

Phase Diagrams for Mixtures

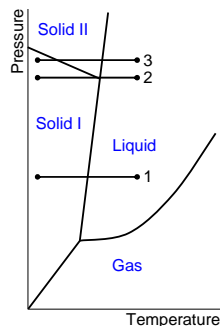
CHEM 323 Physical Chemistry I

Definitions

- Phase
 - Number of phases, P
- Constituent (Chemical Species)
- Component (Independent Constituent)
 - Number of components, C
- Variance, F
 - Degrees of freedom
 - State variables p , T , composition
- Phase Rule: $F = C - P + 2$

One-Component Systems

- $C = 1$, so $F = 3 - P$
 - Meaning of F when $P = 1$
 - Maximum number of phases in equilibrium
- Heating/Cooling Curve along an Isoobar
 - Why do we monitor ΔT when $\Delta p = 0$?
 - Halts



Two-Component Systems

- Variance for Systems of two Components
 - Overall $C = 2$, so $F = 4 - P$; $F_{\max} = 3$
 - Hold one variable constant (e. g., T) decreases F_{\max} to 2 (p, χ_i)
- Consequence: two Types of Phase Diagrams
 - Pressure as a function of composition
 - Temperature as a function of composition
 - Purification of mixtures

Vapor Pressure Diagrams

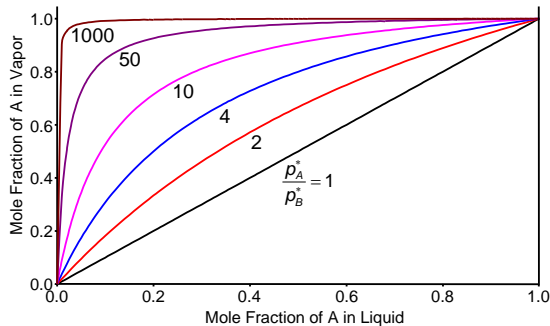
- Observations
 - Composition of vapor and of mixture
 - Phase changes occur over range
- For Ideal Solution
 - Mole fractions in vapor phase

$$y_A = \frac{\chi_A p_A^*}{p_B^* + (p_A^* - p_B^*)\chi_A} \quad y_B = 1 - y_A$$

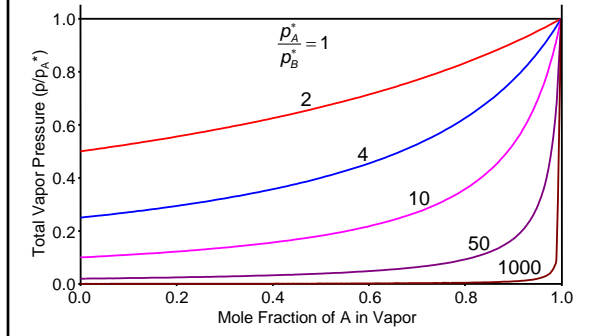
- Total pressure in terms of vapor composition

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$

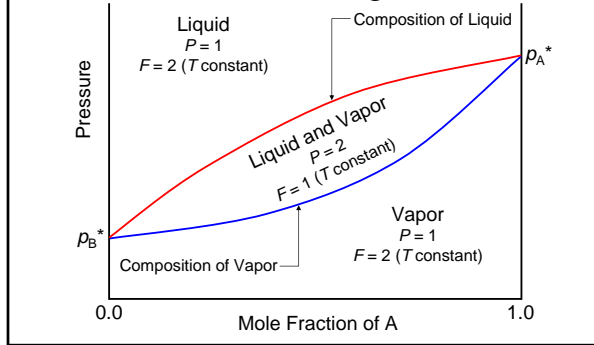
Vapor Composition as Function of Mixture Composition



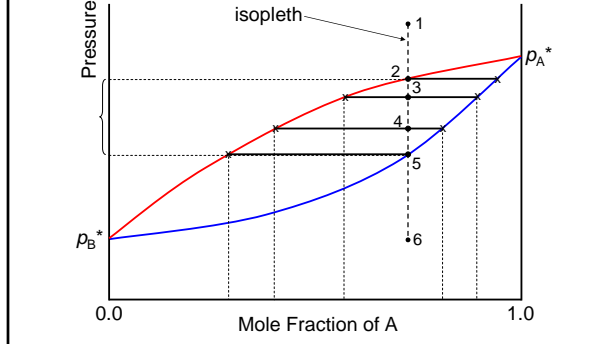
Vapor Pressure as a Function of Vapor Composition

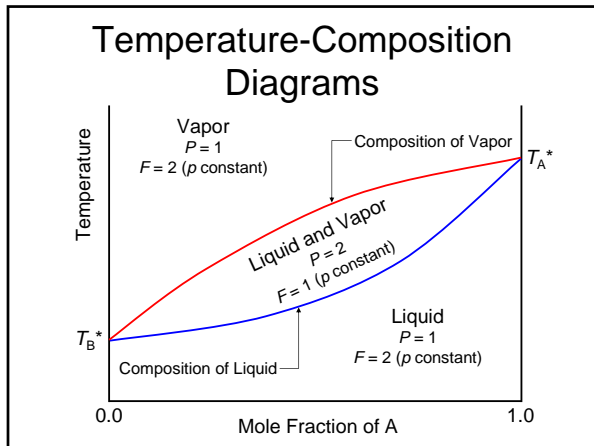


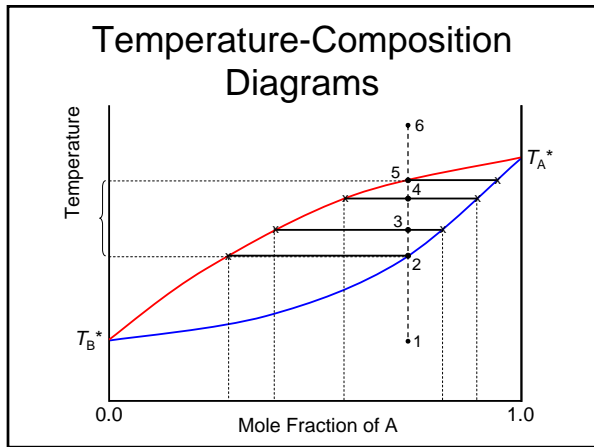
Combined Vapor Pressure Diagram

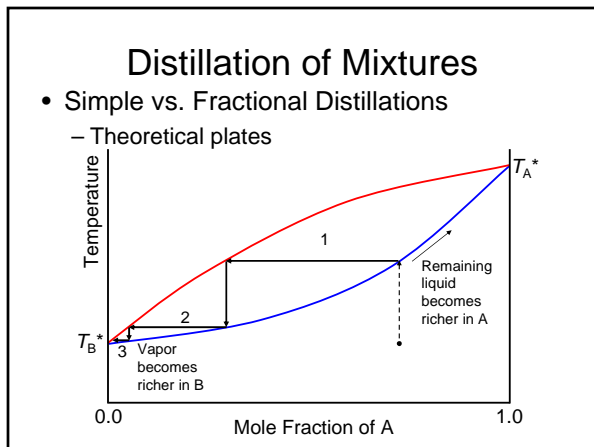


Using Vapor Pressure Diagram the Lever Rule



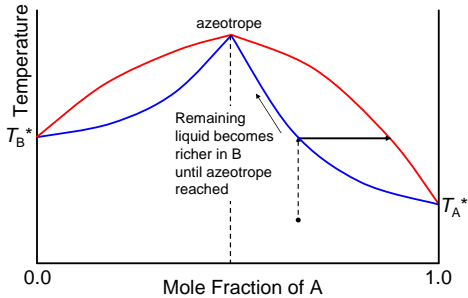






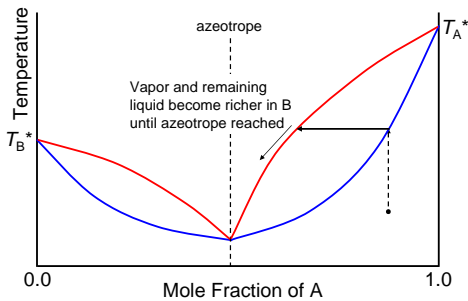
Azeotropes

- High-boiling ($G^E < 0$)



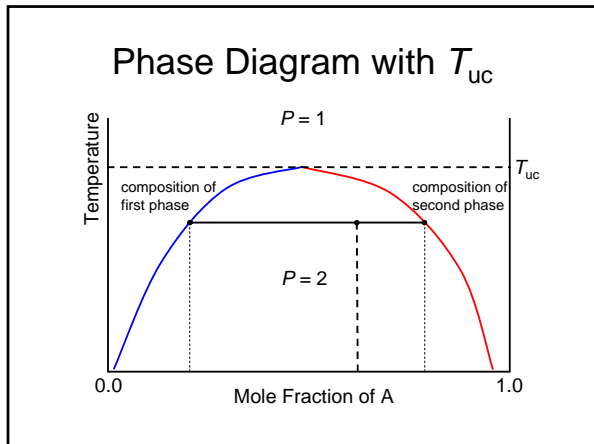
Azeotropes

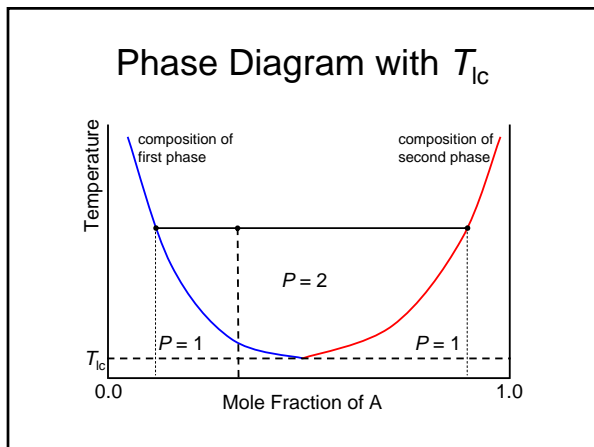
- Low-boiling ($G^E > 0$)

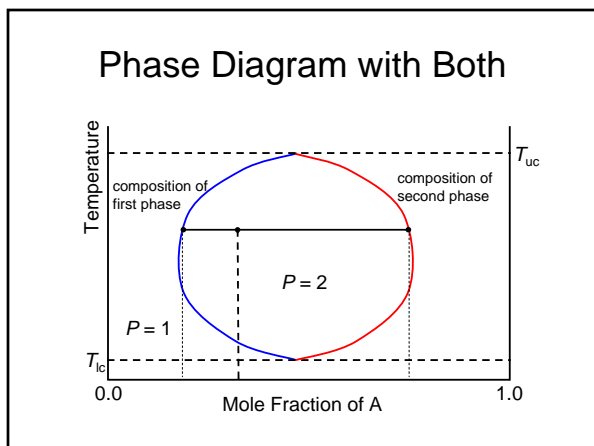


Liquid-Liquid Phase Diagrams

- Phase Separation ($\Delta_{\text{mix}}G > 0$)
 - Remember role of intermolecular interactions (β) in determining sign of $\Delta_{\text{mix}}G$
- Critical Solution Temperatures (depend on Pressure)
 - Upper critical solution temperature, T_{uc}
 - Lower critical solution temperature, T_{lc}
 - A solution may have one, neither or both
- Boiling of Phase Separated Liquids

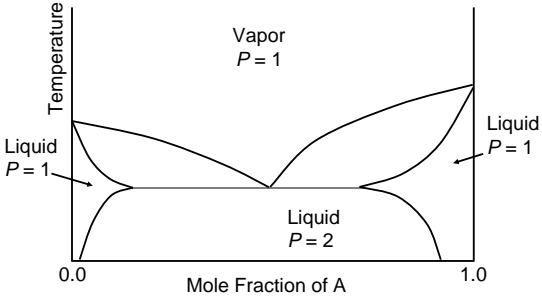






Vaporization occurs before T_{uc} reached

- Vaporization of immiscible Liquids

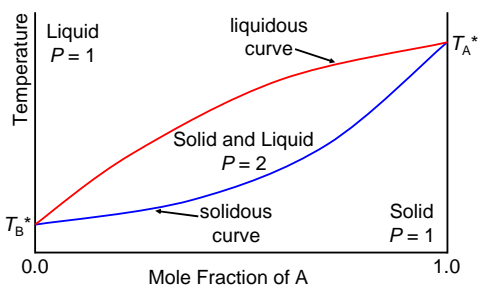


Liquid-Solid Phase Diagrams

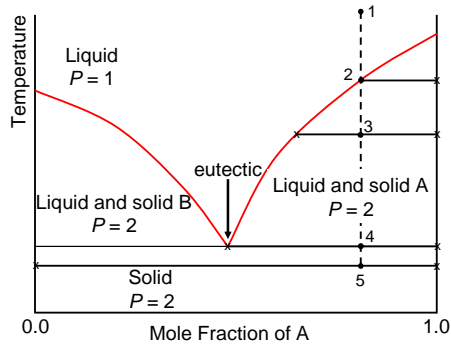
- Observations
 - Formation of solid solutions
 - Some systems can have liquid and either solid
 - Some systems react to form new compounds in solid state
 - Eutectic, monotectic, peritectic points
 - Congruent and incongruent melting

Solid Solutions

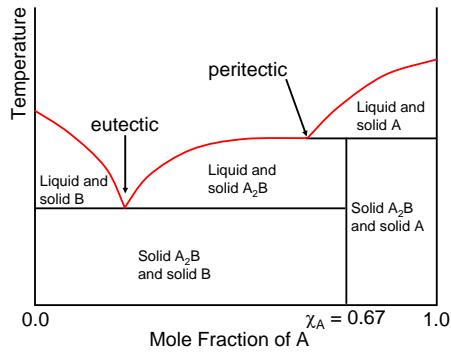
- Common with Isomorphous Solids
 - Gives substitutional alloy (e. g., Mo-V)



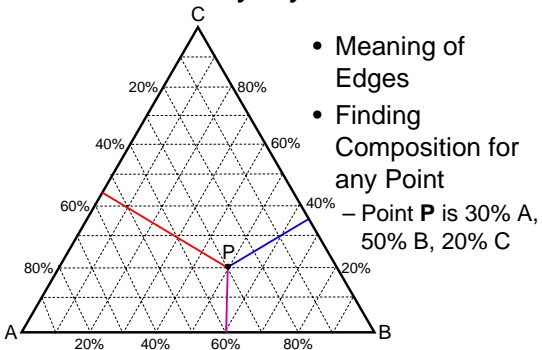
Immiscible Solid, Miscible Liquid



Reacting Systems



Ternary Systems



- Meaning of Edges
- Finding Composition for any Point
 - Point P is 30% A, 50% B, 20% C

Tie Lines in Ternary Systems

- Tie Lines are not necessarily Parallel
 - Binodal
- Isothermal Critical Point
 - Plait point

