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# Chemical Equilibrium and Critical Phenomena: The Solubilities of Iron(III) Oxide and Cobalt(II,III) Oxide in Isobutyric Acid + Water Near the Consolute Point

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**Abstract** The solubilities of iron(III) oxide, formula $Fe_2O_3$, and cobalt(II,III) oxide, formula $Co_3O_4$, have been determined in the liquid mixture, isobutyric acid + water, along the critical isopleth at temperatures above the upper critical solution temperature near 299 K. When plotted in van't Hoff form with $\ln s$ versus $1/T$, the measurements of solubility, $s$, lie on a straight line for values of the temperature, $T$, in kelvin, which are sufficiently in excess of the critical solution temperature, $T_c$. The sign of the slope, $(\partial \ln s/\partial(1/T))$, indicates that in the case of both oxides, the dissolution reaction is *endothermic*. When the temperature is within 1 K of $T_c$, however, the slope departs from its constant value and appears to diverge toward *negative* infinity. The principle of critical-point universality predicts that a divergence in $(\partial \ln s/\partial(1/T))$ is to be expected for $T$ near $T_c$ in those cases where the stoichiometry of the dissolution reaction involves both components of the solvent; moreover, the Gibbs–Helmholtz equation predicts that, if the heat of solution is *endothermic*, the sign of the divergence should be *negative*. Both of these predictions are confirmed by the solubilities of $Fe_2O_3$ and $Co_3O_4$ measured as a function of temperature along the critical isopleth of isobutyric acid + water.

**Keywords** Cobalt(II,III) oxide · Critical phenomena · Iron(III) oxide · Isobutyric acid · Solubility · Water

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## 1 Introduction

In the case of a binary liquid mixture with a miscibility gap, the opposite sides of the coexistence curve in the temperature vs. mole fraction phase diagram converge at the consolute point [1]. The temperature at the point of convergence is called the critical solution temperature. If the coexistence curve is *concave down*, the critical temperature is an *upper* critical solution temperature (UCST), while if it is *concave up*, the critical temperature is a *lower* critical solution temperature (LCST). At the consolute point, the distinction between the coexisting liquid phases disappears.

According to the *principle of critical-point universality,* the consolute point is a member of a class of critical points where certain thermodynamic properties tend to infinity as the temperature approaches the critical temperature [2–8]. The application of the principle of critical-point universality to critical phenomena in binary liquid mixtures is due to Griffiths and Wheeler [2], who divide the thermodynamic variables into two classes called *fields* and *densities*. In a system at thermodynamic equilibrium, a *field* has a uniform value across all coexisting phases. Examples of field variables include the pressure, $P$, the temperature, $T$, the chemical potential of each component, and also the Gibbs energy of reaction, $\Delta G$, 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 enthalpy, the molar volume, and the composition variables represented by the mass fractions of the various components.

To apply the principle of critical-point universality to the dissolution of a metal oxide in isobutyric acid + water (UCST), we consider the following stoichiometric relation,

$$(1/x)\mathrm{M}_x\mathrm{O}_y(c) + \mathrm{Z\,HA(aq)} + (6 - (\mathrm{Z}/2))\mathrm{H_2O(aq)} \rightarrow \mathrm{M(H_2O)}_6^{\mathrm{Z}+}\mathrm{(aq)} + \mathrm{ZA}^-\mathrm{(aq)} \tag{1}$$

in which the generic oxide, $\mathrm{M}_x\mathrm{O}_y$ reacts with isobutyric acid, HA, to form the hexahydrate metal cation [9], $\mathrm{M(H_2O)}_6^{\mathrm{Z}+}$ and the isobutyrate anion, $\mathrm{A}^-$. Here "c" in parentheses refers to the crystalline phase, while "aq" denotes the water-based solvent mixture. We denote the solubility of the metal in the liquid by $s$, which is the metal mass fraction in the units of grams of dissolved metal per gram of solution.

According to Griffiths and Wheeler [2], 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 $(\partial s/\partial T)_\mathrm{e}$, where the subscript, e, refers to chemical equilibrium [10,11]. 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 the critical temperature, $T_\mathrm{c}$. That is to say, there is no observable critical effect [2]. (2) When fewer than two densities are held fixed, the derivative of a density with respect to a field should go to infinity as $|T - T_\mathrm{c}|^{-x}$, where $x$ is called the critical exponent. If only *one* density is held fixed, the value of $x$ is of the order of *tenth*, and the derivative is said to diverge *weakly* [2]. If *no* densities are held fixed, the value of $x$ is of the order of *unity*, and the derivative is said to diverge *strongly* [2]. The exact value of the critical exponent, $x$, depends on the direction of approach to the critical point reckoned with respect to the direction of the liquid–liquid coexistence curve plotted in the space spanned by the fields [2]. The liquid–liquid coexistence curve in a binary mixture is, incidentally, a markedly symmetric function of the fields, $T$ and $P$ [12].

In the case of a chemically reactive liquid mixture at equilibrium under ordinary laboratory conditions, the fixed thermodynamic variables are $T$, $P$, 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. Since the dissolution reaction in Eq. 1 involves *both* components of the solvent, the mixture contains *no* inert components. In the absence of inert components, the thermodynamic derivative, $(\partial s/\partial T)_{\mathrm{e}}$, can be identified with $(\partial s/\partial T)_{P,\Delta G=0}$, where $\Delta G = 0$ is the criterion for dissolution equilibrium [10,11]. Since *no* densities are held fixed, $(\partial s/\partial T)_{P,\Delta G=0}$ is expected to approach infinity *strongly* as $T$ approaches $T_{\mathrm{c}}$ [11].

When solubility data collected *outside* the critical region are plotted in the form, $\ln s$ vs. $1/T$, the van't Hoff law predicts that the slope, $\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, should be a constant. As $T$ approaches $T_{\mathrm{c}}$, however, the critical behavior of $(\partial s/\partial T)_{P,\Delta G=0}$ forces $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ to depart from its expected constant value. At temperatures *inside* the critical region, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ goes to *positive* infinity, if the dissolution is *exothermic,* and it goes to *negative* infinity if the dissolution is *endothermic* [11]. We shall demonstrate that the latter prediction applies in the case of the dissolution of iron(III) oxide or cobalt(II,III) oxide in isobutyric acid + water at temperatures that lie along the critical isopleth.

## 2 Experiment

Isobutyric acid was obtained from Aldrich (Lot # 07710 PB) and was used as received. Water was distilled once from a glass system. The binary solvent mixture was prepared at the critical composition of 0.388 mass fraction isobutyric acid [13] by weighing. Both $Fe_2O_3$ and $Co_3O_4$ were obtained from Fisher and used as received.

To maintain a constant temperature in our experiments, we employed a 14 dm$^3$ water bath heated by a submerged 60 W light bulb powered by a Cole Parmer, 115 V variable output, Model G-02149-20 controller connected to a Philadelphia Roto-Stat differential thermoregulator. The temperature of the bath was read with a precision of 0.007 K by using a magnifying glass to observe the gradations on a long mercury-in-glass thermometer. The 24 h stability of the water bath temperature was better than 0.01 K.

To start a solubility experiment, 0.15 dm$^3$ of the isobutyric acid + water mixture, prepared at the critical composition, was added to the reaction vessel, which was a 3 cm i.d. × 25 cm long flat bottom, Pyrex test tube. Visual observation of critical opalescence in this mixture indicated that the critical temperature was 299.35 K. A magnetic stirring bar and metal oxide in an amount sufficient to cover the bottom of the reaction vessel were added. The vessel was then closed with a stopper, and the contents were stirred for 24 h. The stirrer was turned off, and the mixture was left to stand undisturbed for an additional 24 h to permit the suspended solid to separate from the liquid by gravitational sedimentation.

The dissolution of small amounts of solutes ordinarily causes a noticeable shift in the critical temperature of a binary liquid mixture [14,15]. A check was made for this effect on completion of the 24 h period of sedimentation. The temperature of the thermostat was first lowered until critical opalescence and a meniscus were clearly visible in the liquid phase; then, accompanied by slow stirring, the temperature was raised slightly, the stirring was stopped, and the meniscus was again observed. This process was repeated as needed until the meniscus disappeared. The value of the temperature at which the meniscus disappeared was identified with $T_c$, the critical temperature of the liquid mixture including dissolved oxide. When excess solid comes to solubility equilibrium with a liquid near its consolute point, the observed value of the critical temperature, $T_c$, is said to locate a critical end-point [16]. In the case of the dissolution of $Fe_2O_3$, the value of $T_c$ was 299.30 K, while in the case of the dissolution of $Co_3O_4$, the value of $T_c$ was 299.50 K.

After determination of the temperature of the critical end-point, the contents of the reaction vessel were stirred for another 24 h, the stirring was stopped, and the suspended solid was allowed to sediment for 24 h. At the end of the sedimentation period, a 2 $cm^3$ aliquot of the supernatant liquid was extracted with a serological pipette. The aliquot was diluted with 5 $cm^3$ of an aqueous solution of 20 g/kg nitric acid to prevent precipitation of dissolved metal ions. The temperature of the thermostat was then raised, and the process of stirring, sedimentation, and harvesting of an aliquot was repeated. The concentration of metal dissolved in each aliquot was determined using a Leeman Labs PS 1000 inductively coupled plasma spectrometer. By following the above procedure, the solubility, $s$, was tracked along the critical isopleth of the mixture.

Iron(III) oxide, formula $Fe_2O_3$, can crystallize in either a hexagonal or a cubic close-packed arrangement of $O^{2-}$ anions with $Fe^{3+}$ cations randomly distributed over the octahedrally coordinated and tetrahedrally coordinated interstices of the unit cell [17,18]. Iron(III) oxide dissolves in isobutyric acid + water according to Eq. 1 with stoichiometry specified by coefficients $x = 2$, $y = 3$, and $Z = 3$. For temperatures *outside* the critical region, we can assume that the ions on the right-hand side of Eq. 1 are sufficiently dilute as to make their activity coefficients unity, and that the water and isobutyric acid are in sufficient excess as to make their respective activities independent of the solubility of the metal. Under these conditions, the solubility data can be fitted to the van't Hoff law in the form [11],

$$\ln(s/s^\circ) = -\frac{A}{T} + B \tag{2}$$

where $s$ is the solubility in the units of grams of metal per gram of solution, and $s^\circ = 10^{-6}$ is the solute standard state. In the case of $Fe_2O_3$, the constant $A$ equals $\Delta H^\circ/4R$ where $\Delta H^\circ$ is the standard enthalpy of solution, and $R$ is the universal gas law constant.

The results of our measurements of the solubility of $Fe_2O_3$ in isobutyric acid + water along the critical isopleth are summarized in Table 1. The same data have been plotted

**Table 1** Temperature dependence of the solubility of $Fe_2O_3$ in 0.388 mass fraction isobutyric acid + water

| $T$ (K) | $s/s^\circ$ |
|---|---|
| 299.30 | 3.27 ± 0.07 |
| 299.70 | 3.72 ± 0.21 |
| 300.00 | 3.86 ± 0.14 |
| 300.35 | 4.14 ± 0.14 |
| 300.65 | 4.40 ± 0.21 |
| 301.00 | 5.14 ± 0.14 |
| 301.65 | 5.27 ± 0.21 |
| 302.00 | 5.48 ± 0.42 |
| 302.35 | 5.54 ± 0.21 |
| 302.70 | 5.51 ± 0.14 |
| 303.05 | 5.63 ± 0.35 |
| 303.35 | 5.80 ± 0.35 |
| 303.75 | 5.95 ± 0.28 |
| 306.05 | 6.87 ± 0.70 |
| 307.95 | 7.21 ± 0.35 |
| 310.55 | 7.28 ± 0.21 |
| 312.95 | 7.77 ± 0.21 |

The temperature at the critical endpoint was $T_c = 299.30\,\text{K}$. The solubility, $s$, is in units of mass of iron per unit mass of solvent. In these units, the solute concentration standard state is $s^\circ = 10^{-6}$. The choice of this standard state is the same as reporting the solubility in the units of ppm

in van't Hoff form in Fig. 1. When restricted to the 12 highest values of the temperature, the $Fe_2O_3$ solubility data in Table 1 can be represented by Eq. 2 with $A = (3400 \pm 280)\,\text{K}$ and $B = 12.97 \pm 0.92$ with a least-squares linear correlation coefficient [19], $R^2 = 0.9361$. The points included in the determination of the line are denoted by the squares in Fig. 1. The slope of the line is negative, which indicates that $Fe_2O_3$ dissolves *endothermically* in isobutyric acid + water.

Cobalt(II,III) oxide, formula $Co_3O_4$ or $CoO{\cdot}Co_2O_3$, adopts the normal spinel structure with the $O^{2-}$ anions occupying the lattice points of a face-centered cubic unit cell and the $Co^{2+}$ and $Co^{3+}$ cations occupying at random the tetrahedral and octahedral interstices, respectively [20,21]. Since $Co_3O_4$ contains cobalt in both the +2 and +3 oxidation states, the stoichiometry of the dissolution reaction cannot be summarized by Eq. 1. Rather, the appropriate equation is

$$\begin{aligned} Co_3O_4(s) + 8HA(aq) + 14H_2O(aq) \rightarrow\ & 2Co(H_2O)_6{}^{3+}(aq) \\ & + Co(H_2O)_6{}^{2+}(aq) + 8A^-(aq) \end{aligned} \qquad (3)$$

For dissolution of $Co_3O_4$, the constant $A$ in Eq. 2 equals $\Delta H^\circ/11R$. The results of our measurements of the solubility of $Co_3O_4$ in isobutyric acid + water along the critical isopleth are summarized in Table 2. The same data have been plotted in van't Hoff form in Fig. 2. When restricted to the 15 highest values of the temperature listed in Table 2, the data can be represented by Eq. 2 with $A = (8265 \pm 870)\,\text{K}$ and $B = 31.1 \pm 2.9$ with a linear least-squares correlation coefficient [19], $R^2 = 0.8741$. In Fig. 2, the

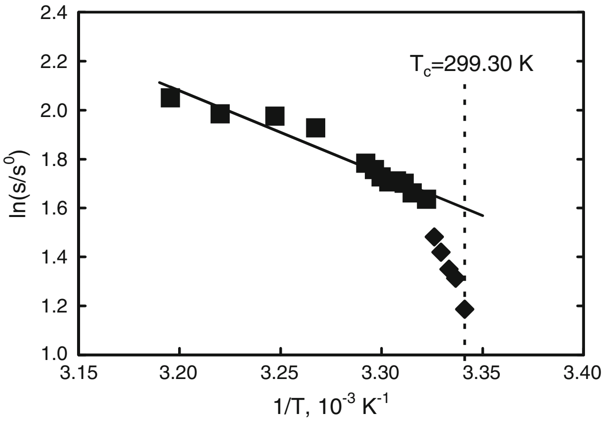

**Fig. 1** Van't Hoff plot of the temperature dependence of the solubility of $Fe_2O_3$ in 0.388 mass fraction isobutyric acid in water. The solubility, $s$, has the units of mass of iron per unit mass of the solvent. In these units, the concentration in the standard state is $s^\circ = 10^{-6}$. The choice of this standard state has the same effect as reporting the solubility in the units of ppm. Points represented by *squares* were used to determine the slope and intercept of the van't Hoff line given by Eq. 2. Points represented by *diamonds* were considered to lie within the critical region. The temperature at the critical end point was $T_c = 299.30\,K$

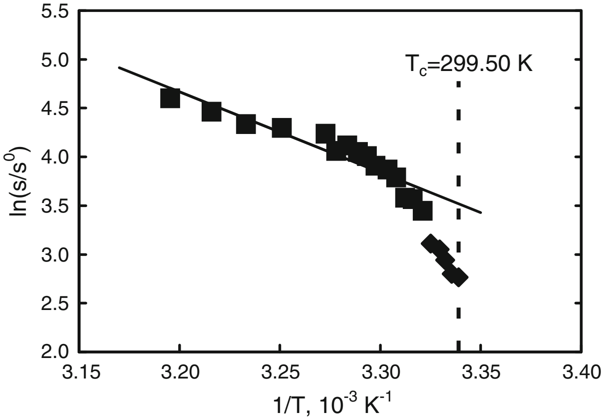

**Fig. 2** Van't Hoff plot of the temperature dependence of the solubility of $Co_3O_4$ in 0.388 mass fraction isobutyric acid in water. The solubility, $s$, is in units of mass of cobalt per unit mass of the solvent. In these units, the solute standard state concentration is $s^\circ = 10^{-6}$. The choice of this standard state has the same effect as reporting the solubility in the units of ppm. Points represented by *squares* were used to determine the slope and intercept of the van't Hoff line given by Eq. 2. Points represented by *diamonds* were considered to lie within the critical region. The temperature at the critical end point was $T_c = 299.50\,K$

points included in the determination of the line are denoted by squares. The slope of the line is negative indicating that $Co_3O_4$ dissolves *endothermically* in isobutyric acid + water.

**Table 2** Temperature dependence of the solubility of $Co_3O_4$ in 0.388 mass fraction isobutyric acid + water

| $T$ (K) | $s/s^\circ$ |
|---|---|
| 299.50 | 15.9 ± 1.4 |
| 299.80 | 16.5 ± 0.6 |
| 300.10 | 19.0 ± 0.7 |
| 300.35 | 21.1 ± 1.4 |
| 300.75 | 22.5 ± 2.1 |
| 301.10 | 31.4 ± 2.8 |
| 301.55 | 35.4 ± 3.5 |
| 301.90 | 35.8 ± 4.2 |
| 302.30 | 44.2 ± 2.1 |
| 302.70 | 48.0 ± 0.7 |
| 303.25 | 49.9 ± 2.8 |
| 303.65 | 55.1 ± 4.9 |
| 304.05 | 58.5 ± 4.2 |
| 304.55 | 61.4 ± 4.9 |
| 305.05 | 58.0 ± 6.3 |
| 305.55 | 69.2 ± 4.9 |
| 307.60 | 73.5 ± 4.9 |
| 309.30 | 76.3 ± 3.5 |
| 310.95 | 87.0 ± 7.0 |
| 312.95 | 99.4 ± 6.3 |

The temperature at the critical endpoint was $T_c = 299.50\,\text{K}$. The solubility, $s$, is in units of mass of cobalt per unit mass of solvent. In these units, the solute concentration standard state is $s^\circ = 10^{-6}$. The choice of this standard state is the same as reporting the solubility in the units of ppm

For temperatures *inside* the critical region, the slope of the van't Hoff plot can be calculated using the equation [11],

$$\left(\frac{\partial \ln s}{\partial(1/T)}\right)_{P,\Delta G=0} = -T\Delta H\left(\frac{\partial \ln s}{\partial \Delta G}\right)_{T,P} \tag{4}$$

The condition for dissolution equilibrium at constant $T$ and $P$ is $\Delta G = 0$; the condition for stability of the dissolution equilibrium is $(\partial \ln s/\partial \Delta G)_{T,P} > 0$ [11]. Being the positive definite derivative of a *density* with respect to a *field*, $(\partial \ln s/\partial \Delta G)_{T,P}$ must diverge toward *positive* infinity as $T \rightarrow T_\text{c}$. Since the enthalpy of solution in the critical region, $\Delta H$, is bounded, Eq. 4 indicates that the slope of the van't Hoff plot in the critical region should go to *negative* infinity when the dissolution is *endothermic*$(\Delta H > 0)$ [11].

As shown in Fig. 1, the van't Hoff slope, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, for dissolution of $Fe_2O_3$ becomes increasingly *negative* in the critical region in agreement with Eq. 4. Table 1 indicates that the critical region extends over the temperature range from 299.30 K to 300.65 K. On the basis of Fig. 2, it is possible to make a similar observation in the case of the dissolution of $Co_3O_4$, which according to Table 2, has a critical region that extends over the temperature range from 299.50 K to 300.75 K.

## 3 Discussion and Conclusions

Binary liquid mixtures with phase diagrams having a consolute point are plentiful; the list includes several *hundred* pairs exhibiting an LCST and several *thousand* pairs exhibiting a UCST [22]. The solvent power of these liquids permits them to be used to study the effect of the critical point on the net rate of reaction [23–33] and also on the position of chemical equilibrium [11,34,35].

Greer et al. [34] 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 the volatile components, 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 the position of equilibrium as the temperature approached the critical value [34]. Because the dissolution reactions of metal oxides in isobutyric acid + water involve a solid in equilibrium with a liquid, they also are *heterogeneous* reactions.

The temperature dependence of the solubilities of $Fe_2O_3$ and $Co_3O_4$ along the critical isopleth of isobutyric acid + water can be compared with the temperature dependence of the solubilities of other metal oxides in this mixture under the same conditions. Like $Fe_2O_3$ and $Co_3O_4$, $MnO_2$ [11] and $In_2O_3$ [35] both dissolve *endothermically* in isobutyric acid + water, and the van't Hoff slope, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, is observed to tend toward *negative* infinity as $T$ approaches $T_c$. In contrast to these three, $Al_2O_3$ [11] dissolves *exothermically*, and the van't Hoff slope tends toward *positive* infinity in the critical region. A *strong* critical effect is observed in the solubility of each of these metal oxides, because the stoichiometry of the dissolution reaction involves both components of the solvent. The observed correlation of *endothermic* dissolution with an increasing *negative* van't Hoff slope in the critical region and *exothermic* dissolution with increasing *positive* van't Hoff slope is in complete agreement with Eq. 4 and the principle of critical-point universality [11].

For metal oxide dissolution in isobutyric acid + water, Tables 1 and 2 permit some conclusions to be drawn concerning the orientation of the critical isopleth with respect to the direction of the liquid–liquid coexistence curve when the two curves are plotted in a coordinate system spanned by field variables. Consider isobutyric acid + water at a temperature $T > T_c$ and a metal oxide that dissolves with stoichiometry as shown in either of Eqs. 1 and 3. The temperature coefficient of the solubility, $(\partial s/\partial T)_{P,\Delta G=0}$, is the derivative of a density with respect to a field with no densities held fixed. According to the principle of critical-point universality, it can be represented in the critical region by

$$(\partial s/\partial T)_{P,\Delta G=0} = C(T - T_c)^{-x} \tag{5}$$

where $x \approx 1$ is an exponent whose value depends only on the orientation of the path of approach to the critical end-point reckoned with respect to the coexistence curve. The proportionality constant, $C$, which depends on both solute and solvent, has a positive value when the metal oxide dissolves endothermically. The integral of Eq. 5 is

$$s(T) = I + \frac{C}{(1-x)}(T - T_c)^{1-x} \tag{6}$$

where $I$ is another constant that depends on both solute and solvent. According to the principle of critical-point universality [2], when the path of approach to the critical end point makes an *angle* with respect to the coexistence curve [2], the exponent that appears on the right-hand side of Eq. 5 should have the universal value $x = 1 - (1/\delta) = 0.78$ [36], which causes the exponent in Eq. 6 to have the *positive* value $1 - x = (1/\delta) = 0.22$. Under these conditions, $(\partial s/\partial T)_{P,\Delta G=0}$ should diverge as $T \rightarrow T_c$, but $s(T)$ should approach the finite limit, $s(T_c) = I$. By contrast, when the path of approach to the critical end point *is parallel* to the coexistence curve [2], the exponent in Eq. 5 assumes the universal value $x = \gamma = 1.23$ [36]. This causes the exponent in Eq. 6 to have the *negative* value, $1 - x = -0.23$. Under these conditions, although $(\partial s/\partial T)_{P,\Delta G=0}$ may be large, $s(T)$ goes to zero before $T$ reaches $T_c$.

In our solubility experiments using isobutyric acid + water as the solvent, we have no a priori knowledge concerning the orientations in field space of either the coexistence curve or the path of approach to the critical end point by way of the critical isopleth. Nonetheless, according to the principle of critical-point universality, the finite value of $s(T)$ at $T = T_c$, which is evident in the tables, suggests that the coexistence curve and the critical isopleth must meet at an *angle*.

The thermodynamic theory of supercritical dissolution was first worked out by Procaccia and Gitterman [37], by Gitterman [38], and by Levelt-Sengers et al. [39]. The thermodynamic treatment outlined in Sect. 2 is very close in spirit and detail to all three of these theories. The main new feature introduced by us is the role played by the stoichiometry in restricting the number of fixed density variables.

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