

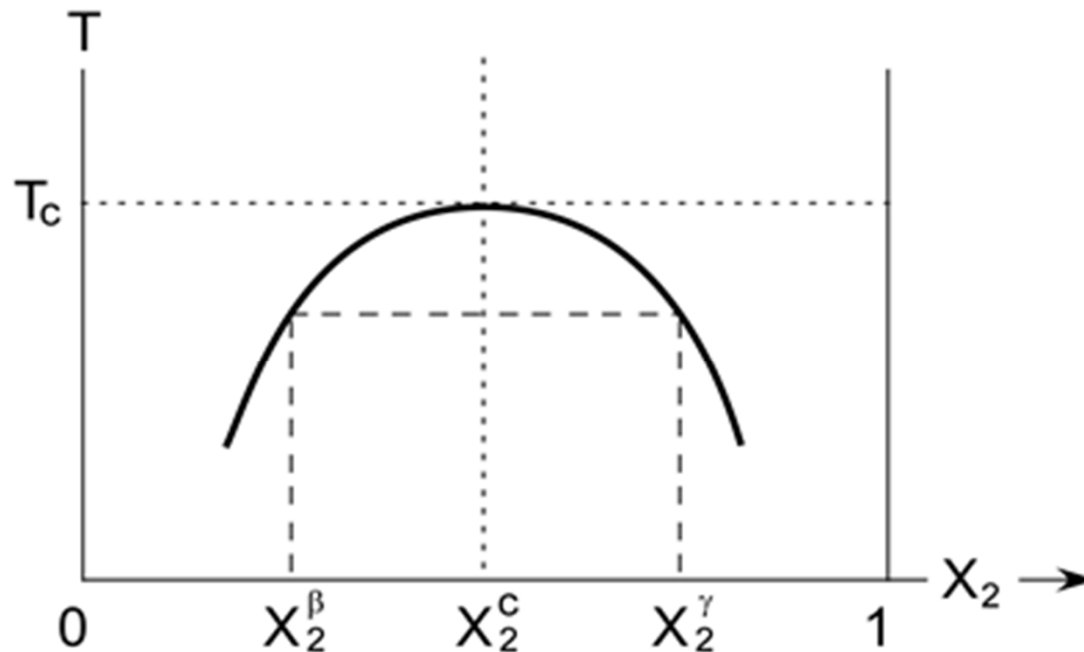
**Diverging Thermodynamic Derivatives Associated with
Heterogeneous Chemical Equilibria in a Binary Liquid
Mixture with a Consolute Point**

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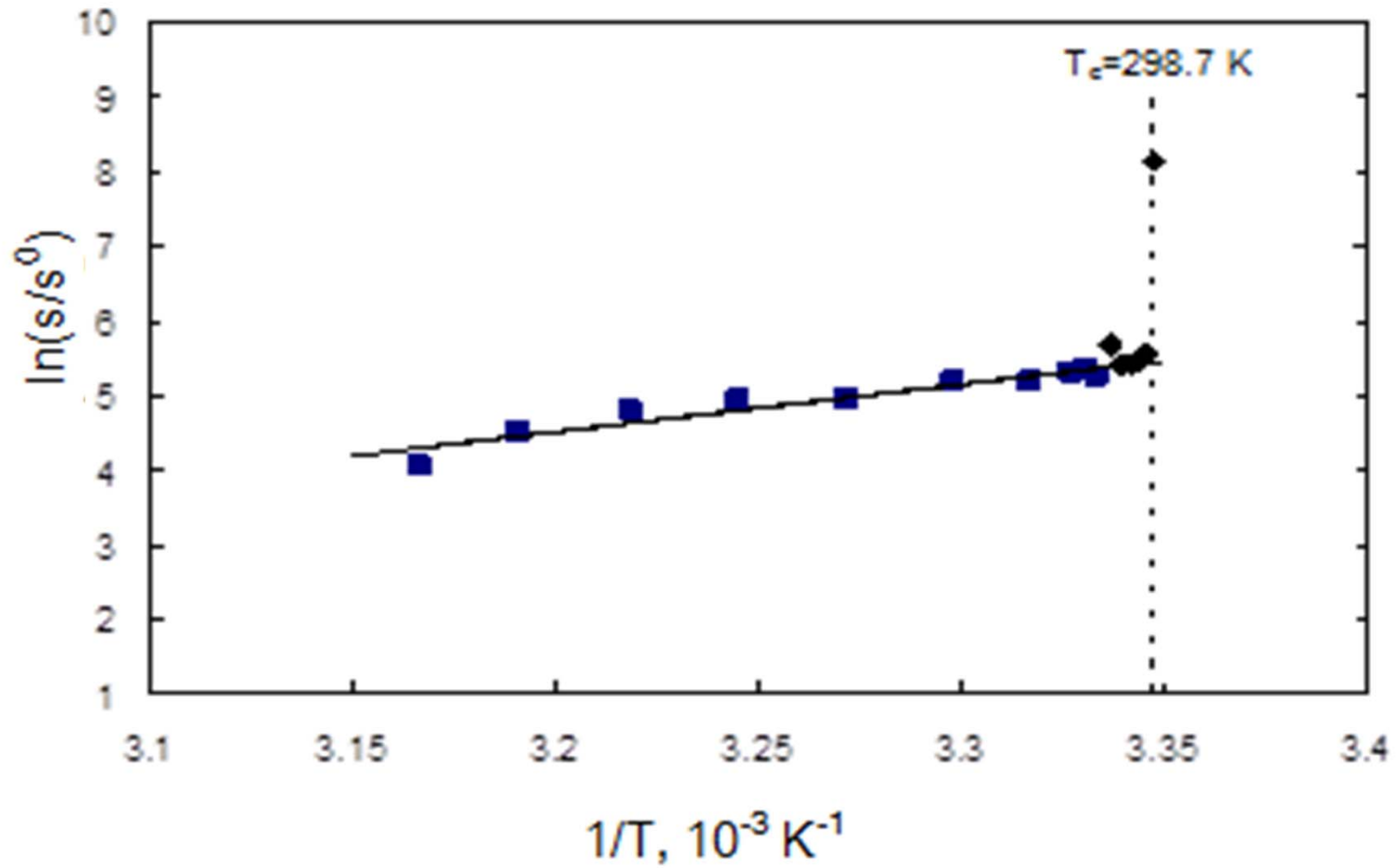
Goal: Test the applicability of the principle of critical point universality to metal oxide dissolution equilibria near the critical point of solution.

Binary liquid mixture with a critical point of solution: $(\text{CH}_3)_2\text{CHCOOH} + \text{H}_2\text{O}$

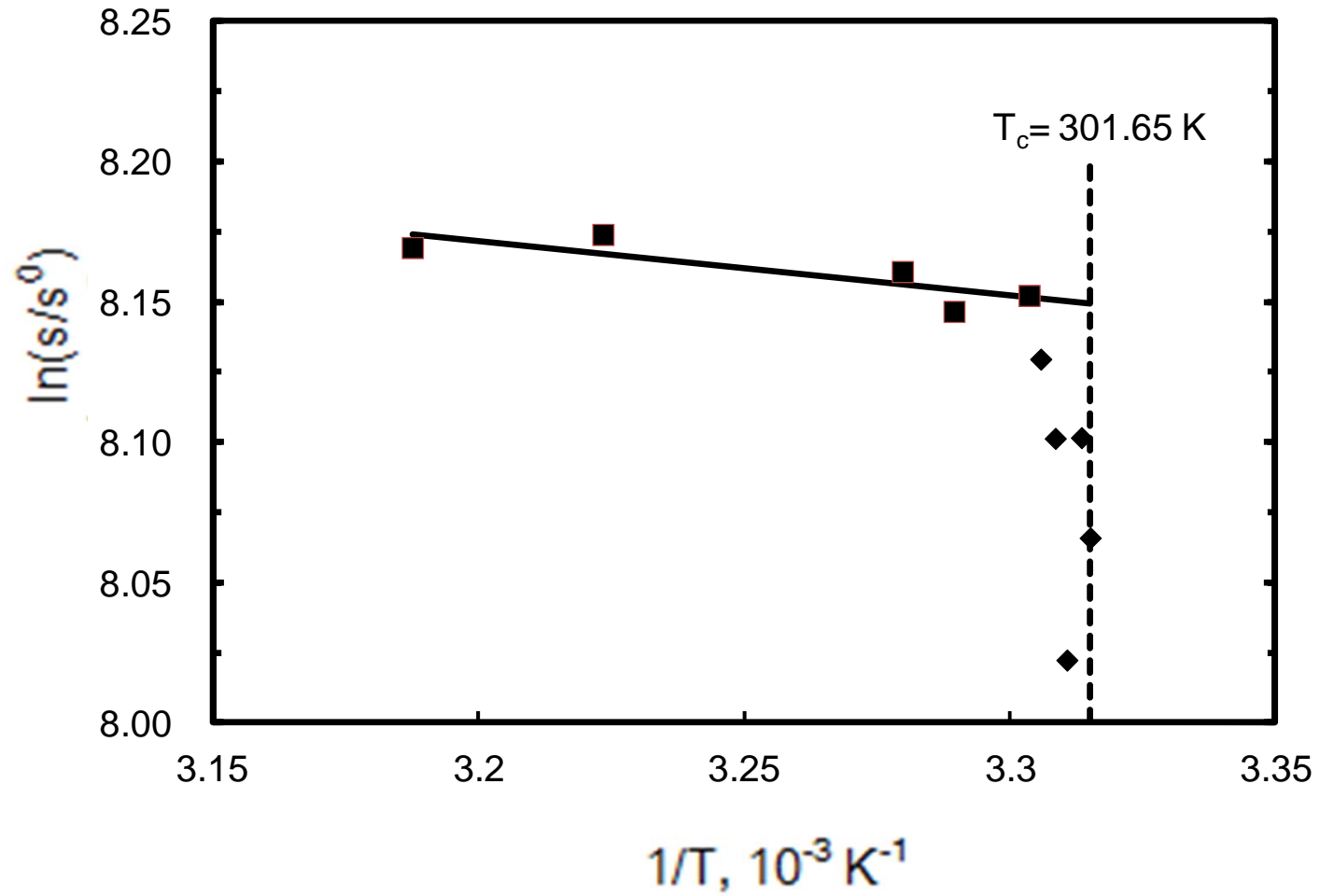
Liquid-Liquid Coexistence Curve for a Binary Liquid Mixture with an Upper Critical Solution Temperature



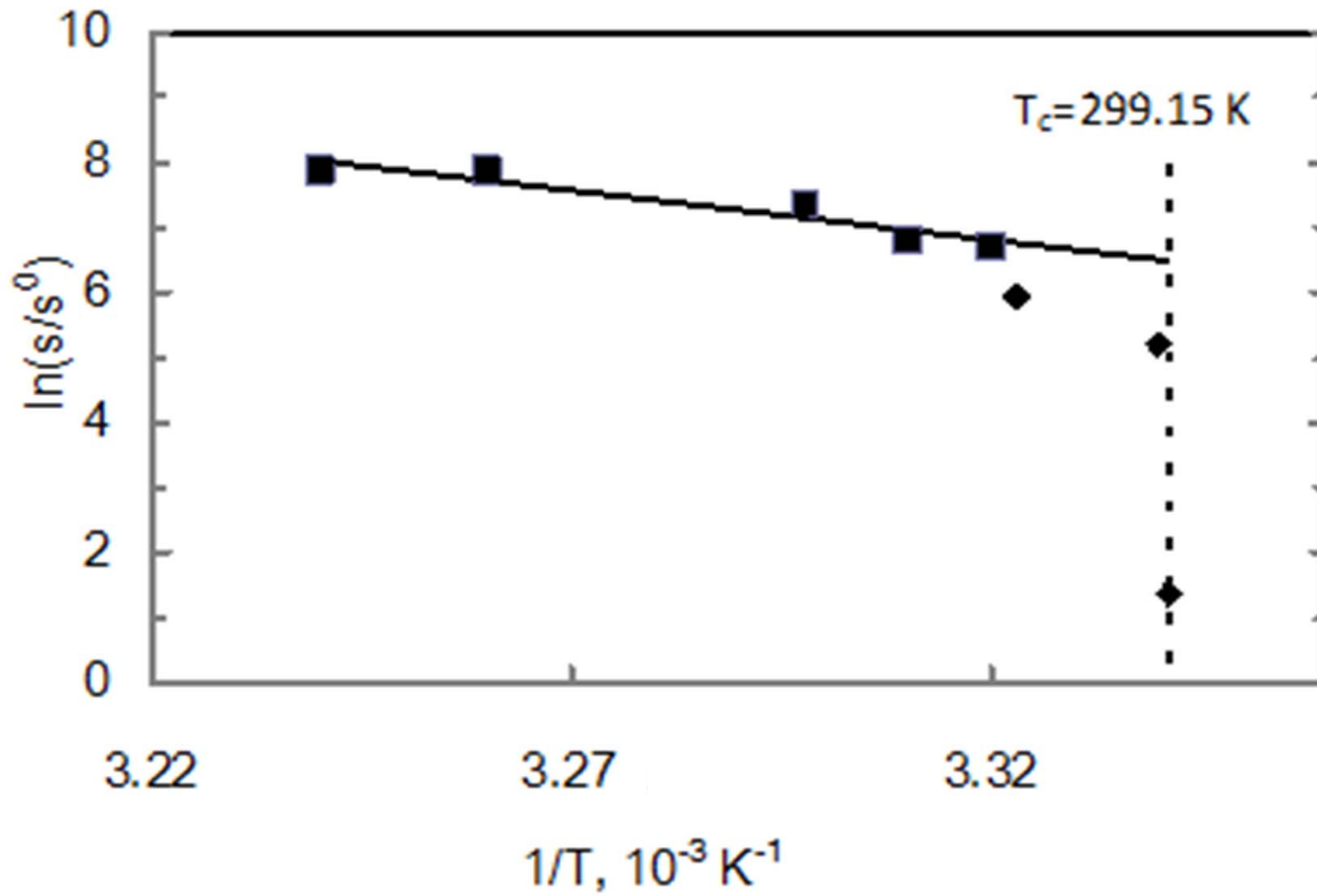
Experimental Results SnO



Experimental Results CuO



Experimental Results CoO



Application of the Principle of Critical Point Universality To the Calculation of the van't Hoff Slope, $\partial \ln s / \partial (1/T)$

I. Griffiths-Wheeler Classification of Thermodynamic Variables

(a) A “field” variable is a variable whose value is *uniform* across all phases coexisting in equilibrium. Examples are P , T , μ and ΔG , which is a linear combination of chemical potentials.

(b) A “density” variable is a variable whose value is *different* in each coexisting phase. Examples are H , \bar{V} , X , and s , which is the solubility in ppm.

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

II. Derivative of a Density with Respect to a Field with No Densities Held Fixed

$\left(\frac{\partial \rho_j}{\partial h_k}\right)$ is the derivative of a density with respect to a field with *no* density variables held fixed. It diverges as $|(T - T_c)/T_c|^{-y}$ with $y \approx 1$. This is called a strong divergence.

$\left(\frac{\partial \ln s}{\partial (1/T)}\right)_{P, \Delta G=0}$ is the derivative of a density with respect to a field with *no* density variables held fixed. It should diverge *strongly*.

III. Method for Determining the Number of Fixed Densities (Gibbs Phase Rule)

- Gibbs Phase Rule

f = number of independent intensive variables (densities and fields)

c = number of independent chemical species

π = number of coexisting phases

$$f = c - \pi + 2$$

III. Method of Determining the Number of Independent Species (Stoichiometry Matrix)

H^+	A^-	O^{2-}	M^{2+}		
1	1	0	0	HA	$HA = (CH_3)_2CHCOOH$
2	0	1	0	H_2O	
3	0	1	0	H_3O^+	
0	1	0	0	A^-	$A^- = (CH_3)_2CHCOO^-$
0	0	1	1	MO	
0	0	0	1	M^{2+}	

Rank of this stoichiometry matrix = 4

$$\rho = 4$$

Ref: S. R. Brinkley, J. Chem. Phys. **14**, 563 (1946)

III. Method for Determining the Number of Independent Species (Constraint Equations)

- Conservation of metal atoms and oxygen atoms.
- When metal oxide is in solubility equilibrium with the liquid, metal atoms are either in the solid or dissolved in the liquid as cations, while oxygen atoms are either in the solid or in the liquid in the form of water or hydronium ions.

$$n_{MO(s)}^o = n_{MO(s)} + n_{M^{2+}(aq)}$$

$$n_{MO(s)}^o = n_{MO(s)} + \Delta n_{H_2O(aq)} + \Delta n_{H_3O^+(aq)}$$

The difference between these two equations is

$$-\Delta n_{H_2O(aq)} + \Delta n_{H_3O^+(aq)} + n_{M^{2+}(aq)} = 0$$

- The liquid phase must be electrically neutral

$$n_{H_3O^+(aq)} + 2n_{M^{2+}(aq)} - n_{A^-(aq)} = 0$$

III. Method Determining the Number of Independent Species (Final Result)

- Rank of stoichiometry matrix

$$\rho = 4$$

- Number of constraint equations

$$S = 2$$

- Calculation of number of independent species

$$c = \rho - S$$

$$= 4 - 2$$

$$= 2$$

IV. Calculation of the Number of Independent Intensive Variables and the Number of Fixed Density Variables

$$f = c - \pi + 2$$

$$c = 2$$

$$\pi = 2$$

$$f = c = 2$$

The two fixed intensive variables are accounted for by the temperature and the pressure, so there are no fixed density variables. A strong critical effect is expected.

Data Analysis and Interpretation

The van't Hoff slope is:

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

(a) For the solubility equilibrium to be stable, $\left(\frac{\partial \ln s}{\partial \Delta G} \right)_{T, P} > 0$. This implies that,

$\left(\frac{\partial \ln s}{\partial \Delta G} \right)_{T, P}$ goes to *positive* infinity *strongly* as $T \rightarrow T_c$.

(b) The sign of $\left(\frac{\partial \ln s}{\partial(1/T)} \right)_{P, \Delta G=0}$ is thus *opposite* to that of ΔH .

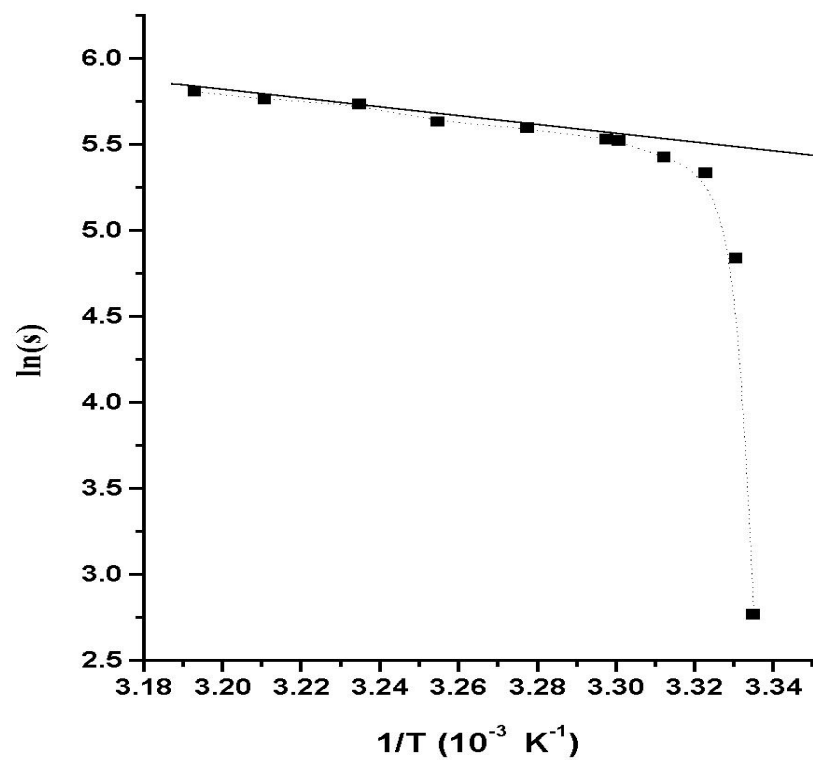
(i) If the dissolution is *endothermic* ($\Delta H > 0$), $\left(\frac{\partial \ln s}{\partial(1/T)} \right)_{P, \Delta G=0}$ goes to *negative* infinity *strongly* as $T \rightarrow T_c$.

(ii) If the dissolution is *exothermic* ($\Delta H < 0$), $\left(\frac{\partial \ln s}{\partial(1/T)} \right)_{P, \Delta G=0}$ goes to *positive* infinity *strongly* as $T \rightarrow T_c$.

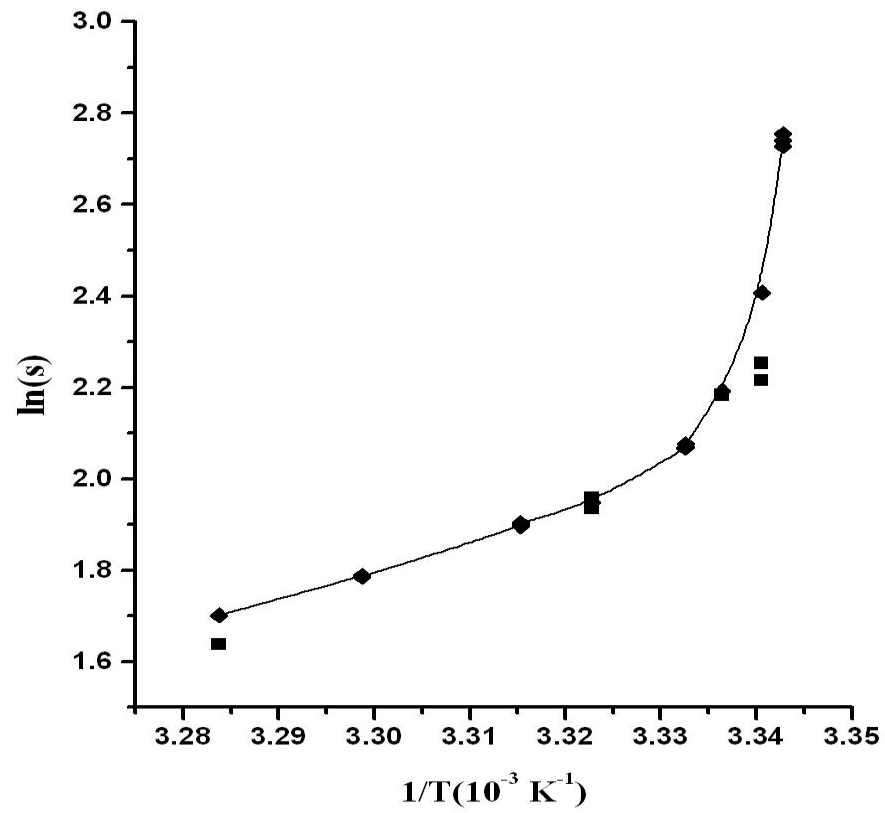
Ref: Y. W. Kim and J. K. Baird, J. Phys. Chem. B **109**, 17262 (2005)

Endothermic Dissolution MnO_2

Ref: Y. W. Kim and J. K. Baird, J. Phys. Chem. B **109**, 17262 (2005).



Exothermic Dissolution Al_2O_3



Summary

Metal Oxide	$\Delta H_{\text{solution}}$	Divergence in ($\partial \ln s / \partial(1/T)$)
SnO	negative	positive
Al ₂ O ₃	negative	positive
CuO	positive	negative
CoO	positive	negative
NiO	positive	negative
MnO ₂	positive	negative
Fe ₂ O ₃	positive	negative
In ₂ O ₃	positive	negative
Co ₃ O ₄	positive	negative

Conclusions

1. Along the critical isopleth at temperatures a few degrees Centigrade or more *above* T_c , a graph of solubility data in the form, $\ln s$ vs. $1/T$, makes a straight line in agreement with the van't Hoff equation.
2. *Within* the critical region, which extends about one degree Centigrade above T_c , the van't Hoff slope, $(\partial \ln s / \partial(1/T))$, diverges towards *positive infinity* when dissolution is *exothermic* and towards *negative infinity* when dissolution is *endothermic*.
3. The requirement that there be no fixed density variables, i.e. $f = 2$, is guaranteed by constraint equations that express conservation of metal atoms, oxygen atoms, and charge. For dissolution in isobutyric acid + water, these constraint equations are satisfied by any ionic metal oxide, peroxide, or hydroxide.
4. In agreement with the principle of critical point universality, the observed departures of $(\partial \ln s / \partial(1/T))$ appear to be *strong* divergences in the Griffiths-Wheeler sense.

Reference:

B. Hu, J. K. Baird, R. D. Richey, and R. G. Reddy, J. Chem. Phys. **134**, 154505 (2011).