

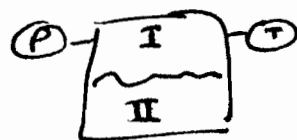
Liquid-Liquid Equilibria (LLE)

Oil and water do not mix; many other ^{non-ideal} systems also have LLE. Used in separations.

$$\mu_{i,I} = \mu_{i,II} \Rightarrow$$

$$f_{i,I} = f_{i,II} \Rightarrow$$

$$\gamma_{i,I} x_{i,I} = \gamma_{i,II} x_{i,II}$$



(Since $f_i(\text{pure})$ is the same)

Example 9.4

Cyclohexane (comp. 1) - Water (comp. 2)

$$x_{1,II} = 1.56 \cdot 10^{-5}$$

$$x_{2,I} = 1.13 \cdot 10^{-3}$$

(Cyclohexane in aqueous phase)

(water in organic phase)

$$\gamma_{1,I} = \gamma_{2,II} = 1$$

Since two phases are almost pure $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$

$$\gamma_{1,II} = \frac{x_{1,I}}{x_{1,II}} = 6.4 \cdot 10^4$$

$$\gamma_{2,I} = \frac{x_{2,II}}{x_{2,I}} = 885$$

very large
non-idealities

How can we understand the thermodynamic origin of LLE?

Entropy mixed, one-phase systems

But... @ const T, P G is min; $G = H - TS$
 \Rightarrow must have favorable enthalpic interactions
 in phase-separated state / unfavorable
 entropy of mixing

Stability condition, two-component systems:

$$\left. \frac{\partial^2 G}{\partial N_1^2} \right)_{T, P, N_2} > 0 \Rightarrow \left. \frac{\partial \mu_1}{\partial N_1} \right)_{T, P, N_2} > 0$$

Consider a system following Margules 1-constant.

$$G^{ex} = C x_1 x_2$$

$$\Delta G_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2) + C x_1 x_2 \Rightarrow$$

$$G = N G = N_1 \mu_1(\text{pure}) + N_2 \mu_2(\text{pure}) + \\ + RT(N_1 \ln x_1 + N_2 \ln x_2) + C N x_1 x_2$$

$$\frac{\partial G}{\partial N_1} = \mu_1(\text{pure}) + RT \left[\ln x_1 + \frac{N_1}{x_1} \frac{d}{dN_1} \left(\frac{N_1}{N_1 + N_2} \right) + \frac{N_2}{x_2} \frac{d}{dN_1} \left(\frac{N_2}{N_1 + N_2} \right) \right] \\ + C \frac{d}{dN_1} \left(\frac{N_1 N_2}{N_1 + N_2} \right) =$$

$$= \mu_1(\text{pure}) + RT \left[\ln x_1 + \frac{N_1}{x_1} \cdot \frac{N_2}{(N_1 + N_2)^2} - \frac{N_2}{x_2} \cdot \frac{N_2}{(N_1 + N_2)^2} \right] \\ + C \frac{N_2^2}{(N_1 + N_2)^2} = \mu_1(\text{pure}) + RT \ln x_1 + C x_2^2$$

$$\frac{d^2 G}{\partial N_1^2} = \frac{RT}{x_1} \cdot \frac{x_2}{N} - \frac{2C x_2^2}{N} = 0 \text{ at limit of stability}$$

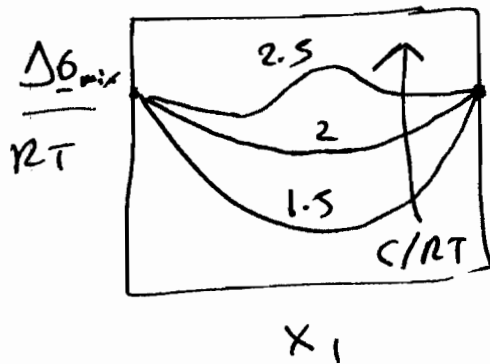
At limit of stability: $\frac{RT}{c} = 2x_1 \Rightarrow$

$$\frac{RT}{c} \equiv T^* = 2x_1(1-x_1) \Rightarrow 2x_1^2 - 2x_1 + T^* = 0$$

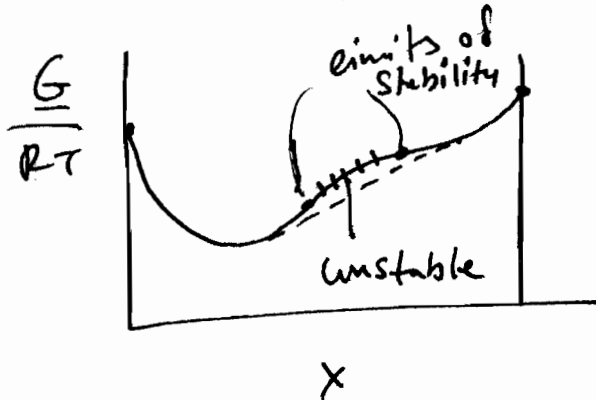
discriminant $d = 4 - 8T^*$, real solutions

$$\text{if } d \geq 0 \Rightarrow 4 \geq 8T^* \Rightarrow T^* \leq \frac{1}{2} \Rightarrow \frac{RT}{c} \leq \frac{1}{2}$$

→ For low temperatures, high c there is liquid-liquid phase separation



↑ decreasing T , increasing c



Equivalent stability condition:

$$\left. \frac{\partial^2 G}{\partial x_1^2} \right|_{T,P} = 0$$

Vapor-liquid-liquid Equilibria (VLLE)



2 components, 3 phases

Gibbs phase rule: $F = 2 - 3 + 2 = 1$

∴ Only 1 degree of freedom

Easiest to analyze if the two liquids are almost pure, assume ideal vapor:

$$f_1(L_1) = f_1(L_2) = f_1(v) \Rightarrow$$

$$\underbrace{\delta_{1,I} x_{1,I} f_1(\text{pure})}_{\delta_{1,I} \approx 1, x_{1,I} \approx 1} = \underbrace{\delta_{1,II} x_{1,II} f_1(\text{pure})}_{\delta_{1,II} \gg 1, x_{1,II} \ll 1} = y_1 P^{3\phi} \Rightarrow$$

$$\delta_{1,I} \approx 1 \quad f_1(\text{pure}) \\ x_{1,I} \approx 1 \quad = P_1^{VP}$$

$$\delta_{1,II} \gg 1 \quad x_{1,II} \ll 1 \\ (\text{ignore})$$

$$\Rightarrow P_1^{VP} = y_1 P^{3\phi} \quad \text{and similarly} \quad P_2^{VP} = y_2 P^{3\phi}$$

$$\therefore P_1^{VP} + P_2^{VP} = P^{3\phi}, \quad y_1 = \frac{P_1^{VP}}{P_1^{VP} + P_2^{VP}}$$

