

Chemical Equilibrium and Critical Phenomena: The Solubilities of Manganese Dioxide and Aluminum Oxide in Isobutyric Acid + Water near Its Consolute Point

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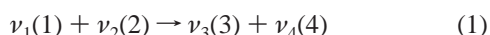
We have measured the solubilities of manganese dioxide and aluminum oxide in isobutyric acid + water along its critical isopleth at temperatures above the upper critical solution temperature at 26.2 °C. Both oxides are basic anhydrides that react with isobutyric acid to produce the metal isobutyrate and water. In both cases, the measured solubility values, s , were in the parts per million range. When the solubility data for either of these oxides were plotted in van't Hoff form with $\ln s$ vs $1/T$, a straight line resulted for absolute temperatures, T , sufficiently in excess of the critical solution temperature, T_c . The sign of the slope of the line indicated that manganese dioxide dissolved *endothermically*, while aluminum oxide dissolved *exothermically*. When the temperature was within 1 K of T_c , however, the local van't Hoff slope, $(\partial \ln s / \partial (1/T))$, appeared to diverge toward *negative* infinity in the case of manganese dioxide, while it appeared to diverge toward *positive* infinity in the case of aluminum oxide. By applying the principle of critical point universality to the critical behavior of thermodynamic derivatives, we have shown that the existence of a divergence in $(\partial \ln s / \partial (1/T))$ as T approaches T_c is to be expected when the dissolution reaction of the oxide involves both components of the solvent. Application of the Gibbs–Helmholtz equation showed that the sign of the divergence must be opposite to the sign of the heat of solution. The experimental solubility data sets for both manganese dioxide and aluminum oxide are in good agreement with these theoretical assertions.

I. Introduction

The consolute point is an extremum in the temperature vs mole fraction phase diagram of a constant pressure binary liquid mixture where the homogeneous solution first begins to separate into two immiscible layers. The extreme value of the temperature along the boundary separating the two immiscible liquids is called the critical solution temperature. A binary mixture having a liquid–liquid phase boundary that is *concave down* has an *upper critical solution temperature* (UCST) and exists as one phase above the boundary and as two phases below it.¹ By contrast, a binary mixture having a liquid–liquid phase boundary that is *concave up* has a *lower critical solution temperature* (LCST) and exists as two phases above the boundary and as a single phase below it.¹ Upon introduction of a reactant or a catalyst to the liquid, a chemical reaction can often be initiated. This permits these mixtures to be used to study the effect of a critical point on the net rate of reaction^{2–9} and also on the position of chemical equilibrium.¹⁰

The principle of critical point universality predicts that when the absolute temperature, T , is sufficiently close to the critical temperature, T_c , certain of the thermodynamic derivatives describing the properties of a pure fluid or a liquid mixture increase without bound.^{11–18} *The purpose of this research is to demonstrate that the principle of critical point universality determines the solubilities of metal oxides in the mixture isobutyric acid + water near its consolute point.*

To exploit the ideas of Griffiths and Wheeler,¹⁸ who have applied the principle of critical point universality to mixtures, we begin by considering the stoichiometry of a general chemical reaction written in the form



where reactants 1 and 2 are converted to the products 3 and 4.

The respective stoichiometric coefficients are ν_1 , ν_2 , ν_3 , and ν_4 . Upon designating $n_i(0)$ as the initial number of moles of the species, i , the number of moles, $n_i(t)$, at a later time, t , is $n_i(t) = n_i(0) \pm \nu_i \eta(t)$, where $\eta = \eta(t)$ is the extent of reaction variable expressed in moles, and the plus sign refers to the products, while the minus sign refers to the reactants. The initial value of $\eta(t)$ is zero, while the value of $\eta(t)$ after the reaction has come to equilibrium is η_e . If we let μ_i be the chemical potential of component, i , then the Gibbs free energy difference separating products from reactants

$$\Delta G = \nu_4 \mu_4 + \nu_3 \mu_3 - \nu_2 \mu_2 - \nu_1 \mu_1 \quad (2)$$

is zero when $\eta = \eta_e$.

Following the lead of Fisher,¹⁷ Griffiths and Wheeler¹⁸ divide the thermodynamic variables into two classes called *fields* and *densities*, respectively. In a system at thermodynamic equilibrium, a field has a uniform value across all coexisting phases. Examples of field variables include the temperature, the pressure, the chemical potential of each component, and also ΔG , which is a linear combination of chemical potentials. By contrast, a density variable has a different value in each coexisting phase. Examples of density variables include the entropy, the volume, and composition variables, such as the extent of reaction variable, η , and the mass fractions of the various chemical components.

Critical effects can manifest themselves in thermodynamic derivatives that involve the differentiation of a density variable with respect to a field variable. An example is $(\partial \eta / \partial T)_e$, where the subscript e refers to chemical equilibrium. There are two distinguishable cases: (1) When the experimental conditions are such that the fixed thermodynamic variables consist of fields and two or more densities, the derivative of a density with respect to a field is expected to be a smooth function of the

temperature as T approaches T_c . That is to say, no observable critical effect in the derivative is to be expected. (2) When fewer than two densities are held fixed, the derivative of a density with respect to a field should go to infinity as $|T - T_c|^{-x}$, where x is called the critical exponent. If only *one* density is held fixed, the value of x is of the order of a tenth,⁹ and the derivative is said to diverge *weakly*.¹⁸ If *no* densities are held fixed, the value of x is of the order of unity,⁹ and the derivative is said to diverge *strongly*.¹⁸

In the case of a chemically reactive liquid mixture *at equilibrium* under ordinary laboratory conditions, the fixed thermodynamic variables are the temperature, T , the pressure, P , and the mass fractions of any inert components that may be part of the system. A component is considered to be inert if it is not involved in at least one chemical reaction. In the absence of inert components, the thermodynamic derivative, $(\partial\eta/\partial T)_e$, can be identified with $(\partial\eta/\partial T)_{P,\Delta G=0}$, which is expected to approach *infinity* strongly as T approaches T_c . Like $(\partial\eta/\partial T)_{P,\Delta G=0}$, the derivative, $(\partial\eta/\partial\Delta G)_{T,P}$ can also be expected to approach *infinity* strongly as T approaches T_c . In the Theory Section, we will demonstrate a proportionality between $(\partial\eta/\partial\Delta G)_{T,P}$ and $(\partial\eta/\partial T)_{P,\Delta G=0}$ and will further show that because $(\partial\eta/\partial\Delta G)_{T,P}$ is positive definite, $(\partial\eta/\partial T)_{P,\Delta G=0}$ can diverge toward either positive or negative infinity depending upon the sign of the heat of reaction.

In the Experimental Section, we describe some measurements of the equilibrium solubilities of manganese dioxide and aluminum oxide in isobutyric acid + water mixtures at temperatures just above the upper critical solution temperature. Manganese dioxide and aluminum oxide are basic anhydrides that dissolve by reacting with isobutyric acid to produce water plus the isobutyrate salt of the metal. We have determined the solubility by using inductively coupled plasma (ICP) spectroscopy to measure the metal content of aliquots harvested from the solution. Since both the oxide solubility and the concentration sensitivity of our ICP spectrometer lie in the parts per million range, we chose as our measure of concentration the mass fraction, s , expressed in the units of ppm. We have observed experimentally that in the critical region, the local slope, $(\partial \ln s / \partial (1/T))_{P,\Delta G=0}$, of a van't Hoff plot tends toward *negative* infinity in the case of manganese dioxide, while it tends toward *positive* infinity in the case of aluminum oxide. On the basis of the fact that s and η are linearly related, and $(\partial\eta/\partial\Delta G)_{T,P}$ is positive definite, we show in the Theory Section that this is to be expected when solubility measurements that are diverging as a function of temperature are plotted versus $1/T$.

II. Theory Section

Our principal object in this section is to determine the temperature behavior of the slope of a van't Hoff plot, $\ln s$ vs $1/T$, for temperatures T near T_c . In this analysis, we exploit the method of DeDonder¹⁹ and Prigogine.¹ We start with the Clausius equation for the differential change in the total Gibbs free energy, G , of the system

$$dG = -S dT + V dP + \sum_i \mu_i dn_i \quad (3)$$

In eq 3, S and V are the entropy and volume, respectively. If we assume that the system contains no inert components and is held at constant T and P , the first two terms on the right are zero, and we can replace dn_i in the sum by $dn_i = \pm \nu_i d\eta$. As in the Introduction, the plus sign refers to products, while the minus sign refers to reactants. After insertion of this expression for dn_i into eq 3 and use of eq 2, we obtain the usual result

$$\left(\frac{\partial G}{\partial \eta}\right)_{T,P} = \Delta G \quad (4)$$

Since at chemical equilibrium the right-hand side of eq 4 is zero, $G(\eta)$ must have an extremum at $\eta = \eta_e$. For the chemical equilibrium to be stable with respect to fluctuations in the value of η about η_e , this extremum should be a minimum;¹ thus at $\eta = \eta_e$, the second derivative of $G(\eta)$ should satisfy

$$\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{T,P} = \left(\frac{\partial \Delta G}{\partial \eta}\right)_{T,P} > 0 \quad (5)$$

We next examine the relationship between the reciprocal of $(\partial \Delta G / \partial \eta)_{T,P}$ and the temperature coefficient, $(\partial \eta / \partial T)_{P,\Delta G=0}$. In the absence of inert components,^{1,19} the variables T , P , and η are sufficient to specify the thermodynamic state of the system; hence

$$\Delta G = \Delta G(T, P, \eta) \quad (6)$$

The total differential of $\Delta G/T$ is

$$d(\Delta G/T) = \left(\frac{\partial(\Delta G/T)}{\partial P}\right)_{T,\eta} dP + \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,\eta} dT + \left(\frac{\partial(\Delta G/T)}{\partial \eta}\right)_{T,P} d\eta \quad (7)$$

If the system is in equilibrium at constant pressure, the first term on the right-hand side disappears, and the left-hand side is identically zero. After dividing the remaining terms through by dT , we can rewrite eq 7 in the form

$$\left(\frac{\partial \eta}{\partial T}\right)_{P,\Delta G=0} = -\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,\eta} T \left(\frac{\partial \eta}{\partial \Delta G}\right)_{T,P} \quad (8)$$

The temperature coefficient of $\Delta G/T$ is given by the Gibbs–Helmholtz equation

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,\eta} = \frac{-\Delta H}{T^2} \quad (9)$$

where $\Delta H = \Delta H(T, P, \eta)$.

We can use the principle of critical point universality to determine the behavior of $(\partial(\Delta G/T)/\partial T)_{P,\eta}$ at temperatures near the critical solution temperature of the mixture. We begin our analysis by examining the behavior of the derivative

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \quad (10)$$

near the critical point of a pure fluid that occupies volume, V . Because $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ are derivatives of densities with respect to fields with no densities held fixed, they must both be proportional to $|T - T_c|^{-x}$ in the critical region, where x is the *strong* exponent. Consequently, near the critical temperature of a pure fluid, $(\partial P/\partial T)_V$ should remain finite. Like $(\partial P/\partial T)_V$, $(\partial(\Delta G/T)/\partial T)_{P,\eta}$ is the derivative of a field, $\Delta G/T$, with respect to a field, T , with one density, η , held fixed. According to the principle of critical point universality, as stated by Griffiths and Wheeler,¹⁸ the occurrence of a divergence in a thermodynamic derivative as $T \rightarrow T_c$ is independent of the physical system and depends only upon the identification of the variables involved as either densities or fields. Thus, the finite behavior of $(\partial P/\partial T)_V$ near the critical point of a pure fluid implies that $(\partial(\Delta G/T)/\partial T)_{P,\eta}$ should remain finite near the consolute point of a

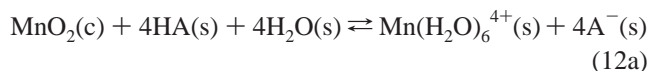
mixture. Because of eq 9, ΔH should also be finite at the consolute point of the mixture.

After substitution of eq 9 into eq 8, we obtain

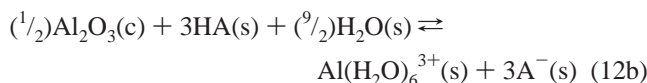
$$\left(\frac{\partial \eta}{\partial T}\right)_{P,\Delta G=0} = \frac{\Delta H}{T} \left(\frac{\partial \eta}{\partial \Delta G}\right)_{T,P} \quad (11)$$

Equation 11 can be applied to any chemically reacting mixture without inert components. According to eq 5, $(\partial \eta / \partial \Delta G)_{T,P}$ is positive definite, which implies that $(\partial \eta / \partial \Delta G)_{T,P}$ must tend toward positive infinity as T approaches T_c ; hence, $(\partial \eta / \partial T)_{P,\Delta G=0}$ will approach either positive or negative infinity depending upon the sign of ΔH .

The oxides on Mn(IV) and Al(III) can be expected to dissolve in an acidic aqueous solvent by forming the complex ions $\text{Mn}(\text{H}_2\text{O})_6^{4+}$ and $\text{Al}(\text{H}_2\text{O})_6^{3+}$, respectively.²⁰ The dissolution MnO_2 should proceed according to the stoichiometric equation



while the dissolution of aluminum oxide should follow the equation



In eqs 12, “c” in parentheses refers to the crystalline phase and “s” refers to the solution phase; HA is isobutyric acid, and A^- is the isobutyrate ion.

To analyze the metal oxide solubility *outside the critical region*, we introduce the equilibrium constant, $K(T)$, appropriate to the stoichiometry represented by eqs 12

$$K(T) = \frac{a_{\text{M}}(a_{\text{A}})^{\nu_{\text{A}}}}{(a_{\text{HA}})^{\nu_{\text{HA}}}(a_{\text{H}_2\text{O}})^{\nu_{\text{H}_2\text{O}}}} \quad (13)$$

Here, a_{M} , a_{A} , a_{HA} , and $a_{\text{H}_2\text{O}}$ are the solution phase activities of the hydrated metal ion, the isobutyrate ion, isobutyric acid, and water, respectively, while ν_{A} , ν_{HA} , and $\nu_{\text{H}_2\text{O}}$ are the corresponding stoichiometric coefficients. At 1 atm pressure, the activity of the solid metal oxide is unity. The activities of HA and H_2O change very little with temperature because these solvent components are in vast excess. If we choose 1 ppm as the standard state of the dissolved metal, then for a dilute, ideal solution, $a_{\text{M}} = s$, and $a_{\text{A}} = \nu_{\text{A}}s$. When we substitute these activities into eq 13, and incorporate $\Delta G^\circ = -RT \ln K(T)$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we obtain the van't Hoff formula

$$\ln s = -\frac{\Delta H^\circ}{(\nu_{\text{A}} + 1)RT} + B \quad (14)$$

that represents the temperature dependence of s in the case of the dissolution reactions in eqs 12. In the derivation of eq 14, R is the universal gas law constant, and ΔG° , ΔH° , and ΔS° are the standard Gibbs energy, enthalpy, and entropy of solution, respectively. The constant, B , involves ΔS° , ν_{A} , and the activities of the solvent components.

For ready comparison of eq 11 with solubility data plotted in van't Hoff form *inside the critical region*, we introduce, $s = 10^6 M\eta/m_{\text{tot}}$, where M is the atomic weight of the dissolved metal and m_{tot} is the total mass of the solution. After use of the simple relations, $ds = 10^6(M/m_{\text{tot}}) d\eta$, $(\partial s / \partial T) = -(s/T^2)(\partial \ln s / \partial (1/T))$, and $(1/s)(\partial s / \partial \Delta G) = (\partial \ln s / \partial \Delta G)$, eq 11 can be

rewritten in the form

$$\left(\frac{\partial \ln s}{\partial (1/T)}\right)_{P,\Delta G=0} = -T\Delta H \left(\frac{\partial \ln s}{\partial \Delta G}\right)_{T,P} \quad (15)$$

Because s and η are proportional, and $(\partial \eta / \partial \Delta G)_{T,P}$ is positive definite, the derivative $(\partial \ln s / \partial \Delta G)_{T,P}$ will also be *positive definite*; hence, eq 15 predicts that $(\partial \ln s / \partial (1/T))_{P,\Delta G=0}$ and ΔH must have *opposite* signs.

According to eq 12, none of the components in the mixture are inert, so the fields, T and P , remain as the only fixed variables, and we can expect $(\partial \ln s / \partial \Delta G)_{T,P}$ to approach *positive* infinity as $T \rightarrow T_c$. On the basis of eq 15, the local van't Hoff slope, $(\partial \ln s / \partial (1/T))_{P,\Delta G=0}$, should then tend toward *negative* infinity in the case of *endothermic* dissolution, while it should tend toward *positive* infinity in the case of *exothermic* dissolution.

III. Experimental Section

Isobutyric acid was obtained from Aldrich and used as received. Water was once distilled from a glass system. The binary solvent mixture was prepared at the critical composition²¹ of 38.8 mass percent isobutyric acid by weighing. Visual observation of critical opalescence indicated that the critical temperature of the mixture was about 26.2 °C. A measurement of the pH of this mixture at a temperature a few degrees above the critical temperature showed pH = 2. Manganese dioxide and aluminum oxide were supplied by Fisher Scientific and used as received. Our thermostat bath, temperature controller, and temperature measuring equipment have been previously described.^{5,6}

Manganese dioxide dissolves in isobutyric acid + water *endothermically*, while aluminum oxide dissolves *exothermically*. To avoid supersaturated solutions that might be subject to nucleation time lags, the equilibria in eqs 12 were traced in the direction of increasing solubility; that is to say, the solubility of manganese dioxide was measured with temperature rising, while the solubility of aluminum oxide was measured with temperature falling. Other than this, the experimental technique was the same for both oxides.

The vessel employed to equilibrate each oxide with the isobutyric acid + water solvent mixture was a well-stoppered, flat bottom, Pyrex glass test tube with a 2.54 cm inside diameter. At the start of each run, oxide was introduced into this test tube in an amount sufficient to cover the bottom, and a stirring bar was added. The temperature of the water bath was adjusted to the desired value using the thermostat. One hundred milliliters of temperature equilibrated solvent mixture was added to the test tube. The metal oxide and solvent were allowed to come to solubility equilibrium by magnetic stirring for 24 h. The stirrer was then turned off, and the test tube was allowed to stand for 24 h in order to permit the liquid and the suspended solid to separate by gravitational sedimentation. At the end of this period of standing, the liquid above the solid sediment was observed to be clear. A 1 mL aliquot of this supernatant was extracted using a calibrated pipet. The aliquot was diluted with 7 mL of 2% nitric acid in order to prevent precipitation of dissolved metal ions. The thermostat temperature was adjusted to the next value, and the process of stirring followed by standing was repeated. By using this procedure, our measurement of the solubility, s , tracked the critical isopleth of the solvent mixture.

The concentration of metal dissolved in each diluted aliquot was determined using a Leeman Labs PS 1000 inductively coupled plasma spectrometer. This spectrometer had been

TABLE 1: Solubility, s , in Parts per Million as a Function of Temperature for Manganese Dioxide in Isobutyric Acid + Water along the Critical Isopleth Composition of 38.8 Mass Percent Isobutyric Acid

| T (°C) | s (ppm) | T (°C) | s (ppm) |
|----------|-----------|----------|-----------|
| 26.70 | 15.9 | 31.95 | 269.7 |
| 27.10 | 126.0 | 34.10 | 279.0 |
| 27.80 | 207.0 | 35.98 | 309.0 |
| 28.75 | 227.1 | 38.30 | 318.0 |
| 29.80 | 249.6 | 40.04 | 333.0 |
| 30.09 | 252.3 | | |

TABLE 2: Solubility, s , in Parts per Million as a Function of Temperature for Aluminum Oxide in Isobutyric Acid + Water along the Critical Isopleth Composition of 38.8 Mass Percent Isobutyric Acid

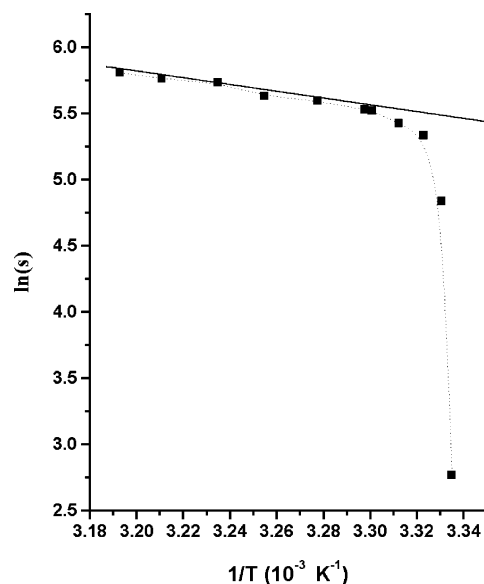
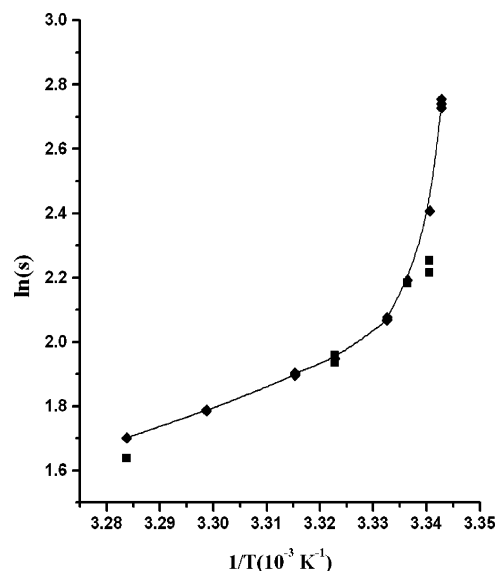
| T (°C) | s (ppm) | T (°C) | s (ppm) |
|----------|-----------|----------|-----------|
| 26.00 | 15.5 | 26.92 | 7.9 |
| 26.00 | 15.3 | 26.92 | 7.9 |
| 26.00 | 15.7 | 26.92 | 8.0 |
| 26.20 | 9.5 | 27.80 | 6.9 |
| 26.20 | 11.1 | 27.80 | 7.0 |
| 26.20 | 9.2 | 27.80 | 7.1 |
| 26.57 | 9.0 | 28.48 | 6.7 |
| 26.57 | 8.9 | 28.48 | 6.7 |
| 26.57 | 8.9 | 28.48 | 6.7 |
| | | 30.00 | 6.0 |
| | | 31.38 | 5.5 |
| | | 31.38 | 5.1 |

previously calibrated with standard solutions of manganese and aluminum. Taking into account the dilution factor, the solubilities of both manganese dioxide and aluminum oxide in isobutyric acid + water at its critical composition were observed to be in the parts per million range. These values are summarized as functions of temperature in Tables 1 and 2, respectively. The solubility of MnO_2 in isobutyric acid + water was substantially higher than the solubility of Al_2O_3 . The same data are shown plotted in van't Hoff form in Figures 1 and 2.

The dissolution of small amounts of solutes ordinarily causes a noticeable shift in the critical temperature of a binary liquid mixture.^{4–9,22,23} The usual relation is $T_c = T_c^\circ + as$, where s is the concentration of the solute, a is an empirical constant that depends on the solute and the binary solvent, and T_c° is the critical temperature of the binary solvent before the addition of the solute.^{4–9} Since $T_c^\circ = 299.35$ K (26.2 °C), the precipitous downward trend in the solubility data in Table 1 that sets in at 27.10 °C suggests that the dissolution of manganese dioxide increases the critical temperature; hence, $a > 0$. In Table 2, on the other hand, the large values of s corresponding to 26.00 °C suggest that the dissolution of aluminum oxide decreases the critical temperature, implying that $a < 0$. Because the solubility, $s(T)$, of the metal oxide depends on the thermostat temperature, T , however, the critical temperature of the ternary mixture does not have a fixed value but is instead an implicit function, $T_c = T_c(s(T))$, of T . Although this phenomenon is peculiar, it does not fall outside the scope of applicability of the principle of critical point universality. According to this principle, the thermodynamic derivative, $(\partial s(T)/\partial T)_{P,\Delta G=0}$, which controls the departure of the van't Hoff plot from linearity, should take the form

$$(\partial s(T)/\partial T)_{P,\Delta G=0} \sim |T - T_c(s(T))|^{-x} \quad (16)$$

in the critical region. Under conditions where the temperature dependence of $T_c(s(T))$ is sufficiently weak that changes in T are able to catch up with $T_c(s(T))$, eq 16 suggests that $|T - T_c(s(T))|$ can still diminish sufficiently for a critical effect in

**Figure 1.** Van't Hoff plot of the solubility, s , in parts per million as a function of the reciprocal of the absolute temperature, T , for manganese dioxide in isobutyric acid + water along the critical isopleth composition at 38.8 mass percent isobutyric acid**Figure 2.** Van't Hoff plot of the solubility, s , in parts per million as a function of the reciprocal of the absolute temperature, T , for aluminum oxide in isobutyric acid + water along the critical isopleth composition at 38.8 mass percent isobutyric acid.

$(\partial s(T)/\partial T)_{P,\Delta G=0}$ to be observed. Figures 1 and 2 are evidence that this was true in the case of the dissolution of manganese dioxide and aluminum oxide in isobutyric acid + water.

IV. Discussion and Conclusions

Heterogeneous equilibria involving binary mixtures with a consolute point have been investigated by Ullman et al.²⁴ and by Greer and collaborators.¹⁰ Ullman et al. extracted organic die molecules from the crystalline state using hexane + methanol (UCST). The solvent composition was consciously chosen, however, to be sufficiently far from the critical composition that no critical effects could intervene. On the other hand, Greer et al.,¹⁰ studied the position of the NO_2 dimerization equilibrium in perfluoromethylcyclohexane + carbon tetrachloride (UCST) as a function of temperature along the critical isopleth. Because the mixture was confined to a closed vessel

with a space above the liquid to accommodate the vapors of volatile components, such as NO₂ and N₂O₄, the reaction was heterogeneous. The position of equilibrium was monitored by making measurements of the dielectric constant of the liquid phase. Greer et al. reported a 4% shift in position of equilibrium toward the side of NO₂ as the temperature approached the critical value.¹⁰

The study of chemical reactions in fluids ordinarily depends on some method for determining the composition of the mixture. Morrison has noted that when a critical point is involved, opalescence can interfere with the determination of the composition using in situ measurements of the optical density.²⁵ Greer has pointed out that critical slowing down can be expected to interfere with the use of thermal conductivity as a measure of composition.²⁶ On the other hand, by extracting aliquots from the critical mixture and quenching them in 2% nitric acid, we presumably could proceed with concentration analysis by ICP spectroscopy without concern for the critical effects that tend to obscure in situ measurements.

The thermodynamic theory of supercritical dissolution has been worked out by Procaccia and Gitterman,²⁷ by Gitterman,²⁸ and by Levelt-Sengers and collaborators.²⁹ The statistical mechanics of a decorated lattice gas model representing supercritical solubility has been studied by Nielson and Levelt-Sengers.³⁰ The Kirkwood–Buff theory of solutions has been applied to this problem by Cochran et al.,³¹ while the molecular dynamics approach has been applied by Chialvo and DeBenedetti.³² Our thermodynamic theory in section II concentrates on the equilibrium between just two phases and is in this respect very close in both spirit and detail to the theories of Levelt-Sengers et al.²⁹ and Gitterman.²⁸ The main new feature that we introduce is the role of chemical reaction in restricting the number of fixed density variables.

In conclusion, the solubility data in Figures 1 and 2 appear to obey eq 14 with ΔH° and B constant at temperatures, T , outside the critical region. The slope of the line in Figure 1 indicates that the dissolution of manganese dioxide in isobutyric acid + water is endothermic ($\Delta H > 0$), while the slope of the linear portion of the curve in Figure 2 indicates that the dissolution of aluminum oxide is exothermic ($\Delta H < 0$). In the case of both reaction equilibria, the dissolution products, as well as both components of the solvent are involved in the overall stoichiometry. Because of this, the mass fractions of all of the dissolved components are functions of the field variables, T and P , which in turn makes the thermodynamic coefficients, $(\partial \ln s / \partial \Delta G)_{P, \Delta G=0}$ and $(\partial \ln s / \partial (1/T))_{P, \Delta G=0}$, derivatives of densities with respect to fields with no densities held fixed. As such, both can be expected to diverge as a function of temperature as T approaches $T_c(s(T))$. Because $(\partial \ln s / \partial \Delta G)_{P, \Delta G=0}$ is positive definite, $(\partial \ln s / \partial (1/T))_{P, \Delta G=0}$ and ΔH must have opposite signs. In Figures 1 and 2, both the existence and the sign of the departure of the data from the van't Hoff background line appear to be consistent with these predictions. Our solubility data thus are in agreement with the principle of critical point universality as expressed by Griffiths and Wheeler.¹⁸

Accurate determination of the critical exponent, x , in eq 16 will require not only more data but also perhaps the use of a

crossover theory to join together the linear and divergent portions of the van't Hoff plot. Of particular interest in this regard are the crossover theories of Kiselev et al.³³ and Wyczalkowska, Sengers, and Anisimov.³⁴ For example, the latter model has proved successful in correcting the van der Waals equation of state, which predicts ideal gas behavior at sufficiently low densities but displays a nonphysical cubic behavior in the critical region. By analogy, one might start with the theory of ideal solutions upon which eq 14 is based and introduce a crossover correction capable of duplicating the nonideal solution behavior that occurs near the consolute point.

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