

Lecture 17

- Gibbs phase rule
- L-V equilibrium in ideal solutions
- L-V equilibrium in non-ideal solutions – azeotrope
- L-L equilibrium

Read Chs. 12 and 13 Sandler

Objectives

- Know Gibbs phase rule
- Have mental image of P-x-y and T-x-y phase diagrams
- Know how to calculate azeotrope
- Know how to compute phase diagrams for L-L equilibrium

Gibbs Phase Rule

For S non-reacting species, in ϕ -phase *coexistence*, the number of independent *intensive* variables (degrees of freedom) to describe the system is

$$f = \phi(S - 1) + 2 - S(\phi - 1) = S + 2 - \phi$$

Single component

$$f = 3 - \phi$$

1-phase

$$f = 2$$

T-P plane

2-phase

$$f = 1$$

Clapeyron line

3-phase

$$f = 0$$

Triple point

Two component

$$f = 4 - \phi$$

Max. degrees of freedom

$$f = 3$$

Max. number of phases

$$\phi = 4$$

- Pertains phases at coexistence
- Doesn't say how many phases are possible

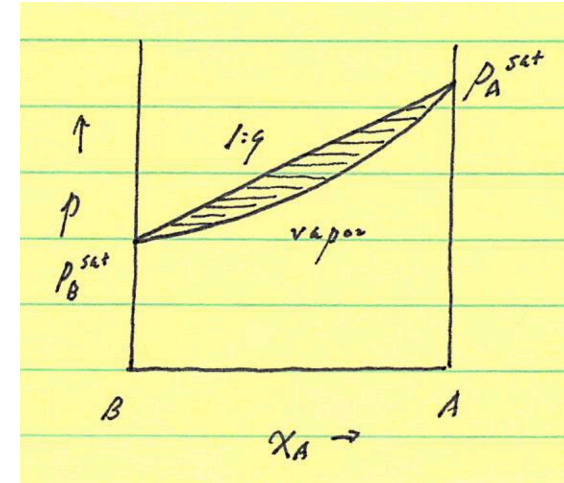
L-V Equilibrium – Ideal Solution

P - x - y diagram

$$P = P_B^{sat} + (P_A^{sat} - P_B^{sat})x_A$$

$$y_A P = \frac{P - P_B^{sat}}{P_A^{sat} - P_B^{sat}} P_A^{sat}$$

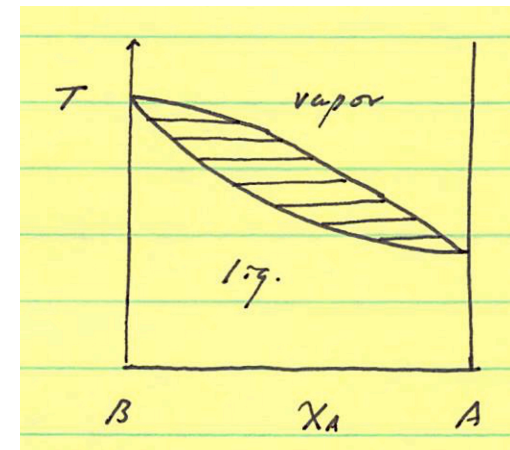
$$\frac{y_A}{y_B} = \frac{x_A P_A^{sat}}{x_B P_B^{sat}} \quad \text{Vapor enriched in more volatile component}$$



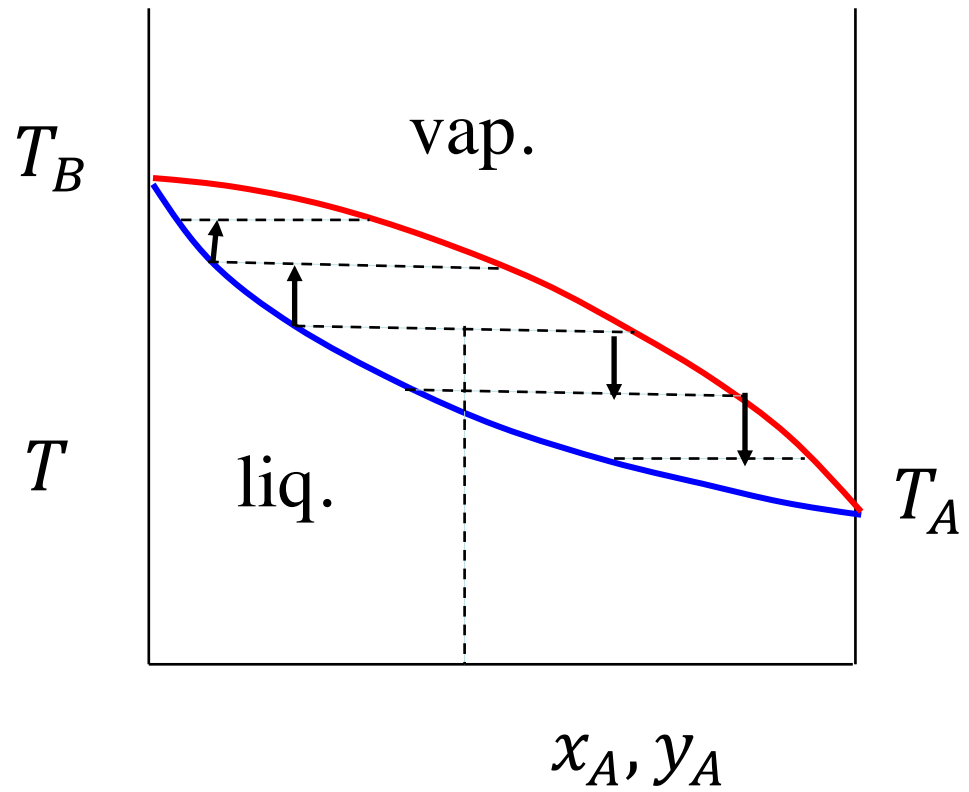
T - x - y diagram: same equations

T -dependence through

$$P_A^{sat}(T), P_B^{sat}(T)$$



Principles of Distillation



L-V Equilibrium – Non-ideal Solution

Deviation from ideality

$$y_A P = \gamma_A x_A P_A^{sat}$$

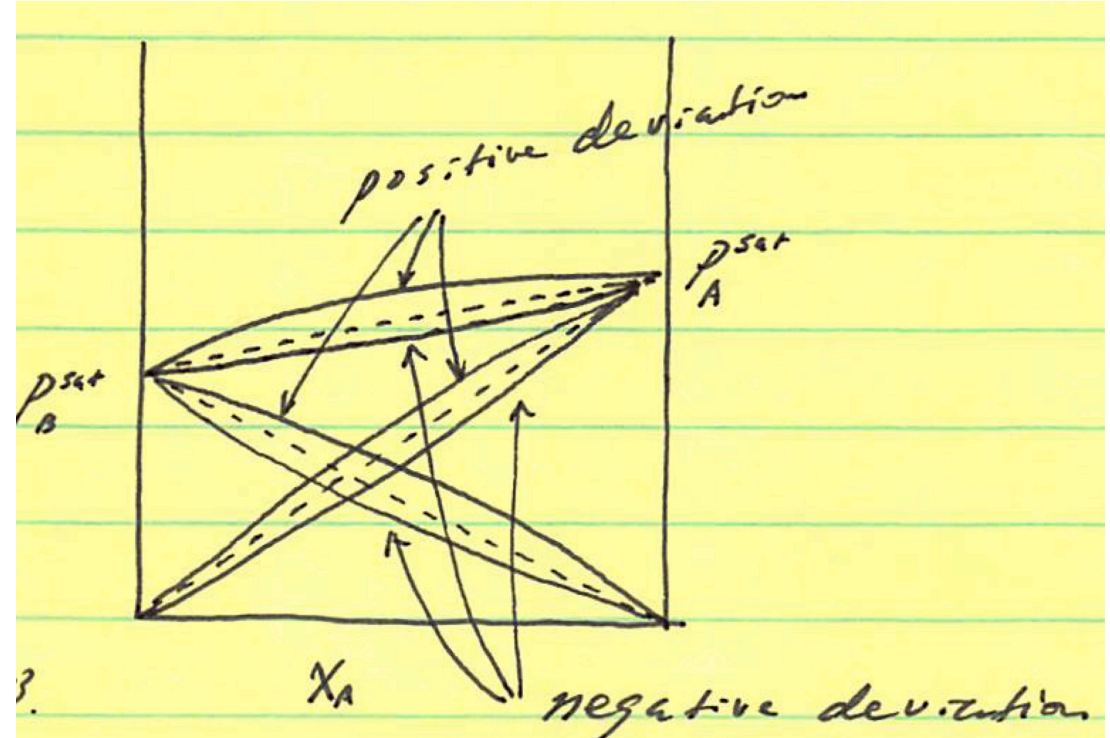
$$y_B P = \gamma_B x_B P_B^{sat}$$

Positive deviation

$$\gamma_A > 1, \gamma_B > 1$$

Negative deviation

$$\gamma_A < 1, \gamma_B < 1$$



L-V Equilibrium – Azeotrope

Azeotrope: liquid and vapor have same composition
(co-boiling)

$$y_A = x_A$$

$$\begin{array}{l} P^* = \gamma_A P_A^{sat} \\ P^* = \gamma_B P_B^{sat} \end{array} \longrightarrow \frac{\gamma_A P_A^{sat}}{\gamma_B P_B^{sat}} = 1$$

Margules model

$$x_A^* = \frac{1}{2} + \frac{RT}{2w} \ln \left(\frac{P_A^{sat}}{P_B^{sat}} \right)$$

Must have

$$-\frac{1}{2} < \frac{RT}{2w} \ln \left(\frac{P_A^{sat}}{P_B^{sat}} \right) < \frac{1}{2}$$

Minimum vs. Maximum Azeotrope

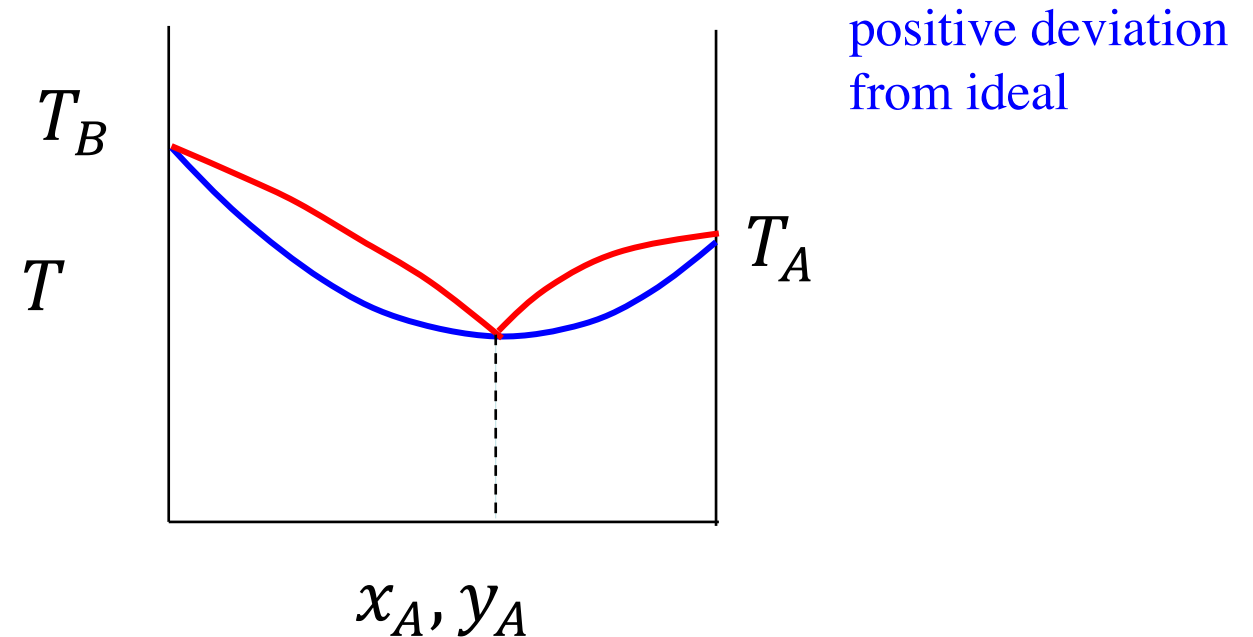
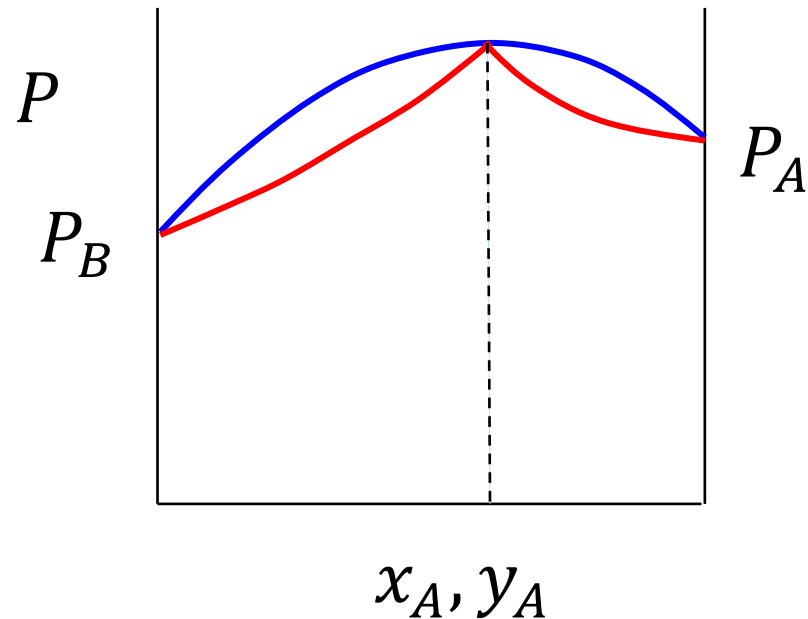
Refers to T - x - y diagram

$$P^* = \gamma_A P_A^{sat}$$

For concreteness let $P_A^{sat} > P_B^{sat}$

$$P^* = \gamma_B P_B^{sat}$$

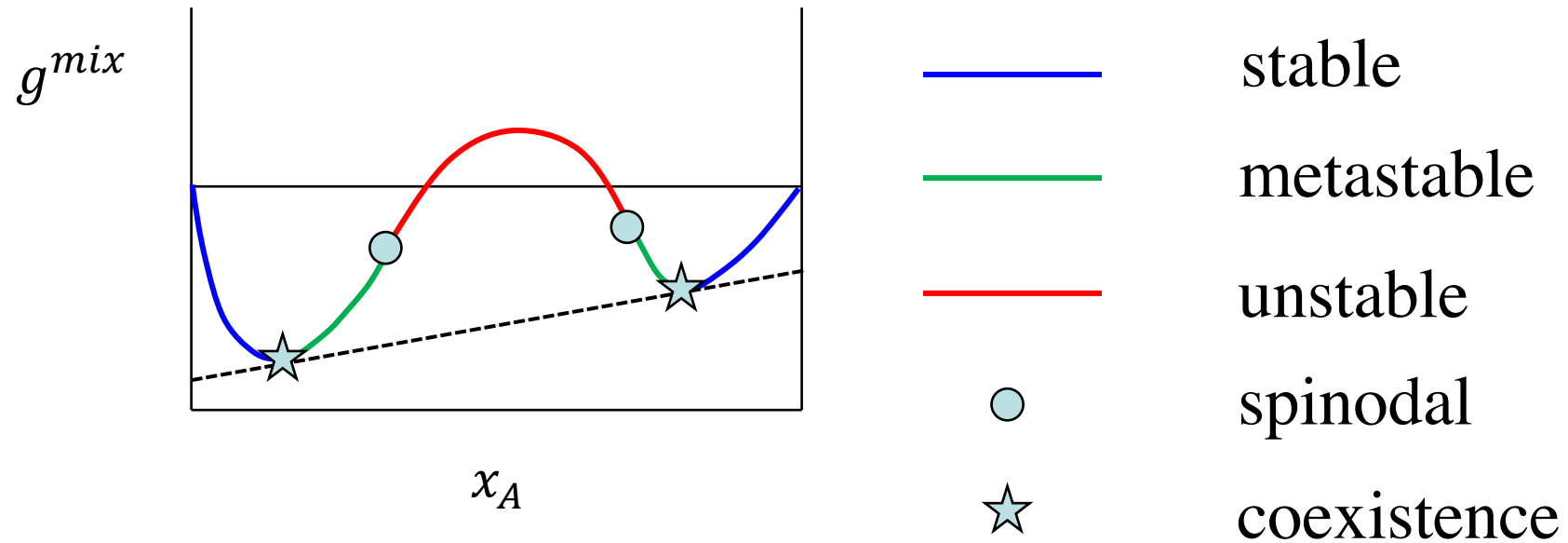
Then minimum azeotrope $P^* > P_A^{sat}$ $x_A^* > \frac{1}{2}$ $w > 0$



Azeotrope is undesirable for separation

L-L Phase Separation

If the Gibbs free energy of mixing has a convex part, system will phase separate into an A-rich and B-rich phases
Coexistence determined by double tangent, or equality of chemical potential



Spinodal:
$$\frac{\partial^2 g^{mix}}{\partial x_A^2} = 0$$

Critical point:
$$\frac{\partial^3 g^{mix}}{\partial x_A^3} = 0$$
 (in addition to the spinodal condition)

Margules Model

$$G^E = nwx_Ax_B$$

$$RT \ln \gamma_A = wx_B^2 \quad \gamma_A = \exp\left(\frac{w}{RT} x_B^2\right)$$

$$RT \ln \gamma_B = wx_A^2 \quad \gamma_B = \exp\left(\frac{w}{RT} x_A^2\right)$$

$$\mu_A = \mu_A^{(0)} + RT \ln x_A + wx_B^2$$

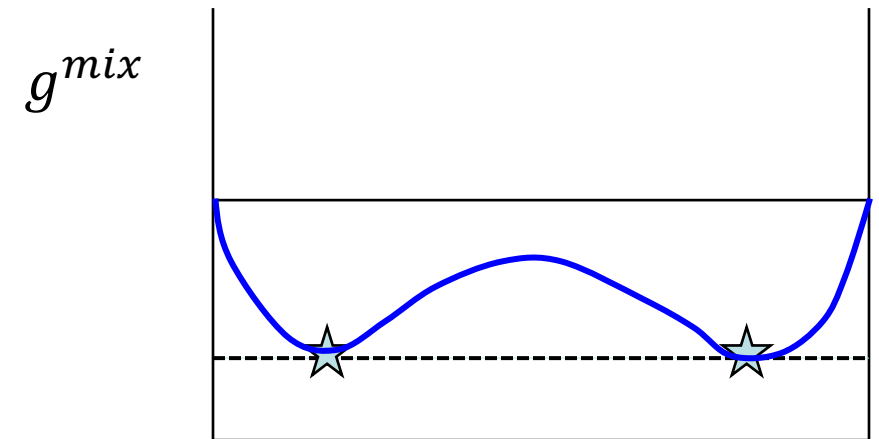
$$\mu_B = \mu_B^{(0)} + RT \ln x_B + wx_A^2$$

symmetric

Coexistence condition

$$\mu_A^\alpha = \mu_A^\beta$$

$$\mu_B^\alpha = \mu_B^\beta$$



only mixing part of chem. potential matters

double tangent same as minimum

Margules Model

$$g^{mix} = RT[x \ln x + (1 - x) \ln(1 - x)] + wx(1 - x)$$

Coexistence: $\frac{\partial g^{mix}}{\partial x} = 0$ (only true for the symmetric case!)

$$RT \ln \frac{x}{1-x} + w(1 - 2x) = 0$$

Spinodal: $\frac{\partial^2 g^{mix}}{\partial x^2} = 0$ $\frac{w}{RT} = \frac{1}{2} \frac{1}{x(1-x)}$

Critical point: $\frac{\partial^3 g^{mix}}{\partial x^3} = 0$

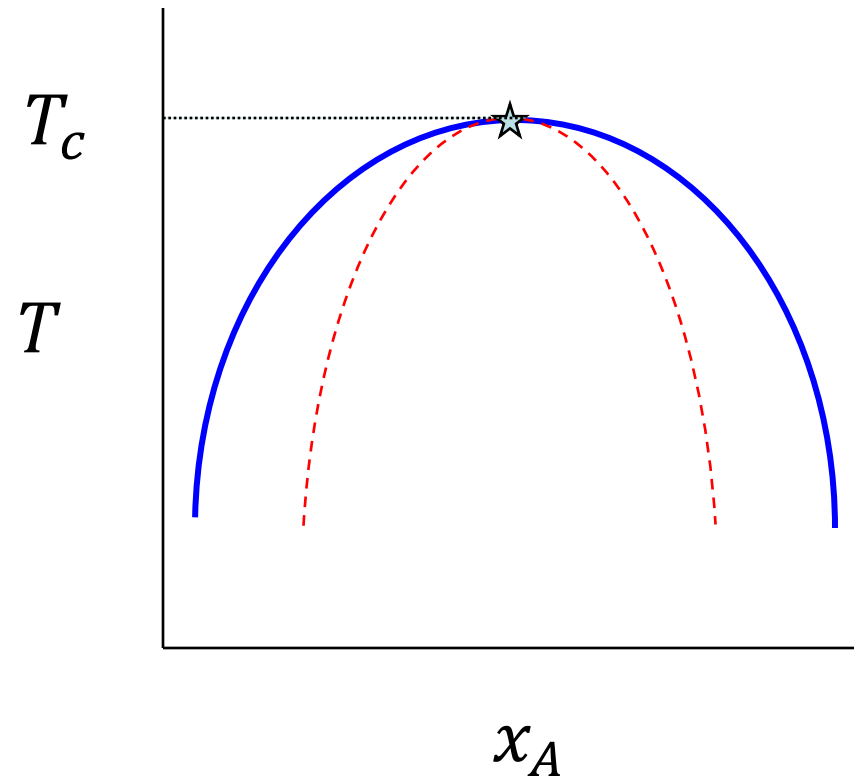
$$x_c = \frac{1}{2}$$

$$\frac{w}{RT_c} = 2$$

critical temperature $T_c = \frac{w}{2R}$

L-L Phase Separation

Phase diagram:



Flory-Huggins Model for Polymer Solutions

$$\frac{G^{mix}}{V} = \frac{RT}{v_0} \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

$$\mu_i = \mu_i^0 + \left(\frac{\partial G^{mix}}{\partial n_i} \right)_{n_{j \neq i}}$$

Noting $V = v_0(n_s + n_p N)$ $\phi = \frac{n_p N}{n_s + n_p N}$

$$\mu_p = \mu_p^{(0)} + RT [\ln \phi - (N - 1)(1 - \phi) + \chi N(1 - \phi)^2]$$

$$\mu_s = \mu_s^{(0)} + RT [\ln(1 - \phi) + \phi - \frac{\phi}{N} + \chi \phi^2]$$

only mixing part of chem. potential matters

Flory-Huggins Model for Polymer Solutions

$$\frac{G^{mix}}{V} = \frac{RT}{v_0} \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

Spinodal: $\frac{\partial^2 g^{mix}}{\partial x^2} = 0$

$$\chi = \frac{1}{2} \left(\frac{1}{N\phi} + \frac{1}{1 - \phi} \right)$$

Critical point: $\frac{\partial^3 g^{mix}}{\partial x^3} = 0$

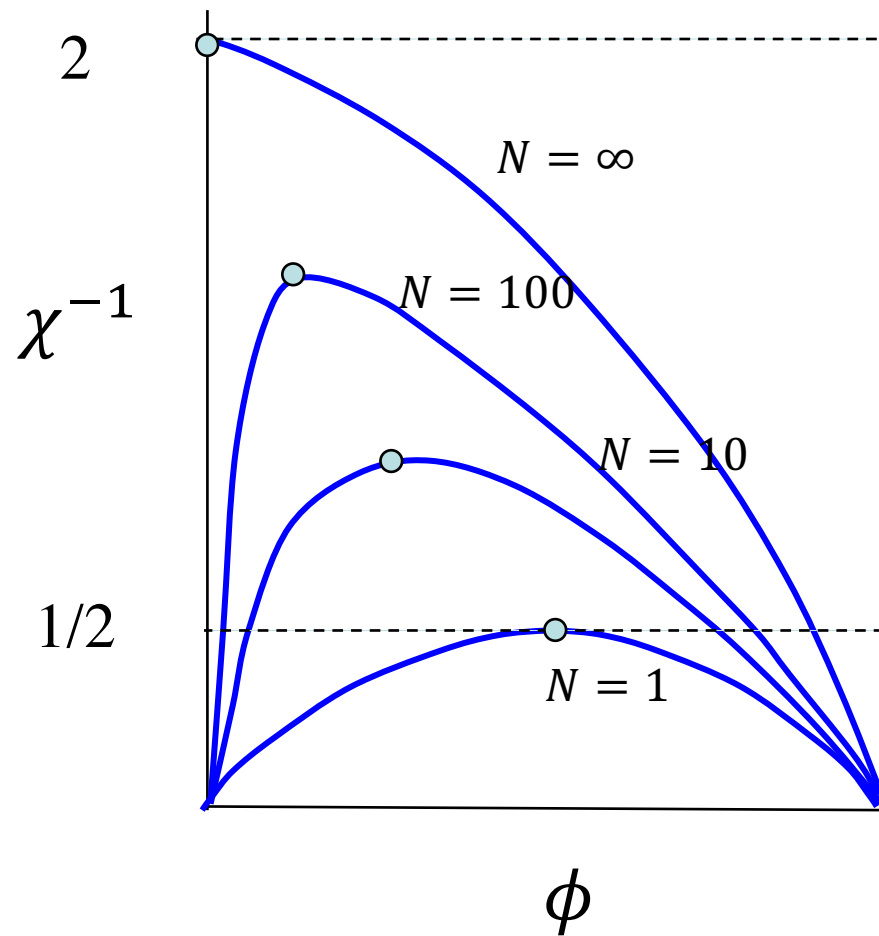
$$\phi_c = (1 + N^2)^{-1} \rightarrow 0$$

for $N \rightarrow \infty$

$$\chi_c = \frac{1}{2} (1 + N^{-1/2})^2 \rightarrow \frac{1}{2}$$

Recovers Margules for $N=1$

Phase Diagram for Polymer Solution



(spinodal not shown)

- Phase diagram skewed for $N > 1$
- Solubility for polymer in poor solvent (below critical temperature) very low

Questions to Think about

- What does positive and negative deviation from Raoult's law mean in molecular terms? How are they related to the minimum vs. maximum azeotrope?
- Work out the expressions for the chemical potential of the polymer and solvent from the Flory-Huggins theory
- Work out the critical point for the Flory-Huggins theory