

Singularity in the degree of dissociation of isobutyric acid, water solutions at the critical solution point

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A recent prediction that the temperature derivative of the ion concentration in isobutyric acid, water solutions should diverge at the critical solution point with an exponent $(\delta - 1)/\delta$ is in error because the author fails to properly account for the variables held constant in taking the derivative, and in the path of approach to the critical point. The correct behavior is a standard weak divergence governed by the exponent α .

Recently Gitterman¹ has proposed that the observed anomaly²⁻⁴ in electrical conductivity in isobutyric acid, water solutions at their critical solution point is due in part to an anomaly in the extent of dissociation of isobutyric acid at this point. Gitterman argues that the ion concentration x in isobutyric acid, water solutions should satisfy [Gitterman's Eq. (10)]

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

where the subscript EL signifies the equilibrium line. The exponent in Eq. (1) corresponds to the behavior of a strongly divergent derivative in the sense of Griffiths and Wheeler⁵ (GW) along a path in which only field variables such as pressure and chemical potential rather than densities such as mole fraction are held constant. (We use the term "field" and "density" in the sense employed by GW.)

This prediction is in error on two counts. First, the derivative in question should be only weakly divergent rather than strongly because the derivative is one in which a density corresponding to the total mole fraction of isobutyric acid is held constant. Second, the path of approach is also one in which this density is held constant. As a consequence, the correct behavior for the ion concentration will be

$$\left[\frac{dx}{dT} \right]_{EL, P=P_c} = \left(\frac{T - T_c}{T_c} \right)^{-\alpha} \quad (2)$$

where $\alpha \approx 0.12$.

Gitterman's error results from not accounting carefully for all of the relevant thermodynamic variables required to specify the derivative and the path of approach to the critical point. We have recently discussed similar errors in the prediction of anomalies in NO₂, N₂O₄ equilibria near the critical point of CO₂ (Ref. 6) at some length elsewhere,⁷ and so restrict ourselves here to a brief thermodynamic treatment of the isobutyric acid, water problem. Following Gitterman, we neglect the ionic dissociation of water in the following argument. It can easily be included with no change in the results.

We consider a solution consisting of the constituents HA, H₂O, H⁺, and A⁻ which are related through the chemical equilibrium



The thermodynamic condition for chemical equilibrium

$$\mathcal{A} = \mu_{HA} - \mu_{H^+} - \mu_{A^-} = 0 \quad (4)$$

corresponds to holding one field variable fixed. Making use of the constraint of electrical neutrality

$$N_{H^+} = N_{A^-} \quad (5)$$

the Gibbs free energy of the solution may be written in the following convenient form:

$$dG = -S dT + V dp - \mathcal{A} dN_{A^-} + (\mu_{HA} - \mu_{H_2O}) dN_A^{\text{tot}} + \mu_{H_2O} dN_{\text{tot}} \quad (6)$$

where \mathcal{A} is given by Eq. (4) and

$$N_A^{\text{tot}} = N_{HA} + N_{A^-} \quad , \quad N_{\text{tot}} = N_{H_2O} + N_A^{\text{tot}} \quad (7)$$

N_A^{tot} measures the total number of moles of HA both dissociated and undissociated and N_{tot} the total number of moles of H₂O and HA. They are constant in a system closed with respect to matter flow, independent of the extent of dissociation of HA to H⁺ and A⁻.

It is convenient to introduce the following density variables

$$\xi = N_{A^-} / N_{\text{tot}} \quad , \quad \chi = N_A^{\text{tot}} / N_{\text{tot}} \quad (8)$$

as well as $g = G/N_{\text{tot}}$, $s = S/N_{\text{tot}}$, $v = V/N_{\text{tot}}$, and to reexpress Eq. (6) in the form

$$dg = -s dT + v dp - \mathcal{A} d\xi + (\mu_{HA} - \mu_{H_2O}) d\chi \quad (9)$$

The density ξ conveniently measures the extent of dissociation. It ranges over the possible values $0 \leq \xi \leq \chi$. The density χ measures the "total mole fraction" of isobutyric acid in the sense that both dissociated and undissociated acid is counted. It is a density variable that remains constant in a system closed with respect to matter flow, independent of the extent of dissociation ξ . The ion concentration is given by 2ξ .

The derivative of interest is thus

$$\left[\frac{\partial \xi}{\partial T} \right]_{p, \chi, \mathcal{A}=0} \quad (10)$$

This is a derivative in which two field-type variables (in the

sense of GW) p and \mathcal{A} , and one density variable χ , are held fixed. According to the very general thermodynamic arguments of GW as well as to detailed decorated lattice model calculations (see, e.g., Ref. 5 and 7, and references therein) such a derivative should be only weakly divergent in the GW sense. Moreover, since experiments are generally carried out in a system closed with respect to matter flow (or as close as possible thereto), the path of approach to the critical point is also one of constant χ . The expected behavior for the derivative in Eq. (10) is then that given in Eq. (2).

One might be tempted to think that, since χ is automatically constant in a system closed with respect to matter flow, it is therefore somehow "irrelevant" to the temperature dependence of the extent of reaction. This seems to be the rationale for omitting certain densities from the list of variables held constant in derivatives in both Refs. 1 and 6. However, the density χ plays a very important role in the phase separation of isobutyric acid and water. It is strongly coupled to the order parameter of the transition. (Indeed, it could very well be taken to be the order parameter.) Holding χ constant amounts to taking a derivative with the order parameter held fixed and thus produces a derivative that is weakly rather than strongly divergent. A generally sound strategy seems to be to make a linear transformation of the extensive composition variables into one set of variables that are constant in any system closed with respect to matter

flow and a set of extents of reaction that change when one reaction proceeds, but are independent of all other reactions. One out of the first set can be chosen to measure the "size" of the system and the thermodynamics can thereby be expressed naturally in terms of densities and fields. It is to be expected, in general, that all of the resulting densities and fields will play a significant role in any phase separation or critical point.

Experimentally,^{2,4} the exponent characterizing the divergence of the temperature derivative of the electrical conductivity is larger than the heat-capacity exponent α , the values falling in the range 0.3–0.67. This does not imply a contradiction with the conclusion reached above, of course, but rather suggests that the dominant mechanism leading to the anomaly in conductivity must be other than the thermodynamic anomaly in the extent of dissociation. This possibility was recognized by the authors of both Refs. 2 and 4, who proposed nonthermodynamic mechanisms leading to the exponents they observed.

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¹M. Gitterman, Phys. Rev. A **28**, 358 (1983).

²A. Stein and G. F. Allen, Phys. Rev. Lett. **29**, 1236 (1972); J. Chem. Phys. **59**, 6079 (1983).

³P. M. Gammell and C. A. Angell, Phys. Lett. **40A**, 49 (1972); J. Chem. Phys. **60**, 584 (1974).

⁴C. H. Shaw and W. I. Goldburg, J. Chem. Phys. **65**, 4906 (1976).

⁵R. B. Griffiths and J. C. Wheeler, Phys. Rev. A **2**, 1047 (1970).

⁶I. Procaccia and M. Gitterman, Phys. Rev. A **27**, 555 (1983).

⁷J. C. Wheeler and R. G. Petschek, Phys. Rev. A **28**, 2442 (1983).