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Phase Equilibria and Critical Phenomena in Closed Reactive Systems

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It is shown that the interplay between chemical reactions and criticality gives rise to some novel phenomena manifested both in a change of critical indices and in some pecularities in the course of chemical reactions. To cite a single example, one can mention the existence of a single point on the hypersurface of the diffusion instability where the slowing down of chemical reactions occurs. The requirements for phase separation in reactive systems are illustrated on simple models of a nonelectrolytic binary mixture and a ternary mixture including electrolytes. The general criterion for the existence of azeotropic points and the upper (lower) critical solution temperatures in reactive systems is formulated. The influence of a chemical reaction on the form of the solubility curve near the melting point in a binary and a dilute ternary mixture is analyzed in detail. A new general approach is formulated to the decay of metastable state in reactive systems. Finally, some possible experimental verifications are considered.

KEY WORDS: Phase equilibria; chemical reactions; slowing down; metastable states; azeotropic mixtures.

1. INTRODUCTION

This review deals with the coexistence of different phases, especially near the critical points in systems in which chemical reactions occur. A chemical reaction clearly leads to the existence of a number of components in a system. Many-component reactive systems, and especially fluids, are the subject of the investigation, which is restricted to the case of closed systems, as distinct from the open systems where many peculiarities in chemical reactions are well known.(1)

This article is a tribute to my dear colleague C. Domb, who has done so much in the understanding of phase transitions and critical phenomena. It is a great pleasure to contribute to this volume honoring him on the occasion of his official retirement.

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The approach is physicochemical in the sense that physical forces of interaction as well as chemical reactions are considered. However, the division of the forces into "physical" and "chemical" is relative in itself. It is convenient$^{(2)}$ to distinguish between strong attractive (chemical) forces leading to the formation of chemical species, and weak attractive (physical) forces, usually called van der Waals forces. It should be remembered, therefore, that when one considers the "ideal" ternary mixture A, B, and A_nB_m the strong bonding interactions between A and B atoms have been already taken into account via the formation of chemical complexes $A_n\,B_m$, and the term "ideal" only means that there are no "physical" forces. The growth of clusters in a metastable state is an example of an unclear distinction between physical and chemical forces. An arbitrary decision has to be made in numerical simulations in order to decide whether a given particle belongs to a "chemical" cluster.

The usefulness of a "chemical" approach to physical problems should be noted. I have considered$^{(3)}$ the mean field theopry of the phase transition in the Ising lattice of nonstoichometric AB alloys. The temperature dependence of the long- and short-range order parameters was found from "the law of mass action" for two appropriately chosen "chemical reactions." The latter are the exchange of position of one atom A from one sublattice and one atom B from the second sublattice. The change of the interaction energy for such transitions when both atoms are or are not the nearest neighbors determines the "constants of chemical reactions."

Such an approach allows one to avoid the calculation of entropy provided that one is interested only in the value of the critical temperature rather than in the behavior of all thermodynamic quantities, which are determined by the same classical critical indices in all versions of the mean field theory.

This "chemical" method, in which a given atom with all its z neighbors is considered as the basic group, gives better results than the Bragg–Williams or the Bethe–Peierls methods. In the Bragg–Williams method, each atom is exposed to the (self-consistent) average influence of all other atoms, while in the Bethe method a pair of adjacent atoms is considered as a basic group.

Many other examples of the "chemical" approach to "physical" phenomena can be found in textbooks on chemical thermodynamics. For example, the typical "physical" process of diffusion can be considered (ref. 4, Chapter 15) as a "chemical reaction" in which some amount of substance A passes from the volume element a to b while a different amount of B passes from b to a.

While the borderline between chemical and physical forces is arbitrary, one usually considers first the "physical" forces in the equation of state, and after that the "chemical" forces in the law of mass action based on the nonideal equation of state. I follow this approach below.

This review is written by a physicist for physicists. My aim is therefore to indicate some new phenomena arising from the mutual influence of criticality and chemistry, rather than to perform the numerical calculations for complicated systems that are so important for practical engineering purposes. Therefore, I consider everywhere the simple case of a single chemical reaction and the simplest equations of state. In a few cases it is enough to consider the ideal equation of state: the azeotropic points in reactive systems exist even for ideal substances.(5) However, the ideal systems do not show phase separation even with chemical reactions. Only for $n \rightarrow \infty$ does the association reaction $A_n \rightleftarrows nA$ result in phase separation even for ideal substances.(6) Therefore, I use the simplest models of strictly regular solutions for neutral systems, and the Debye–Hückel approximation for solutions of electrolytes.

In the wake of the impressive advance in the study of critical phenomena, it seems that the influence of criticality on chemical reaction and vice versa has not received widespread atention. I hope that this interesting subject will attract more attention in the future.

2. GENERAL STABILITY CONDITIONS. CHEMICAL INSTABILITY

The thermodynamic state of an n-component one-phase system is determined by $n+1$ variables, say the temperature T and the chemical potentials of each component μ_i $(i=1, 2,..., n)$. The free energy ϕ as a function of all these "field" variables has the following form:

$$\phi = \phi(T, \mu_1, ..., \mu_n) \tag{1}$$

However, for a reactive system the chemical potentials are not independent. Thus, for the reaction $\sum_{i=1}^{n} v_i A_i = 0$, where A_i are the chemical symbols of the reagents and the v_i are positive or negative integers, one has an additional constraint on μ_i, namely, according to the law of mass action,(4) in equilibrium

$$A \equiv - \sum_{i=1}^{n} v_i \mu_i = 0 \tag{2}$$

The unconstrained free energy $\tilde{\phi}$ can be written as

$$\tilde{\phi}(T, \mu_1, ..., \mu_n) = \phi(T, \mu_1, ..., \mu_n) + \xi \sum_{i=1}^{n} v_i \mu_i \tag{3}$$

where ξ is a Lagrange multiplier. By differentiating Eq. (3) with respect to μ_i, one obtains the particle number densities

$$n_i = n_i^0 + \xi v_i \tag{4}$$

Equation (4) means that for a given system (with initial n_i^0) the change in n_i is completely determined by the extent ξ of the reaction. The latter quantity defines, for given P and T, the trajectory of all possible thermodynamic states of a system in the n-dimensional phase space. The thermodynamic behavior near the critical point for given n_i^0 has been analyzed recently.(7,8)

However, the complete analysis of stability at given T and P requires a consideration of all possible changes of n_i coming both from n_i^0 and ξ in Eq. (4). In multicomponent systems the stability with respect to diffusion is broken first, before the thermal or the mechanical stability. In terms of the Gibbs free energy $G(T, P, n_1,..., n_n)$ the condition for diffusion stability for given P and T has the form

$$d^2G = \sum_{ij} dn_i\, \mu_{ij}\, dn_j > 0; \qquad \mu_{ij} \equiv \partial\mu_i/\partial n_j \tag{5}$$

One can easily show(4) that the matrix μ_{ij} is semipositive, i.e., the determinant of this matrix $\|\mu_{ij}\|$ vanishes and the rank of μ_{ij} is equal to $n-1$ and all but one eigenvalue of μ_{ij} are positive. Let N_j^0 be the eigenvector corresponding to zero eigenvalues:

$$\sum_j \mu_{ij} N_j^0 = 0 \tag{6}$$

Equations (6), which are the Gibbs–Duhem relations, have a simple physical meaning of invariance with respect to proportional change of all particle numbers. On substituting (4) in (5), one obtains

$$d^2G = \sum_{i,j} [dn_i\, \mu_{ij}\, dn_j + 2dn_i\, \mu_{ij} v_j\, d\xi + v_i \mu_{ij} v_j\, (d\xi)^2] > 0 \tag{7}$$

The form $q \equiv \sum_{i,j} x_i \mu_{ij} x_j$ vanishes only when $\|\mu_{ij}\| = 0$. (The opposite, however, is not true; namely, for $\|\mu_{ij}\| = 0$, q may remain positive.) Therefore, the existence of a chemical reaction does not change the stability conditions. The equivalence of the stability conditions with respect to chemical changes and those with respect to diffusion becomes evident when one considers(4) them as results of homogeneous and nonhomogeneous perturbations of an initially homogeneous system.

On the critical hypersurface the expression (5) vanishes, i.e., new zero eigenvalues of μ_{ij} appear which correspond to some eigenvector N_j such that

$$\sum \mu_{ij} N_j = 0 \tag{8}$$

Among all points on the critical hypersurface, those are worthy of notice where not only the condition (5) is violated, but also the sum $\sum_{i,j} \nu_i \mu_{ij} \nu_j$ vanishes. I shall call them the "chemical" instability points. The latter name is justified in that near these points and only near them does the slowing down of chemical reactions occur. In fact, one can show in different ways that the sum $\sum_{i,j} \nu_i \mu_{ij} \nu_j$, which, according to Eq. (7), is equal to $(dA/d\xi)_{\text{eq}}$, determines the slowing down. The affinity A and the derivative $d\xi/dt$ are two conjugate parameters in the entropy production; both vanish in equilibrium and therefore, near equililbrium, one can assume an Onsager-type relation:

$$d\xi/dt = LA \approx L(dA/d\xi)(\xi - \xi_{\text{eq}}) = L \sum_{i,j} \nu_i \mu_{ij} \nu_j (\xi - \xi_{\text{eq}}) \tag{9}$$

Mode-coupling analysis shows(8) that the Onsager coefficient L has no singularity at the critical point. Therefore, the slowing down will take place when

$$\sum_{i,j} \nu_i \mu_{ij} \nu_j = 0 \tag{10}$$

The same results can be obtained from the usual kinetic relations for the rate of chemical reactions.(9) For the chemical reaction

$$\sum_{i=1}^{k} \nu_i A_i = \sum_{j=1}^{l} \nu'_j A'_j$$

the observe rate of reaction r is the difference between the forward and backward processes,

$$r = \vec{r} - \overleftarrow{r} = r_+ C_1^{\nu_1} \cdots C_k^{\nu_k} - r_- C_1^{\nu'_1} \cdots C_l^{\nu'_l} \tag{11}$$

where r_+ and r_- are microscopically determined rate coefficients for the forward and backward reactions, while C_i are the concentrations (or fugacities) of the ith species in an ideal (or nonideal) solution. Using the definition of the chemical potentials $\mu_i = \mu_i^0 + RT \ln C_i$ and the fact that(4)

$$r_+/r_- = \exp\left[\left(\sum_{i=1}^{k} \nu_i \mu_i^0 - \sum_{j=1}^{l} \nu'_j \mu_j^0\right)\Big/ RT\right]$$

one can rewrite Eq. (11) as

$$\begin{aligned} r &= r_+ C_1^{\nu_1} \cdots C_k^{\nu_k} [1 - (r_-/r_+)(C_1^{\nu'_1} \cdots C_l^{\nu'_l} / C_1^{\nu_1} \cdots C_k^{\nu_k})] \\ &= r_+ C_1^{\nu_1} \cdots C_n^{\nu_k} [1 - \exp(-A/RT) \equiv LRT[1 - \exp(-A/RT)] \end{aligned} \tag{12}$$

One concludes from Eq. (12) that the rate of reaction r which is proportional to $d\xi/dt$ is, in general, a nonlinear function of A. However, in equilibrium $A = 0$, and for small enough deviations from equilibrium $A/RT \ll 1$ and Eq. (12) reduces to the Onsager relation (9).

Let us consider when the condition (10) for the critical slowing down is satisfied. Equations (6) and (8) mean that the slowing down (10) will take place if and only if

$$v_i = \alpha N_i + \beta N_i^0 \tag{13}$$

where α and β are arbitrary constants. The important formula (13) has been obtained by Patashinsky *et al.*(10)

There are $n-2$ constraints (13) equal to the rank of the matrix μ_{ij} on the critical hypersurface. Together with two critical conditions, they define n conditions on $n+1$ independent variables. Thereby only one free parameter is left, which will be fixed by the law of mass action (2). Therefore, the slowing down may appear only at an isolated point on the critical hypersurface provided that all constraints are compatible. Each chemical reaction decreases by one the dimension of the critical hypersurface. In the case of an n-component system with $n-1$ chemical reactions (e.g., a binary mixture with a single chemical reaction), the only existing critical point will be where slowing down occurs. The rate of the chemical reaction near this isolated critical point will be proportional to $[(T-T_c)/T_c]^\gamma$, where γ is the susceptibility critical index.

For an n-component mixture with the number of chemical reactions less than $n-1$, the chemical instability point will be an isolated point on the critical hypersurface, which makes the experimental verification more complicated than was expected.(8) However, in addition to binary mixture with a single chemical reaction, the slowing down is very probable(10) in reactions in multicomponent systems involving the separation of weakly-dissolved substances from a solvent.

3. THE EFFECT OF CRITICALITY ON CHEMISTRY

3.1. Critical Slowing Down of Chemical Reactions

Our analysis of the slowing down based on Eq. (9) is not complete for the following reason. Only homogeneous changes of the extent of reaction ξ are allowed by (9). If, however, a system is large enough, the K-dependent changes connected with the sound, heat, or diffusion modes become more important.(13) Indeed, the relaxation rates of the latter processes will become smaller (for some small wave numbers K) than the fixed K-independent rate of the chemical reaction.

The general mean-field approach which goes back to Van Hove$^{(11)}$ is the straightforward generalization of Eq. (9). On the left-hand side of the equation, instead of ξ, the column matrix of the "density"-type variables x (density, concentrations, entropy, etc.) apprars, and instead of A, their conjugate "fields" X (pressure, chemical potentials, temperature, etc.), which are connected by the matrix of Onsager coefficients $L(K)$, i.e.,

$$i\omega x(K, \omega) = L(K)\, X(K, \omega) \tag{14}$$

The field variables X are connected, in turn, with the density variables x by the susceptibility matrix χ^{-1}, i.e., $X(K, \omega) = \chi(K)^{-1} x(K, \omega)$ (the constituent equation). Finally,

$$i\omega x(K, \omega) = L(K)\, \chi^{-1} x(K, \omega) = M x(K, \omega) \tag{15}$$

The matrix $M = L\chi^{-1}$ is the hydrodynamic matrix. One has, therefore, to write the hydrodynamic equations for a reactive system. I consider here the linearized equations for binary mixtures, leaving the analysis of the nonlinearities to Section 4.2.

The linearized hydrodynamic equations can be obtained as a straightforward generalization of the equation of motion of a nonreactive binary mixture. We may choose the mass fraction of one component as the extent of reaction ξ and write

$$\partial\rho/\partial t + \rho \nabla \cdot \mathbf{v} = 0 \tag{16}$$

$$\rho\, \partial \nabla \cdot \mathbf{v}/\partial t = -\nabla^2 P + (\tfrac{4}{3}\eta + \eta_v)\, \nabla^2\, \nabla \cdot \mathbf{v} \tag{17}$$

$$\partial\xi/\partial t = D[\nabla^2 \xi + (k_T/T)\, \nabla^2 T + (k_P/P)\, \nabla^2 P] + LA \tag{18}$$

$$\begin{aligned}\partial S/\partial t = {} & (\lambda/\rho T)\, \nabla^2 T + (D k_T/T)(\partial A/\partial\xi)_{P,T}[\nabla^2 \xi + (k_P/P)\, \nabla^2 P] \\ & + (\partial S/\partial \xi)_{P,T}\, D[\nabla^2 \xi + (k_P/P)\, \nabla^2 P + (k_T/T)\, \nabla^2 T]\end{aligned} \tag{19}$$

Here ρ, $\mathbf{v}$, η, η_v, D, λ, and k_T are the density, velocity field, shear and bulk viscosities, diffusion constant $[D \equiv \alpha(\partial A/\partial\xi)_{P,T}]$, heat conductivity, and the thermodiffusion constant, respectively. The quantity k_P/P is thermodynamic and equals $(\partial A/\partial P)_{T,\xi}/(\partial A/\partial \xi)_{T,P}$.

Notice that the chemistry term LA appears only in (18) and not in (19). The reason is that the chemical reaction contributes only quadratic terms to the entropy production.$^{(4)}$ Since A vanishes at equilibrium, we expand A in P, T, and ξ:

$$LA = L(\partial A/\partial \xi)_{P,T}\, \delta\xi + L(\partial A/\partial T)_{\xi,P}\, \delta T + L(\partial A/\partial P)_{\xi,T}\, \delta P \tag{20}$$

By using thermodynamic identities, we can write Eq. (20) in the form

$$LA = -(1/\tau_{T,P})[\delta\xi - (\partial\xi/\partial T)_{P,A}\,\partial T - (\partial\xi/\partial P)_{T,A}\,\delta P] \tag{21}$$

where $\tau_{T,P} \equiv (1/L)(\partial A/\partial\xi)^{-1}_{T,P}$.

The system of equations (16)–(19) contains four hydrodynamic degrees of freedom from the existing six variables because the transverse components of the velocity are not coupled with other variables. Moreover, the sound modes connected with density and longitudinal velocity are much faster than the nonpropagating diffusive and reacting modes. Therefore, two more equations of (16)–(19) can be eliminated, leaving only two equations, (18) and (19). What remains is a 2×2 matrix whose eigenvalues can easily be calculated.(8) I use here the simple physical analysis performed by Milner and Martin.(13)

One can see from Eq. (18) that the relaxation of ξ comes through chemical processes (with characteristic time τ away from the critical point), through diffusion [for which $(DK^2)^{-1}$ is the typical relaxation time], and through thermal diffusion. In the latter case the characteristic time is $(\lambda K^2)^{-1}$, where $\lambda = (k_T D/C_{P,\xi})(\partial A/\partial\xi)_{P,T}$ and the concentration–temperature coupling is treated by Eqs. (18) and (19). Let us defined now two characteristic lengths (inverse wave numbers) by $K_c^{-2} = D\tau$ and $K_H^{-2} = \lambda\tau$, where generally $K_H^{-1} \gg K_c^{-1}$.

The possible values of the wave numbers fall into three intervals: $K < K_H$, $K_H < K < K_c$, and $K > K_c$. In the first interval the chemical reaction is more rapid than both heat conduction and particle diffusion, while in the third interval diffusion dominates the chemical relaxation. Only for the processes with wave numbers located in the "window" between K_H and K_c is the relaxation dominated by chemistry. For the typical values of $\lambda = 0.1$ cm^2/sec and $D = 10^{-5}$ cm^2/sec and for a reaction rate $\tau^{-1} = 10^5$ Hz we have $K_H = 10^3$ cm^{-1} and $K_c = 10^5$ cm^{-1}. Therefore, light-scattering experiments at different temperatures in the vicinity of the critical temperature should evidence the slowing down of chemical reactions near the critical points. According to theoretical "mean-field" predictions,(8, 13) the slowing down is governed by the "strong" critical index γ, while the renormalization group analysis (see Section 4.2) leads to small corrections to γ.

Notice that the "slowing down of the chemical reaction" does not imply that the forward or backward reaction is slowed down. It is the measured rate, which is the net difference between the forward and backward reactions, which is affected by criticality. In fact, the condition (10), which is no other than $(\partial A/\partial\xi)_{P,T} = 0$, means that the system becomes indifferent to changes in the species concentration. In equilibrium, when $A = 0$, the reaction is balanced and the measured rate is zero. Usually, a change of ξ from ξ_{eq} builds up an affinity $A \neq 0$ which acts as a driving force to restore the equilibrium. However, due to the thermodynamic properties of the critical region, a change in ξ does not create a restoring force (i.e., affinity) and the reaction continues to be balanced although $\xi \neq \xi_{eq}$. The net rate continues to the zero. In other words, the physical explanation of the slowing down of the chemical reaction is the same as that of diffusion near the critical points. The only difference is that the chemical perturbation is homogeneous, in contrast to the inhomogeneous diffusion changes.

All the above consideration hold for a two-component mixture with a single chemical reaction. For more complicated systems the slowing down is weaker (with the "weak" critical index α) or does not exist at all.$^{(13)}$

3.2. Critical Anomalies of Chemical Equilibria

In addition to singularities in the rate of reaction, some peculiar behavior of equilibrium concentrations of reagents takes place near the critical point. The dissociation–recombination reaction of the form $B_2 \rightleftarrows 2B$ near the single liquid–gas critical point of the binary mixture of B_2 and B has been considered in ref. 14, which, however, suffered from some inaccuracies that have been corrected by Wheeler and Petshek.$^{(15)}$ According to common sense, one expects that increasing (decreasing) the temperature should result in increasing (decreasing) the concentration of monomers in all dissociation–recombination reactions. Indeed, both energy (due to bond energy) and entropy (due to number of particles) considerations seem to lead to this very same conclusion. Quite unexpectedly, the opposite has been observed in qualitative experiments performed by Krichevskii and his collaborators,$^{(16)}$ who studied the equilibrium $N_2O_4 \rightleftarrows 2NO_2$ in dilute solution in CO_2 in proximity to the critical point of the mixture. While another interpretation of this almost 20-year-old experiment exists,$^{(15,17)}$ it does not question the very existence of the anomalies in chemical equilibrium near critical points, no matter how small they are. Consider a variation of the temperature along an equilibrium line of a reactive binary mixture $B_2 \rightleftarrows 2B$ at, say, constant pressure. Since the affinity $A = \mu_{B_2} - 2\mu_B$ vanishes for any equilibrium state, we can write along the equilibrium line

$$0 = dA = (\partial A/\partial T)_{\xi,P}\, dT + (\partial A/\partial \xi)_{T,P}\, d\xi \tag{22}$$

where $d\xi = dn_{B_2} = -dn_B/2$ is, according to (4), the change in the extent of the reaction.

From Eq. (22) it follows that

$$(d\xi/dT)_{P,\text{equil line}} = -[(\partial H/\partial \xi)_{T,P}]/[T(\partial A/\partial \xi)_{T,P}] \tag{23}$$

where the thermodynamic identity(4)

$$(\partial A/\partial T)_{P,\xi} = (\partial S/\partial \xi)_{T,P} = [A + (\partial H/\partial \xi)_{T,P}]/T \tag{24}$$

has been used, with H and S being the entalpy and entropy, respectively. The derivative $(\partial H/\partial \xi)_{T,P}$ has no critical singularity; therefore, the slope of concentration curves $\xi(T)$ is inversely proportional to the same derivative $(\partial A/\partial \xi)_{T,P}$, which, according to (21), determines the critical slowing down. Hence, the derivative $(d\xi/dT)_{P,\mathrm{eq}}$ exhibits a strong divergence at the critical point which is characterized(15) by critical indices γ or $(\delta - 1)/\delta$, depending on whether the critical point is approached at constant critical volume or pressure, respectively.

It should be noted that we used(18) similar arguments for an explanation of the technologically important phenomenon of "supercritical extraction"—the substantial increase in the ability of near-critical fluids to dissolve solids. Let us denote the solid phase by s and the fluid phase by g. The equality of the chemical potentials in the two phases is a necessary condition for the coexistence of these phases. Thus, for the solid,

$$\mu^s(T, P) - \mu^g(T, P, x) \equiv \Delta\mu = 0 \tag{25}$$

where use has been made of the fact that the solid phase is composed only of solid, i.e., its concentration x is equal to unity in this phase. Consider now isobaric changes in temperature along the equilibrium line:

$$0 = d\,\Delta\mu = (\partial\mu^s/\partial T)_P\,dT - (\partial\mu^g/\partial T)_{P,x}\,dT - (\partial\mu^g/\partial x)_{T,P}\,dx \tag{26}$$

Equation (26) can be rewritten as

$$(\partial x/\partial T)_P = (\bar{s} - s^s)/(\partial\mu^g/\partial x)_{T,P} \tag{27}$$

where we defined the molar entropy of the solid $s^s = -(\partial\mu^s/\partial T)_P$ and the partial entropy of the solid in the fluid phase $\bar{s} = -(\partial\mu^g/\partial T)_{P,x}$.

Equations (26)–(27), which are analogous to (22)–(23), explain the supercritical extraction. Indeed, near the critical points the denominator in (27) goes to zero, leading to a strong divergence of the slope in the solubility curve.

The system outlined above contains a small amount of solid dissolved in fluid. One may use also the binary mixture as the solvent and the solid as the solute.

We have suggested(19) the use for supercritical extraction of the neighborhood of a consolute point rather than usually used liquid–gas critical point. The former are characterized by much lower pressures and temperatures, and so have clear technological advantages.

4. THE EFFECT OF CHEMISTRY ON CRITICAL PHENOMENA

4.1. Modification of Critical Indices

The preceding section considered the influence of the criticality on an existing chemical reaction. However, such influence is mutual, and I raise now the problem of changes in critical phenomena arising from the presence of a chemical reaction.

The singularities of the thermodynamic (and kinetic) quantities near the critical points are determined by the critical indices. Theoretical calculations of these indices assume the constancy of some intensive variables ("fields"),' say, the pressure P or the chemical potentials μ, while in practice it is impossible, for example, to ensure the constancy of μ (one has to vary the concentrations during the course of the experiment). Similarly, P remains practically unchanged near the liquid–liquid critical points because the experiment is carried out in the presence of saturated vapor. On the other hand, it is quite difficult to ensure the constancy of P near the liquid–gas critical point where a fluid is highly compressible.

In order to compare theoretical calculations for an ideal one-component system and experimental data obtained on the "real" objects, Fisher(20) established the theory of renormalization of critical indices. The main idea of the renormalization can be explained by the following simple arguments. For a pure substance, the mechanical stability is determined by $(\partial P/\partial v)_T < 0$. The condition for diffusion stability in a binary mixture has the form $(\partial \mu/\partial x)_{T,P} > 0$, which by a simple thermodynamic transformation can be rewritten as $(\partial P/\partial v)_{T,\mu} < 0$. One can say, therefore, that at constant chemical potential μ, the critical behavior of a binary mixture, which is defined by the stability conditions, will be the same as that of a pure substance. Multicomponent systems behave in a perfectly analogous manner, namely, the stability condition for an n-component mixture is determined by the condition $(\partial P/\partial v)_{T,\mu_1\cdots\mu_{n-1}} < 0$, where $n-1$ chemical potentials are held constant. However, the critical parameters now depend on the variables μ_i, and in order to obtain experimentally observable quantities which correspond to constant concentrations x_i, one has to pass, say, from $T(\mu)$ to $T(x)$. As a result, when one goes from a pure substance to a binary mixture the critical indices above and below a critical point are multiplied by $\pm(1-\alpha)^{-1}$,(20) where the minus sign refers to the specific heat at constant volume, the plus sign refers to all other critical indices, and α is the critical index of the specific heat at constant volume. We have considered(21) the renormalization of the critical indices associated with the presence of chemical reactions. As an example, let us again consider a binary fluid mixture A_1–A_2 with the single reaction $\nu_1 A_1 + \nu_2 A_2 = 0$ (say, the isomerization reaction). The latter means that the law of mass action

(2) is satisfied, i.e., $-A \equiv \nu_1 \mu_{A_1} + \nu_2 \mu_{A_2} = 0$, which, in turn, reduces by one the number of thermodynamic degrees of freedom in a binary mixture. The reactive binary system, therefore, has an isolated critical point, and the critical indices of this system are the same as of a pure fluid, namely,

$$\begin{aligned} &(\partial v/\partial P)_{T,A=0} \sim C_{P,A=0} \sim [(T-T_c)/T_c]^{-\gamma} \\ &(\partial v/\partial P)_{s,A=0} \sim C_{v,A=0} \sim [(T-T_c)/T_c]^{-\alpha}, \quad \text{etc.} \end{aligned} \tag{28}$$

It is interesting to compare (28) with the case of frozen chemical reaction (no catalyst is added). Then, the system considered is a binary mixture with a liquid–gas critical line. The renormalizations of critical indices of such systems are well known⁽²⁰⁾:

$$\begin{aligned} &C_{P,\xi} \sim (\partial v/\partial P)_{T,\xi} \sim [(T-T_c)/T_c]^{-\alpha/(1-\alpha)} \\ &C_{v,\xi} \sim (\partial v/\partial P)_{s,\xi} \sim [(T-T_c)/T_c]^{\alpha/(1-\alpha)} \end{aligned} \tag{29}$$

The correspondence between (28) and (29) becomes obvious from the thermodynamic relation⁽⁴⁾

$$C_{P,A=0} = C_{P,\xi} - h^2(\partial \xi/\partial A)_{T,P} \tag{30}$$

where h is the heat of reaction. In fact, the asymptotic behavior of the left-hand side of Eq. (30) on approaching a critical point is determined by the second term on the right-hand side, rather than by the first one, which has a weaker singularity there.

Thus, the occurrence of a chemical reaction in a system under consideration modifies the critical indices of the experimentally observable specific heats at constant volume and constant pressure (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. Thus, 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.

The singularities become weaker for many-component mixtures. A common situation is when the solutes undergo various chemical transformations while the solvent does not participate in them. Consider, as an example, the critical system containing the reactive binary mixture dissolved in some solvent. Due to the existence of a neutral third component, the system considered has a line of critical points rather than an isolated critical point, as in the case of the reactive binary mixture.

Let us consider first the frozen chemical reaction. The singularities of the thermodynamic quantities in a ternary mixture at constant chemical potential μ_0 of the solvent are similar to those of a binary mixture. The liquid–liquid critical points hardly depend on the pressure, so that the parameter $R\rho_c\, dT_c/dp$ (ρ_c is the critical density) is very small. It is this parameter which determines the region of renormalization.(22) Therefore, in this case, as for the vicinity of the λ line in helium, the renormalization is absent, and

$$C_{P,\xi,\mu_0} \sim \tau(\mu_0)^{-\alpha}; \qquad C_{v,\xi,\mu_0} \sim \tau(\mu_0)^{-\alpha}; \qquad \tau(\mu_0) = [T - T_c(\mu_0)]/T_c(\mu_0)$$

However, measurements are taken at the constant number of solvent particles rather than at $\mu_0 = \text{const}$. According to renormalization procedure, near the liquid–liquid critical points one obtains

$$C_{P,\xi,N_0} \sim C_{v,\xi,N_0} \sim [(T - T_c)/T_c]^{\alpha/(1-\alpha)} \tag{31}$$

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

$$C_{P,\xi,\mu_0} \sim \tau^{-\alpha/(1-\alpha)}; \qquad C_{v,\xi,\mu_0} \sim \tau^{\alpha/(1-\alpha)} \tag{32}$$

and for $N_0 = \text{const}$

$$C_{P,\xi,N_0} \sim \tau^{\alpha/(1-\alpha)}; \qquad C_{v,\xi,N_0} \sim \text{const} \tag{33}$$

Comparing (31) and (33), one concludes that without chemical reactions 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 points.

Let us turn now to the case where a chemical reaction takes place. The singularities near the critical points can be found from the thermodynamic relations, analogous to (30):

$$\begin{aligned} C_{P,N_0,A=0} &= C_{P,N_0,\xi} - T(\partial\xi/\partial A)_{P,T,N_0}(\partial A/\partial T)^2_{P,N_0,\xi} \\ C_{v,N_0,A=0} &= C_{v,N_0,\xi} - T(\partial\xi/\partial A)_{v,T,N_0}(\partial A/\partial T)^2_{v,N_0,\xi} \end{aligned} \tag{34}$$

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. (34). The factor $\partial A/\partial T$ in the latter term remains finite at the critical point, while the second factor has the assymptotic behavior

$$(\partial\xi/\partial A)_{P,T,\mu_0} \sim \tau(\mu_0)^{-\gamma}, \qquad (\partial\xi/\partial A)_{v,T,\mu_0} \sim \tau(\mu_0)^{-\alpha} \tag{35}$$

and after the renormalization

$$\begin{aligned} (\partial\xi/\partial A)_{P,T,N_0} &\sim [(T-T_c)/T_c]^{-\alpha/(1-\alpha)} \\ (\partial\xi/\partial A)_{v,T,N_0} &\sim [(T-T_c)/T_c]^{\alpha/(1-\alpha)} \end{aligned} \tag{36}$$

Therefore for a system with chemical reaction one obtains from (34) and (36)

$$\begin{aligned} C_{P,N_0,A=0} &\sim (\partial v/\partial P)_{T,N_0,A=0} \sim \tau^{-\alpha/(1-\alpha)} \\ C_{v,N_0,A=0} &\sim (\partial v/\partial P)_{s,N_0,A=0} \sim \tau^{\alpha/(1-\alpha)} \end{aligned} \tag{37}$$

Hence, by comparing (31) and (33) with (37), one can conclude that the 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 at atmospheric pressure and room temperature.

4.2. Singularities of Transport Coefficients in Reactive Systems

In order to find critical contributions to transport coefficients, one must go beyond the linear hydrodynamic equations (16)–(19). The different ways of attacking this problem include, among others, the mode–mode coupling(23) [taking into account nondissipative nonlinear terms in Eqs. (16)–(19)] and the dynamic renormalization group methods(24) (including both dissipative and nondissipative interactions).

The description of these methods is clearly beyond the scope of this article. I present, instead, results of the application of the above methods to reactive systems, and compare them with those for nonreactive systems.

4.2.1. Mode-Coupling Analysis. The nonlinear contribution to the following three transport coefficients has been found: the microscopic, Onsager part of the chemical relaxation time L $[\tau_{T,P}^{-1} = L(\partial A/\partial\xi)_{P,T}]$, the diffusion constant D, and the shear viscosity η. According to the famous Green–Kubo formula, the transport coefficients can be written as time integrals of the correlations of appropriate fluxes, which, in turn, are expanded in powers of the hydrodynamic variables. One has to find the implications of the chemical reactions for the usually calculated divergences in α $[D=\alpha(\partial A/\partial\xi)_{P,T}]$ and η, as well as to see whether L has any nonlinear critical anomaly.

One can show$^{(8)}$ from general symmetry considerations that L has no mode-coupling corrections and it remains finite, as in the conventional theory of critical slowing down.$^{(11)}$ Such a notable difference in the critical behavior of L and α (which characterizes the diffusion process and has a strong singularity at a critical point) can be understood in the following manner. In contrast to diffusion, the homogeneous chemical reaction has no characteristic length, and therefore it is not influenced by the correlation length λ, which diverges at the critical point.

In calculations of critical corrections ΔD and $\Delta\eta$, we neglected the small critical index, assuming the Ornstein–Zernike form for the susceptibility. In turns out that the most significant contribution to $\Delta\eta$ is the integral over the wave numbers K of the form

$$\Delta\eta \sim \int_{K_1}^{K_2} [K^2\, dK/(K^3+LK^2)] \tag{38}$$

While the upper limit K_2 of the integral is related to an unimportant cutoff, the lower limit K_1, the inverse correlaqtion length λ^{-1} vanishes at the critical point. Where there is no reaction $(L=0)$ this integral diverges logarithmically at the critical point, $\Delta\eta \sim \ln\tau$. (In fact, a more careful calculation of $\Delta\eta$ leads to a weak-power divergence rather than a logarithmic one.) However, when $L\neq 0$ the integral (38) does not diverge. From this fact it turns out that the viscosity in reactive systems remains finite at the critical point. Notice that if L is extremely small (i.e., extremely slow chemical reaction), then η would grow approaching the critical point, but its growth would be terminated once the correlation length becomes of order of L^{-1}, $\lambda^{-3} \sim L\lambda^{-2}$.

The final result of calculations of the mode-coupling corrections to the wave number-(frequency)-dependent diffusion coefficient in reactive binary ΔD is$^{(18)}$

$$\Delta D = [K_{\mathrm{B}} T\lambda^{-1}/6\pi\rho\eta X^2][K(X) - \beta(X^3/Y^3)\,K(Y)] \tag{39}$$

where λ is the correlation length, $X=K\lambda$; $Y=X[\partial/(1+\partial+X)]^{1/2}$, $\partial = L/\eta$; $\beta = \partial/(1+\partial)$. The function $K(X)$ is

$$K(X) = (3/4)[(1+X^2)+(X^3-X^{-1})\,\mathrm{tg}^{-1}X]$$

When $L=0$ one comes back to the well-known result for nonreactive mixtures.$^{(23)}$ The influence of the chemical reaction on the diffusion coefficient can be easily seen in the two limiting cases of low frequencies $K\lambda < 1$ (the "hydrodynamic" region) and of high frequencies $K\lambda > 1$ (the "critical" region).

(a) For $K\lambda \ll 1$, $K(X) \sim X^2$, then

$$\Delta D \sim [K_B T \lambda^{-1}/6\pi\rho](1-\beta^{1/2}) \tag{40}$$

The usual result[23] $\Delta D \cdot \eta \sim \lambda^{-1}$ is recaptured. However, the coefficient is renormalized. Remembering that $D = \alpha(\partial A/\partial\xi)_{T,P}$, we conclude that since η is not divergent in reactive systems, α diverges like λ.

(b) For $K\lambda \gg 1$, $K(X) \sim (3\pi/8)X^2$, and

$$\Delta D \sim [K_B T \cdot K]/[16(\eta + L)\rho] \tag{41}$$

Again this result is similar to the case of a nonreactive binary mixture, except for the renormalization of the coefficient of K.

One concludes that the diffusion coefficient in reactive systems still vanishes like λ^{-1} with a modified coefficient of proportionality due to the chemical reaction.

The mode-coupling method has been used[25] for the analysis of the propagation of the sound in a reactive binary mixture near the critical point. Such an experiment, where the equilibrium state is minimally perturbed, could be a useful test for verification of the abovementioned singularities of rate of reaction and kinetic coefficients in reacting systems.

The general formula for the complex sound attenuation coefficient $\hat{\alpha}(\omega)$ has been obtained by Kawasaki.[23] The real and imaginary parts of $\hat{\alpha}(\omega)$ determine the observable sound attenuation $\alpha(\omega)$ and sound velocity changes $\Delta C(\omega)$, respectively. The existence of a chemical reaction results in an additional mechanism for the relaxation of the composition back to its equilibrium value. For nonreactive systems, relaxation is associated with diffusion. Just as diffusion processes show critical slowing down with a time scale $\tau_D \sim (DK^2)^{-1} \sim \lambda^3 \sim [(T-T_c)/T_c]^{-3\nu}$, the sound attenuation will show this critical behavior. On the other hand, if the chemical reaction is on a faster time scale than diffusion and shows the critical slowing down, then the sound attenuation will relax on a time scale $\tau_c \sim [(T-T_c)/T_c]^{-\gamma}$ (see Section 3.1). As $\gamma < 3\nu$, the chemistry is faster and will dominate the diffusion, which can be seen in sound experiments.

Notice that the diffusion coefficient $D(K)$ is wave number dependent and, according to Eq. (41), at high frequencies, $D \sim K$, i.e., the characteristic diffusion time scale will then be $\tau_D \sim (DK^2)^{-1} \sim K^{-3}$. This will finally occur on a faster time scale than the chemical reaction and the crossover will occur back to diffusion-controlled sound attenuation.

Finally, by plotting $\alpha(\omega)/\omega^2$ versus ω at various temperatures, one can see whether $\tau_D \sim [(T-T_c)/T_c]^{-3\nu}$ or $\tau_c \sim [(T-T_c)/T_c]^{-\gamma}$ yields a better dynamic scaling function. The calculated change in sound velocity $\Delta C/\omega^2 C$ for $\omega\tau \ll 1$ turns out(25) to be proportional to $(\omega\tau)^{1/2}$ in the nonreactive and to $\omega\tau$ in the reactive case.

4.2.2. Renormalization Group Methods.

The hydrodynamic equations (16)–(19) are written for the local space-averaged variables $\rho(r, t)$, $T(r, t)$. Similarly, the renormalization group technique allows one to use averages over increasing ranges, thereby reducing the number of effective degrees of freedom of the system considered. Such a procedure is of special importance near the critical points, where, due to divergence of the correlation length, the increasing number of degrees of freedom becomes important. The efficient computing schemes which have been developed for studying the static critical phenomena(26) have been extended to cover the dynamic critical phenomena.(24)

The starting point for the latter theory is the identification of the slow mode(s), whose relaxation times go to zero at small wave numbers, and also (if the order parameter is not conserved) the order parameter mode. Classifilcation of all possible cases (models A–H) with the proper results is given in ref. 24. One has therefore to allocate each system in which we are interested to the appropriate model of ref. 24. Such an identification depends also on the regions of wave numbers which define the relative importance of different modes.

The distinctive feature of reactive systems is the existence of a homogeneous chemical mode, which strictly speaking, converts the concentration into a nonconserved parameter. Milner and Martin(13) performed the renormalization group analysis of a reactive binary mixture, improving thereby the results of the linear analysis of the critical slowing down described in Section 3.1.

The results obtained(13) are presented in Table I for different regions of wave number defined (see Section 3.1) as $K_c = (D\tau)^{-1}$ and $K_H = (\lambda\tau)^{-1}$, where $\lambda = (k_T D/C_{P,\xi})(\partial A/\partial\xi)_{P,T}$.

Table I

Region	Slow critical mode	Type of model(24)	RG correction to critical slowing down
$K < K_H$	Heat	H	$\gamma - (18/19)\nu \approx 0.64$
$K_H < K < K_c$	Chemical	C	$\gamma + \alpha + \eta\nu \approx 1.37$
$K > K_c$	Diffusive	H	$\gamma - (18/19)\nu \approx 0.64$

Thus, the critical slowing down of a chemical reaction which occurs for $K_H < K < K_c$ is governed by the strong critical index $\gamma + \alpha + \eta\nu \approx 1.37$ rather than by $\gamma \approx 1.26$ obtained in the linear theory.(33)

5. PHASE SEPARATION IN REACTIVE SYSTEMS

5.1. Multiple Solutions of the Law of Mass Action

Until now we have considered single-phase reactive systems near their critical points. Another interesting problem is the phase separation in reactive systems as compared to that in nonreactive systems. Will the addition of a very small amount of catalyst [which promotes a chemical reaction(s) in a system] stimulate or restrict the coexistence of different phases, and accelerate or slow down the kinetics of phase separation? I consider the thermodynamic requirements in Section 5.2 and the kinetics in Section 5.3. To begin with, I consider the possibility of multiple solutions of the law of mass action. The two (or more) coexisting phases which have the same temperature and pressure are different, however, in concentrations of different components and, therefore, in conducting chemical reactions(s). The latter means that the law of mass action (2) has more than one solution at some temperatures and pressures. This existence of more than one equilibrium composition is very important for chemical engineers who calculate the phase diagrams of multicomponent reactive systems.

Let us clarify the physical reasons for the appearance of multiple solutions of the law of mass action. For a reaction taking place in a fluid the chemical potentials have the form

$$\mu_i = \mu_i^0(P, T) + K_B T \ln(x_i \gamma_i) \tag{42}$$

where the activities γ_i determine the deviation from the ideal systems where $\gamma_i = 1$. Using (42), one can write the law of mass action (2) as

$$x_1^{\nu_1} x_2^{\nu_2} \cdots x_n^{\nu_n} = K_{\text{id}}(P, T)\gamma_1^{-\nu_1} \cdots \gamma_n^{-\nu_n} \equiv K \tag{43}$$

The chemical equilibrium constant for the ideal system K_{id} is determined by the functions μ_i^0 in (42), i.e., by the properties of individual nonreacting components, while for the nonideal systems K depends also on the interactions among components. For the ideal systems all $\gamma_i = 1$, and Eq. (43) has a single set of solutions $x_1 \cdots x_n$ (The mathematical proof has been given by Aris.(27)) For nonideal systems the activities γ_i depend on the x_i; therefore for certain values of P and T, Eq. (43) can have more than one solution for the concentrations of reagents.

It is clear from these arguments that a system has to be considerably nonideal for the existence of multiple solutions of (43), i.e., the interaction energy must be of the order of the characteristic energy of a single particle. One possibility is for the interaction energy between particles to be high, as, for example, in a gas consisting of charged particles (plasma, electrolytes, molten salts, metal–ammonium solutions, solid-state plasma). Another possibility is when the characteristic energies of single particles are small, as in the case of isomers. We have considered in detail both the isomerization(28) and the dissociation(29) reactions. The isomerization reaction between different nonideal substances has also been considered by Caram and Scriven.(30) Othmer(31) extended this analysis to three-component mixtures with different single reactions.

Consider the ionization equilibrium of the chemical reaction of the form $A \rightleftarrows i + e$ (dissociation–recombination of the neutral particles into positive and negative charges). Neglecting the complications associated with the infinite number of bound states, assume that $K_{\mathrm{id}} \sim \exp(I_0/K_{\mathrm{B}}T)$, where I_0 is the ionization potential of a neutral particle. Under the assumption of Debye screening of the electrostatic interaction, one readily finds(29, 32) that

$$\begin{aligned} K = K_{\mathrm{id}} \exp[-\Phi(x, T)/K_{\mathrm{B}}T] &\approx \exp\{[I_0 - \phi(x, T)]/K_{\mathrm{B}}T\} \\ \phi(x, T) &\approx (8\pi x)^{1/2}(e^2/K_{\mathrm{B}}T)^{3/2} + Bx + \cdots \end{aligned} \tag{44}$$

where x is the concentration of charges, and the function B, which determines the pair correlation between charges, is tabulated in ref. 27.

At certain T (and P), Eq. (44) manifests several solutions for x which have a simple physical meaning. The function $\phi(X, T)$ in (44) diminishes the ionization potential I_0 as a result of screening. This means that the phase with the larger degree of ionization has higher energy and a higher entropy than the second phase. Hence, these two phases can have equal chemical potentials and can therefore coexist. The chemical reaction proceeds thereby in different ways in two coexisting phases. Therefore, the appearance of multiple solutions of the law of mass action is a necessary condition for the phase separation in reactive systems, where a chemical reaction proceeds in all phases.

5.2. Phase Equilibria in Reactive Binary Mixture: Isomerization and Dissociation Reactions

Let us assume that two components A_1 and A_2 participate in a chemical reaction of the form $\nu_1 A_1 \rightleftarrows \nu_2 A_2$ (Isomerization reaction corresponds to $\nu_1 = \nu_2$). The law of mass action (2) for this reaction becomes

$$\nu_1 \mu_1 - \nu_2 \mu_2 = 0 \tag{45}$$

If the system separates into two phases, their temperatures, pressures, and chemical potentials have to be equal:

$$\mu_i(P, T, x') = \mu_i(P, T, x''); \qquad i = 1, 2 \tag{46}$$

where x' and x'' stand for the concentrations of one of the two components in two phases. The ideal system is unique, but the range of nonideal behavior is so wide that the general analysis is very hard. I illustrate the general behavior on the simplest model of a strictly regular A_1–A_2 solution where the chemical potentials have the following form^(4):

$$\begin{aligned} \mu_1 &= \mu_1^0(P, T) + K_B T \ln x + w(1-x)^2 \\ \mu_2 &= \mu_2^0(P, T) + K_B T \ln(1-x) + wx^2 \end{aligned} \tag{47}$$

The coexistence curve is defined by Eq. (46), which by using (47), gives^(4) for the concentrations of the two coexisting phases $x' = 1 - x''$ and the symmetric coexistence curve:

$$\omega/K_B T = [\ln x - \ln(1-x)]/(2x-1) \tag{48}$$

The law of mass action (45) can be written, using (47), as

$$\omega/K_B T = [\ln(1-x) - \delta \ln x]/[\Delta + \delta(1-x)^2 - x^2] \tag{49}$$

where

$$\delta = -(\nu_1/\nu_2); \qquad \Delta = (\delta\mu_1^0 - \mu_2^0)/\omega \tag{50}$$

Phase separation in a reactive binary mixture will occur if and only if Eqs. (48) and (49) have a common solution. One can immediately see that Eqs. (48) and (49) coincide if both $\Delta = 0$ ("symmetric" mixture) and $\delta = 1$ (isomerization reaction). If $\delta = 1$, $\Delta \neq 0$, these equations have no common solution, and the strictly regular reactive binary mixture will not separate into two phases. In all other cases, one can equate the right-hand sides of Eqs. (48) and (49) to obtain

$$[(1-x)^2 \ln(1-x) - x^2 \ln x]/[\ln x - \ln(1-x)] = \Delta/(\delta - 1) \equiv q \tag{51}$$

The concentration x ranges from zero to unity. Therefore, Eq. (51) has a solution only for $q < (2 \ln 2 - 1)/4 = 0.097$. Only for substances and chemical reactions satisfying this inequality does the model of a strictly regular reactive binary mixture allow phase separation. If, for instance, $\Delta = 0.09$ and $\delta = 2$, the criterion $q < 0.097$ is satisfied, two phases may coexist, and their concentrations are given by intersection of the coexistence curve (48) and the law of mass action (49). In contrast, for $\Delta = 0.02$ and $\delta = 1$, the above-mentioned criterion is not satisfied, these two curves have no intersection, and hence there is no phase separation for this reactive system.

The noncompatibility of Eqs. (48) and (49) for some P, T, i.e., the nonexistence of a common solution for the concentrations in the range from zero to unity, may appear in the framework of some models in an n-component system with $n-1$ independent chemical reactions. In all other cases the existence of r chemical reactions will decrease by r the dimension of a coexistence hypersurface.

A ternary mixture with an ionization reaction is another example of phase separation in reactive systems. Let us consider a system composed of neutral particles which are partially dissociated into positive and negative charges. Now suppose that the Gibbs free energy has the following form:

$$G = N_A \mu_A^0 + N_1 \mu_1^0 + N_c \mu_c^0 + N_A K_B T \ln x_A + 2N_1 K_B T \ln x_1 + u_0 N_1 x_1^\alpha + N_1 I \tag{52}$$

where N_A is the number of neutral particles, N_1 (N_c) is the number of ions (electrons), and I is the dissociation energy. Owing to electron neutrality, $N_1 = N_c$. Here $x_A(x)$ is the concentration of atoms (ions): $x_A \equiv N_A/(N_A + 2N_1) = 1 - 2x$.

The first three terms in Eq. (52) describe the ideal gases of the particles. The next two terms are the entropy, and the sixth term represents the interaction between the charged particles. I keep the arbitrary power α in this term, although later I shall pass to the Debye–Hückel approximation, where

$$\alpha = 1/2; \qquad \mu_0 = -(e^3/3K_B T)(P/2\varepsilon^3 \varepsilon_0^3 \pi^2)^{1/2} \tag{53}$$

One can formulate the Debye–Hückel approximation using either the Gibbs or the Helmholtz free energy. If one goes from one to the other by using the ideal-gas equation of state in the correction term, the Debye–Hückel approximation looks slightly different. I use here the Gibbs free energy, and Eq. (53) follows from Eqs. (94.1) and (75.14) of Landau and Lifshitz.(33)

The chemical potentials of the neutral and charged particles can be easily found from (52),

$$\begin{aligned} \mu_A &= \mu_A^0 + K_B T \ln x_A - \alpha u_0 x^{\alpha+1} \\ \mu_q &= \mu_1 + \mu_c = \mu_1^0 + \mu_c^0 + 2K_B T \ln x + u_0[(\alpha+1)x^\alpha - 2\alpha x^{\alpha+1}] + I \end{aligned} \tag{54}$$

In order to find the coexistence curve, one has to equate according to (46) the chemical potentials in the two phases. Solving these two equations for $\alpha u_0/K_B T$ yields

$$\begin{aligned}\alpha\mu_0/K_B T &= [\ln(1-2x') - \ln(1-2x'')]/(x'^{\alpha+1} - x''^{\alpha+1})\\ &= 2\alpha(\ln x' - \ln x'')/[2\alpha(x'^{\alpha+1} - x''^{\alpha+1}) - (\alpha+1)(x'^{\alpha} - x''^{\alpha})] \qquad (55)\end{aligned}$$

One can immediately verify that Eq. (55) gives the following connection between the charge concentrations in the coexisting phases:

$$(x'/x'')^{\alpha} = (1-2x'')/(1-2x') \qquad (56)$$

For the Debye–Hückel interaction (53), the coexistence curve has the following form:

$$\begin{aligned} x' &= [1 - x'' - (2-3x'')^{1/2} x''^{1/2}]^{1/2}\\ -[e^3/6(K_B T)^2](P/2\varepsilon^3\varepsilon_0^3\pi^2)^{1/2} &= (\ln x' - \ln x'')/(x'^{3/2} - x''^{3/2}) \end{aligned} \qquad (57)$$

If the dissociation reaction $A \rightleftarrows I + e$ takes place, one has to add to the formula obtained the restriction stemming from the law of mass action, $\mu_A - \mu_1 - \mu_c = 0$. Using Eqs. (53) and (54), one can write the latter equation in the form

$$\mu_A^0 - \mu_1^0 - \mu_c^0 - I + K_B T \ln[(1-2x)/x^2] + (u_0/2)(3x^{1/2} - x^{3/2}) = 0 \qquad (58)$$

Neglecting the difference in the masses of atom and ion, we put $\mu_A^0 = \mu_1^0$. Furthermore, using the well-known expression for an ideal gas of electrons, one obtains from (58)

$$\begin{aligned}\ln[(P/K_B T)(2\pi h^2/m_e kT)^{3/2}] + I/K_B T - [\ln(1-2x)/x^2]\\ - [e^3/6(K_B T)^2](P/\pi^2 2\varepsilon^3\varepsilon_0^3)^{1/2}(3x^{1/2} - x^{3/2}) = 0 \qquad (59)\end{aligned}$$

Equation (59) gives the required restriction on the parameters of the coexisting phases following from the chemical reaction. One now has to find the simultaneous solutions of Eqs. (57) and (59). Unfortunately, it is hard to obtain analytical solutions. I will refer to these equations in Chapter 6, analyzing the liquid mercury experiments.

In the two simple examples under discussion(34) the concentrations of the coexisting phases have been found analytically. Usually one has to use numerical calculations already on this level.

5.3. Kinetics of Phase Separation in Reactive Systems

The behavior of nonreactive many-component systems "quenched" from an initial homogeneous stable state to a metastable state is well known.(35) The kinetics of phase separation proceeds in two clearly distinguished stages. During the first stage the system is located at the quenched state "waiting" for the appearance of a significant number of critical nuclei due to fluctuations (it is the duration of this stage that it usually called "the lifetime of the metastable state"). At the end of this first stage the system starts to separate into two phases, and after some "completion" time it achieves the two-phase equilibrium state.

This picture will change if one adds a small amount of catalyst to initiate a chemical reaction in this system. The thermodynamic consideration [the common solution of Eqs. (45) and (46)] gives necessary conditions for the phase separation. These conditions, however, turn out to be insufficient. Even when thermodynamics allows phase separation, it may be impossible from the kinetic point of view. Indeed, a chemical reaction leads to an additional driving force $A \neq 0$, shifting a system homogeneously from an initial quenched state to an equilibrium one. Only in the latter does the affinity A of the reaction vanish. Strictly speaking, for a reactive system the first stage of the nucleation does not exist. Immediately after a quench a system is shifted by the chemistry to the closest state on the coexistence curve (at the same temperature if one neglects the heat of reaction).

If a chemical reaction is fast enough, the homogeneous transition will occur before the appearance of the nuclei of the new phase, and the system will never separate into two phases. If the chemical reaction is slow compared with the rate of appearance of critical nuclei of a new phase, its presence does not influence the lifetime of the metastable state. For all intermediate rates of chemical reactions, their presence will increase the lifetime of the metastable state due to the shift toward the coexistence curve where the radius of the critical nuclei drastically increases.

These physical arguments can be supported by simple calculations.(36)

The traditional phenomenological approach to the decay of a metastable state in a pure substance is based on the distribution function $W(r, t)$ of nuclei of size r at time t.(35) The continuity equation has the form

$$\partial W(r, t)/\partial t = -[\partial J(r, t)|\partial r] = (\partial/\partial r)[FW + D(\partial W/\partial r)] \qquad (60)$$

where the flux $J(r, t)$ of nuclei along the size axes is determined by two unknown functions F and D. We have recently developed the critical dynamics approach to metastability,(37) according to which, for a nonconserved order parameter,

$$F(r) = D_0[(1/r) - (1/r_c)]; \qquad D(r) = D_0 K_B T/8\pi\sigma r^2 \qquad (61)$$

where D_0 is a typical diffusion coefficient far from the critical point and σ is the surface tension.

According to ref. 37, the problem of nucleation is subsumed within the larger class of general dynamic phenomena in the critical region. Then, one reduces the equation(s) of the critical dynamics to the Langevin equation for the radius of nuclei with a known random force, which, finally, can be transformed to the Fokker–Planck equation (60) with functions F and D given by Eq. (61).

The nucleation process in a binary mixture can be described in analogous fashion.$^{(38)}$ The formation energy of a nucleus containing n_1 molecules of component 1 and n_2 molecules of component 2 will be

$$\Delta G = (\mu_1^n - \mu_1)n_1 + (\mu_2^n - \mu_2)n_2 + 4\pi\sigma r^2 \tag{62}$$

where μ_1 and μ_2 are the chemical potentials of the components when they are in the homogeneous phase and μ_1^n and μ_2^n are the corresponding quantities when they are in nuclei. The size r of a nucleus is connected with its structure, namely $4\pi r^3/3 = v_1 n_1 + v_2 n_2$, where v_1 and v_2 are the volumes per molecule.

In contrast to a pure substances, the critical nucleus is now defined not only by its size r, but also by the concentration $x_1 = n_1/(n_1 + n_2)$. Therefore, the height of the potential barrier is defined by $\partial(\Delta G)/\partial r = \partial(\Delta G)/\partial x = 0$, which gives r_c (and x_c) of the critical nucleus:

$$r_c = 2\sigma[x_c v_1 + (1 - x_c)v_2]/[x_c\,\Delta\mu_1 + (1 - x_c)\,\Delta\mu_2] \tag{63}$$

where $\Delta\mu_i = \mu_i^n - \mu_i$.

Let us turn now to reacting systems. Here the concentration x changes as a result of a chemical reaction, which shifts the initial quanched state to the closest equilibrium state on the coexistence curve. Each intermediate state corresponds to a different radius of critical nucleus $r_c(t)$, increasing toward the coexistence curve, where $r_c \to \infty$. Hence, everywhere one has to replace r_c by $r_c(t)$. The latter function can be found from Eq. (63) under the assumption of a quasistatic chemical shift. This shift is caused by a chemical reaction, and can be described in the linear approximation as

$$dx/dt = -(x - x')/\tau \tag{64}$$

where τ^{-1} is the rate of the chemical reaction.

On substituting the solution of Eq. (64), $x - x' = (x_0 - x')e^{-t/\tau}$, into Eq. (63), one obtains

$$\begin{aligned} r_c(t) &= 2\sigma[x''v_1 + (1 - x'')v_2]/K_B T[(x''/x') - (1 - x'')/(1 - x')](x' - x'') \\ &\equiv r_0 e^{t/\tau} \end{aligned} \tag{65}$$

where I have used the coexistence condition (46), and the leading logarithmic part of the chemical potentials.

The next step will be to obtain and solve the Fokker–Planck equation for the distribution function $W(r, x, t)$ of nuclei of size r and composition x at time t. To this end, I make the following approximation. Assume that all the nuclei which are important for the phase separation have the same composition x'' and therefore omit the argument x in $W(r, x, t)$. In other words, one assumes that a chemical reaction brings the path leading to the saddle point closer to that of $x = x''$.

Substituting (61) and (65) into the Fokker–Planck equation (60) one obtains

$$\partial W/\partial t = \partial/\partial r\{D_0[1/r - 1/r_0 \exp(t/\tau)]\, W + (D_0 K_B T/8\pi\sigma r^2)\, \partial W/\partial r\} \tag{66}$$

Equation (66) contains two different time scales connected with the transient processes (of order of r_0^2/D_0) and with the chemical reaction (of order τ). Consider the quasi-steady-state regime which will be established once the transient process is over. The quasi-steady-state solution $W_{\mathrm{qss}}[r, r_c(t)]$ does not have an explicit time dependence, so that $\partial W_{\mathrm{qss}}/\partial t = 0$. The Fokker–Planck equation (66) can then be rewritten as

$$D_0[1/r - 1/r_0 \exp(t/\tau)]\, W_{\mathrm{qss}} + (D_0 K_B T/8\pi\sigma r^2)\, \partial W_{\mathrm{qss}}/\partial r = J_{\mathrm{qss}}(t/\tau) \tag{67}$$

The quasi-steady-state flux J_{qss} reduces to the steady-state flux J_{ss} when the chemical reaction is absent:

$$J_{\mathrm{qss}}[(t/\tau) = 0] = J_{\mathrm{ss}} \tag{68}$$

There is no stationary state at all for the reacting system considered here. Therefore, one is forced to given a new definition of the lifetime of a metastable state in reactive systems. The simplest generalization of the usual definition is

$$1 = \int_0^{T_{\mathrm{ch}}} dt\, J_{\mathrm{qss}}(t) \tag{69}$$

i.e., the time required to produce one critical nucleus. For the time-independent case J_{qss} is replaced, according to (68), by J_{ss} and T_{ch} by the lifetime of the metastable state in the nonreacting system $T_0 = J_{\mathrm{ss}}^{-1}$.

Let us turn now to the solution of Eq. (67). The boundary conditions for this equation are determined by the requirements that the distribution of nuclei of minimal size ξ will be the equilibrium one and that the total number of nuclei in the system is bounded:

$$W_{\mathrm{qss}}(\xi) = W_{\mathrm{eq}}(\xi); \qquad W_{\mathrm{qss}}(r \to \infty) = 0 \tag{70}$$

where W_{eq} corresponds to zero flux.

The solution of Eq. (67) which satisfies the boundary condition (70) has the form(37)

$$W_{\mathrm{qss}} = W_{\mathrm{eq}}(r)\left[1 - J_{\mathrm{qss}} \int_{\xi}^{r} (dr')/D(r')\, W_{\mathrm{eq}}(r')\right] \tag{71}$$

where

$$J_{\mathrm{qss}}^{-1} = \int_{\xi}^{\infty} dr'/[D(r')\, W_{\mathrm{eq}}(r')] \tag{72}$$

The function $W_{\mathrm{eq}}^{-1}(r')$ has a sharp maximum at r_c which reflects the existence of a barrier to nucleation. Therefore, the integral (72) can be evaluated easily by steepest descent. Then

$$J_{\mathrm{qss}} = (K_{\mathrm{B}} T/4\pi^2\sigma)^{1/2}(D_0/2r_0^2) \exp\{-2t/\tau - [\Delta G(r_0)/K_{\mathrm{B}} T]\, e^{2t/\tau}\} \tag{73}$$

where $\Delta G(r_0) = 4\pi\sigma r_0^2/3$ is the minimal work for producing the critical nucleus in the initial state immediately after a quench.

On introducing J_{ss} defined by (68) into (73), one obtains

$$J_{\mathrm{qss}} = J_{\mathrm{ss}} \exp[-2t/\tau - u(e^{2t/\tau} - 1)]; \qquad u \equiv \Delta G(r_0)/K_{\mathrm{B}} T \tag{74}$$

Finally, introducing (74) and $T_0 = J_{\mathrm{ss}}^{-1}$ in (69) gives the equation for the lifetime T_{ch} of a metastable state in a reacting system as a function of that in the nonreacting system T_0 (the latter depending on the volume under observation), the extent of quench u, and the rate τ^{-1} of the chemical reaction:

$$1 = (\tau e^{u} u/2T_0) \int_{u}^{u \exp(2T_{\mathrm{ch}}/\tau)} [\exp(-z)/z^2]\, dz \tag{75}$$

Equation (75) for T_{ch} has been solved numerically. This equation has no solution if τ is too small, i.e., if the chemical reaction is too fast. Then, although the thermodynamics allows phase separation in a reactive system, such a separation is impossible from the kinetic point of view. The system is dragged by a chemical reaction to a homogeneous equilibrium state on the coexistence curve before the nuclei of the new phase appear. The minimal τ which still allows the phase separation for different quenches (with characteristic u and T_0) is given approximately by the following formula:

$$(\tau/T_0)_{\mathrm{min}} \approx 3.03 + 2.08u \tag{76}$$

For all smaller values of τ, the system will never separate into two phases. The two possible sets of experiments performed with and without catalyst (different quenches for a given chemical reaction and different chemical reactions for the same quench) will be discussed in the next section.

5.4. Comments on the Geometry of Reactive Phase Diagrams

The effect of a chemical reaction on some characteristic points (surfaces) of the phase diagrams will be illustrated here with the help of three simple examples. I consider the types of critical points in reactive binary mixtures and the azeotropic and melting points of many-component reactive systems.

5.4.1. Upper and Lower Critical Solution Temperatures in Binary Reactive Mixtures. Different binary liquid mixtures show either concave-down coexistence curves on a temperature–concentration phase diagram with a so-called upper critical solution temperature (UCST) or concave-up curves with a lower critical solution temperature (LCST). Under the assumption of analyticity of the thermodynamic functions at the critical points, one can obtain the general thermodynamic criterion for the existence of UCST or LCST.(4) We show here that the existence of the chemical reaction may lead to the replacement of a UCST by an LCST and vice versa.(39) Moreover, the Clapeyron–Clausius equation for a binary mixture is determined by the chemical reaction in addition to the latent heat and the volume difference between the two phases.

Consider a mole of a binary mixture which separates into two phases B' and B''. The system can be described by four parameters P, T, x'_2, and x''_2 which satisfy the following conditions:

$$\mu'_1(P, T, x'_2) = \mu''_1(P, T, x''_2); \qquad \mu'_2(P, T, x'_2) = \mu''_2(P, T, x''_2) \tag{77}$$

Along the equilibrium surface between B' and B'' one can differentiate the equilibrium conditions (77). Using some simple thermodynamic relaxations, one obtains(4)

$$\begin{aligned} \Delta v_1\, dP - (\Delta h_1/T)\, dT - x'_2\, g'_{2x}\, dx'_2 + x''_2 g''_{2x}\, dx''_2 &= 0 \\ \Delta v_2\, dP - (\Delta h_2/T)\, dT + (1 - x'_2)\, g'_{2x}\, dx'_2 - (1 - x''_2)\, g''_{2x}\, dx''_2 &= 0 \end{aligned} \tag{78}$$

where h_i and v_i are the partial molar volume and enthalpy,

$$\Delta v_i \equiv v'_i - v''_i; \qquad \Delta h_i \equiv h'_i - h''_i$$

$$g'_{2x} \equiv (\partial^2 g'/\partial x'_2)_{P,T}; \qquad g''_{2x} \equiv (\partial^2 g''/\partial x''_2)_{P,T}$$

The partial derivatives of the intensive properties can be found from Eqs. (78) at constant pressure or constant temperature or constant concentration.(4) There is no need, however, to consider these special section of the coexistence surface when we deal with a reactive system. Indeed, for a reaction $\nu_1 A_1 + \nu_2 A_2 = 0$ an additional restriction to (78) exists in the form of the law of mass action

$$\nu_1 \mu'_1 + \nu_2 \mu'_2 = 0 \tag{79}$$

On differentiating the latter equation along the equilibrium surface, one finds

$$\begin{aligned}(\nu_1 v'_1 + \nu_2 v'_2)\, dP - [(\nu_1 h'_1 + \nu_2 h'_2)/T]\, dT \\ + [\nu_1(-x'_2 g'_{2x}) + \nu_2(1 - x'_2)\, g'_{2x}]\, dx'_2 = 0\end{aligned} \tag{80}$$

The common solutions of Eqs. (78) and (80) determine the slopes of the equilibrium line of a two-phase reactive binary mixture:

$$T\left(\frac{\partial P}{\partial T}\right)_{\text{chem}} = \frac{v'_{2x}(\Delta x_2)^2 - (2\Delta x_2/n')(\nu_1 h'_1 + \nu_2 h'_2)}{h'_{2x}(\Delta x_2)^2 - (2\Delta x_2/n')(\nu_1 v'_1 + \nu_2 v'_2)} \tag{81}$$

$$\left(\frac{\partial T}{\partial x'_2}\right)_{\text{chem}} = \frac{2Tg'_{2x}\,\Delta x_2 + Tn' v'_{2x}(\Delta x_2)^2(\nu_1 v'_1 + \nu_2 v'_2)^{-1} g'_{2x}}{h'_{2x}(\Delta x_2) - v'_{2x}(\Delta x_2)(\nu_1 h'_1 + \nu_2 h'_2)(\nu_1 v'_1 + \nu_2 v'_2)^{-1}} \tag{82}$$

where $n' \equiv \nu_1 x'_2 - \nu_2(1 - x'_2)$; here $h' \equiv (1 - x'_2) h'_1 + x'_2 h'_2$ and $v' \equiv (1 - x'_2) v'_1 + x'_2 v'_2$ are the heat of reaction and the volume change of reaction in phase B'.

In the absence of a chemical reaction, all but the first terms in the denominators and numerators of Eqs. (81) and (82) vanish and those reduce to the well-known forms(4)

$$T\left(\frac{\partial P}{\partial T}\right)_{x'_2} = \frac{v'_{2x}}{h'_{2x}} \tag{83}$$

$$\left(\frac{\partial T}{\partial x'_2}\right)_P = \frac{2Tg'_{2x}\,\Delta x_2}{h'_{2x}(\Delta x_2)^2} \tag{84}$$

Equation (81) provides the generalized form of the Clapeyron–Clausius equation (83) for a reactive mixture, while Eq. (82) determines the criterion of UCST and LCST. The latter can be obtained just as one obtains it from (84) for nonreactive systems.(4)

The "classical" expansion near the critical points $[g'_{2x} \approx \frac{1}{8} g'_{4x}(\Delta x_2)^2 - (h^{\text{cr}}_{2x}/T)\,\delta T$, etc.] results in

$$\left(\frac{\partial T}{\partial x'_2}\right)_P \sim \frac{Tg'_{4x}(x'_2 - x''_2)}{4h^{\text{cr}}_{2x}} \tag{85}$$

If $x_2'' > x_2^{\text{cr}} > x_2'$, then $(\partial x_2'/\partial T)_P$ is positive if $h_{2x}^{\text{cr}} \equiv (\partial^2 h/\partial x^2)^{\text{cr}}$ is negative. These signs define a UCST. Analogously, an LCST corresponds to $(\partial^2 h/\partial x^2)^{\text{cr}} > 0$.

Performing a similar expansion near the single critical point of a reactive binary mixture, one obtains from Eqs. (81) and (82)

$$T\left(\frac{\partial P}{\partial T}\right)_{\text{chem}} \sim \frac{\nu_1 h_1^{\text{cr}} + \nu_2 h_2^{\text{cr}}}{\nu_1 v_1^{\text{cr}} + \nu_2 v_2^{\text{cr}}} \tag{86}$$

$$\begin{aligned}\left(\frac{\partial T}{\partial x_2}\right)_{\text{chem}} &\sim T g_{4x}'(x_2' - x_2'')\left(h_{2x}^{\text{cr}} - v_{2x}^{\text{cr}}\frac{\nu_1 h_1^{\text{cr}} + \nu_2 h_2^{\text{cr}}}{\nu_1 v_1^{\text{cr}} + \nu_2 v_2^{\text{cr}}}\right)^{-1} \\ &\sim T g_{4x}'(x_2' - x_2'')h_{2x}^{\text{cr}}\left(1 - \frac{\nu_1 h_1^{\text{cr}} + \nu_2 h_2^{\text{cr}}}{\nu_1 v_1^{\text{cr}} + \nu_2 v_2^{\text{cr}}}\,\frac{dT_c}{T_c dP}\right)^{-1}\end{aligned} \tag{87}$$

Equation (83) was used in the last relation in (87). As is clear from (87), the existence of a chemical reaction may change the type of the critical point (UCST to LCST or vice versa) if the last bracket in (87) is negative. The ratio of the second derivatives $v_{2x}^{\text{cr}}/h_{2x}^{\text{cr}}$ can be replaced by the ratio of excess volume V_E and excess entalphy h_E at the critical point.

Thus, a chemical reaction will change the type of the critical point if the following (equivalent) inequalities are satisfied:

$$\frac{\nu_1 h_1^{\text{cr}} + \nu_2 h_2^{\text{cr}}}{\nu_1 v_1^{\text{cr}} + \nu_2 v_2^{\text{cr}}}\,\frac{V_E^{\text{cr}}}{h_E^{\text{cr}}} > 1 \quad \text{or} \quad \frac{\nu_1 h_1^{\text{cr}} + \nu_2 h_2^{\text{cr}}}{\nu_1 v_1^{\text{cr}} + \nu_2 v_2^{\text{cr}}}\,\frac{1}{T_c}\,\frac{dT_c}{dP} > 1 \tag{88}$$

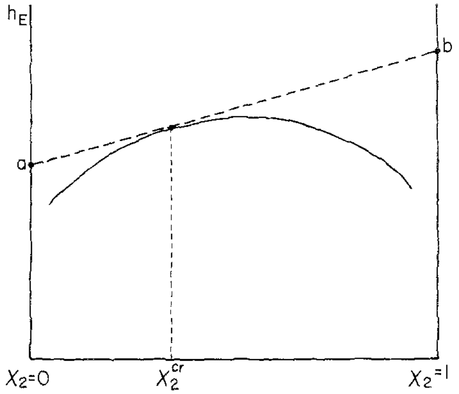

Fig. 1. The typical form of the excess enthalpy h_E (or excess volume V_E) for a binary mixture as a function of concentration. Points a and b correspond to the critical molar enthalpy of pure substances.

The form of the critical line near the critical point dT_c/dP as well as V_E and h_E can be found in refs. 40 and 41. Some typical examples of positive V_E and h_E are shown in Fig. 1. Using the definition of the partial molar quantity $y_1 = y - x_2(\partial y/\partial x_2)_{T,P}$, where $y \equiv \{h, v\}$, one can see that the points a, b in Fig. 1 give h_1^{cr} and h_2^{cr} (or analogously, $v_1^{\text{cr}}, v_2^{\text{cr}}$). For an isomerization reaction, $\nu_1 = -\nu_2 = 1$ and (88) becomes

$$\frac{h_1^{\text{cr}} - h_2^{\text{cr}}}{h_E^{\text{cr}}} \frac{V_E^{\text{cr}}}{v_1^{\text{cr}} - v_2^{\text{cr}}} > 1 \tag{89}$$

There are no physical reasons why the criterion (89) should not be satisfied for some mixtures. Then, the presence of a chemical reaction will change USCT to LSTP and vice versa.

5.4.2. Azeotropic Points in Reactive Many-Component Systems.

A typical temperature–composition projection of the T–x'–x'' equilibrium surface (at constant pressure) is shown in Fig. 2. This mixture forms an azeotropic point A, where(40) "distillation (or condensation) takes place without change of composition." The azeotropic states, like the critical states, do not exist for ideal nonreactive mixtures.

The situation is quite different for reactive mixtures. It turns out(5) that for reactive systems an azeotropy exists even for ideal mixtures, and it is no

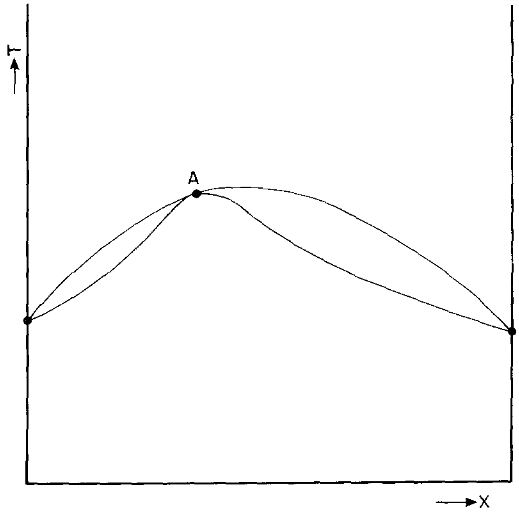

Fig. 2. Liquid–gas equilibrium in a binary mixture, showing the azeotropic point A.

longer defined by the equality of phase compositions. For reactive mixtures the latter condition is replaced for c-component two-phase systems by

$$(x_1''-x_1')/(\nu_1-\nu_T x_1')=(x_i''-x_i')/(\nu_i-\nu_T x_i'); \qquad i=1,2,\dots,c-1 \tag{90}$$

where $\nu_T=\sum_{i=1}^{c}\nu_i$.

A simple proof$^{(5)}$ of Eq. (90) is based on the conservation laws in a closed system in which a c-component liquid mixture is being vaporized at constant pressure (or at constant temperature). The material balance for component i gives

$$\frac{d(V'x_i')}{dt}+\frac{d(V''x_i'')}{dt}=\nu_i\frac{d\xi}{dt}; \qquad i=1,2,\dots,c-1 \tag{91}$$

where V' and V'' are the molar volumes of the two phases and ξ is the extent of reaction. Using now the overall balance

$$dV'/dt+dV''/dt=\nu_T\,d\xi/dt \tag{92}$$

one can rewritte Eq. (91) in the following form:

$$V'\frac{dx_i'}{dt}+V''\frac{dx_i''}{dt}=(\nu_i-\nu_T x_i')\frac{d\xi}{dt}-(x_i''-x_i')\frac{dV''}{dt}; \qquad i=1,2,\dots,c-1 \tag{93}$$

During the azeotropic transformation, the composition of each phase is constant, i.e., $dx_i'/dt=dx_i''/dt=0$, and (93) reduces to

$$(x_i''-x_i')/(\nu_i-\nu_T x_i')=(d\xi/dt)/(dV/dt); \qquad i=1,2,\dots,c-1 \tag{94}$$

The right-hand side of (94) does not depend on i, which thereby proves Eq. (90).

5.4.3. Effect of Chemistry on the Solubility Curves of Binary Mixtures.

Consider the phase diagram near the melting point for a two-phase system consisting of a solid component AB which dissociates completely on melting and the liquid of the same composition. The T–x_B projection of the phase diagram is shown in Fig. 3, where T^+ is the melting point, the vertical line at $X_B=1/2$ describes a solid phase, and the dashed lines relate to liquid phases with concentrations larger and smaller than 1/2. The existence of two branches of the solubility curve can be explained by the lowering of the melting point by the addition or removal of one component. The solubility lines, therefore, meet in a point at $T=T^+$.

Let us now allow a chemical reaction (dissociation) in the liquid phase:

$$\mathrm{AB}\rightleftarrows \mathrm{A}+\mathrm{B} \tag{95}$$

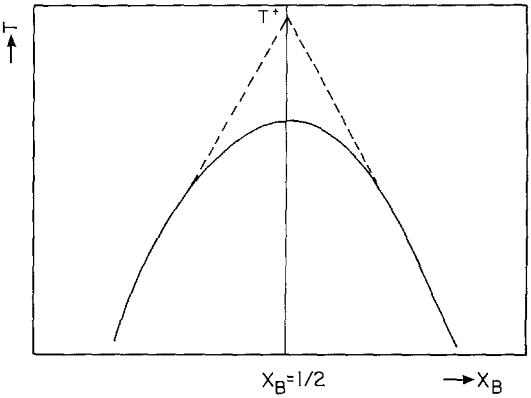

Fig. 3. Liquid–solid solubility curves for compound AB with (solid curve) and without (dashed lines) the dissociation reaction.

Then, the solubility curves will be rounded at $T = T^+$, as is shown in Fig. 3 by the solid curves. The solubility curves become more and more rounded with an increase of the degree of dissociation. This may be shown as follows.

Let the liquid solution have the total compositions X_A, X_B and the detailed composition y_A, y_B, y_{AB} $(y_A + y_B + y_{AB} = 1)$. The chemical potential of AB in the solution must be equal to that in the solid (which plays the role of the chemical potential "bath" for the solution). The chemical potential of the solid depends only on temperature, and therefore one may assume that for small degrees of dissociation y_{AB} is a function of T alone, say $y_{AB} = f(T)$.

Let us introduce now the small parameter ξ to describe the left part of the melting curves $(X_B < \frac{1}{2})$:

$$\xi = 2(\tfrac{1}{2} - X_B) \tag{96}$$

The x, y variables are connected by the relation

$$X_B = (y_B + y_{AB})/(y_{AB} + y_B + y_{AB} + y_A) \tag{97}$$

Using Eqs. (95) and (96) and the relations $y_{AB} = f(T)$ and $y_A + y_B + f(T) = 1$, one obtains

$$y_A = \frac{1 - f(T)}{2} + \frac{\xi}{2}[1 + f(T)]; \qquad y_B = \frac{1 - f(T)}{2} - \frac{\xi}{2}[1 + f(T)] \tag{98}$$

Assuming that the dissociation is small and therefore the solution is ideal, one can write the law of mass action for the reaction (95):

$$y_A y_B = K(T) \tag{99}$$

Substituting (98) in (99), one can rewrite the latter in the form

$$\xi^2 = [1 - f(T)]^2/[1 + f(T)]^2 - 4K(T)/[1 + f(T)]^2 \equiv Q(T)^2 - R(T)^2 \tag{100}$$

At $T = T^+$, $\xi = 0$, i.e., $Q(T^+) = R(T^+)$. Expanding Eq. (100) near (T^+, $\xi = 0$), one obtains

$$\xi^2 = 2Q(T^+)[R'(T^+) - Q'(T^+)](T^+ - T) + \cdots \tag{101}$$

Equation (101) describes a melting line in the presence of a chemical reaction (solid curve in Fig. 3).

We now turn to the case of a nonreacting mixture. Then, $K(T) = 0$, and the first term in a series expansion of Eq. (100) near T^+, $\xi = 0$ is of the second order in $(T^+ - T)$:

$$\xi^2 = Q'(T^+)^2 (T^+ - T)^2 + \cdots \tag{102}$$

i.e., the melting lines in this case meet at a point (the dashed curves in Fig. 3).

The reason for the difference between Eqs. (101) and (102) was explained as early as 1892.(42) If in the solution there were any appreciable dissociation of AB into its constituents, then, in contrast to the nondissociated solution, an infinitesimal addition of either component does not change the equilibrium temperature. Therefore, the melting point is a true maximum of a solid curve [Eq. (101)] and not a kink [Eq. (102)].

A more general consideration, including the more complicated compounds(43) $A_n B_m$ and the strictly regular solution model(44) (instead of an ideal one), leads to similar results.

A further development of these ideas has been presented recently by Krichevskii *et al.*(45,46) They considered the influence of a third component on the thermodynamics of the three-phase equilibrium among a solid phase (a compound of AB_m, a solvent B with a dissolved substance A), a liquid phase (a solution saturated with this component and extremely dilute with respect to component C), and a gas phase (the vapor of the pure solvent B, as the components A and C are assumed to be nonvolatile).

For a nondissociated system the change of the fugacity of the solvent B (which for the low saturated vapor pressure coincides with the partial pressure) due to the addition of a small amount of C is given by(47)

$$\ln[P_{B,(ABC)}/P_{B,(AB)}] = -n_C/n_B\,; \qquad dP = 0; \qquad dT = 0 \tag{103}$$

where $P_{B(AB)}$ and $P_{B(ABC)}$ are the respective partial pressures of the solvent in binary and ternary solutions at the same temperature; n is the number of moles of the components.

Let us allow now the chemical reaction (dissociation) in the solution

$$AB_m \rightleftarrows A + mB \tag{104}$$

The chemical potential of the compound AB_m in solution which coexists with a solid is fixed and depends only on the temperature. The fugacity γ of the nonvolative component A can be replaced by the activity a. Therefore, the law of mass action for the reaction (104) can be written as

$$a_A \gamma_B^m = K \tag{105}$$

or in differential form

$$d(\ln a_A) + md(\ln \gamma_B) = 0; \qquad dP = 0; \qquad dT = 0 \tag{106}$$

Combining the last equation with the Gibbs–Duhem equation[4]

$$n_A\, d(\ln a_A) + n_B\, d(\ln \gamma_B) + n_C\, d(\ln a_C) = 0; \qquad dP = 0; \qquad dT = 0 \tag{107}$$

one obtains

$$d(\ln \gamma_B) = -n_C\, d(\ln a_C)/(n_B - mn_A) \tag{108}$$

Assuming that the solution is very dilute with respect to C, one can replace the activity a_C by the number of moles n_C.

After integration of Eq. (108), we have

$$\ln \frac{\gamma_{B,(ABC)}}{\gamma_{B,(AB)}} = \ln \frac{P_{B(ABC)}}{P_{B(AB)}} = -\frac{n_C}{n_B^0 - mn_A^0} \tag{109}$$

For the chemical reaction of the form (104) the difference $n_B - mn_A$ remains constant. Consequently, we replace n_B and n_A in (109) by the total number of moles of the components n_B^0 and n_A^0 in both liquid and solid phases.

At $m = 0$, Eq. (109) is reduced to Eq. (103). At the melting point in Fig. 3 (which was drawn for $m = 1$) where two branches of the solubility curves meet, the compositions of the solid and liquid phases are equal, and the denominator of Eq. (109) is reduced to zero. Addition of component C to solutions must, on the left branch ($n_B > mn_A$) decrease, and on the right branch ($n_B < mn_A$) increase, the value of $P_{B(ABC)}$.

The immediate vicinity of the melting point is of special interest. On approaching the melting point along the left branch, the right-hand side of

Eq. (109) tends to $-\infty$, and on approaching along the right branch, it tends to $+\infty$. Then, $P_{B(ABC)}$ must correspondingly decrease to zero and increase to infinity. Both of these values (0 and ∞) are physically impossible. In fact, $P_{B,(ABC)}$ on the left branch may not be less than the dissociation pressure of the compound in solution and on the right branch $P_{B,(ABC)}$ cannot exceed the saturated vapor pressure of the pure solvent.

I consider in Section 6 some of the experimental verifications of these predictions for nonelectrolyte(45) and electrolyte(46) systems.

6. POSSIBLE EXPERIMENTAL VERIFICATION

6.1. Chemical Anomalies

Although there are no systematic experimental results concerning the mutual influence of the chemical reactions and the critical phenomena, I have found some indications of the critical slowing down reported as early as 1931.(48) A very rapid decrease of the reaction velocity was found there near the critical point of hydrogen chloride and propylene.

In 1946 Toriumi *et al.*(49) reported increases in the rate of oxidation of NH_3 and of SO_2 near their respective critical points.

The distinguished Russian physical chemist I. R Krichevskii in his pioneering experiments studied the influence of the critical environment on the chemical reactions. He studied(16) the dissociation–recombination equilibria $N_2O_4 \rightleftarrows 2NO_2$ in dilute solution in CO_2 in proximity to the critical point of the mixture (which for this dilute solution is very close to that of pure CO_2). A strong increase was found in the concentrations of NO_2 when the temperature was lowered toward the critical temperature. Two other experiments performed by Krichevskii and his collaborators are concerned with chemical kinetics. They irradiated pure Cl_2 in one case(50) and I_2 in CO_2 in the other case(51) with light. In both cases the irradiation results in the dissociation of the diatomic molecules into atoms. Under normal conditions, when the irradiation is stopped, a rapid recombination restores the chemical equilibrium. When the experiment was conducted under critical conditions (near the liquid–gas critical point of the pure Cl_2 or the binary CO_2–I_2 mixture, respectively) the recombination rate according to Krichevskii is dramatically slowed down. Although Krichevskii's interpretation of his experiments was wrong (see below), he should be given credit for his attention to the issues.

To make the picture complete, one should mention the experiments of Snyder and Eckert,(52) where two types of reactions were run in a binary mixture (such as water–triethylamine) that served as a solvent. The reaction rates were measured near the critical point of phase separation. In one case the reaction rate somewhat decreased (by 25%) compared to noncritical conductions, but in the other case it increased.

Krichevskii's experiments gave the initial impetus for our interest in chemistry in the "critical wonderland," and we tried(8, 14) to explain his experiments. It turns out, however, that the situation is more complicated than expected. First, the equilibrium experiments(16) were performed at constant volume rather than at constant pressure as considered in Section 3.2. Second, Krichevskii's photoexcitation experiments(50, 51) probe fluctuations of vanishing wavenumber rather than those located in the region K_H–K_c discused in Section 2.1. According to refs. 13 and 15, in both these cases the singularities do exist, but they are governed by the weak rather than by the strong critical index. Moreover, Morrison insists(17) on a different interpretation of Krichevskii's equilibrium results,(16) considering them as due to critical opalescence rather than a result of the critical enhancement in the extent of reaction.

Recently, Greer(53) repeated the experiment of Krichevskii(50) and found that for the $Cl_2 \rightleftarrows 2Cl$ reaction the recombination time near the critical point is still very fast, and the slowing down, if any, can be checked by the use of picosecond spectroscopy. The latter result does not contradict the theoretical prediction described in Section 3.1 about the absence of a strong singularity in the chemical relaxation rate of spatially homogeneous fluctuations. Greer concludes(53) that the long relaxation times obtained by Krichevskii(50) are connected with thermal effects and not with the slowing down of the reaction rate.

Recently Tveekrem *et al.*(54) studied the dimerization of NO_2 ($2NO_2 \rightleftarrows N_2O_4$) near the liquid–liquid critical point of the binary mixture perfluoromethylohexabe + carbon tetrachloride. They observed a small decrease in dimerization near T_c (of about 4%) decribed by the weak critical index. In another article Greer(55) suggested measuring a one-component system near its liquid–gas critical point, in which the reaction is an intramolecular transformation, such as the boat-chair conformation transformation in cyclohexane. According to Section 3, one expects a strong effect in this case.

6.2. Critical Points and Critical Indices in Reactive Mixtures

Due to the additional constraint (the law of mass action), a chemical reaction decreases the number of thermodynamic degrees of freedom. For example, a binary mixture with a chemical reaction behaves like a one-component system, i.e., has an isolated critical point instead of a line of critical points. To my knowledge, even this basic statement has not been proved experimentally.

Reactive binary mixtures having a miscibility gap are the simplest objects for an experimental test of the theoretical predictions. In order to have a second instability analogous to the liquid–liquid instability in a reactive mixture, the liquid–gas critical curves in the P–T or P–X planes for this mixture (without chemical reaction) must differ significantly from straight lines.(28) The comparative values of the heat of reaction H and the heat of mixing J give another indication of the existence of both a chemical reaction and a miscibility gap. This is the case when H is of order J (the model consideration(28) gives $|H| \lesssim 4J$). The *cis–trans* mixtures might show such behavior. For example, for the mixture *cis–trans* dichlorethylene, $J \approx 155$ cal/mole(56) and $H \approx 500$ cal/mole.(57) Once an appropriate system is chosen, one expects to find different critical indices for, say, specific heat measurements with and without a chemical reaction, i.e., when the interconversion of the isomers (the chemical reaction) is stimulated by adding a catalyst or by photochemistry.

It should be noted that miscibility and isomerization contradict one another. In fact, the isomers have to be similar enough to allow interconversion. On the other hand, miscibility requires substantial differences between isomers. It is likely, therefore, that such an experiment can be performed more easily in a many-component system.

6.3. Attenuation of Sound in Reactive Systems

Only sound experiments have been performed so far for revealing the critical contribution to the transport coefficients in reactive systems. Sound attenuation and the velocity of ultrasound have been measured(58) in the homogeneous solution of isobutyric acid and water near the liquid–liquid critical point. All the parameters were known from independent experiments. However, it turned out that one cannot describe the experimental data by the use of these parameters unless the additional mechanism of absorption is taken into account. The latter is caused by a chemical reaction whose rate has an anomaly in the critical point described by the critical index in the interval 1.0–1.25, while the theory (Section 4) predicts the weak critical index for this case. Therefore, this experiment needs an additional refinement.

6.4. Phase Separation in Systems with Dissociation Reactions

Order–disorder phase transitions and critical phenomena in electrically neutral systems originate from the competition between the repulsive and attractive forces. When charged particles appear due to the dissociation–recombination reaction, they give rise to new attractive forces (the Coulomb interaction between ions, which is, on average, an attractive interaction) and repulsive forces (say, the hard-core interaction at short distances). These new competing forces result in an additional first-order phase transition in a three-component plasma with a critical point. The coexisting phases for a new phase transition following from the chemical reaction are determined by Eqs. (57) and (59) of Section 5.2. It has been proposed(59,21,34) that these arguments can be used for an explanation of some experiments in metallic vapors at high pressures and in the metal–ammonia solutions.

Metal–ammonia solutions provide a type of system where an increase of a (small) concentration of metal results in a huge increase of electroconductivity manifesting a transition from nonmetallic to metallic conductivity. Metallic vapors are another example of the latter behavior. The continuous decrease in the density of metals with heating above the critical temperature causes transition into the nonmetallic state and a significant decrease of the electrical conductivity.

The most common and general explanation of the nature of this transition has been given by Mott,(60) who considered the following elegant physical argument. Mott argued that changing the number density n of charges interacting with the screened Coulomb interaction eliminates the bound states when $a_B n^{-1/3} \approx 0.25$, and hence the system will become metallic. (Here, a_B is the Bohr radius in the medium.) Despite the generality of the Mott criterion, not all metal–nonmetal transitions can be thus explained. Sometimes the transitions take place at densities lower than those predicted by the Mott criterion(61); in other systems there is more than one transition. Let us consider two examples in more detail.

The liquid–gas critical point of mercury occurs at a density $\rho_c = 5.77 \text{ g cm}^{-3}$ ($P_c = 1670$ bar; $T_c = 1750$ K). Upon expansion, a metal–nonmetal transition takes place at $\rho \approx 9 \text{ g cm}^{-3}$. It is generally accepted (see, however, ref. 62) that the latter transition is adequately explained by the Mott criterion. However, a dielectric anomaly has recently been found(63) at a density $\rho \approx 3 \text{ g cm}^{-3}$. The latter was interpreted as a transition from a weakly ionized mercury plasma to a new inhomogeneous phase with charged droplets. This transition, probably of first order, occurs at densities much lower than those in the Mott theory, and therefore requires further explanation.

The second example is even more conclusive. The heat capacity of sodium–ammonia solution has been measuired for three different molar fractions of metal ($x = 0.045$, 0.0462, and 0.0631).(64) Starting at low temperatures, the heat capacity shows a jump across the liquid–gas separation curve of this mixture. However, upon further heating, two more jumps in the heat capacity occur(64) at two distinct temperatures above the critical one. The changes in slope of the electromotive force take place at the same temperatures,(65) providing additional evidence for the first-order phase transition above the liquid–gas critical point. Experimental observation of this new phase transition is very difficult because of the very small density differences between two phases and the existence of slow diffusion processes. The former calls for high homogeneity of the temperature, and the latter results in very long relaxation times. I believe that the above-mentioned and other experimental problems prevent the observation of this new thermodynamic phase transitions for other systems, while its existence seems to be obvious for a broad class of systems. In addition to the metal vapors and the metal–ammonia solutions, one can mention molten salts, weak electrolytes, solutions of metals in their salts, electron–hole plasmas in optically excited semiconductors, etc.

One has to assume very detailed models in order to explain a new phase transition in metal–ammonia solutions. Therefore, I restrict myself to an application of Eqs. (57) and (59) for an explanation of the dielectric anomaly in liquid mercury. I adopt the following numerical procedure. For a given I and ε, one starts from some x' which gives x'' and two equations for T and P. The ionization potential is taken to be 10.43 eV, which is the value for the isolated mercury atom. The choice of the dielectric constant ε is much more complicated, and I choose the two reasonable values $\varepsilon = 1.7$ and $\varepsilon = 1.8$. Assuming values for I and ε, one can proceed now to the calculation of the x', x'', P, and T for the two coexisting phases using Eqs. (57) and (59). The locus of the temperature and pressure of our phase transition is very close(34) to the locus of the onset of the dielectric anomaly observed in ref. 63. I do not claim to have a quantitative explanation of the experimental results, due to the specific model used and the uncertainty of the value of the dielectric constant in two coexisting phases.

6.5. Decay of Metastable States in Reactive Systems

I do not know of any experiments of this kind. The *cis–trans* isomeric systems seem to be appropriate substances where the chemical transformations can be induced by a catalyst or by photochemical methods.

6.6. Criterion for Upper (Lower) Critical Point in Reactive Mixtures

I do not know of any experimental study of the influence of a chemical reaction on the critical point. A possible experimental strategy is to measure the equilibrium line near the critical point with and without a small amount of catalyst. Then, if the criterion (88) or (89) is satisfied, heating will bring the reactive mixture to the critical point, in contrast to cooling for the equivalent nonreactive mixture.

6.7. Azeotropy in Reactive Mixtures

In contrast to the previous two subjects, the experimental use of chemical reactions for the distillation process goes back to the 1920s. All the usual methods of separation do not work for mixtures of components with boiling temperatures close to each other, such as isomers. The idea of reactive distillation is to add a catalyst (entrainer) which reacts preferentially with one of the isomers. Then the second isomer will be taken off as distillate, and the first isomer, a catalyst, and reaction products will remain. The process can be repeated until the full separation of isomers. There are dozens of examples(66,67) widely used in many chemical processes.

6.8. The Solubility Curve of Dissociable Solute

The classical examples of the influence of dissociation in the liquid state on the curvature of the solubility curve near the melting point are hydrated salts such as sodium thiosulfate $Na_2SO_4 \cdot 5H_2O$, sodium acetate $NaC_2H_3O_2 \cdot 3H_2O$, and the best known example, calcium chloride hexahydrate $CaCl_2 \cdot 6H_2O$. This salt may dissociate in the liquid according to $CaCl_2 \cdot 6H_2O = CaCl_2 + 6H_2O$, which flattens the solubility curve in Fig. 3. The influence of a third component on the above phenomenaon has been studied experimentally by Krichevskii *et al.*(45,46) They added small amounts of sucrose, fructose, and urea to saturated acqeous solution of crystal hydrates of $Na_2SO_4 \cdot 10H_2O$ and $Mg(NO_3)_3 \cdot 6H_2O$. The data obtained for all systems were in very good agreement with Eq. (109). The results of measurements of $\ln(P_{B(ABC)}/P_{B(AB)})$ as a function of $n_C/(n_B - mn_A)$ lay on a single straight line havinig a slope -1.(45) Moreover, the information relating to partial pressures was used to calculate m in the dissociation equation (104). The results, $m = 10.1 \pm 0.1$ for $Na_2SO_4 \cdot 10H_2O$ and $m = 5.9 \pm 0.1$ for $Mg(NO_3)_2 \cdot 6H_2O$, support the use of this method of determining m for cases where it is difficult to analyze the basic phase directly, say, due to high solution viscosity.

The interesting task of studying the immediate vicinity of the melting point is still awaiting experimental verification.

Additional experiments have been performed for the cases when the third component is a strong electrolyte [NaCl, KCl, $Mg(NO_3)_2$]. Experiments again supported the theoretical predictions.(46)

We are looking forward to new experiments relating to the peculiar chemical behavior near the critical point.

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