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Singularity in the degree of dissociation near a critical point

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Anomalies in the degree of dissociation near a critical point of a ternary mixture are analyzed for a reaction of the type $A \rightleftarrows B + C$. The concentration-temperature curve has, at the critical point, an infinite slope $(T - T_c)^{-(\delta-1)/\delta}$, where δ is the critical index. An isobutyric acid and water mixture, which consists of four components, has the same singularity in the charge density near a critical point. In any of the anomalies in the electrical conductivity in this mixture, or in similar systems, the singularity in the charge density must be considered.

The mixture isobutyric acid and water has an upper consolute point located at atmospheric pressure and room temperature ($T_c \approx 26.23\,^\circ\mathrm{C}$ and 38% weight fraction of acid). The chemical reaction $HA + H_2O \rightleftarrows A^- + (H_3O)^+$ produces charges that show anomaly in electroconductivity near the critical point. Stein and Allen found[1] that the singular part of the resistance has an energy-density-type anomaly approaching the critical point. Theoretical explanations for this anomaly have been based on different models for scattering of charges by strongly enhanced concentration fluctuations.[2] However, Jasnow, Goldburg, and Semura, at the end of their 1973 article,[3] referred to an unpublished remark by Griffiths, who noted that the ion density itself may have a singularity near the critical point due to the chemical reaction. As will be shown, this Griffiths supposition is correct. Therefore, an analysis of the electroconductivity near the critical point must include the singularity in the ion density together with (or instead of) possible anomalies of scattering processes.

Recently[4] we have discussed anomalies in the chemical equilibria near critical points for simple reactions of the type $B_2 \rightleftarrows 2B$. In this paper, we extend the results of Ref. 4 to (a) a two-phase system, and (b) a wide range of different reactions. This should stimulate experimental verification.

Let us start with a ternary mixture (components 1, 2, and 3) existing in two phases, which we will label α and β. The chemical reaction allowed is of the form $1 \rightleftarrows 2 + 3$. We are interested in the singularities (if any) of the number densities near the critical point of a considered system. Our model describes, for example, a one-component system (say, HI) near its liquid-gas critical point (≈ 150 K for HI) dissociated into two species ($2HI \rightleftarrows H_2 + I_2$). The question is, how will the concentrations of the reagents vary near the critical points of a three-component system? In the case of a small equilibrium constant of reaction, these critical points are slightly shifted from the critical point of a one-component system.

Denoting by μ_i^α and μ_i^β the chemical potentials of the ith component in each phase, we can write for an equilibrium state

$$\mu_1^\alpha = \mu_1^\beta, \;\; \mu_2^\alpha = \mu_2^\beta, \;\; \mu_3^\alpha = \mu_3^\beta \; . \tag{1}$$

The condition of chemical equilibrium (the law of mass action) has the following form for reactions considered here:

$$\mu_1^\alpha - \mu_2^\alpha - \mu_3^\alpha = 0 \; . \tag{2}$$

We omit the chemical equilibrium condition for a reaction taking place in the second phase $\mu_1^\beta - \mu_2^\beta - \mu_3^\beta = 0$ because the latter is a linear combination of Eqs. (1) and (2) and, therefore, does not result in any additional restrictions.

We choose as independent variables the mole fractions of the first and second components in each phase x_1^α, x_2^α, x_1^β, and x_2^β, as well as the temperature T and the pressure P, which are the same in both phases. For these six variables we have the four equations of Eqs. (1) and (2); i.e., the system had two degrees of freedom, in accordance with the Gibbs phase rule ($f = c + 2 - p - r$; in our case, $c = 3$, $p = 2$, and $r = 1$).

We are interested here in equilibrium properties. Therefore, the thermodynamic path we choose is a displacement along an equilibrium line. Moreover, we consider an equilibrium process under constant pressure, in accordance with the usual experimental procedure where the temperature is changed (isothermal changes of pressure can be considered analogously).

Equations (1) and (2) have to be satisfied along the equilibrium line; hence,

$$\begin{aligned} d(\mu_1^\alpha - \mu_1^\beta) &= d(\mu_2^\alpha - \mu_2^\beta) = d(\mu_3^\alpha - \mu_3^\beta) \\ &= d(\mu_1^\alpha - \mu_2^\alpha - \mu_3^\alpha) = 0 \; . \end{aligned} \tag{3}$$

Using x_1^α, x_2^α, x_1^β, x_2^β, and T as independent variables, and adopting the notations

$$\left(\frac{\partial \mu_i^{\alpha,\beta}}{\partial x_j^{\alpha,\beta}} \right)_{P,T,x_i \neq x_j} \equiv \mu_{ij}^{\alpha,\beta} \; ,$$

$$\left(\frac{\partial \mu_i^{\alpha,\beta}}{\partial T} \right)_{P,x_j} \equiv \mu_{iT}^{\alpha,\beta} \; ,$$

we can rewrite Eqs. (3) in the following form:

$$\begin{aligned} &\mu_{11}^\alpha dx_1^\alpha + \mu_{12}^\alpha dx_2^\alpha - \mu_{11}^\beta dx_1^\beta - \mu_{12}^\beta dx_2^\beta = (\mu_{1T}^\beta - \mu_{1T}^\alpha) dT \; , \\ &\mu_{21}^\alpha dx_1^\alpha + \mu_{22}^\alpha dx_2^\alpha - \mu_{21}^\beta dx_1^\beta - \mu_{22}^\beta dx_2^\beta = (\mu_{2T}^\beta - \mu_{2T}^\alpha) dT \; , \\ &\mu_{31}^\alpha dx_1^\alpha + \mu_{32}^\alpha dx_2^\alpha - \mu_{31}^\beta dx_1^\beta - \mu_{32}^\beta dx_2^\beta = (\mu_{3T}^\beta - \mu_{3T}^\alpha) dT \; , \\ &(\mu_{11}^\alpha - \mu_{21}^\alpha - \mu_{31}^\alpha) dx_1^\alpha + (\mu_{12}^\alpha - \mu_{22}^\alpha - \mu_{32}^\alpha) dx_2^\alpha \\ &\qquad = -(\mu_{1T}^\alpha - \mu_{2T}^\alpha - \mu_{3T}^\alpha) dT \; . \end{aligned} \tag{4}$$

Dividing both sides of Eqs. (4) by dT we can solve the inhomogeneous system of equations for $dx_i^{\alpha,\beta}/dT$ and find

$$\left[\frac{dx_i^{\alpha,\beta}}{dT}\right]_{\mathrm{EL},\ P=\mathrm{const}}=\frac{\Delta_i^{\alpha,\beta}}{\Delta}\ , \tag{5}$$

where EL is the equilibrium line, Δ is the determinant of Eqs. (4), and $\Delta_i^{\alpha,\beta}$ is the same determinant where one of the four rows (namely, that containing $dx_i^{\alpha,\beta}$) is replaced by the row of coefficients from the right-hand side of Eqs. (4). Solutions for different dx_i^{α}/dT and dx_i^{β}/dT are qualitatively similar and, therefore, we omit superscript and subscript indices in our following discussion.

The 4×4 determinant Δ can be simplified by an expansion in its four line elements, two of which are zeros. In doing this we use the Gibbs-Duhem relations[5] $\sum_{j=1}^{3}(n_j^{\alpha,\beta}d\mu_j^{\alpha,\beta}+S^{\alpha,\beta}dT)=0$, where $n_j^{\alpha,\beta}$ are the number of moles of species j in the α or β phase. After some tedious transformations, we obtain

$$\Delta=\frac{n_1^{\alpha}(n_2^{\beta}-n_3^{\beta})-n_2^{\alpha}(n_3^{\beta}-n_1^{\beta})-n_3^{\alpha}(n_1^{\beta}-n_2^{\beta})}{n_3^{\alpha}n_3^{\beta}}$$
$$\times[\mu_{11}^{\alpha}\mu_{22}^{\alpha}-(\mu_{12}^{\alpha})^2][\mu_{11}^{\beta}\mu_{22}^{\beta}-(\mu_{12}^{\beta})^2]\ . \tag{6}$$

It can be seen from Eq. (6) that, apart from the case of some special connection between the mole numbers, Δ vanishes when each of the two last factors on the right-hand side of Eq. (6) vanishes, $[\mu_{11}^{\alpha,\beta}\mu_{22}^{\alpha,\beta}-(\mu_{12}^{\alpha,\beta})^2]=0$. However, the latter formulas are merely the boundary of stability of a ternary mixture in α or β phases.[5] Equation (6) can be rewritten in the equivalent form

$$\mu_{11}^{\alpha,\beta}\mu_{22}^{\alpha,\beta}-(\mu_{12}^{\alpha,\beta})^2\equiv\left[\frac{\partial\mu_2^{\alpha,\beta}}{\partial x}\right]_{T,P,\mu_1}=0\ . \tag{7}$$

The line of the critical points is determined[5] by Eq. (7) and by the vanishing of the next derivative of $\mu_2^{\alpha,\beta}$ with respect to x.

On the other hand, it is easy to check that the numerator in Eq. (5) is not singular at the critical point. Thus, we conclude from Eqs. (5)–(7) that x-T curves have an infinite slope at the critical point.

Let us now find the temperature dependence of the derivative dx/dT as the critical point is approached, which according to Eq. (5) will be determined completely by that of Δ; i.e., by the limiting behavior of the derivative entering Eq. (7). This equation describes, in fact, the critical behavior of a binary mixture at constant chemical potential μ_1, reflecting the well-known "isomorphism principle": The stability conditions for a ternary mixture are identical to those of a binary mixture under an additional constraint, namely, $\mu_1=\mathrm{const}$.

Combining two asymptotic expressions for the susceptibility when $t=0$ and $x=0$, respectively, we write the following interpolation formula:

$$\left[\frac{\partial\mu_2}{\partial x}\right]_{T,P,\mu_1}=a_1p^{\gamma}+a_2t^{\gamma}+a_3x^{\delta-1}+\cdots\ , \tag{8}$$

where a_1, a_2, and a_3 are constants, γ and δ are the so-called critical exponents, and p, t, and x are the dimensionless pressure, temperature, and concentration, respectively, which are measured from their critical values

$$p=\frac{P-P_c(\mu_1)}{P_c(\mu_1)},\quad t=\frac{T-T_c(\mu_1)}{T_c(\mu_1)},\quad x=\frac{x-x_c(\mu_1)}{x_c(\mu_1)}\ .$$

The critical parameters now depend upon μ_1, and in order to obtain experimentally observable quantities, we have to pass, say, from $T_c(\mu_1)$ to $T_c(x)$ according to the following relation:

$$T_c(\mu_1)=T_c(x)+\frac{dT_c}{d\mu_1}\Delta\mu_1\ ,$$

taking into account that $\mu_1=\mu_1(P,T,x)$. By so doing, we can obtain three different results[6]: (1) In the major portion of the experimentally accessible region on the phase diagram, critical indices remain unchanged; (2) inside the "renormalization region," these indices will be multiplied by the factor $1/(1-\alpha)\approx 1.12$; and (3) some cases, like points of singularity of the function $T_c=T_c(\mu)$, need special consideration.

We restrict ourselves to the first case, which is the simplest, and consider therefore the critical parameters appearing in Eq. (8) as p_c, T_c, and x_c. Note that the second case could bring an increase of 10% of the critical indices.

The temperature dependence of the susceptibility in Eq. (8) is determined by the thermodynamic path to the critical point. In our case, this path can be found from a natural assumption that the chemical potential is a smooth function of pressure. Integrating Eq. (8) with respect to x, we obtain $\mu\sim a_1p^{\gamma}x+a_2t^{\gamma}x+(a_3/\delta)x^{\delta}+a_4t+a_5p+\cdots$. Then, if μ is a smooth function of p, the comparability of the other variables has to be $t\sim x^{\delta}$. Substituting the latter relation into Eq. (8) and keeping the t term with the smallest power, we obtain for $P=P_c$

$$\left[\frac{\partial\mu_2}{\partial x}\right]_{T,P}\sim t^{(\delta-1)/\delta}\ . \tag{9}$$

Using now Eqs. (9), (8), and (7), we obtain finally for the change in composition in the vicinity of the critical point

$$\left[\frac{dx}{dT}\right]_{\mathrm{EL},\ P=P_c}\sim\left[\frac{T-T_c}{T_c}\right]^{-(\delta-1)/\delta}\ . \tag{10}$$

The numerical value of the critical index δ is $\delta\approx 5$, very close to the critical point (within the so-called "Ginzburg region"[7]), or $\delta=3$ outside this region but still not too far from the critical point.

Returning now to the isobutyric acid and water mixture we see that, as a result of the chemical reaction, this system consists of four components: HA, H_2O, A^-, and $(H_3O)^+$. (We neglect all possible association of the water molecules.) However, the electroneutrality condition results in an important constraint, namely, that the numbers of moles of the positive and negative charges must be equal in each phase $n_3^{\alpha}=n_4^{\alpha}$ and $n_3^{\beta}=n_4^{\beta}$. These restrictions bring us back to the previously considered case of a three-component mixture. It can easily be shown that the boundary of stability of the four-component mixture with the condition of electroneutrality, in fact, coincides with that of a ternary mixture. On the other hand, the isobutyric acid and water mixture can be described in each phase by two mole fractions, say, x_1 and x_2, while $x_3=x_4=(1-x_1-x_2)/2$. Therefore, the equilibrium equations will have the same form, Eq. (4), resulting in Eq. (10). In summary, as the critical point is approached, the ion concentrations in the isobutyric acid and water mixture and in similar systems increase in accordance with formula (10); i.e., as $[(T-T_c)/T_c]^{1-(\delta-1)/\delta}$, which is $[(T-T_c)/T_c]^{0.20}$ within, and $[(T-T_c)/T_c]^{0.33}$ outside the Ginzburg region.

Measurements of the charge concentrations would be the most direct way to check our predictions. Note that we have considered only the case of constant pressure. If experiments are performed at constant volume, an additional renormalization must be made,[8] which will decrease the singularity.

Comparisons with electrical-conductivity measurements[2] are more problematic because near the critical-point singularities of both the charge density and the mobility must be considered. However, the predicted critical indices do not appear to be inconsistent with the experimental values given in Ref. 2.

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