

Introduction

The position of equilibrium in the case of a solid-liquid phase equilibrium in a multicomponent mixture can be determined by specifying various “density” variables, such as mole fractions, and “field” variables, such as temperature and pressure. If the system has a critical point, then according to the principle of critical point universality, the derivative, $(\partial\rho/\partial h)_{\{x\}}$, of any density variable, ρ , with respect to any field variable, h , can be expected to go to infinity in the critical region if the fixed variable set, $\{x\}$, contains no more than one density variable.

Gibbs Phase Rule Theory

Under ordinary experimental conditions, the temperature and pressure are the only field variables used to specify equilibrium. If a total of F variables are required to specify the equilibrium, then necessarily, $F-2$, of these are density variables. The phase rule predicts:

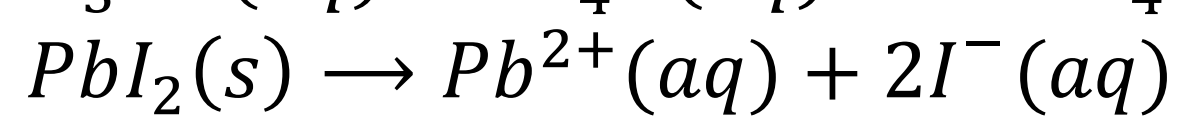
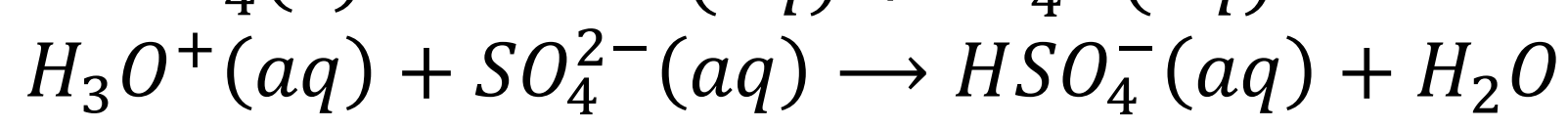
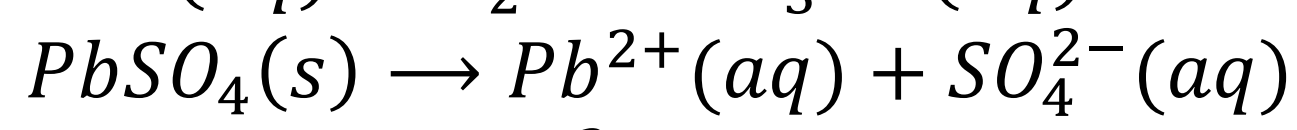
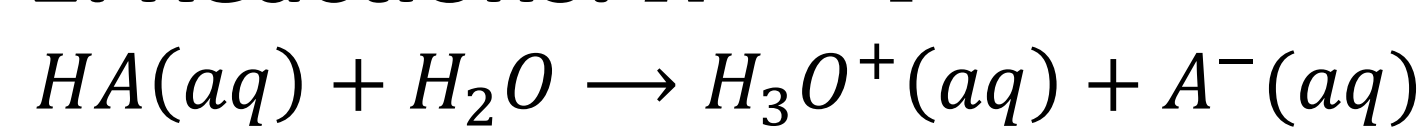
$$F = C - P - R - \sum_{k=1}^{\phi} I_k + 2$$

where C is the total number of chemical species, P is the number of coexisting phases, R is the number of linear independent chemical reactions, and I_k is the number of constraint equations associated with k -th phase.

Example

A mixture of isobutyric acid (HA) + water has a miscibility gap ending in an upper critical solution point at 26 °C and 0.11 mole fraction HA . Consider the simultaneous dissolution of $PbSO_4(s)$ and $PbI_2(s)$ in the mixture.

1. Reactions: $R = 4$



2. Components: $C = 10$

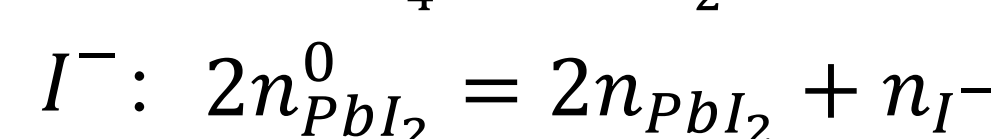
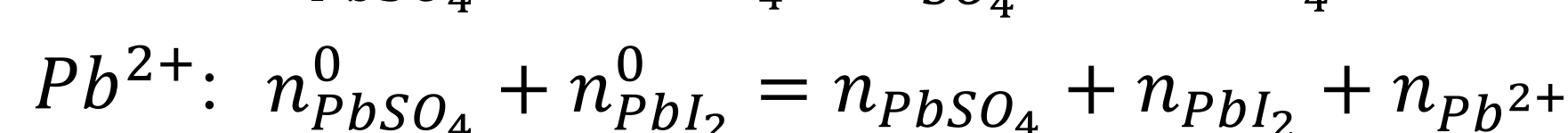
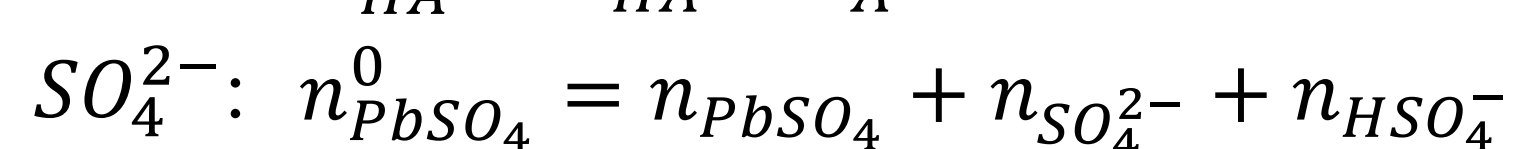
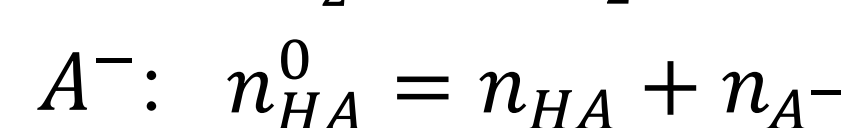
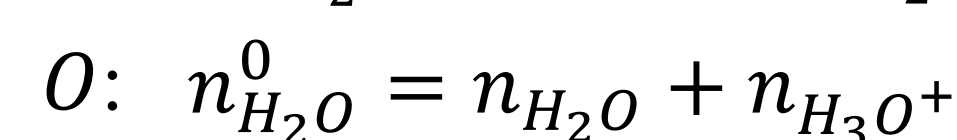
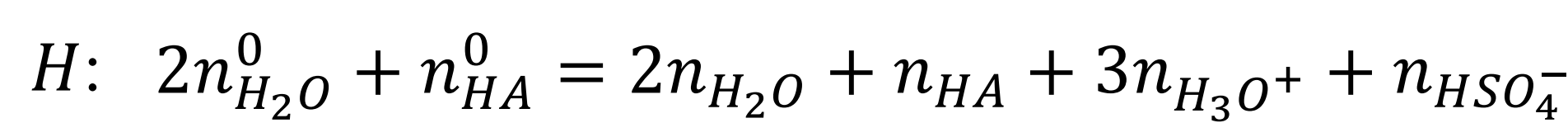
$H_2O, HA, H_3O^+, A^-, PbI_2, Pb^{2+}, SO_4^{2-}, PbSO_4, I^-, HSO_4^-$. Note: These ten components are spanned by the six “elements”: $H, O, A^-, Pb^{2+}, SO_4^{2-}$ and I^- . Ten components spanned by six elements can support a maximum of $R = C - E = 10 - 6 = 4$ linearly independent reactions.

3. Phases: $P = 3$

$PbSO_4(s)$ and $PbI_2(s)$, plus the liquid phase.

4. Constraint Equations: $I = 2$

We first write the conservation equations for the six elements:



where n_Z^0 and n_Z are the initial and equilibrium number of moles of substance, Z , respectively.

Linear combination of the above equations gives two relations independent of temperature and pressure and free of initial conditions. In terms of mole fractions, X_Z , these are

H^+ balance condition:

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

charge neutrality condition:

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

5. Evaluation of F

$$F = C - R - P - I + 2 \\ = 10 - 4 - 3 - 2 + 2 = 3$$

6. Predictions:

- Because $F = 3$ (one density fixed), the slope, $(\partial \ln s / \partial(1/T))$, of a van't Hoff plot of Pb^{2+} solubility, s , a density variable, as a function of $1/T$, a field variable, should diverge as T approaches the critical temperature, T_c .
- The Gibbs-Helmholtz equation predicts that the sign of the divergence should be the same as the sign of $(\partial \ln s / \partial(1/T))$ outside the critical region.

Experimental Method

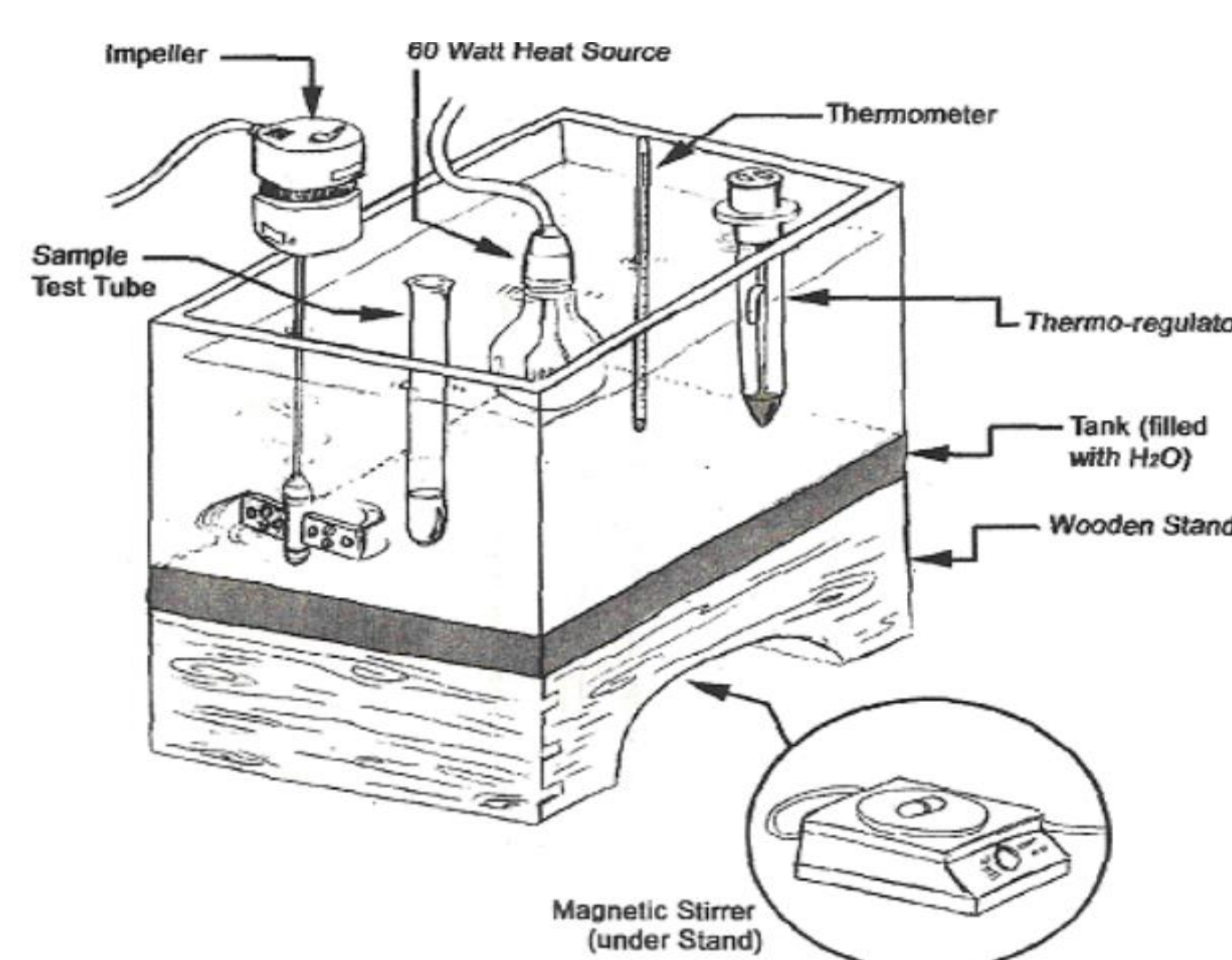


Fig 1. Schematic diagram of water bath

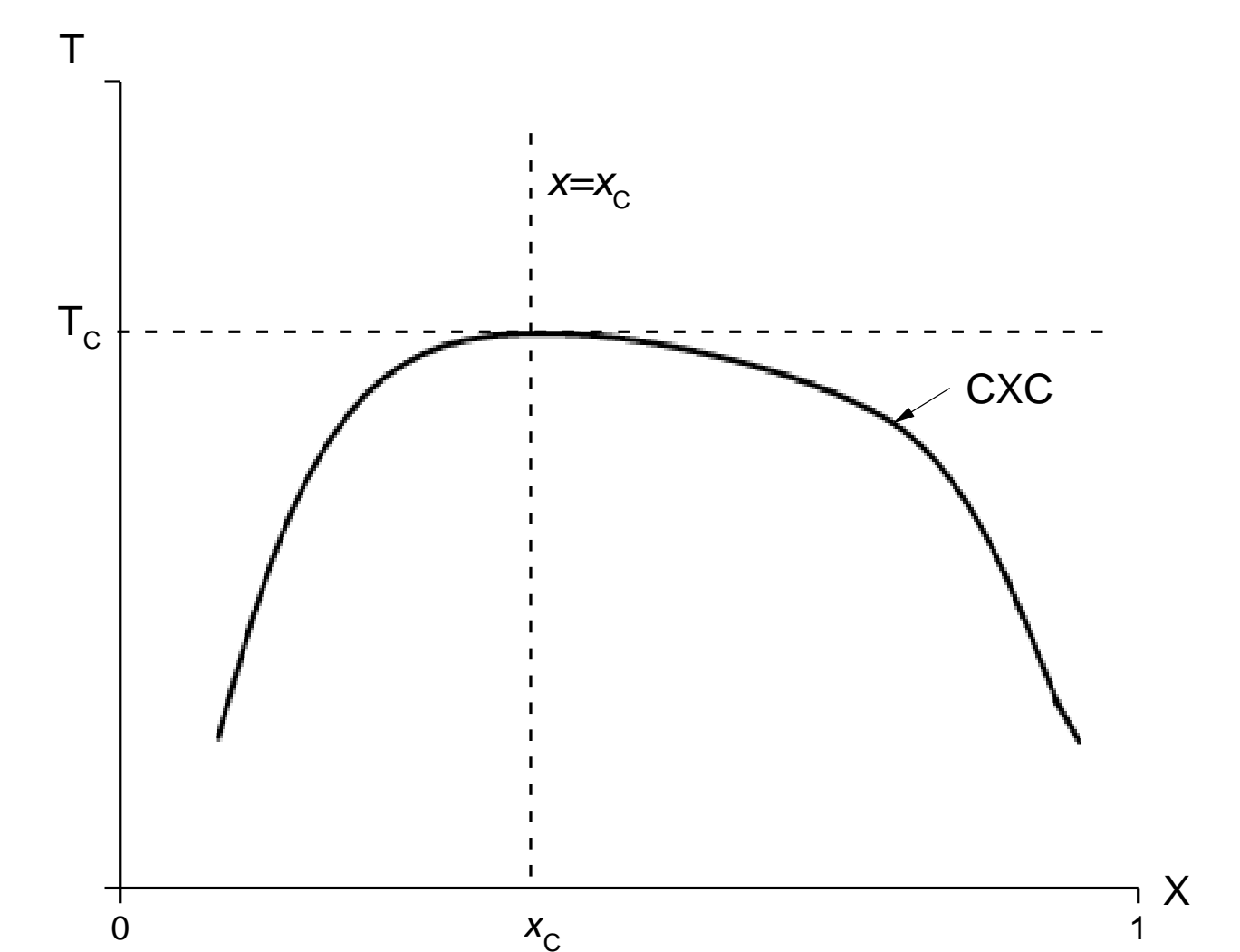


Fig 2. Phase Diagram of IBA and water mixture

Results

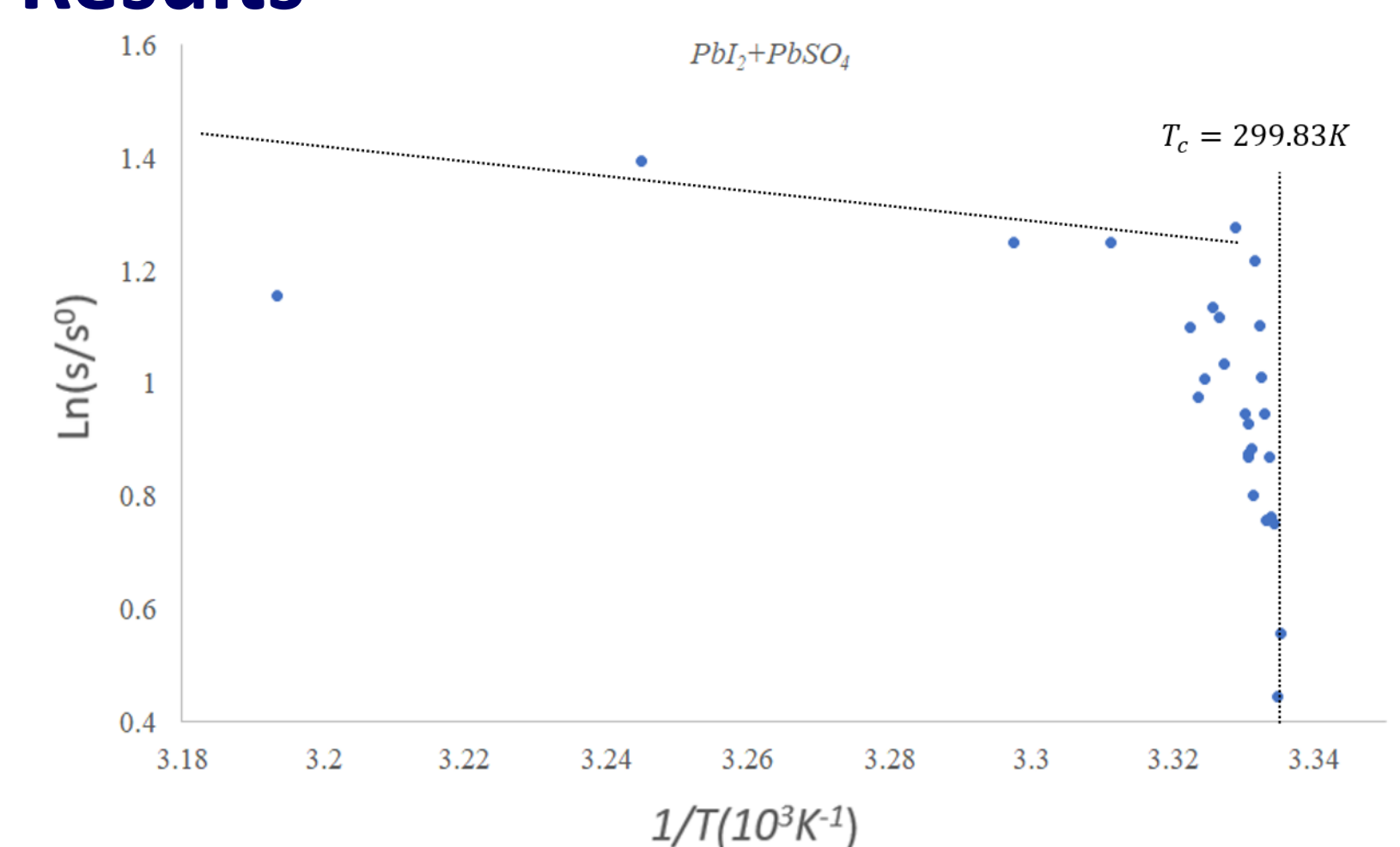


Fig 3. van't Hoff plot of the solubility of Pb^{2+} in isobutyric acid and water mixture

Supporting Results

- Dissolution of $BaCrO_4$ in IBA + water.** In this case, because $C = 9, R = 4, P = 2$ and $I = 2$, which makes $F = 3$, the phase rule correctly predicts the critical effect.

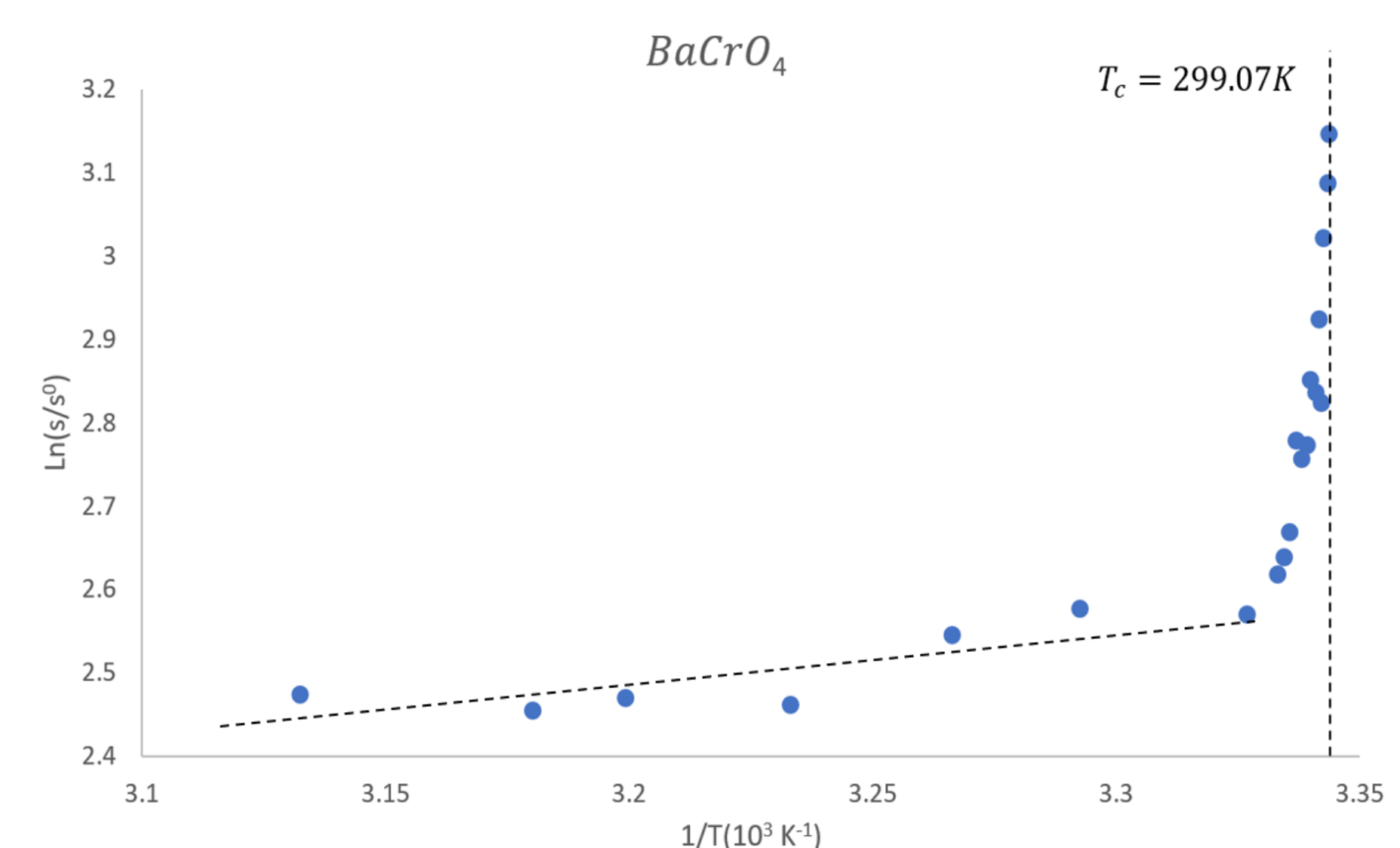


Fig 4. van't Hoff plot of the solubility of CrO_4^{2-} in isobutyric acid and water mixture

- Phenolphthalein in nitrobenzene + dodecane.** In this case, because $C = 3, R = 0, P = 2$ and $I = 0$, which makes $F = 3$, the phase rule correctly predicts the critical effect.

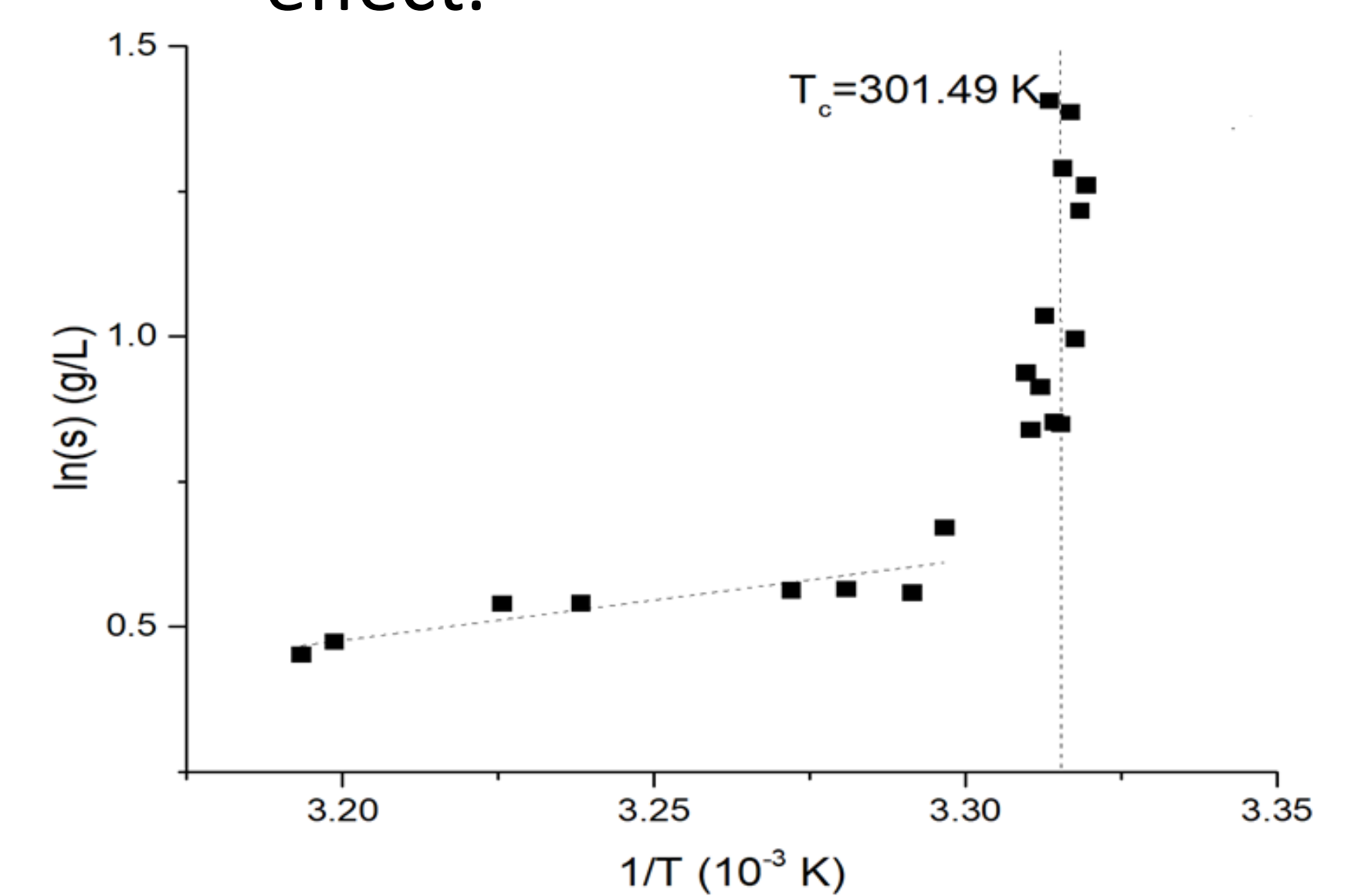


Fig 5. van't Hoff plot of the solubility of CrO_4^{2-} in isobutyric acid and water mixture

Conclusion

The phase rule analysis appears to be a satisfactory method to predict the critical effect in solid-liquid phase equilibria. Our future work should focus on systems with $F > 3$ which means no critical effect should be observed.