Universality of Physical and Chemical Critical Effects in Liquid Mixtures

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Introduction to Critical Phenomenon

The point in the phase diagram of a system where the structural difference between two coexisting phases disappears defines a **critical point**. Systems as diverse as superconductors, pure fluids, and binary liquid mixtures exhibit critical points [1,2]. The critical behaviors of the thermophysical properties of these systems are sufficiently similar from case to case as to constitute an "isomorphism"[1]. Figure 1 shows a phase diagram for a binary liquid mixture with a critical point of solution
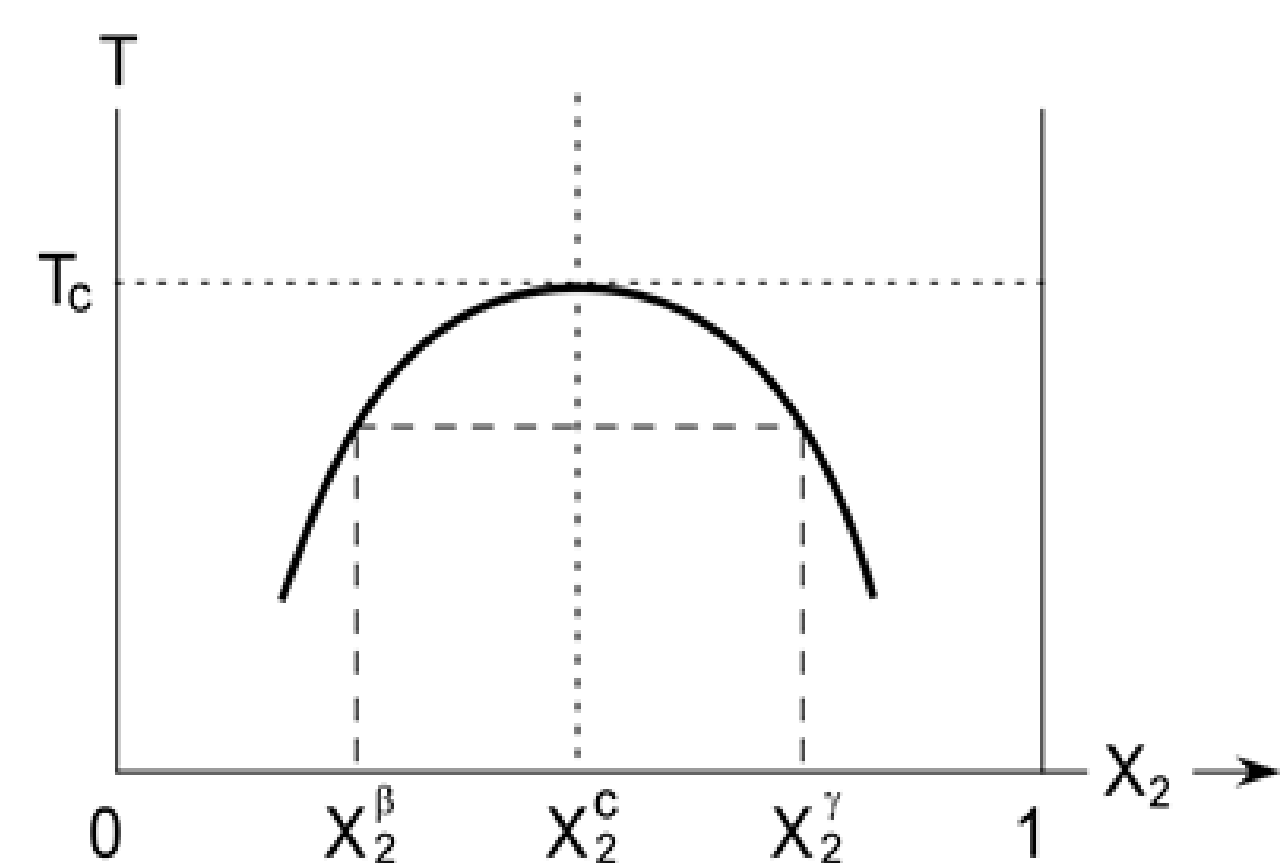
Fig. 1. The coordinates are the temperature, T vs. the mole fraction, X_2, of one of the components. The solid curve is the liquid-liquid coexistence boundary. On the convex side to this curve, the two components are miscible and form a single liquid phase. On the concave side, complete miscibility fails, and a meniscus appears separating two liquid phases, one with composition X_2^{β} and the other with composition X_2^{γ}. The critical temperature for the phase transition is T_c, and the critical composition is X_2^c.

Physical Properties of The Critical Point

The intensive thermodynamic variables describing a binary liquid mixture with a critical point of solution can be divided into two classes, called "fields" and "densities". A **"field"** variable, h, such as temperature, pressure, or chemical potential, has a value which is uniform across all coexisting phases. A **"density"** variable, ρ, such as a mole fraction or the specific entropy has a unique value in each phase [2].

- The derivative of a "density" with respect to a "field" $(\partial \rho / \partial h)_{\{X\}}$ will diverge toward infinity near the critical point, if the set of fixed variables, $\{X\}$, defines a path of approach to the critical point that contains no more than one fixed "density".
- The isobaric heat capacity is given by $C_{P,X_2} = T(\partial \bar{S}/\partial T)_{\{P,X_2\}}$. Here $\bar{s}$ is the specific entropy, (a "density" variable) and T is the temperature (a "field variable"); $(\partial \bar{S}/\partial T)_{(P,X_2)}$ is the derivative of a "density" with respect to a "field". The path of approach to the critical point lies along the critical isopleth, $X_2 = X_2^c$, so only one "density" variable is held fixed; hence, $\lim_{T \to T_c} C_{P,X_2} \to \infty$.

The G-W Rules are Based Upon a Count of the Independent Intensive Variables

In the case of a liquid mixture under ordinary laboratory conditions, the temperature and pressure (both are "fields") are fixed by the experimenter. Any additional fixed variable is necessarily a mole fraction (i.e. a "density"). The condition that the path of approach to the critical point should contain no more than one fixed "density" is satisfied when the phase rule [3] predicts $F = 3$, where $F = C - R - \phi - I + 2$ and F = the number of independent intensive thermodynamic variables, C = the number of chemical components making up the system, E = the total number of chemical elements required to express the stoichiometry, $R = C - E$, the maximum number of linearly independent chemical reactions, ϕ = the number of coexisting phases, I = the number of constraint equations derivable from the law of conservation of mass.

Application of The Phase Rule

1. Chemically inert mixture: aniline and cylcohexane [4]
- Components: $C = 2$; aniline and cyclohexane
- Reactions: $R = 0$
- Phases: $\phi = 1$; Liquid phase above T_c
- Constraints: In the absence of chemical reaction, $I = 0$
- Evaluation of the Phase Rule: $F = C - R - \phi - I + 2 = 2 - 0 - 1 - 0 + 2 = 3$
- Experimentally $\lim_{T \to T_c} C_{P,X_2} \to \infty$

2. Chemically reactive mixture: triethylamine and water [5]
The components undergo acid-base reaction according to $R_3N + H_2O \to R_3NH^+ + OH^-$
- Components: $C = 4$; R_3N, H_2O, R_3NH^+, OH^- (R = ethyl)
- Chemical "Elements": $E = 3$; R_3N, H, O
- Reactions: $R = C - E = 4 - 3 = 1$
- Phases: $\phi = 1$; Liquid phase above T_c

Element Conservation Equations:
Conservation of H: $2n^o_{H_2O} = 2n_{H_2O} + n_{R_3NH^+} + n_{OH^-}$ (1)

Conservation of O: $n^o_{H_2O} = n_{H_2O} + n_{OH^-}$ (2)

where, n_Y^0 is the initial number of moles and n_Y is the equilibrium number of moles of substance Y. A relation, which is independent of $n^o_{H_2O}$, can be derived by forming the linear combination, Eq.(1) – 2 x Eq.(2). The result is the electroneutrality condition: $n_{R_3NH^+} = n_{OH^-}$

- Hence, constraint equations: $I = 1$
- Evaluation of the Phase Rule: $F = C - R - \phi - I + 2 = 4 - 1 - 1 - 1 + 2 = 3$
- Experimentally $\lim_{T \to T_c} C_{P,X_2} \to \infty$

CONCLUSION: The diverging temperature behavior of C_{P,X_2} as T goes to T_c is correlated with $F = 3$.

Chemical Properties of The Critical Point

If we designate the extent of reaction by s, the slope, $(\partial \ln s / \partial (1/T))$ of a van't Hoff plot of $\ln s$ vs. $1/T$ is the derivative of a "density" with respect to a "field". The sign of the slope is given by the following equation

$$\left(\frac{\partial \ln s}{\partial (1/T)} \right) = -T \Delta H \left(\frac{\partial \ln s}{\partial \Delta G} \right) \qquad (3)$$

The chemical equilibrium stability condition is $(\partial \ln s / \partial \Delta G) > 0$. Because $(\partial \ln s / \partial \Delta G)$ involves differentiation of s (a "density") with respect to ΔG (linear combination of chemical potentials, and hence a "field"), then when we have $F = 3$, the $\lim_{T \to T_c} (\partial \ln s / \partial \Delta G) \to +\infty$. According to Eq.(3), we can expect

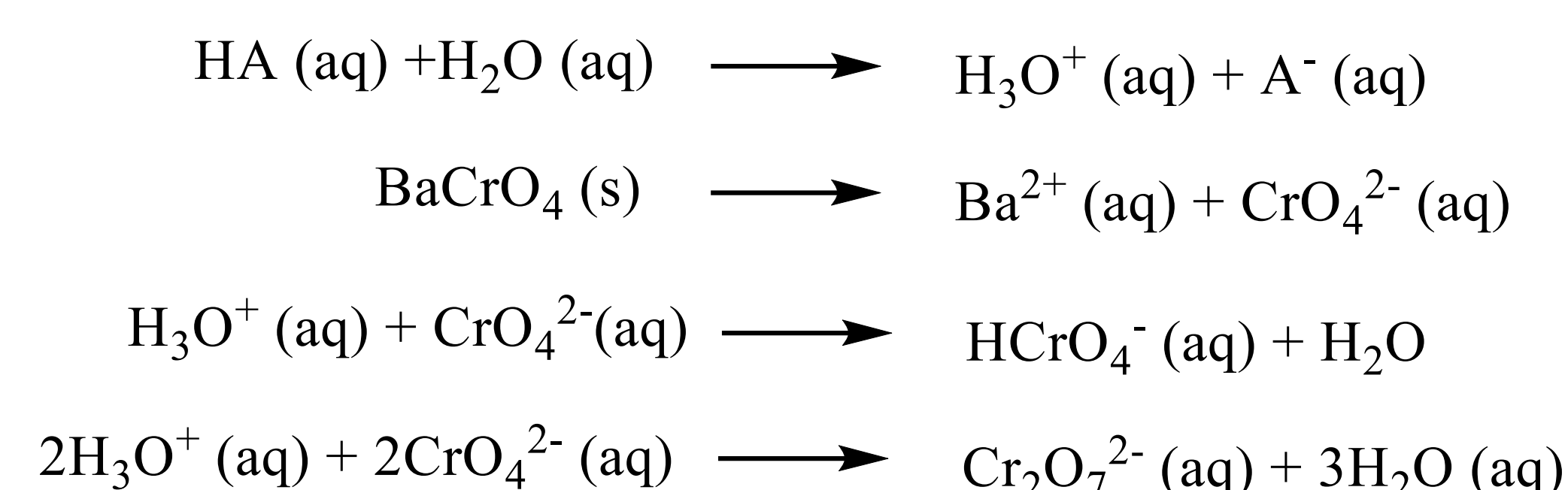$$\lim_{T \to T_c} \left(\frac{\partial \ln s}{\partial (1/T)} \right) \to -\infty \quad \text{if } \Delta H > 0 \qquad (4)$$

$$\lim_{T \to T_c} \left(\frac{\partial \ln s}{\partial (1/T)} \right) \to +\infty \quad \text{if } \Delta H < 0 \qquad (5)$$

Observation of Critical Effects in the van't Hoff Slope

Solubility of Barium Chromate in Isobutyric Acid (HA) + Water [7]	Reaction of Lead Sulfate with Potassium Iodide in Isobutyric Acid (HA) + Water [6]

Reaction Scheme

$HA\ (aq) + H_2O\ (aq) \longrightarrow H_3O^+\ (aq) + A^-\ (aq)$

$BaCrO_4\ (s) \longrightarrow Ba^{2+}\ (aq) + CrO_4^{2-}\ (aq)$

$H_3O^+\ (aq) + CrO_4^{2-}(aq) \longrightarrow HCrO_4^-\ (aq) + H_2O$

$2H_3O^+\ (aq) + 2CrO_4^{2-}(aq) \longrightarrow Cr_2O_7^{2-}\ (aq) + 3H_2O\ (aq)$

- Components: $C = 9$, HA (aq), H_2O, H_3O^+ (aq), A^- (aq), $BaCrO_4$ (s), Ba^{2+} (aq), CrO_4^{2-} (aq), $HCrO_4^-$ (aq) and $Cr_2O_7^{2-}$ (aq)
- Elements: $E = 5$; H, A⁻, O, Ba²⁺, Cr
- Reactions : $R = C - E = 4$
- Phase: $\phi = 2$; $BaCrO_4$ (solid) and liquid phase

Conservation of H, A, O, Ba^{2+} and Cr leads to two constraint equations as shown below

$n_{Ba^{2+}} = n_{CrO_4^{2-}} + n_{HCrO_4^-} + 2n_{Cr_2O_7^{2-}}$

$2n_{Ba^{2+}} + n_{H_3O^+} = 2n_{CrO_4^{2-}} + n_{HCrO_4^-} + 2n_{Cr_2O_7^{2-}} + n_{A^-}$

- Constraint Equations: $I = 2$
- Evaluation of the Phase Rule

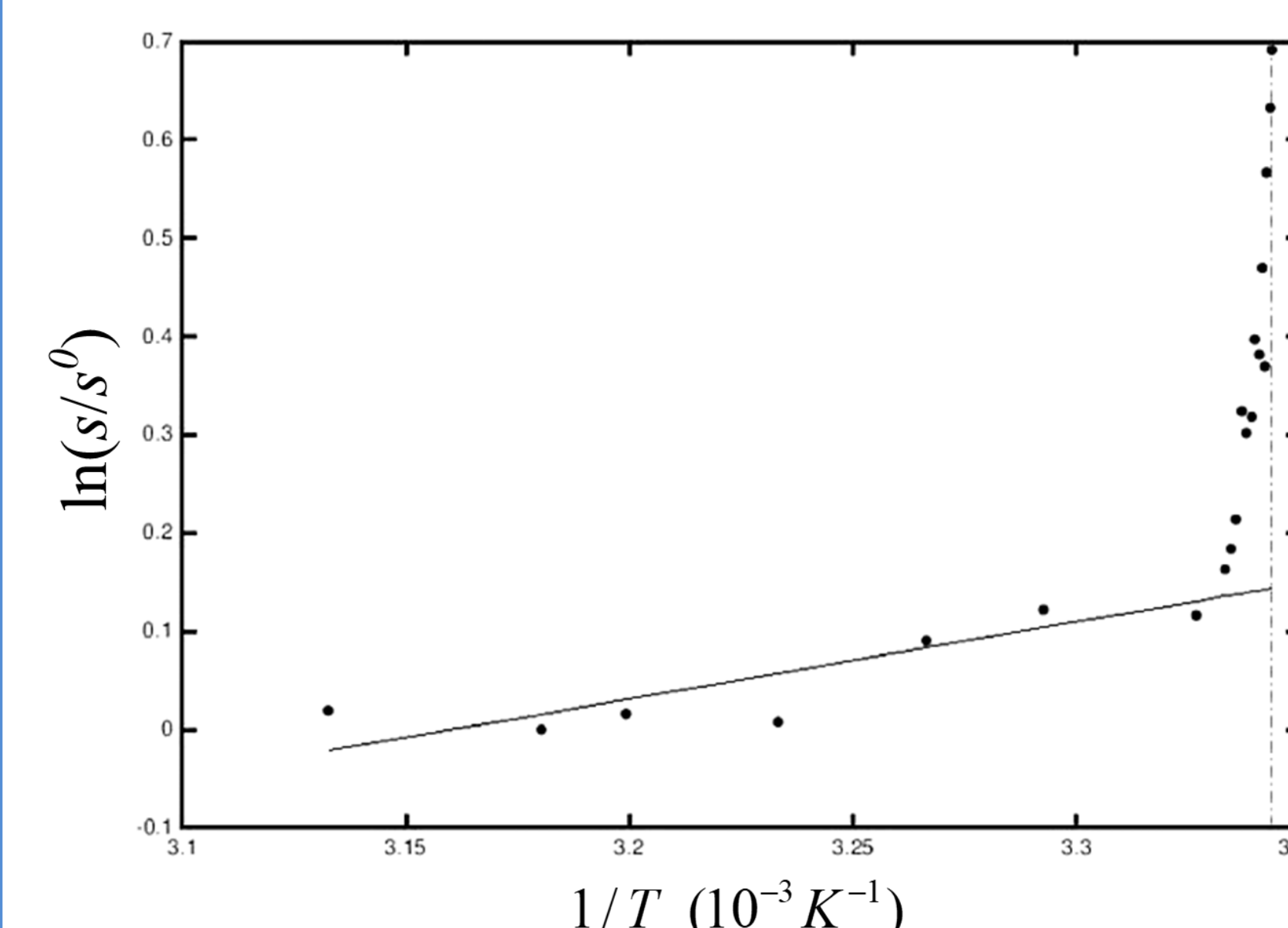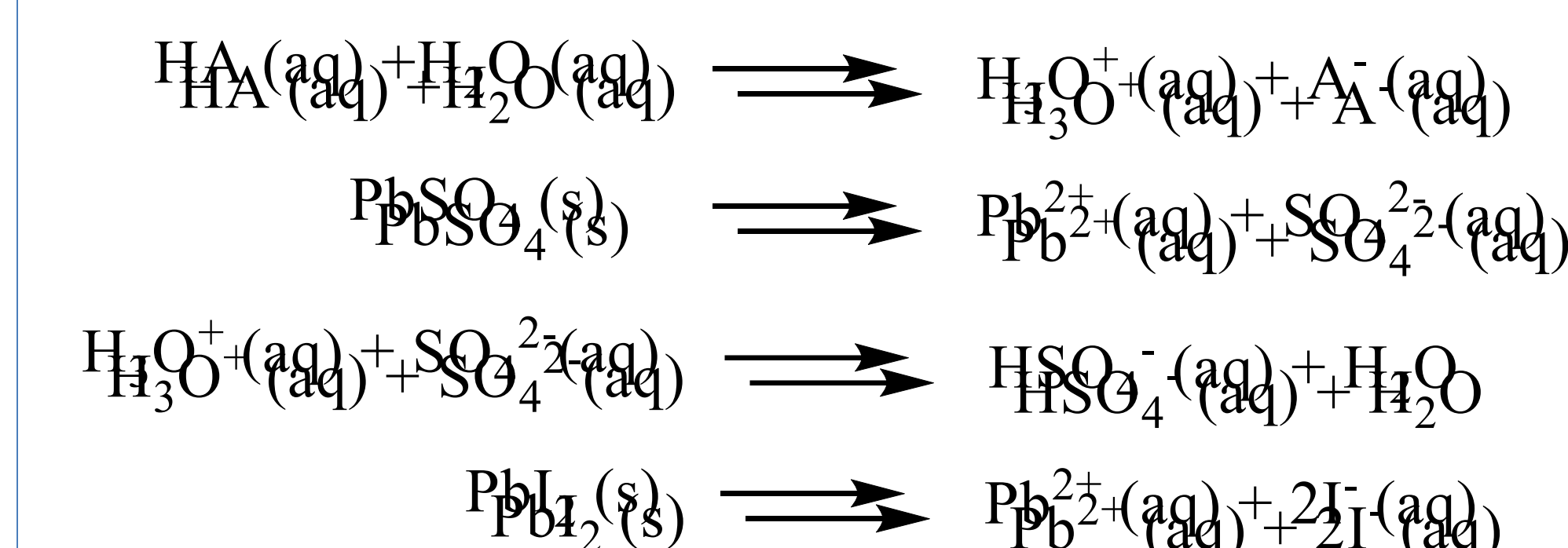$F = C - R - \phi - I + 2$
$= 9 - 4 - 2 - 2 + 2 = 3$

Fig. 2. Van't Hoff plot of the dependence of the concentration, s vs temperature, T, of total chromium dissolved in critical 38.8 mass % aqueous isobutyric acid in equilibrium with excess barium chromate. The standard state of dissolved chromium was taken to be $s^0 = 0.00275$ g/L. The solid line was fitted to data collected above the critical point and then extrapolated into the critical region. The vertical dashed line locates the critical temperature at $T_c = 299.07$ K.

The slope of the van't Hoff plot outside the critical region is positive, implying that $\Delta H < 0$. In agreement with Eq.(5), the sign of the divergence in the critical region is positive.

Reaction Scheme

$HA\ (aq) + H_2O\ (aq) \longrightarrow H_3O^+\ (aq) + A^-\ (aq)$

$PbSO_4\ (s) \longrightarrow Pb^{2+}\ (aq) + SO_4^{2-}\ (aq)$

$H_3O^+\ (aq) + SO_4^{2-}(aq) \longrightarrow HSO_4^-\ (aq) + H_2O$

$PbI_2\ (s) \longrightarrow Pb^{2+}\ (aq) + 2I^-\ (aq)$

- Components: $C = 11$, HA (aq), H_2O, H_3O^+ (aq), A^- (aq), $PbSO_4$ (s), Pb^{2+} (aq), SO_4^{2-} (aq), (aq), PbI_2 (s), I⁻ (aq) and K^+(aq)
- Elements: $E = 7$; H, A⁻, O, Pb, SO_4^{2-}I⁻ and K^+
- Reactions : $R = C - E = 4$
- Phase: $\phi = 3$; $PbSO_4$ (solid), PbI_2 (solid) and liquid phase

Conservation of H, A, O, Pb, SO_4^{2-}, I⁻ and K^+ leads to two constraint equations as shown below

$n_{H_3O^+} + n_{HSO_4^-} = n_{A^-}$

$n_{K^+} + n_{H_3O^+} + 2n_{Pb^{2+}} = 2n_{SO_4^{2-}} + n_{HSO_4^-} + n_{I^-} + n_{A^-}$

- Constraint Equations: $I = 2$
- Evaluation of the Phase Rule

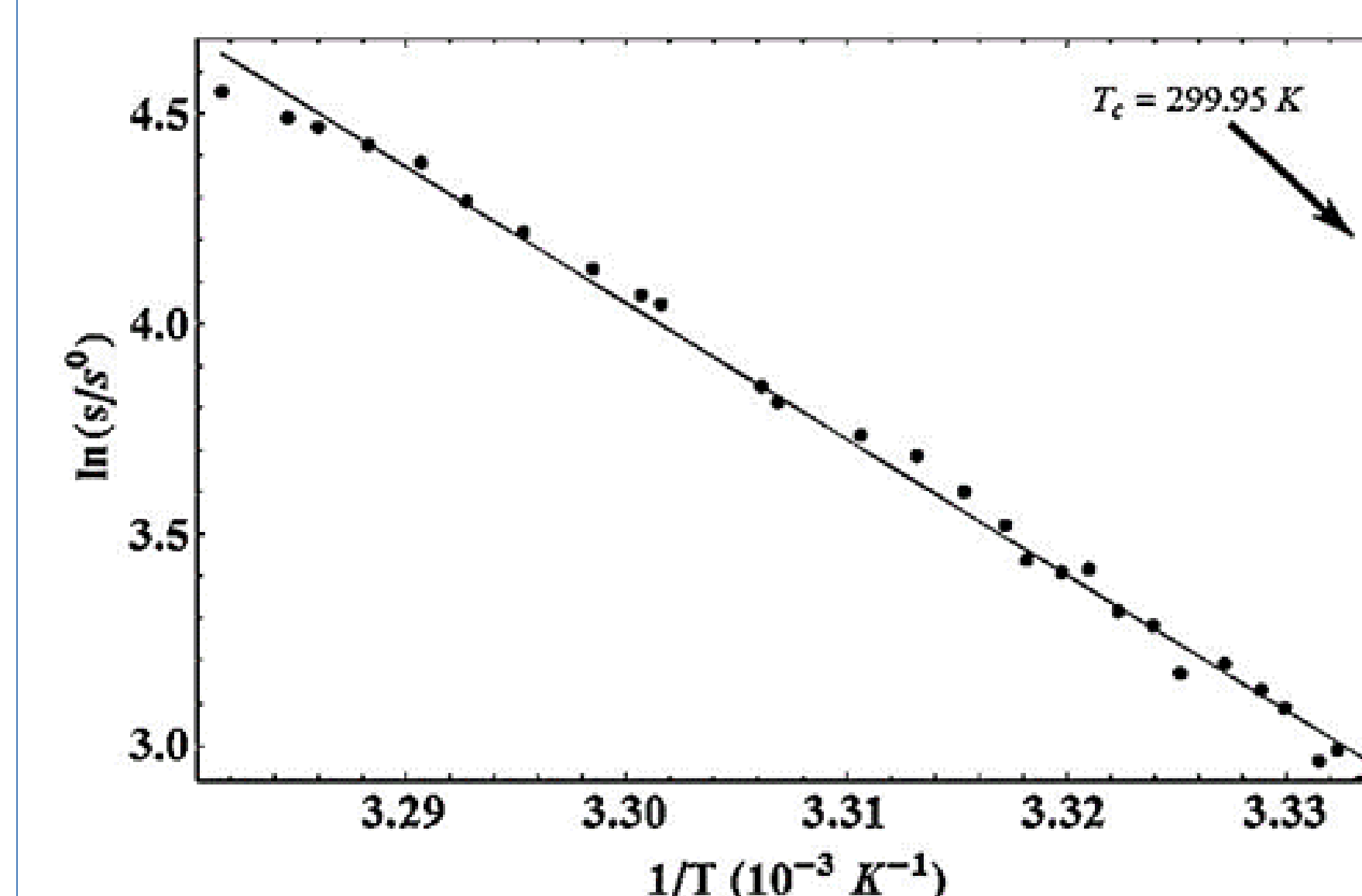$F = C - R - \phi - I + 2$
$= 11 - 4 - 3 - 2 + 2 = 4$

Fig. 3. Van't Hoff plot of the concentration, s of Pb^{2+} vs. temperature, T, for the reaction of $PbSO_4$ with KI in a mixture of 38.8 mass % isobutyric acid + water. The standard state concentration is $s^0 = 1$ ppm. The vertical dashed line locates the critical temperature at $T_c = 299.95$ K.

The slope of van't Hoff plot of the data within the critical region is finite and continuous with that outside the critical region. Because F = 4, there is no evidence of a critical effect.

References

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Conclusion

- The critical effect in the van't Hoff slope has been observed experimentally in the case $F = 3$ for more than 20 different chemical reactions, including examples of both homogeneous and heterogeneous equilibria and liquid mixtures with upper and lower critical solution temperatures [6,7]. In every case, the sign of the divergence in the van't Hoff slope was correlated with the sign of ΔH in agreement with Eqs.(4) and (5).
- At constant temperature and pressure and $F = 3$, a liquid mixture with a critical point of solution satisfies the Griffiths-Wheeler rule [2] that the derivative of a "density" with respect to a "field" will diverge in the critical region. This conclusion applies to both the physical and the chemical properties.