§13.1 - 13.6 → Review on your own

13.7 Differential Relationships on Phase Boundaries

We have seen for C=1 a very useful general relationship,

$$(dP/dT)_{\alpha-\beta\ coex} = \frac{\Delta S}{\Delta V} = \frac{\Delta h}{T\Delta V}$$ [Clapeyron Equation]

How about multicomponent systems? [Set $\alpha = L$, $\beta = G$]

$$d\mu_1^L = d\mu_1^G \Rightarrow -\bar{S}_1^L dT + \bar{V}_1^L dP + \frac{\partial \mu_1^L}{\partial x_1} dx_1 = -\bar{S}_1^G dT + \bar{V}_1^G dP + \frac{\partial \mu_1^G}{\partial y_1} dy_1$$

$$d\mu_2^L = d\mu_2^G \Rightarrow -\bar{S}_2^L dT + \bar{V}_2^L dP + \frac{\partial \mu_2^L}{\partial x_1} dx_1 = -\bar{S}_2^G dT + \bar{V}_2^G dP + \frac{\partial \mu_2^G}{\partial y_1} dy_1$$

[$\Delta = G - L$]

[note we are using the same vars, $T, P, y_1/x_1$ for both L and G]

Multiply 1st equation by x_1, 2nd by x_2 and add:

$$+\left[x_1 \Delta\bar{S}_1 + x_2 \Delta\bar{S}_2\right] dT - \left[x_1 \Delta\bar{V}_1 + x_2 \Delta\bar{V}_2\right] dP +$$

$$+ \underbrace{\left[x_1 \frac{\partial \mu_1^L}{\partial x_1} + x_2 \frac{\partial \mu_2^L}{\partial x_1}\right]}_{(A)} dx_1 - \underbrace{\left[x_1 \frac{\partial \mu_1^G}{\partial y_1} + x_2 \frac{\partial \mu_2^G}{\partial y_1}\right]}_{(B)} dy_1 = 0$$

Recall from Gibbs-Duhem: $N_1 d\mu_1 + N_2 d\mu_2 = 0$

$\partial/\partial x_1$ (1/N) $\Rightarrow$ $x_1 \frac{\partial \mu_1^L}{\partial x_1} + x_2 \frac{\partial \mu_2^L}{\partial x_1} = 0$ (A) vanishes @ const T + P

$\partial/\partial y_1 \Rightarrow y_1 \frac{\partial \mu_1^G}{\partial y_1} + y_2 \frac{\partial \mu_2^G}{\partial y_1} = 0 \Rightarrow \frac{\partial \mu_2^G}{\partial y_1} = -\frac{y_1}{y_2} \frac{\partial \mu_1^G}{\partial y_1}$

$$\Rightarrow (B) = \left[x_1 - x_2 \frac{y_1}{y_2}\right] \frac{\partial \mu_1^G}{\partial y_1}$$

$\therefore$

$$+\left[x_1 \Delta\bar{S}_1 + x_2 \Delta\bar{S}_2\right] dT - \left[x_1 \Delta\bar{V}_1 + x_2 \Delta\bar{V}_2\right] dP + - \left[x_1 - x_2 \frac{y_1}{y_2}\right] \frac{\partial \mu_1^G}{\partial y_1} dy_1 = 0$$

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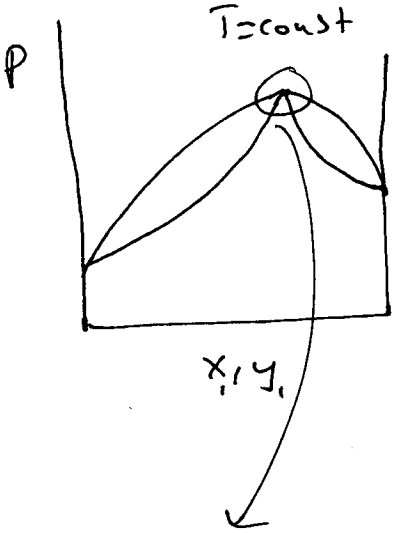
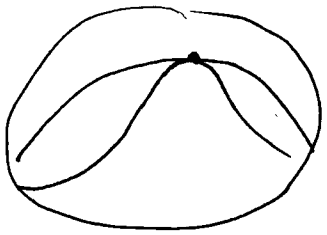
This is the generalization of the Clapeyron equation for C=2.



At azeotropic point,

$x_1 = y_1$, $x_2 = y_2$

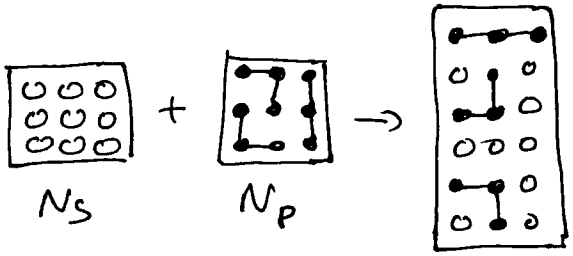
$$\left(\frac{dP}{dy_1}\right)_{T,coex} = \frac{\left[x_1 - x_2\frac{y_1}{y_2}\right]\frac{\partial \underline{G}}{\partial y_1}}{x_1\Delta\bar{V}_1 + x_2\Delta\bar{V}_2} = 0$$



Slope of (P,x) (P,y) envelopes must be <u>zero</u> at azeotropic point

13.8 Polymer Solutions

Flory-Huggins model:
(monomeric solvent + chains of M beads)



To derive the entropy of mixing, we assume no interactions (athermal), $\Delta V_{mix} = 0$

N_S solvent molecules find themselves in a bigger volume

$$\frac{\underline{O}_S(\text{final})}{\underline{O}_S(\text{initial})} = \left[\frac{N_S + MN_P}{N_S}\right]^{N_S}$$

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For polymer chains, $\frac{\Omega_p(\text{final})}{\Omega_p(\text{initial})} = \left(\frac{N_s + MN_p}{MN_p}\right)^{N_p}$

Total entropy change: $\Delta S_{mix} = k_B \ln\left(\frac{\Omega_s \Omega_p(\text{final})}{\Omega_s \Omega_p(\text{initial})}\right)$

$= k_B\left[N_s \ln\frac{N_s+MN_p}{N_s} + N_p \ln\frac{N_s+MN_p}{MN_p}\right] =$

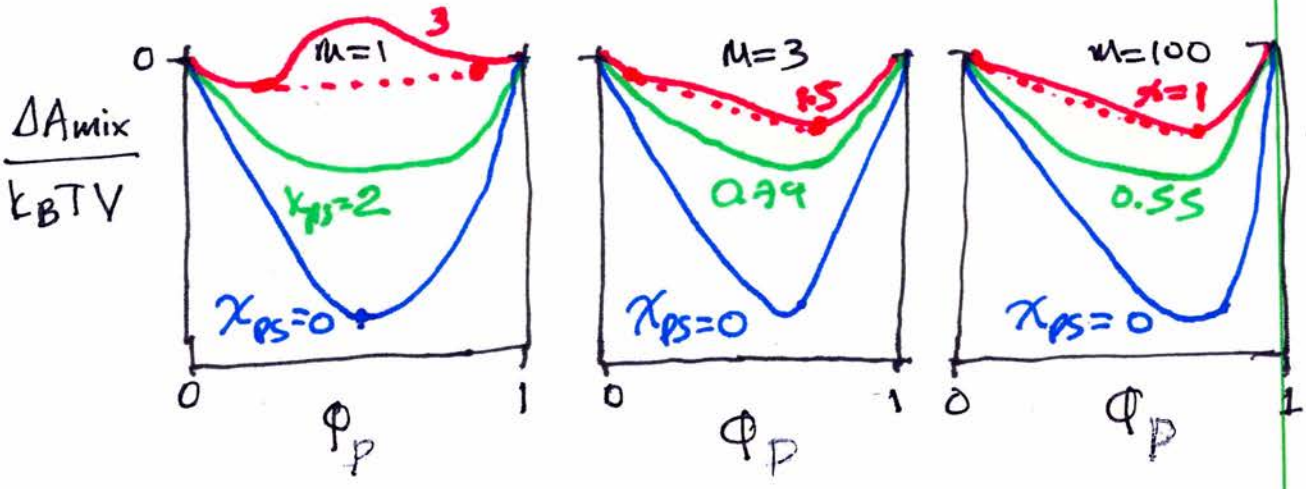
$= -k_B\left[N_s \ln\varphi_s + N_p \ln\varphi_p\right]$, where $\varphi_s = \frac{N_s}{N_s+MN_p}$, $\varphi_p = \frac{MN_p}{N_s+MN_p}$ } volume fraction

For the energy of mixing, we make the "standard" mean-field assumption we used previously for interacting mixtures:

$\Delta E_{mix} = k_B T V \chi_{ps} \varphi_p \varphi_s$ with $\chi_{ps} = \frac{z}{k_B T}\left[w_{ps} - \frac{w_{pp}+w_{ss}}{2}\right]$

$\Delta A_{mix} = \Delta E_{mix} - T\Delta S_{mix} \Rightarrow$ $\boxed{\frac{\Delta A_{mix}}{k_B T V} = \chi_{ps}\varphi_s\varphi_p + \frac{\varphi_p}{M}\ln\varphi_p + \varphi_s \ln\varphi_s}$

Phase separation is seen for $\chi_{ps} > 0$, depends on M



as M goes up, ΔA_{mix} becomes more asymmetric
→ phase boundary moves to left (polymer lean)

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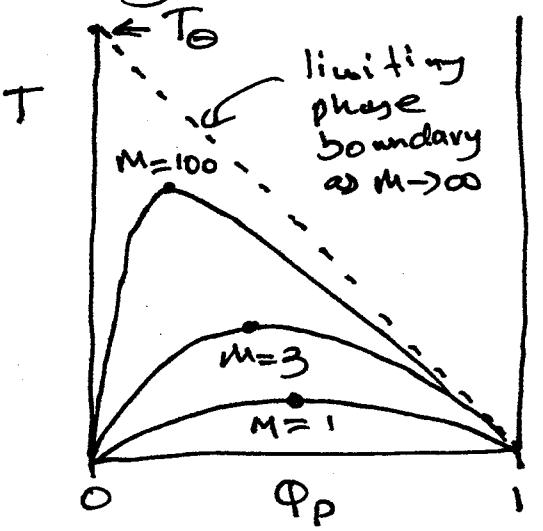
Recall that χ_{ps} depends on T (goes ↓ as T ↑).
The phase boundaries and critical points are strongly M-dependent.



ϕ_c ↓, T_c ↑ as M ↑

At the limit $M \to \infty$

$T_c \to T_\Theta$ (Theta temperature)

$\phi_c \to \emptyset$

The Θ temperature T_Θ is:

- The limiting critical temp. for phase separation as $M \to \infty$
- The temperature for which chain dimensions scale the same as a random walk: (R_G: radius of gyration)

$$R_G \propto M^{0.5}$$

- The temperature at which the second virial coefficient B is zero:

$$B(T_\Theta) = 0$$

$B(T)$