Diverging Thermodynamic Derivatives Associated with Heterogeneous Equilibria in a Binary Liquid Mixture with a Consolute Point

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The opposite sides of the coexistence curve of a binary liquid mixture with a miscibility gap converge at the consolute temperature, T_c, where certain of the thermodynamic derivatives go to infinity [1]. A heterogeneous equilibrium exists when such a liquid mixture comes into contact with a reactive solid. We examine three cases of solids in contact with a mixture of isobutyric acid + water, which has a critical solution temperature near 26 ^{o}C: (a) In the presence of a basic metal oxide, the acid reacts with the oxide to form the metal isobutyrate and water [2]. The temperature derivative (ds/dT) of the solubility, s , goes to infinity as the temperature, T approaches T_c.(b) When charcoal comes into contact with the liquid mixture, the isobutyric acid (and to a certain extent also the water) is adsorbed onto the charcoal [3]. The derivative ($dX/d\mu$) of the isobutyric acid mole fraction,X , with respect to its chemical potential, μ, goes to infinity as T approaches T_c. (c) When the hydroxide form of an anion exchange resin comes into contact with isobutyric acid + water, the isobutyrate anion exchanges with the hydroxide ion. Assuming that the fraction of resin sites, θ, occupied by isobutyrate anions is governed by the Langmuir adsorption isotherm, then the derivative ($dX/d(1/\theta)$) diverges as T approaches T_c. We will show that all of these diverging derivatives follow as a consequence of the principle of critical point universality [1].

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