

Chemistry 163B
Multicomponent Phase Rule
Solution Behavior
Handout

1 component

$$f = 3 - p$$

- 1 phase: T,P vary independently
- 2 phases present: T and P covary
- 3 phases present: fixed T and P

multi-component phase rule $f = 2 + c - p$ $f=3-p$ for $c=1$

- c = number of components (molecular species)
 p = number of coexisting phases
- *intensive* variables required to specify system
 $T, P, X_i^{(\alpha)}$ (mole fraction of component i in phase α)
- total variables to specify
total vars = $2 + (c-1)p$
[2 from T, P ; $(c-1)$ independent mole fractions in each phase]
- total restrictions for equilibrium
total restrictions = $c(p-1)$
[already T, P same in each phase]

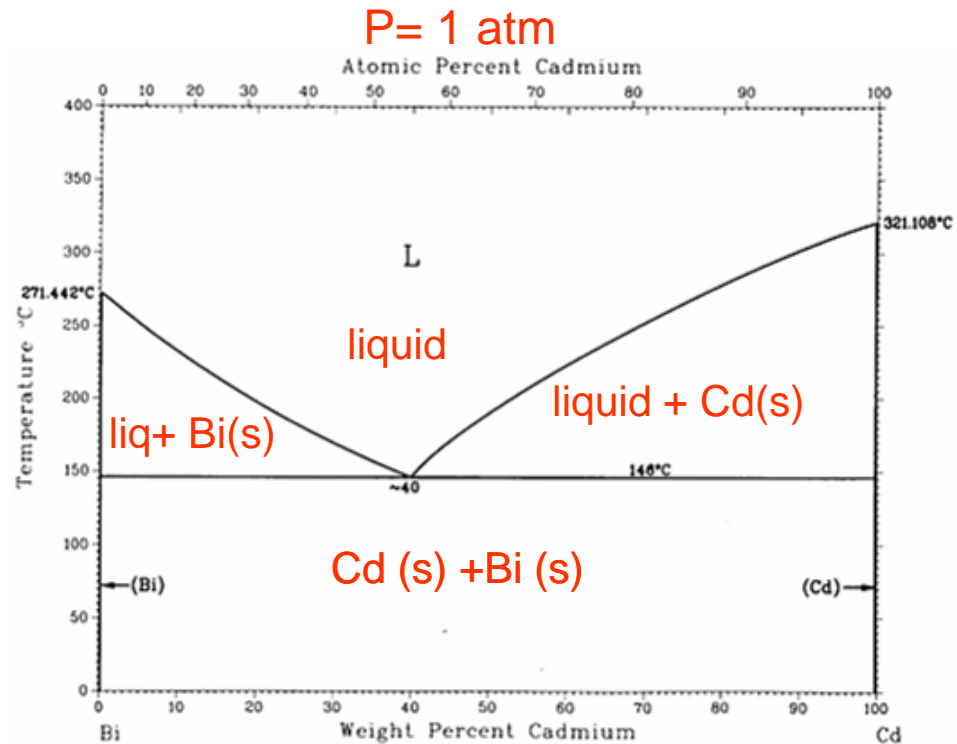
set $\mu_i^{(\alpha)}$ then $\mu_i^{(\alpha)} = \mu_i^{(\beta)} = \dots \mu_i^{(p)}$ ($p-1$ restrictions for each component)

$c(p-1)$ total restrictions for c components

- $f = \text{total variables} - \text{total restrictions}$
- $f = 2 + (c-1)p - c(p-1) = 2 + c - p$

phase rule and Cd-Bi phase diagram (P=1 atm)

- $f=2+c-p$
- $c=2$ (Bi, Cd)
- $f=4-p$
- set $P=1\text{ atm}$
- $f_{\text{remaining}}=3-p$
- variables:
 T, χ_{Cd}^l in liquid



$\chi_{\text{Cd}}^l \rightarrow$

Listen up!!!

**UNDERSTAND THE FOLLOWING DISCUSSION
OF THE PHASE RULE AND THIS
BINARY COMPONENT PHASE
DIAGRAM**



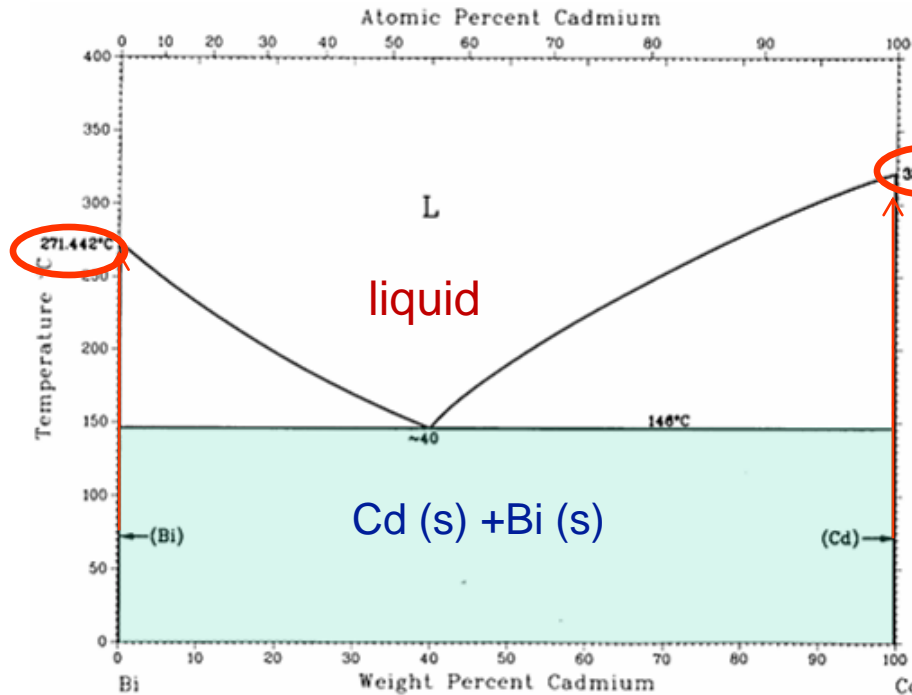
it may be very good for your future



happiness

phase rule and Cd-Bi phase diagram (P=1 atm)

- $f=2+c-p$
- $c=2$
- $f=4-p$
- set $P=1\text{ atm}$
- $f_{\text{remaining}}=3-p$
- variables:
 T, χ_{Cd}^l



liquid,
 $p=1, f=2$
 T, χ_{Cd}^l can vary

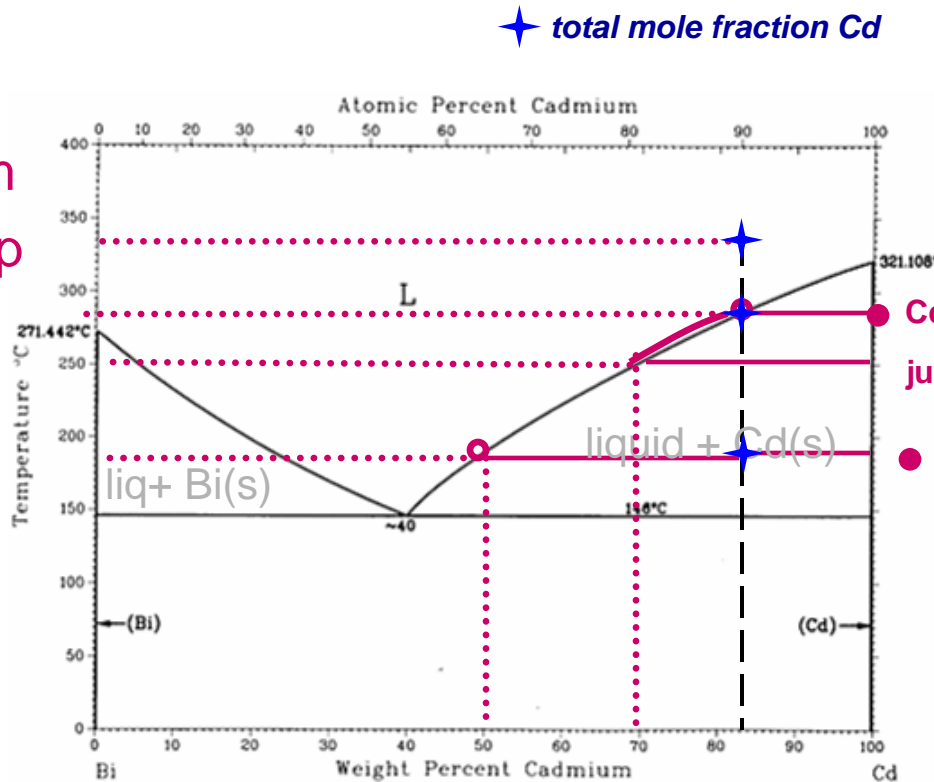
solid $< 146^\circ\text{C}$,
 $p=2, f=1$
 T can vary
 note: Cd(s)
 and Bi(s) are
 pure solids,
 not solution (alloy),
 $\chi_{\text{Cd}}^s=1 \quad \chi_{\text{Bi}}^s=1$

" χ_{Cd} " →

m.p. of pure Bi= 271.4°C
 m.p. of pure Cd= 321.1°C

phase rule and Cd-Bi phase diagram (P=1 atm)

- $f=2+c-p$
- $c=2$
- $f=4-p$
- set $P=1\text{ atm}$
- $f_{\text{remaining}}=3-p$
- variables:
 T, χ_{Cd}^l



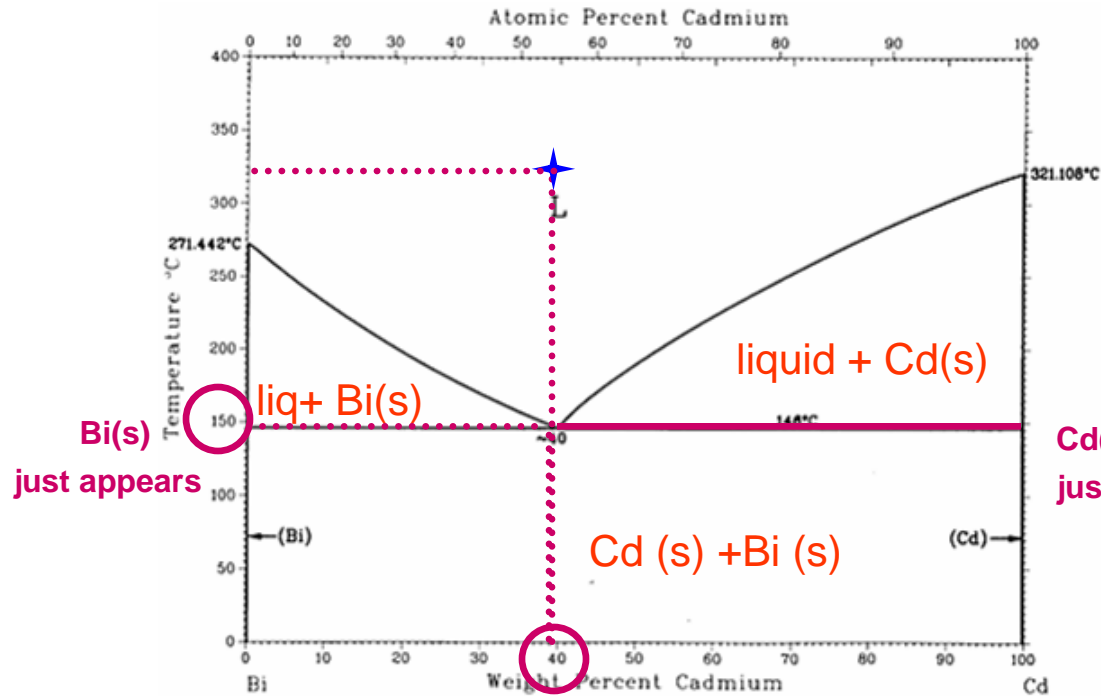
liquid + Cd(s),
 $p=2, f=1$
 only T or χ_{Cd}^l
 can independently
 vary (i.e.
 T and χ_{Cd}^l covary)

just appears lower T
 $\chi_{\text{Cd}}^{\text{total}}$ fixed

χ_{Cd}^l

phase rule and Cd-Bi phase diagram (eutectic)

$$f_{\text{remaining}} = 3 - p$$



liquid + Cd(s) + Bi(s)

$$p = 3, f = 0$$

T and $\chi_{\text{Cd}}^{\text{L}}$

fixed

$$T = 146^\circ \text{C},$$

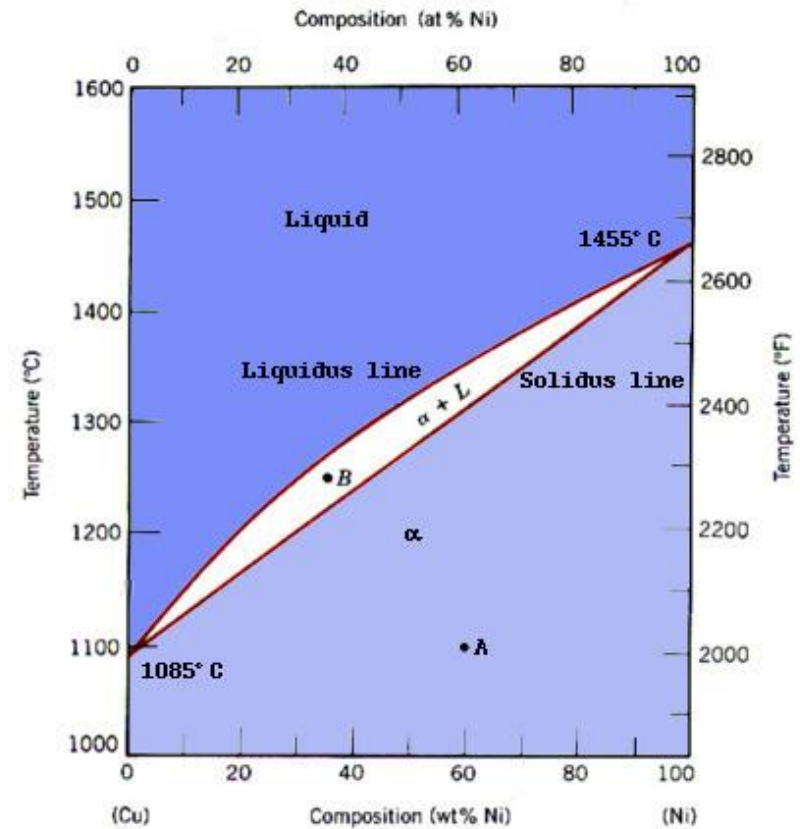
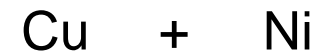
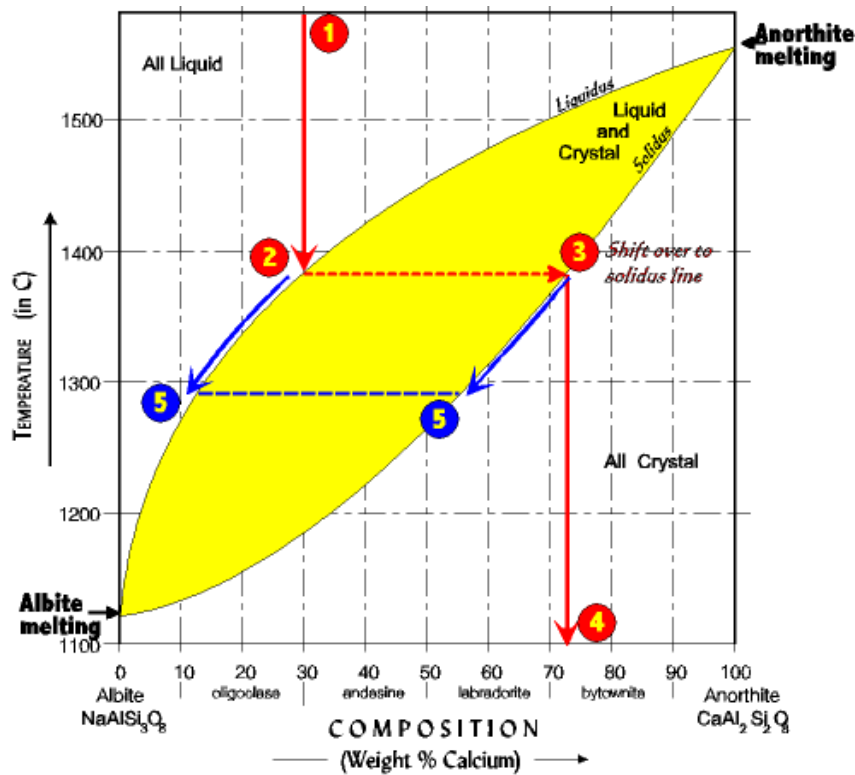
$$\chi_{\text{Cd}}^{\text{L}} = 0.55$$

$$= 0.39 \text{ wt\%}$$

" $\chi_{\text{Cd}}^{\text{L}}$ " →

eutectic = constant freezing composition (mixture)

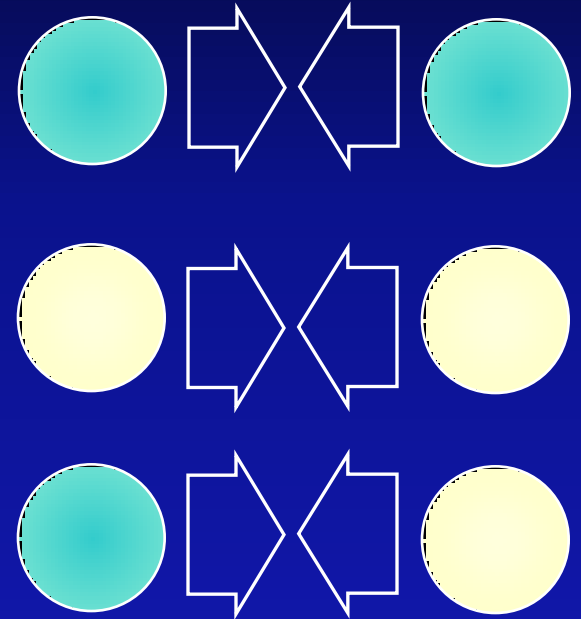
not all solid-solid mixtures form eutectics



Ideal Solutions

Molecular Basis for Ideal Sol'ns.

- In pure liquid A, there are only **A-A** interactions.
- In pure liquid B, there are only **B-B** interactions.
- In solutions of A and B, there are **A-B** interactions as well.
- $\Delta H_{\text{mixing}} = 0$
means that all three interactions are of equal strength.



ideal solutions

properties of the solution depend only on the properties of components in bulk (pure) and the mole fractions of the components.

for example partial vapor pressure of components:

mole fraction A in liquid

$$P_A^{(v)} = X_A^{(\ell)} P_A^{\bullet} \leftarrow \text{vapor pressure of pure A}$$

$$P_B^{(v)} = X_B^{(\ell)} P_B^{\bullet} \leftarrow \text{vapor pressure of pure B}$$

$$\begin{aligned} P_{total} &= P_A^{(v)} + P_B^{(v)} = X_A^{(\ell)} P_A^{\bullet} + X_B^{(\ell)} P_B^{\bullet} \\ &= X_A^{(\ell)} P_A^{\bullet} + (1 - X_A^{(\ell)}) P_B^{\bullet} \\ &= X_A^{(\ell)} (P_A^{\bullet} - P_B^{\bullet}) + P_B^{\bullet} \leftarrow \text{linear } P_{total} \text{ vs } X_A^{(\ell)} \end{aligned}$$

correction
for non-ideality
activity

HW #8 prob 55

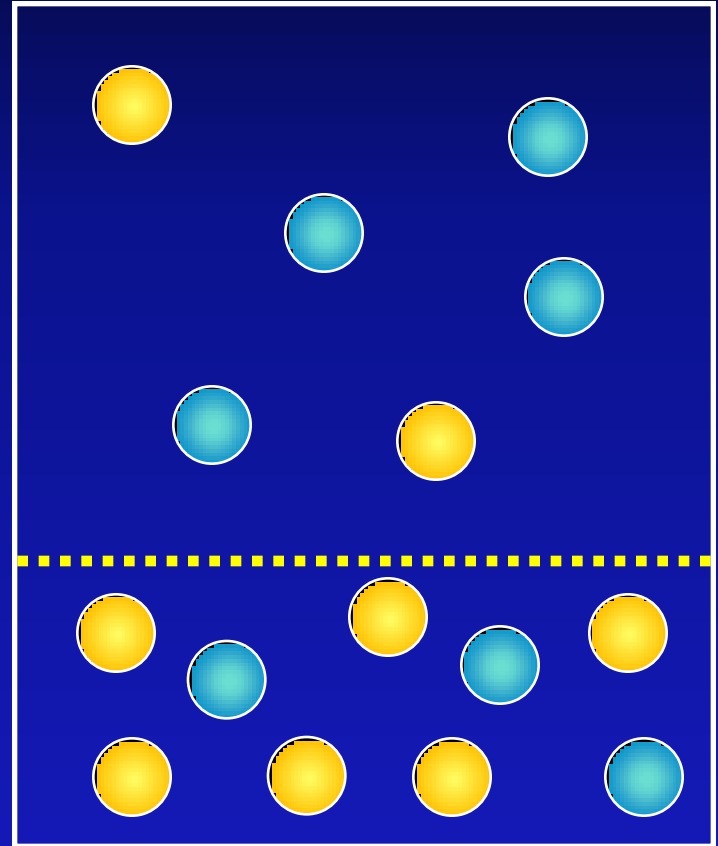
$$P_i^{(v)} = a_i^{(\ell)} P_i^{\bullet}$$

$$\text{ideal } a_i^{(\ell)} = X_i^{(\ell)}$$

$$\text{non-ideal } a_i^{(\ell)} = \gamma_i^{(\ell)} X_i^{(\ell)}$$

liq \leftrightarrow *vap* Eq. in Binary Mixtures

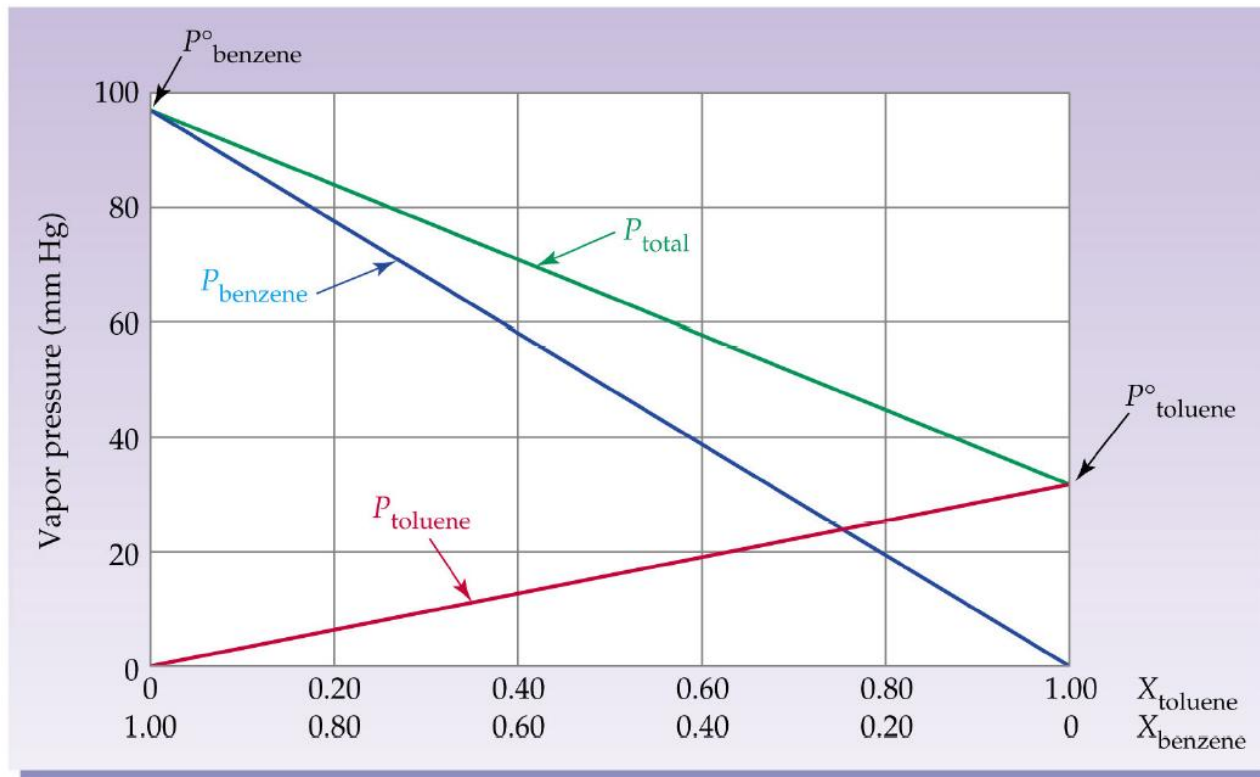
- Both the liquid and the vapor phase are binary mixtures of A and B.
- x_A, x_B are the mole fractions in the liquid.
- y_A, y_B are the mole fractions in the vapor.
- p_A, p_B are the partial pressures in the vapor.



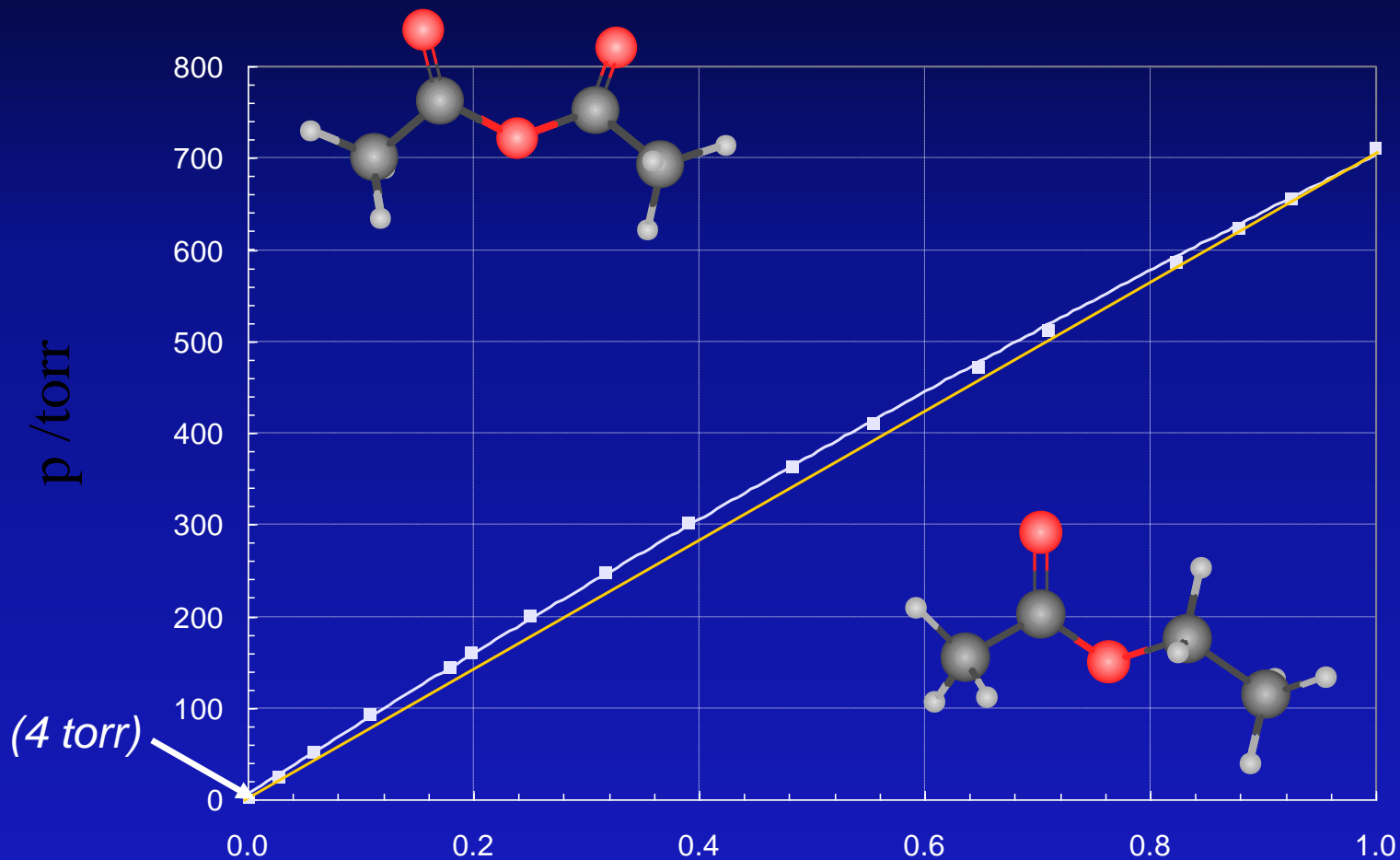
benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

$$P_{total} = X_A^{(\ell)} (P_A^* - P_B^*) + P_B^*$$

Benzene and Toluene



Ethyl Acetate/Acetic Anhydride



$X^{(l)}$ vs $X^{(v)}$ (notation conventions)

conventions :

mole fraction liquid component A:

$X_A^{(l)}$ or $X_A^{(solution)}$ most descriptive;

but also X_A (sloppy) and x_1 (**E & R**)

mole fraction gas (vapor) component A:

$X_A^{(v)}$ most descriptive;

but also y_1 (**E & R**) [not very descriptive and weird??;

but note for E&R HW probs]

relate $X^{(\ell)}$ vs $X^{(v)}$ assuming vapor is ideal gas

$$P_{total} = P_A + P_B = n_{total}^{(v)} \frac{RT}{V}$$

$$P_A = n_A^{(v)} \frac{RT}{V} \quad P_B = n_B^{(v)} \frac{RT}{V}$$

$$\frac{P_A}{P_{total}} = \frac{n_A^{(v)}}{n_{total}^{(v)}} = X_A^{(v)} \quad \text{and} \quad \frac{P_B}{P_{total}} \frac{n_B^{(v)}}{n_{total}^{(v)}} = X_B^{(v)}$$

$$P_A = X_A^{(\ell)} P_A^{\bullet} \quad \text{or} \quad P_A = \gamma_A X_A^{(\ell)} P_A^{\bullet}$$

$$X_A^{(v)} = \frac{P_A}{P_{total}} = \frac{X_A^{(\ell)} P_A^{\bullet}}{P_{total}} \quad (E \& R's y_A)$$

HW#8 probs 50, 55 use E&R's y_i

ideal solution thermodynamics: key ideas

similar to sec 6.4 E&R

have proven $\mu_A^{(\ell)} = \mu_A^{(v)}$ single component A

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

$$dG = -SdT + VdP + \sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)}$$

ω phase
 i component

at equilibrium

$$dG_{T,P} = 0 = \sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)}$$

for each component i $\ell \rightleftharpoons v$ $dn_i^{(v)} = -dn_i^{(\ell)}$

$$\sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)} = 0 \Rightarrow \sum_i (\mu_i^{(\ell)} - \mu_i^{(v)}) dn_i^{(\ell)} = 0 \Rightarrow \mu_i^{(\ell)} = \mu_i^{(v)} \text{ for each component}$$

how does $\mu^{(v)}$ relate to $X^{(\ell)}$? ($\gamma_i^{(v)} = 1$ for ideal gas; $\gamma_i^{(\ell)} = 1$ for ideal solution)

$$\mu_i^{(v)}(T, P, X_i^{(\ell)}) = \mu_i^{\circ(v)}(T) + RT \ln \underbrace{(\gamma_i^{(v)} P_i^{(v)}(T))}_{f_i}$$

$$P_i^{(v)} = \gamma_i^{(\ell)} X_i^{(\ell)} P_i^{\circ(v)}$$


$$\mu_i^{(v)}(T, P, X_i^{(\ell)}) = \underbrace{\mu_i^{\circ(v)}(T) + RT \ln(\gamma_i^{(v)} P_i^{\circ(v)}(T))}_{\mu_i^{\circ(v)}(T, P_i^{\circ})} + RT \ln(\gamma_i^{(\ell)} X_i^{(\ell)})$$

$$\mu_i^{(v)}(T, P, X_i^{(\ell)}) = \mu_i^{\circ(v)}(T, P_i^{\circ}) + RT \ln(\gamma_i^{(\ell)} X_i^{(\ell)})$$

a little more of how does $\mu^{(\ell)}$ relate to $X^{(\ell)}$?

$$\mu_i^{(v)}(T, P, X_i^{(\ell)}) = \mu_i^{\bullet(v)}(T, P_i^{\bullet}) + RT \ln(X_i^{(\ell)})$$

solution \rightleftharpoons vapor components in equilibrium at T


$$\mu_i^{(\ell)}(T, P, X_i^{(\ell)}) = \mu_i^{(v)}(T, P, X_i^{(\ell)})$$

pure liquid \rightleftharpoons pure vapor components in equilibrium at T

$$\mu_i^{\bullet(\ell)}(T, P_i^{\bullet}) = \mu_i^{\bullet(v)}(T, P_i^{\bullet})$$

we get

$$\mu_i^{(\ell)}(T, P, X_i^{(\ell)}) = \mu_i^{\bullet(\ell)}(T) + RT \ln(X_i^{(\ell)}) \quad \text{ideal solution}$$

$$\mu_i^{(\ell)}(T, P, X_i^{(\ell)}) = \mu_i^{\bullet(\ell)}(T) + RT \ln(\underbrace{\gamma_i^{(\ell)} X_i^{(\ell)}}_{a_i}) \quad \text{corrected for nonideality}$$

Ideal Solutions

from: http://switkes.chemistry.ucsc.edu/teaching/CHEM163B/Winter14/handouts_W14.html



Handout #53

- I. **The partial molar volume of each component in solution is the same as its molar volume in pure liquid and thus the volume of the solution is the additive volume of the pure components**

$$\bar{V}_i = \bar{V}_i^\ell \quad V = \sum_i n_i \bar{V}_i$$

- II. **The enthalpy of mixing is zero:** $\Delta H_{mix} = 0$

- III. **The free energy of mixing is:** $\Delta G_{mix} = \sum_k n_k RT \ln X_k^\ell$

- IV. **The entropy of mixing is:** $\Delta S_{mix} = \frac{\Delta H_{mix} - \Delta G_{mix}}{T} = -\sum_k n_k R \ln X_k^\ell$

Listen up!!!

**UNDERSTAND THE FOLLOWING DISCUSSION
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DIAGRAM**

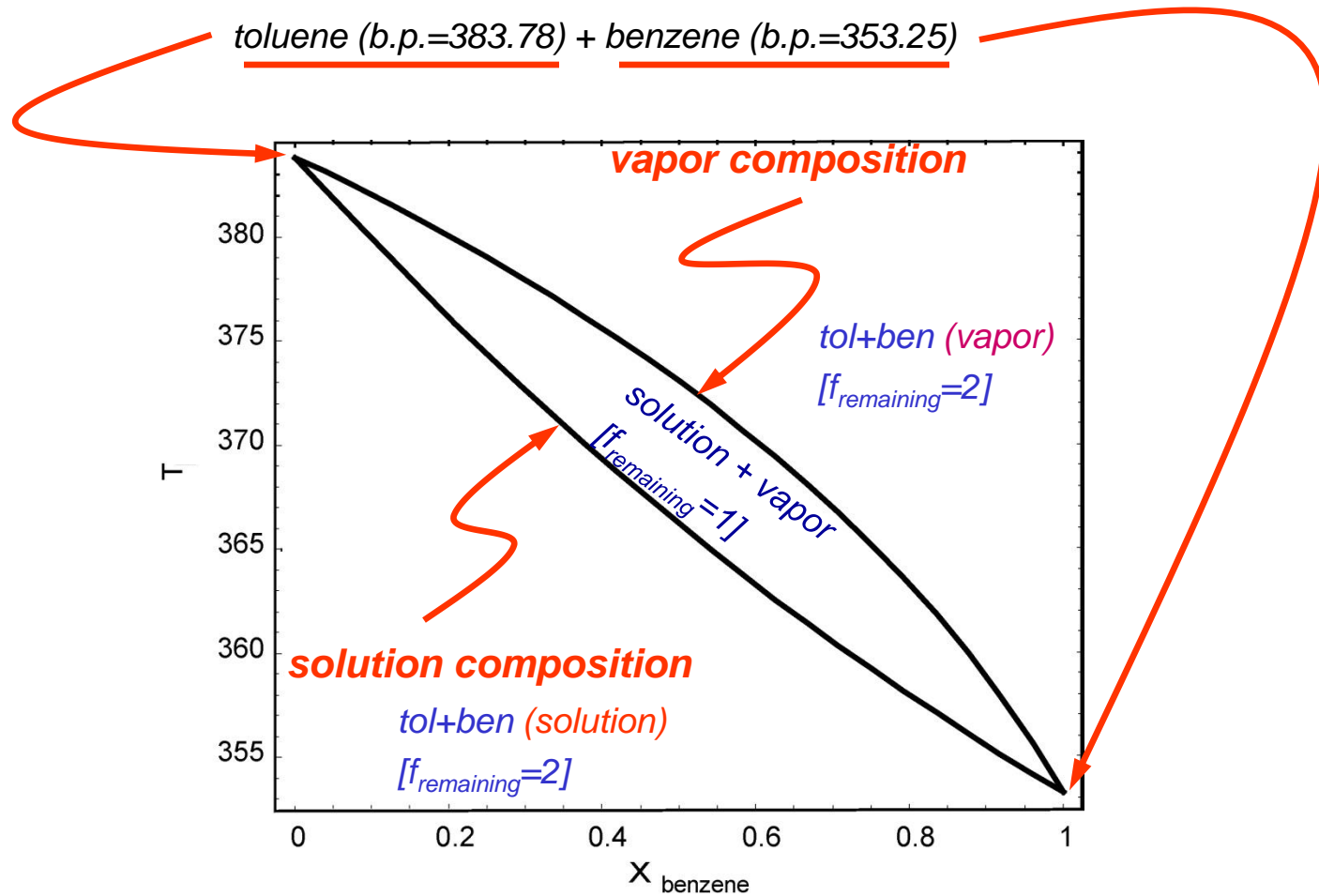


it may be very good for your future

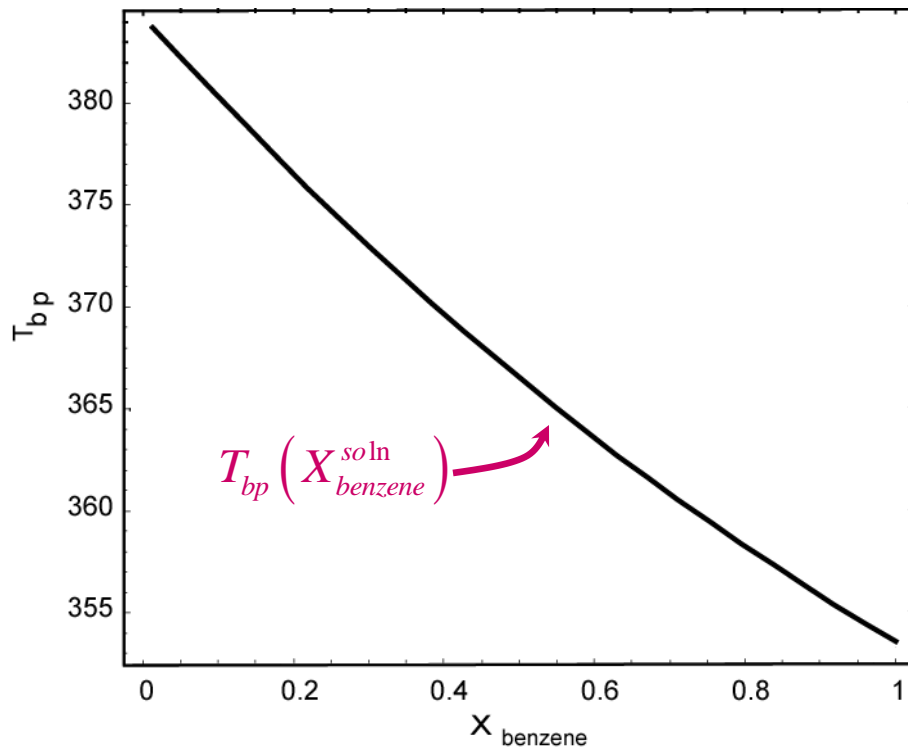


happiness

T vs X ($P=1$ atm) for solution-vapor equilibrium **TOLUENE + BENZENE**

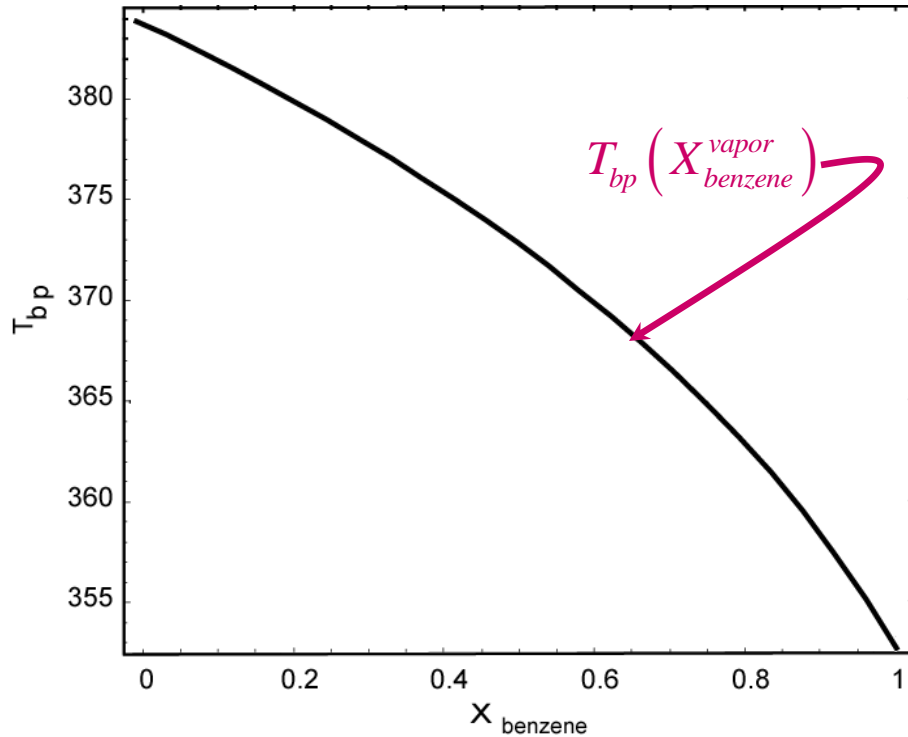


fractional distillation [T_{bp} vs $(X_{benzene})^{solution}$]



- $\ln\left(\frac{P_{benzene}^*(T)}{1 \text{ atm}}\right) = -\frac{(\Delta\bar{H}_{vap})_{ben}}{R} \left[\frac{1}{T} - \frac{1}{(T_{bp}^*)_{ben}} \right]$
- $\frac{P_{benzene}^*(T)}{1 \text{ atm}} = e^{-\frac{(\Delta\bar{H}_{vap})_{ben}}{R} \left[\frac{1}{T} - \frac{1}{(T_{bp}^*)_{ben}} \right]}$ **vapor pressure of benzene at T**
- $\frac{P_{toluene}^*(T)}{1 \text{ atm}} = e^{-\frac{(\Delta\bar{H}_{vap})_{tol}}{R} \left[\frac{1}{T} - \frac{1}{(T_{bp}^*)_{tol}} \right]}$ **vapor pressure of toluene at T**
- **in ideal solution**
 $P_{benzene}(T) = X_{benzene}^{solution} P_{benzene}^*(T)$ and $P_{toluene}(T) = X_{toluene}^{solution} P_{toluene}^*(T)$
- **at boiling** $\Rightarrow P_{benzene} + P_{toluene} = 1 \text{ atm}$
 $1 \text{ atm} = X_{benzene}^{solution} P_{benzene}^*(T_{bp}^{solution}) + (1 - X_{benzene}^{solution}) P_{toluene}^*(T_{bp}^{solution})$
- **for a given $X_{benzene}^{solution}$ solve for $T_{bp}^{solution}$**
(or better have Mathematica solve equations see handout #54)

fractional distillation [T_{bp} vs $(X_{benzene})^{vapor}$]



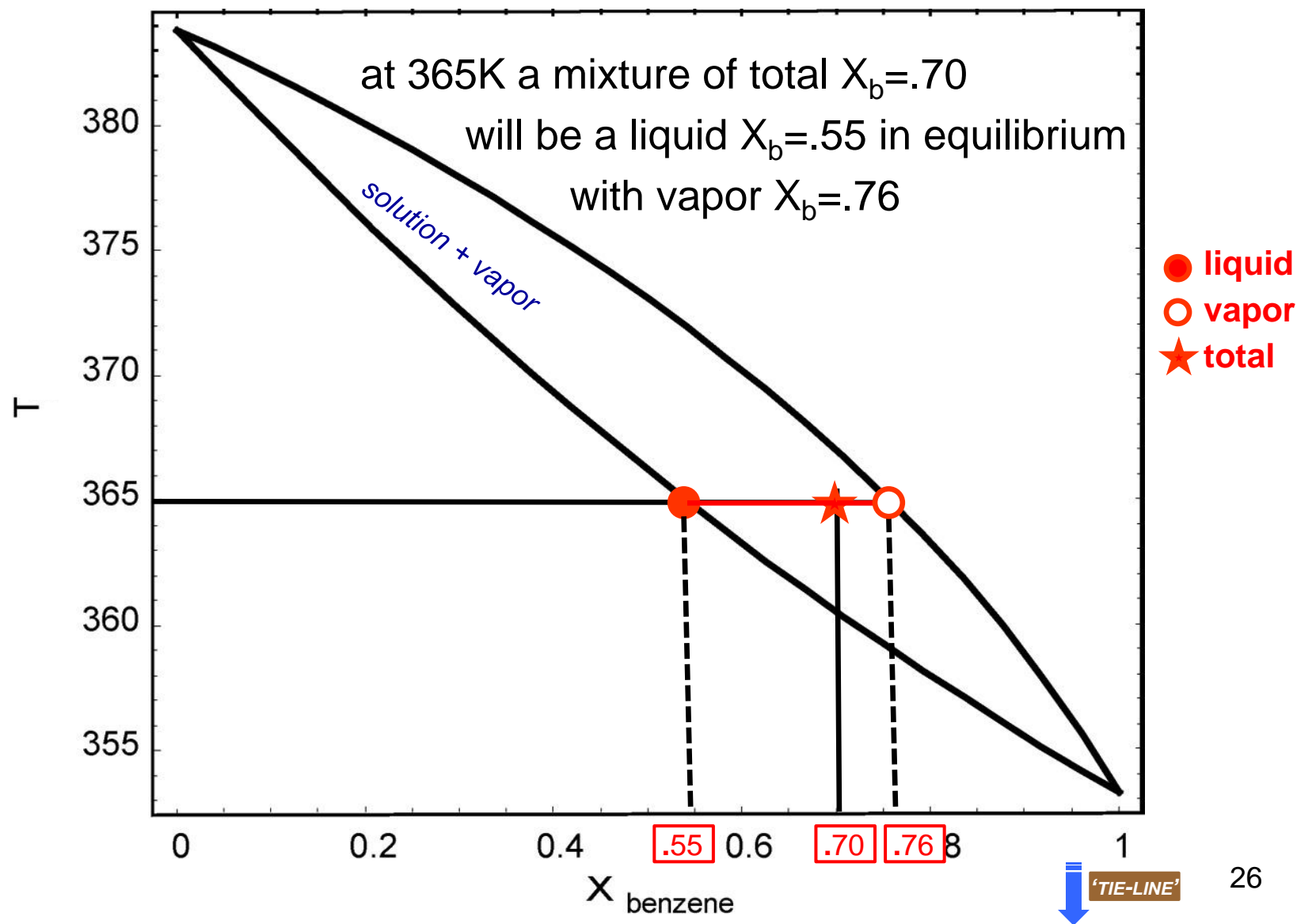
$$X_{benzene}^{vapor} = \frac{P_{benzene}}{P_{total}} = \frac{X_{ben}^{soln} P_{ben}^*(T_{bp}^{solution})}{P_{total}}$$

$$X_{benzene}^{vapor} = X_{ben}^{soln} P_{ben}^*(T_{bp}^{solution})$$

since $P_{total} = 1 \text{ atm}$ at $T_{bp}^{solution}$

get $T_{bp}^{solution}$ from equations on previous slide

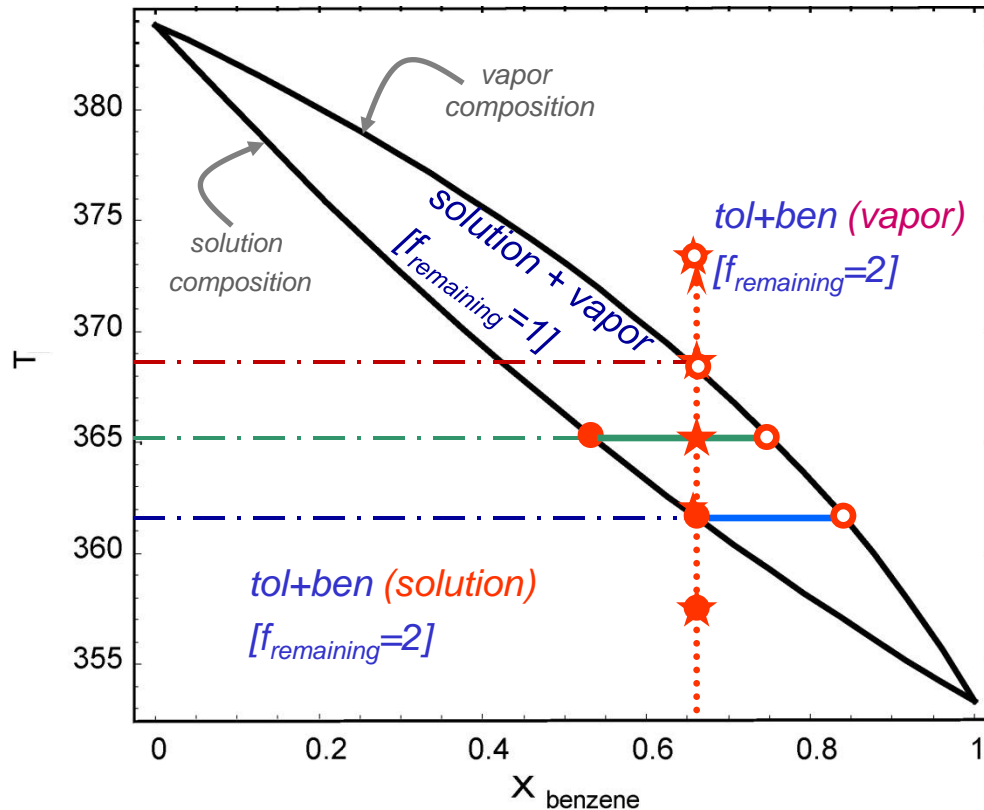
two-phase region ($P=1\text{ atm}$) TOLUENE + BENZENE ($l \rightleftharpoons v$)



T vs X (P=1 atm) for solution-vapor equilibrium TOLUENE + BENZENE

toluene (b.p.=383.78) + benzene (b.p.=353.25)

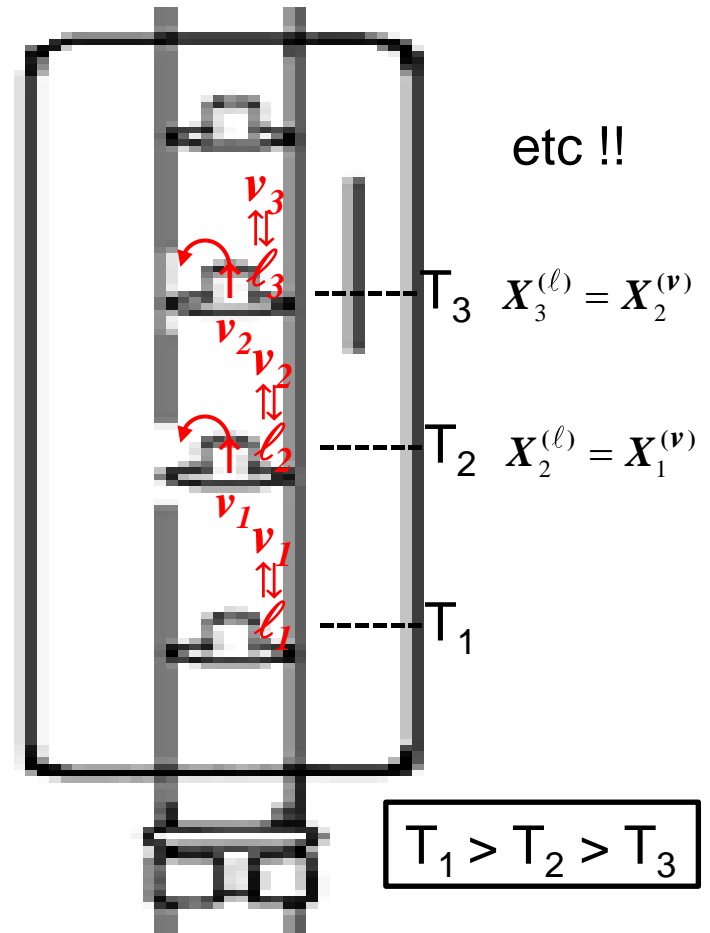
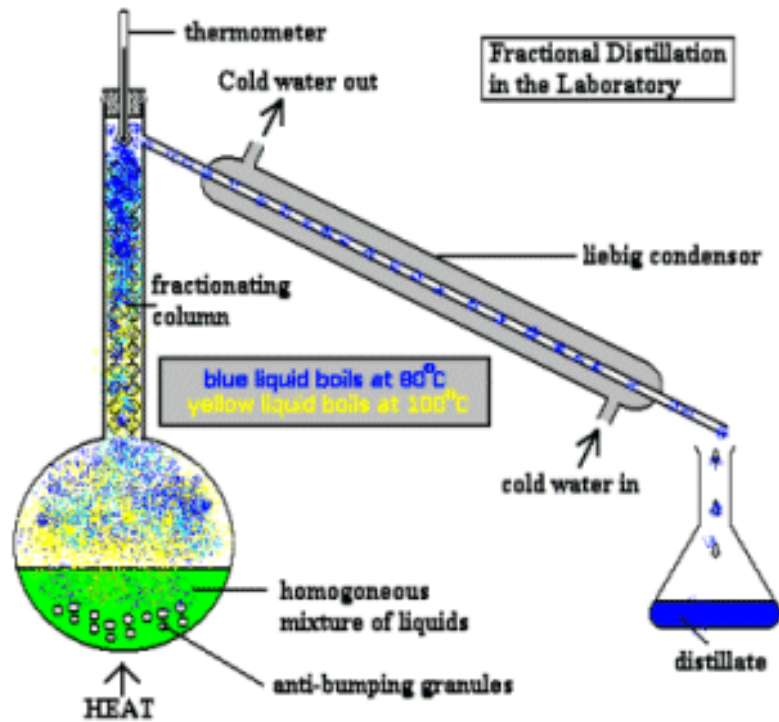
$$X_{benz}^{total} = 0.65$$



- liquid
- vapor
- ★ total

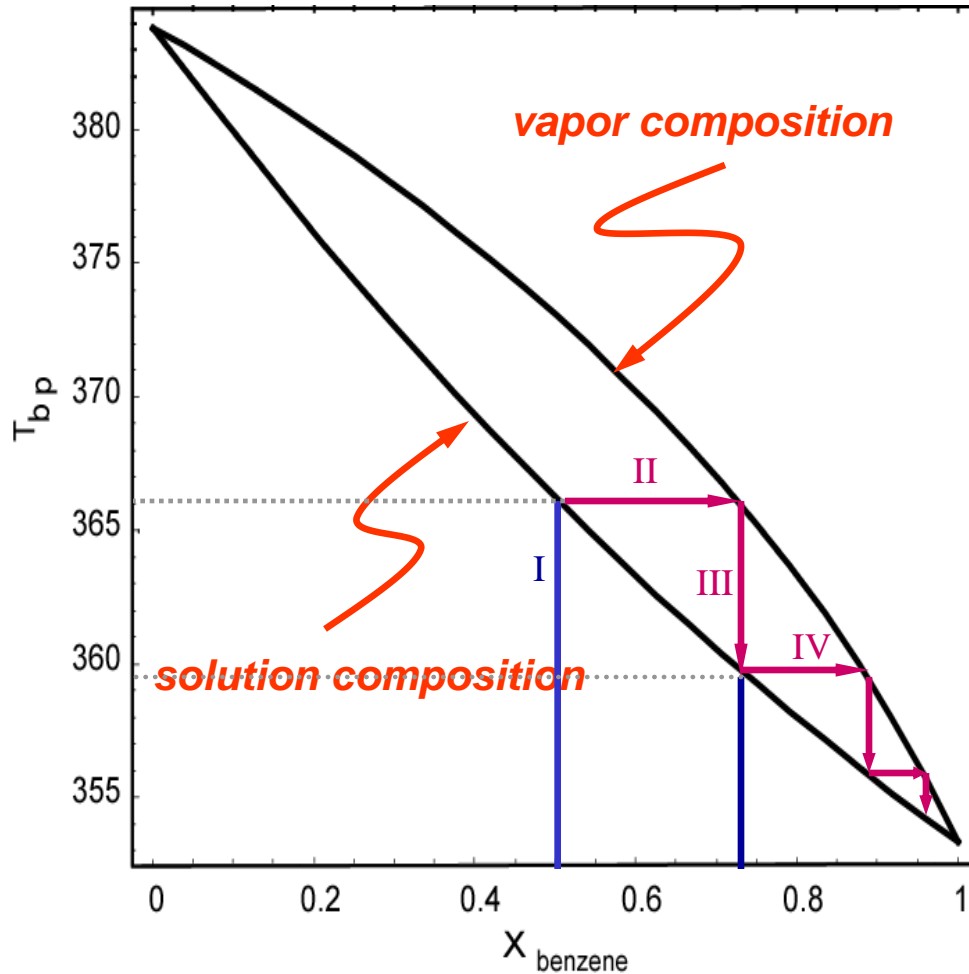
- a solution of $X_{benz}^{(l)} \approx 0.65$ at $T=357K$ is a liquid
- that boils at $\sim 362K$ ($P_{total}=1atm$)
- at $T \sim 362K$ the solution is in equilibrium with vapor $X_{benz}^{(v)} = .83$
- if the system is maintained at $P_{total} = 1 atm$ and T is raised to $365K$, liquid will evaporate until $X_{benz}^{(l)}=0.53$ and $X_{benz}^{(v)}=0.74$
- above $T=389.6K$ the system is all vapor with $X_{benz}^{(v)} = 0.65$

fractional distillation



<http://www.wpbschoolhouse.btinternet.co.uk/page12/gifs/FracDistRed.gif>

Fractional Distillation

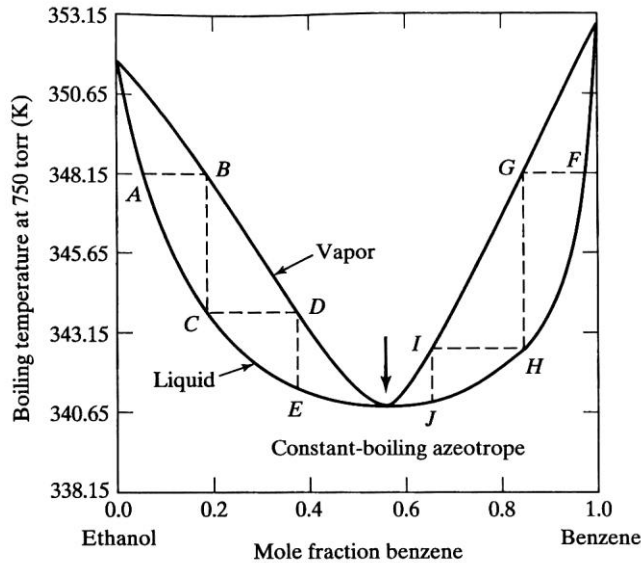


top of column (cooler)

- VI. approaches
 $X_{benzene} = 1$
- V. etc, ...
- IV. • evaporate
 - vapor $X_{benzene}^v \approx .88$
- III. • condense $X_{benzene}^{soln} \approx .72$
 - $T_{bp} \approx 359.5$
- II. • vapor $X_{benzene}^v \approx .72$
- I. • start with 50-50 mixture
 - $T_{bp} \approx 366$

bottom of column (warmer)

azeotrope (non-ideal solution)

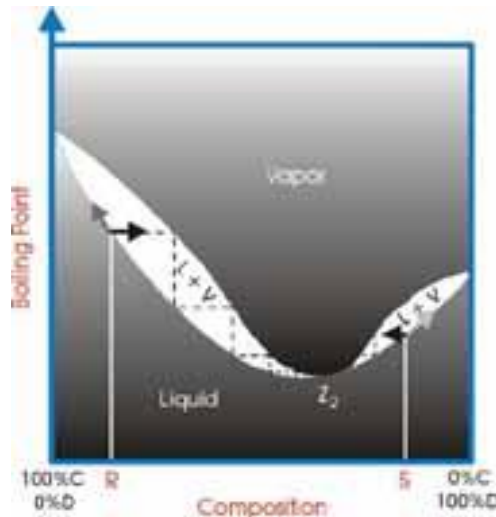


- fractional distillation leads to constant boiling azeotrope in vapor

- and (in pot after azeotrope boils off)

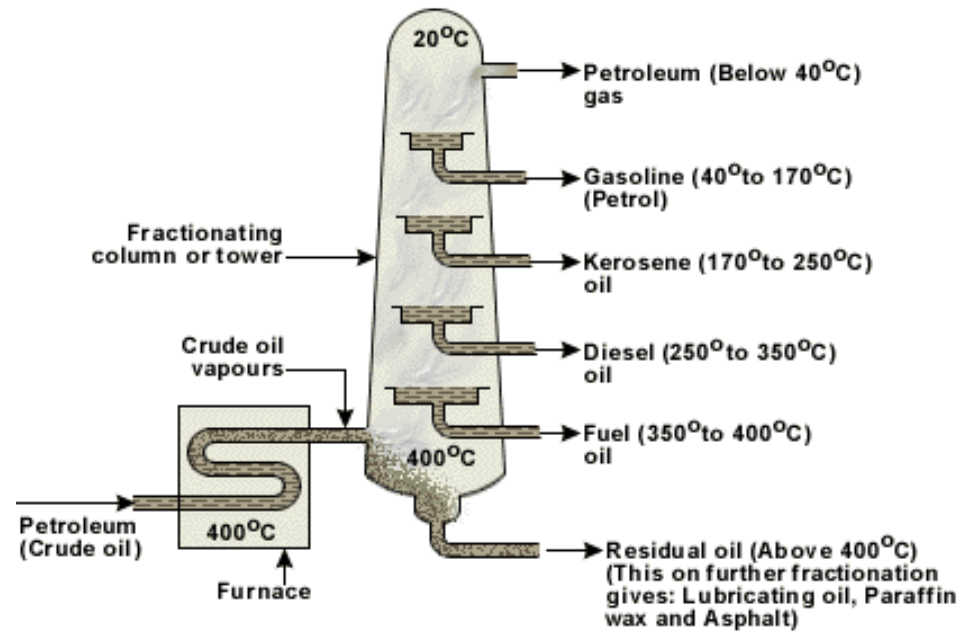
- $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$ pure A

- $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$ pure B



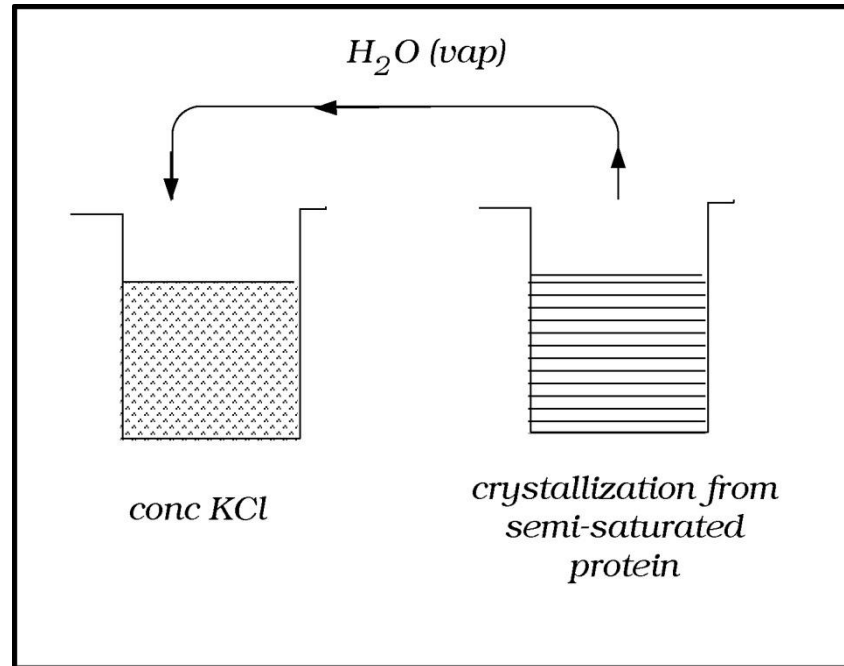
http://www.solvent--recycling.com/azeotrope_1.html

fractional distillation

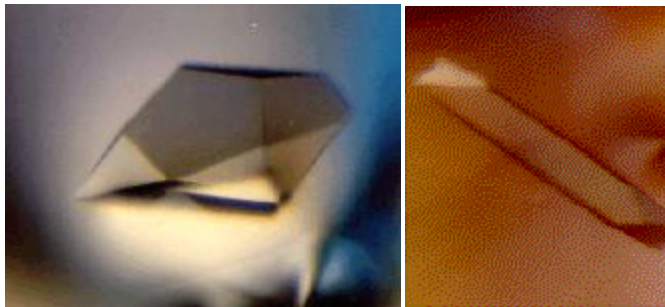
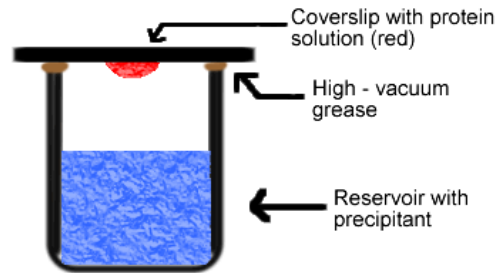


Fractional distillation of petroleum.

Vapor Diffusion Crystal Growth



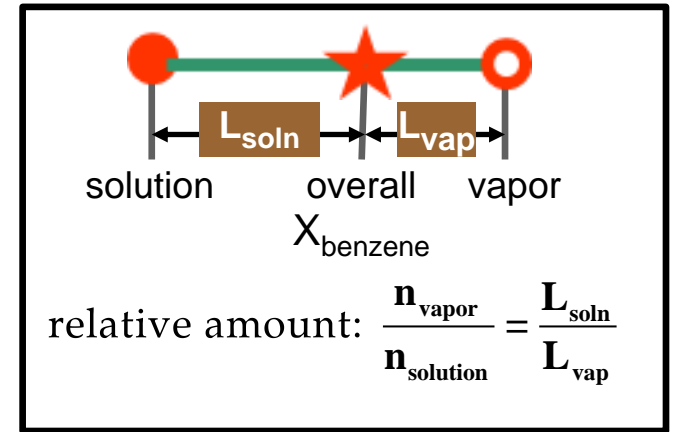
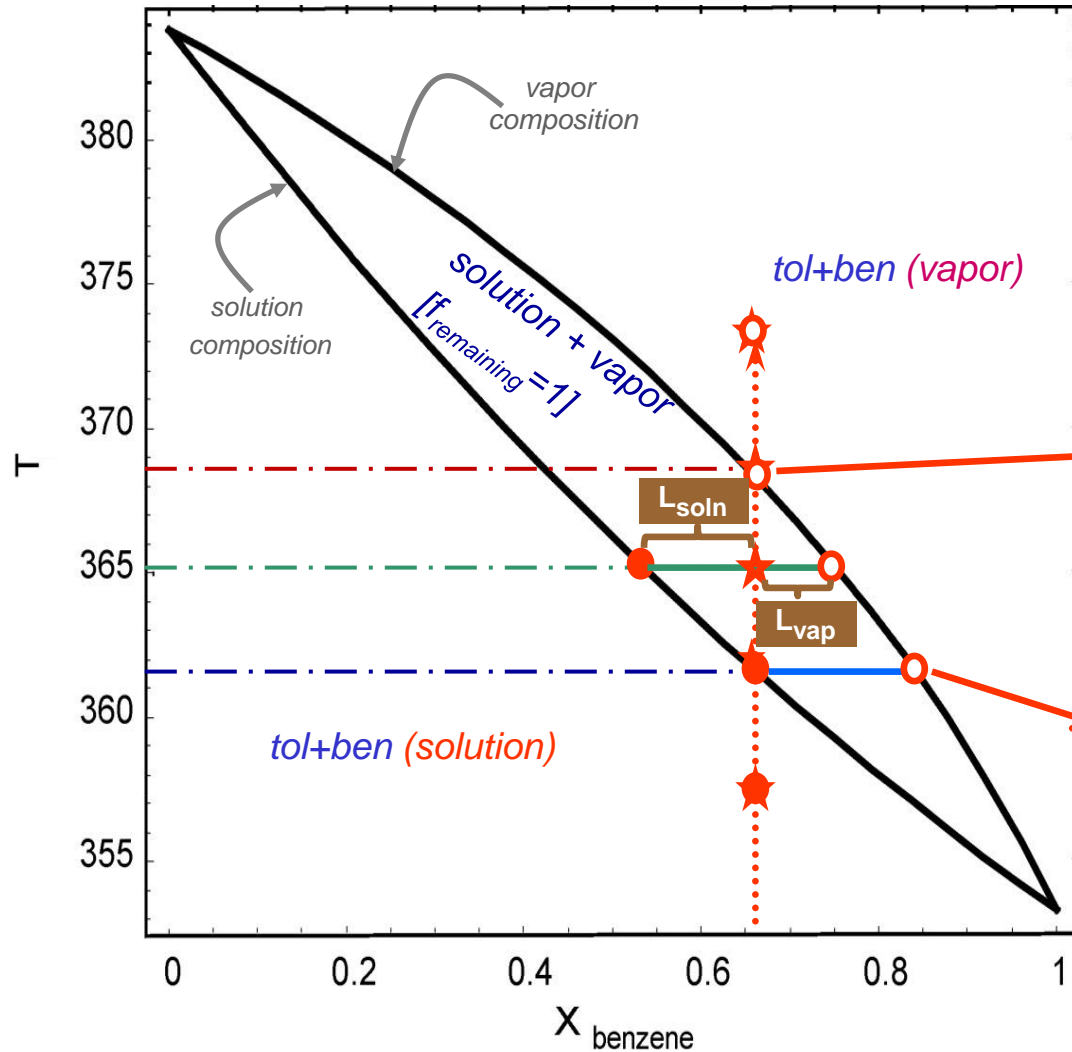
Vapor Diffusion Crystal Growth



<http://science.nasa.gov/ssl/msad/pcg/#HARDWARE>

End of Lecture

relative amounts of components in two-phase region



$(L_{\text{vap}}=0)$ all vapor

$$\frac{n_{\text{solution}}}{n_{\text{vapor}}} = \frac{L_{\text{vap}}}{L_{\text{soln}}}$$

$(L_{\text{soln}}=0)$ all solution

$$\frac{n_{\text{vapor}}}{n_{\text{solution}}} = \frac{L_{\text{soln}}}{L_{\text{vap}}}$$