-component fluid and constrained by the requirement of constancy of the total number of impurities. The free energy $F(T, h, \mu)$ depends now not only on the temperature T and the second intensive parameter h conjugated to an order parameter (pressure in the case of fluids, magnetic field for ferromagnetics, etc.) but also on an additional parameter μ conjugated to the new extensive variable x (μ is the chemical potential for the case of impurities). In accordance with Ref. 1 for fixed μ, the critical indices remain the same as in the ideal case. However, the critical parameters now depend on the variable μ, and in order to obtain experimentally observable quantities one has to pass, say, from $T(\mu)$ to $T(x)$. As a result of this, the critical indices above and below a phase-transition point obtain the additional factor $\pm(1-\alpha)^{-1}$ where the minus sign refers to the specific heat at constant volume, the plus sign relates to all other critical indices, and α is the critical index of the specific heat at constant volume of the ideal system. [The logarithmic dependence and points of singularity of the function $T=T(\mu)$ have been considered separately.[1]]

One has to introduce some assumptions as one passes from ideal to real critical indices. It would therefore be interesting to measure the ideal indices directly and also together with the real ones, as this would enable us to refine the theory of critical phenomena.

It is the aim of this article to indicate a whole class of systems where the thermodynamic path with a variable concentration (constant chemical potentials) is the only possible way of measurement. Therefore, such measurements will give the ideal critical indices. This class of objects is a fluid mixture with chemical reaction(s).

II. MIXTURE WITH ONE CHEMICAL REACTION

For the thermodynamic description of a system with a chemical reaction one has to use, in addition to T and P, say, an extra chemical variable ξ, which determines the progress of the chemical reaction. For the reaction $\sum \nu_i M_i = 0$, where M_i are the chemical symbols of the reagents and ν_i are the stoichometric coefficients, the changes of the number N_i of the particles of the ith component during chemical reaction are given by $dN_i = \nu_i d\xi$. Therefore the system is characterized by a Gibbs free energy G whose differential form is

$$\begin{aligned} dG &= -S\,dT + V\,dP + \sum \mu_i dN_i \\ &= -S\,dT + V\,dP - A\,d\xi, \quad A = -\sum \nu_i \mu_i \end{aligned} \tag{1}$$

where μ_i is the chemical potential of the ith component and A is the affinity of the reaction.[2]

The affinity A is the measure of the departure of a system from the equilibrium as a result of a chemical reaction. In equilibrium

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = -A(P,T,\xi) = 0\,. \tag{2}$$

As one can see from Eq. (1) the reacting system becomes unstable when the first derivative of the affinity A with respect to the extent of reaction ξ vanishes. Accordingly, the critical point is determined by the following relations:

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T} = \left(\frac{\partial^2 A}{\partial \xi^2}\right)_{P,T} = 0\,. \tag{3}$$

As an example, let us consider a binary fluid mixture AB with the isomerization reaction $A \rightleftharpoons B$. Equation (2) determines ξ as a function of the thermodynamic parameters $\xi = \xi(P,T)$, i.e., the number of degrees of freedom in a binary mixture with a chemical reaction is the same as in a pure one-component fluid. Therefore such a system, according to Eqs. (2) and (3), has an isolated critical point. Thus, the critical indices of this system are the same as of pure fluid, namely,

$$\begin{gathered} \left(\frac{\partial V}{\partial P}\right)_{T,A=0} \sim C_{P,A=0} \sim \tau^{-\gamma}, \\ \left(\frac{\partial V}{\partial P}\right)_{S,A=0} \sim C_{V,A=0} \sim \tau^{-\alpha}, \\ \tau \equiv \frac{T-T_c}{T_c}\,. \end{gathered} \tag{4}$$

If the chemical reaction is frozen the system considered is a binary mixture with a liquid-gas critical line. The renormalization of critical indices of such systems has been considered in Refs. 3 and 4. According to these references

$$\begin{gathered} C_{P,\xi} \sim \left(\frac{\partial V}{\partial P}\right)_{T,\xi} \sim \tau^{-\alpha/(1-\alpha)}, \\ C_{V,\xi} \sim \left(\frac{\partial V}{\partial P}\right)_{S,\xi} \sim \tau^{\alpha/(1-\alpha)}\,. \end{gathered} \tag{5}$$

The correspondence between Eqs. (4) and (5) becomes obvious from the well-known thermodynamic relation[2]

$$C_{P,A=0} = C_{P,\xi} - \left(\frac{\partial \xi}{\partial A}\right)_{T,P} h^2, \tag{6}$$

where h is the heat of reaction at constant T and P. In fact, the asymptotic behavior of the left-hand side (lhs) of Eq. (6) on approaching a critical point is determined by the second term on the right-hand side (rhs) of this equation which according to Eq. (3) has a singularity at a critical point, rather than by the first one which has a weaker singularity there.

Thus, the occurrence of a chemical reaction in a system under consideration magnifies the critical indices of the experimentally observable specific heats (or inverse velocities of sound) compared to a system with frozen chemical reactions, and they are changed from $\alpha/(1-\alpha)$ and $-\alpha/(1-\alpha)$ to $-\alpha$ and $-\gamma$, respectively. The specific heat at constant volume, for example, has a weak singularity at a critical point when a chemical reaction proceeds instead of a finite, although cusped, behavior in the absence of a chemical reaction.

Unfortunately, we do not know any measurements of critical indices in systems with a chemical reaction. The possibility exists, for example, of using the chrome-aluminum catalyst for the mixture of butene isomers, especially *cis-trans* mixture. Equilibrium in this system is achieved very rapidly, and the liquid-gas critical point is located at 430 K and 40 atm.[5] Hence one can expect to find different critical indices from, say, the specific-heat measurements with and without a chemical reaction.

An analogous result may be expected for the mixture of iso- and n-butanols. The solid lines in Fig. 1 show the experimentally observed[6] liquid-gas critical line and the coexistence curves for this mixture. The isomerization reaction takes place in the presence of a catalyst. The dotted line in Fig. 1 indicates the curve of the phase equilibrium $P(T)$ for this system calculated in Ref. 7. Measurements of the asymptotic behavior of the thermodynamic quantities on approaching the critical point A along the line AB (with a chemical reaction) and on approaching one of the critical points on the line $00'$ along the path $x = \text{const}$ (without a chemical reaction) must give different critical indices.

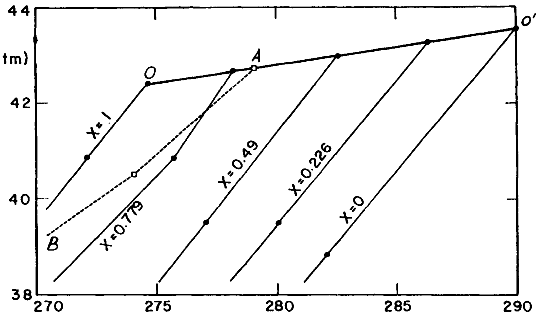

FIG. 1. The P-T phase diagram for the isobutanol-n-butanol system (Ref. 6). 00′ is the line of the liquid-gas critical point. The dotted line AB shows the coexistence curve, calculated in (Ref. 7), for this system, in the presence of an isomerization reaction.

III. CHEMICAL REACTION IN SOLUTION

In solutions, a common experimental situation is that while the solutes undergo various chemical transformations, the solvent does not participate in them. We are interested in the influence of a chemical reaction on the critical phenomena in a solvent-solute system compared with the case of frozen chemical reaction.

Stability conditions for such a system are considered in the Appendix. By analogy with the previous section, we find that, in equilibrium,

$$A(P,T,N_0)=0\,, \tag{7}$$

and the critical points are the solutions of the equations

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T,\mu_0}=\left(\frac{\partial^2 A}{\partial \xi^2}\right)_{P,T,\mu_0}=0\,, \tag{8}$$

where μ_0 and N_0 are the chemical potential and number of particles of solvent, respectively.

As before, let us restrict our consideration to a mixture of isomers dissolved in some solvent. Examples of such systems are the aqueous solution of the mixture of iso- and n-butanol near the liquid-gas critical points of one of the isomers and water, or the so-called Menschutkin reaction of ethyl iodide and triethylamine near a lower liquid-liquid critical point of a water-triethylamine system.

Some characteristic properties of chemical kinematics near the critical point for the latter reaction have been found in Ref. 8. Let us note that in this reaction, as well as in some others, one can "switch on" the chemical reaction not only by catalysts but also by changes of pressure, because the chemical reaction constant strongly depends on the pressure (see, for example, Ref. 9).

Without a catalyst, the chemical reaction is frozen, i.e., in addition to $N_0=\text{const}$ we have $\xi=\text{const}$, while if a chemical reaction takes place, $N_0=\text{const}$ (the solvent does not take part in a chemical reaction) and, according to (7), $A=0$. In other words, there exists a full plane of P-T-N_0 phase equilibrium with coexistence curves of the types AB (Fig. 1) depending on the initial solvent's concentration. Analogously, a considered system with chemical reactions has a line of critical points rather than an isolated critical point as in Fig. 1.

Let us consider first the frozen chemical reaction. According to the hypothesis of renormalization of critical indices^1 ("isomorphism of critical phenomena" in the language of Ref. 4), the singularities of the thermodynamic quantities in a ternary mixture at constant chemical potential μ_0 of the third component are similar to those of a binary mixture. Although the liquid-liquid and liquid-gas critical points are determined from the same thermodynamic relations (8), one has to distinguish the behavior of thermodynamic quantities near these points.

The liquid-liquid critical points hardly depend on the pressure. In this case, according to Ref. 4, the region of renormalization of critical indices is, in fact, absent, and the thermodynamic quantities vary as

$$\begin{gathered} C_{P,\xi,\mu_0}\sim\tau(\mu_0)^{-\alpha}\,,\quad C_{V,\xi,\mu_0}\sim\tau(\mu_0)^{-\alpha}\,,\\ \left(\frac{\partial V}{\partial P}\right)_{S,\xi,\mu_0}\sim\left(\frac{\partial V}{\partial P}\right)_{T,\xi,\mu_0}\sim\text{const}\,. \end{gathered} \tag{9}$$

However, measurements are taken at $N_0=\text{const}$ rather than at $\mu_0=\text{const}$. According to renormalization procedure, in the vicinity of the liquid-liquid critical point one obtains

$$C_{P,\xi,N_0}\sim C_{V,\xi,N_0}\sim\tau^{\alpha/(1-\alpha)}\,. \tag{10}$$

Unlike the liquid-liquid critical point, there are two renormalizations for the neighborhood of liquid-gas critical point: the first one when one passes from the binary to the ternary mixture, and the second renormalization takes place when passing from $\mu_0=\text{const}$ to the experimentally observable situation of $N_0=\text{const}$. Accordingly, in the region of renormalization of the ternary mixture we have

$$\begin{gathered} C_{P,\xi,\mu_0}\sim\left(\frac{\partial V}{\partial P}\right)_{T,\xi,\mu_0}\sim\tau^{-\alpha/(1-\alpha)}\,,\\ C_{V,\xi,\mu_0}\sim\left(\frac{\partial V}{\partial P}\right)_{S,\xi,\mu_0}\sim\tau^{\alpha/(1-\alpha)}\,, \end{gathered} \tag{11}$$

and for $N_0=\text{const}$

$$\begin{gathered} C_{P,\xi,N_0}\sim\left(\frac{\partial V}{\partial P}\right)_{T,\xi,N_0}\sim\tau^{\alpha/(1-\alpha)}\,,\\ C_{V,\xi,N_0}\sim\left(\frac{\partial V}{\partial P}\right)_{S,\xi,N_0}\sim\text{const}\,. \end{gathered} \tag{12}$$

On comparing Eqs. (10) and (12), one concludes that without chemical reaction the cusplike behavior exists for both specific heats near the liquid-liquid critical points and only for the specific heat at constant pressure near the liquid-gas critical point.

Let us turn now to the case where a chemical reaction takes place. The singularities near the critical points can be found from the well-known thermodynamic relations, analogous to (6):

$$C_{P,N_0,A=0}=C_{P,N_0,\xi}-T\left(\frac{\partial\xi}{\partial A}\right)_{P,T,N_0}\left(\frac{\partial A}{\partial T}\right)^2_{P,N_0,\xi},$$
$$C_{V,N_0,A=0}=C_{V,N_0,\xi}-T\left(\frac{\partial\xi}{\partial A}\right)_{V,T,N_0}\left(\frac{\partial A}{\partial T}\right)^2_{V,N_0,\xi}. \tag{13}$$

For both types of critical points, the singularities of thermodynamic quantities in a system with chemical reaction ($A=0$) are determined by the second term on the right-hand side of Eq. (13). The factor $(\partial A/\partial T)$ in the latter term remains finite at the critical point, while the second factor has the asymptotic behavior

$$\left(\frac{\partial\xi}{\partial A}\right)_{P,T,\mu_0}\sim\tau(\mu_0)^{-\gamma},\quad\left(\frac{\partial\xi}{\partial A}\right)_{V,T,\mu_0}\sim\tau(\mu_0)^{-\alpha}, \tag{14}$$

and after the renormalization

$$\left(\frac{\partial\xi}{\partial A}\right)_{P,T,N_0}\sim\tau^{-\alpha/(1-\alpha)},\quad\left(\frac{\partial\xi}{\partial A}\right)_{V,T,N_0}\sim\tau^{\alpha/(1-\alpha)}. \tag{15}$$

Therefore for a system with chemical reaction one obtains from (13) and (15):

$$C_{P,N_0,A=0}\sim\left(\frac{\partial V}{\partial P}\right)_{T,N_0,A=0}\sim\tau^{-\alpha/(1-\alpha)},$$
$$C_{V,N_0,A=0}\sim\left(\frac{\partial V}{\partial P}\right)_{S,N_0,A=0}\sim\tau^{\alpha/(1-\alpha)}. \tag{16}$$

Hence, by comparing (10) with (16) and (12) with (16) one can conclude that existence of a chemical reaction leads to a magnification of singularities of the specific heat at constant pressure for both types of critical points [from cusplike behavior $\alpha/(1-\alpha)$ to the weak singularity $-\alpha/(1-\alpha)$]. On the other hand, the specific heat at constant volume changes its asymptotic behavior (from constant to cusp) only near the liquid-gas critical points. One can, in principle, detect such a magnification experimentally. Experiments might be slightly easier near the liquid-liquid critical points, because these points are usually located near atmospheric pressure and room temperature.

IV. OTHER CHEMICAL REACTIONS

In all the examples considered above, it is possible to freeze the chemical reaction by using the dependence on a catalyst or on the pressure of the constant of chemical reaction, and to compare, therefore, the critical indices with and without chemical reaction. There are, however, a vast number of systems in which a chemical reaction always takes place, and one expects them to show magnified critical indices. Let us cite a few examples.

In the aqueous solution of acetic acid the dimerization reaction $(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH$ takes place in both the liquid and the vapor phases.[10-12] Therefore one should find the magnified critical indices (13) near the liquid-gas critical points of these substances.

Solutions of alkaline or alkaline-earth metals in salts (halogenides, iodides, etc.) or in liquid ammonia (metal-ammonia solutions) have been very thoroughly investigated. Liquid-liquid stratification occurs in both systems, and there is a metal-dielectric transition near the liquid-liquid critical point. The metal-dielectric transition is connected, in our opinion,[13] with the ionization reaction. Therefore one can apply Eqs. (12) to the metal-ammonia solution.

There are experimental data, obtained by Bowen,[14] concerning the adiabatic velocity of sound $(\partial P/\partial V)_S^{1/2}$ in Li-NH_3 which show no singularity approaching the critical point. This fact is in agreement with our Eq. (12). However, there is no singularity also in the absence of a chemical reaction [compare Eq. (10) and experimental data[15] for nitroethane-iso-octane mixture without chemical reaction]. Experimental data of specific heat at constant-pressure measurements for metal-ammonia solutions are given in Ref. 16. They show a very strange critical index 0.7 which contradicts both our estimates (12) and (16), 0.15 and −0.15, for a system with and without chemical reaction, respectively.

In conclusion, we have described a whole class of systems where a chemical reaction magnifies the singularities of the thermodynamic quantities near the critical points. The same consideration is applicable to other processes with an additional parameter ξ, and not only to phase transitions, for instance, to systems with internal degrees of freedom or for the glass-formation processes. It would be interesting to perform an experimental verification of this phenomenon for the above-mentioned or some other systems.

APPENDIX: ON THE STABILITY OF CHEMICAL EQUILIBRIUM IN SOLUTIONS

The Gibbs free energy G of the studied system has the following form[2]:

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{r+1} \mu_i dN_i = -S\,dT + V\,dP + \mu_0 dN_0 + \sum_{i=1}^{r} \mu_i dN_i^0 - A\,d\xi\,, \quad A = -\sum_{i=1}^{r} \nu_i \mu_i \tag{A1}$$

where ν_i are stoichiometric coefficients of the chemical reaction, N_0 and μ_0 are number of particles and chemical potential of solvent, N_i^0 are numbers of particles of solutes at zero time, and μ_i $(i = 1, 2, \ldots, r)$ are the chemical potentials of the r components of solute partaking in a chemical reaction. The extent of reaction ξ determining the numbers of particles taking part in a reaction, $N_i = N_i^0 + \nu_i \xi$, is introduced in the last equality in (A1).

For simplicity let us assume that at zero time the solute was composed of only one component, $N_1^0 \neq 0$, $N_j^0 = 0$ $(j = 2, 3, \ldots, r)$. Introducing the chemical potential $\mu = \mu_1/m_1 - \mu_0/m_0$, where m_1 and m_0 are masses of particles, and the concentration $x = m_1 N_1^0$, one can rewrite Eq. (A1) as

$$dG = -S\,dT + V\,dP + \mu\,dx - A\,d\xi\,. \tag{A2}$$

The only difference between (A2) and (A1) is that, in the former, diffusion instability occurs in two-component systems, while in the latter occurs in many-component systems. However, diffusion can be described as some chemical reaction with "extent of reaction" ξ_{diff}, where ξ_{diff} determines the passage of components from one volume element to the other. On the other hand, the chemical equilibrium is stable with respect to diffusion.[2,17] Therefore the stability conditions for the system under consideration could be formulated as a stability of a ternary system with respect to diffusion or, equivalently, as a stability of a system with two simultaneous reactions. It means that for stability of a system, except for conditions $(\partial\mu/\partial x)_{P,T,\xi} > 0$ and $(\partial A/\partial\xi)_{P,T,x} < 0$, the second-order determinant of coefficients of Eq. (A2) must be positive, i.e.,

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,\xi}\left(-\frac{\partial A}{\partial\xi}\right)_{P,T,x} - \left(\frac{\partial\mu}{\partial\xi}\right)_{P,T,x}\left(-\frac{\partial A}{\partial x}\right)_{P,T,\xi} > 0\,. \tag{A3}$$

Using the simple thermodynamic relations

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,A=0} = \left(\frac{\partial\mu}{\partial x}\right)_{P,T,\xi} + \frac{(\partial A/\partial x)^2_{P,T,\xi}}{(\partial A/\partial\xi)_{P,T,x}}\,, \tag{A4}$$

$$\left(\frac{\partial A}{\partial\xi}\right)_{P,T,\mu} = \left(\frac{\partial A}{\partial\xi}\right)_{P,T,x} + \frac{(\partial A/\partial x)^2_{P,T,\xi}}{(\partial\mu/\partial x)_{P,T,\xi}}\,, \tag{A5}$$

one can show that the stability conditions reduce to

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,\xi} > 0, \quad \left(\frac{\partial A}{\partial\xi}\right)_{P,T,x} < 0, \quad \left(\frac{\partial\mu}{\partial x}\right)_{P,T,A=0} > 0,$$

or (A6)

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,\xi} > 0, \quad \left(\frac{\partial A}{\partial\xi}\right)_{P,T,x} < 0, \quad \left(\frac{\partial A}{\partial\xi}\right)_{T,P,\mu} < 0\,.$$

The first term in the rhs of Eq. (A4) is positive while in Eq. (A5) it is negative. Let $(\partial A/\partial\xi)_{P,T,x}$ or $(\partial\mu/\partial x)_{P,T,\xi}$ tend to zero. Then, as is clear from Eqs. (A4) and (A5) the lhs of these equations will vanish before either of the derivatives $(\partial A/\partial\xi)_{P,T,x}$, $(\partial\mu/\partial x)_{P,T,\xi}$ vanishes. Therefore, finally, the stability conditions for a system described by Eq. (A2) are

$$\left(\frac{\partial A}{\partial\xi}\right)_{P,T,\mu} < 0$$

or (A7)

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,A=0} > 0\,.$$

One can show in analogous manner that the critical point of a system under consideration is determined by

$$\left(\frac{\partial A}{\partial\xi}\right)_{P,T,\mu} = \left(\frac{\partial^2 A}{\partial\xi^2}\right)_{P,T,\mu} = 0$$

or (A8)

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T,A=0} = \left(\frac{\partial^2\mu}{\partial x^2}\right)_{P,T,A=0} = 0\,.$$

The relations (A7) and (A8) must be considered, for example, in the stability analysis of solution of weak electrolytes, metal-ammonium solution, molten salts, etc., where the "ionization reaction" occurs.[13]

Recall that for a pure substance the mechanical stability is determined by $(\partial P/\partial V)_T < 0$. The condition for the diffusional instability in binary mixtures has a form $(\partial\mu/\partial x)_{P,T} > 0$ which, however, can be rewritten as $(\partial P/\partial V)_{T,\mu} < 0$. Such an "isomorphism" principle is quite general. In our case the stability condition for a system with additional degrees of freedom has the same form as for the original system with some additional constraints, namely, the diffusion instability with $A = 0$, or the chemical instability with $\mu = \text{const}$.

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