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 behavior of the thermophysical properties of these systems is 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, X2, 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 X2 and the other with composition X2'. The critical temperature for the phase transition is Tc, and the critical composition is Xc.](image)

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” (δρ/δh)Xj will diverge toward infinity near the critical point, as the set of fixed variables, {Xj}, defines a path to the critical point that contains no more than one fixed “density”.
- The isobaric heat capacity is given by Cρ = T(δS/δT)ρ, where T is the temperature (a “field variable”); (δS/δT)Xj is the derivative of a “density” with respect to a “field”. The path of approach to the critical point lies along the isotherm, X2 = X2’, so only one “density” variable is held fixed; hence, limit Cρ→∞.

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 - ϕ + 1 + 2 and F is the number of independent intensive thermodynamic variables, C is the number of chemical components making up the system, E is the total number of chemical elements required to express the stoichiometry, R = C - E, the maximum number of linearly independent chemical reactions, ϕ is 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 cyclohexane [4]**
   - Components: C = 2, aniline and cyclohexane
   - Reactions: R = 0
   - Phases: ϕ = 1; Liquid phase above Tc
   - Constraints: In the absence of chemical reaction, I = 0
   - Evaluation of the Phase Rule: F = C - R - ϕ + 1 + 2 = 2 - 0 - 1 + 2 = 3
   - Experimentally limit Cρ→∞.

2. **Chemically reactive mixture: triethylene and water [5]**
   - Components: C = 4; R, N, H2O, R2NH3; OH (R = ethyl)
   - Chemical “Elements”: E = 3; R, N, H, O
   - Reactions: R = C - E = 4 - 3 = 1
   - Phases: ϕ = 1; Liquid phase above Tc
   - Element Conservation Equations:
     - Conservation of H: 2nH2O = 2nH₂O + nR₂NH₃ + nOH⁻
     - Conservation of O: nH₂O = nH₂O + nOH⁻

   where, n$_{H₂O}$ is the initial number of moles and n$_j$ is the equilibrium number of moles of substance Y. A relation, which is independent of R₂NH₃, can be derived by forming the linear combination, Eq.(1) - 2 x Eq.(2). The result is the electroneutrality condition: R₂NH₃ = nOH⁻.
   - Hence, constraint equations: I = 1
   - Evaluation of the Phase Rule: F = C - R - ϕ + 1 + 2 = 4 - 1 - 1 - 1 + 2 = 3
   - Experimentally limit C$_{ρ/T}$→∞.

CONCLUSION: The diverging temperature behavior of C$_{ρ/T}$ as T goes to Tc is correlated with F = 3.

Chemical Properties of The Critical Point

If we designate the extent of reaction by s, the slope, (δln s/δ(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:

$$\left(\frac{\partial \ln s}{\partial \left(1/T\right)}\right)_{T \rightarrow \infty} = -T \Delta H_f$$

(3)

The chemical equilibrium stability condition is (δln s/δG) > 0. Because (δln s/δG) 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 limit (δln s/δG) → ∞. According to Eq.(3), we can expect

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

(4)

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

(5)

Observation of Critical Effects in the van’t Hoff Slope

**Solubility of Barium Chromate in Isobutyl Alcohol (HA) + Water [7]**

**Reaction of Lead Sulfate with Potassium Iodide in Isobutyl Alcohol (HA) + Water [6]**

**Reaction Scheme**

- HA (aq) + H₂O (aq) → H₃O⁺ (aq) + A⁻ (aq)
- BaCrO₄ (s) → Ba₂⁺ (aq) + CrO₄²⁻ (aq)
- H₂O (aq) + CrO₄²⁻ (aq) → HCrO₄ (aq) + H₂O
- 2H₂O (aq) → 2CrO₄²⁻ (aq) + 3H₂O (aq)

**Components:** C = 9, HA (aq), H₂O, H₂O⁻ (aq), A⁻ (aq), BaCrO₄ (s), Ba₂⁺ (aq), CrO₄²⁻ (aq), HCrO₄ (aq) and Cr₂O₇²⁻ (aq)

- Elements: E = 5; H, A, O, Ba⁴⁺, Cr
- Reactions: R = C - E = 4
- Phase: ϕ = 2; BaCrO₄ (solid) and liquid phase

Conservation of H, A, O, Ba²⁺ and Cr leads to two constraint equations as shown below

$$\text{Conservation of } H: 2n_{H₂O} = 2n_{H₂O} + n_{R₂NH₃} + n_{OH⁻}$$

$$\text{Conservation of } O: n_{H₂O} = n_{H₂O} + n_{OH⁻}$$

where, n$_{H₂O}$ is the initial number of moles and n$_j$ is the equilibrium number of moles of substance Y. A relation, which is independent of R₂NH₃, can be derived by forming the linear combination, Eq.(1) - 2 x Eq.(2). The result is the electroneutrality condition: R₂NH₃ = nOH⁻.

• Constraint Equations: I = 2
• Evaluation of the Phase Rule
  - F = C - R - ϕ + 1 + 2 = 4 - 1 - 1 - 1 + 2 = 3

**Conclusion**

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

**References**