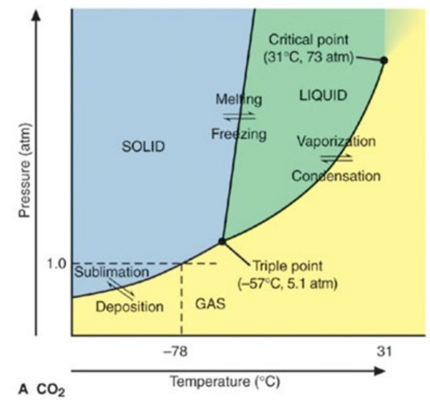
Lectures 20-21
Chemistry 163B W2020
Multicomponent Phase Rule and Solution Behavior

le menu

- phase rule for multicomponent systems
- solid A-solid B phase diagram
- ideal solutions
- solution-vapor phase diagrams
- fractional distillation and vapor diffusion crystal growth

1 component

P



T

$$f = 3-p$$

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]

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

$$c(p-1) \text{ total restrictions for c components}$$

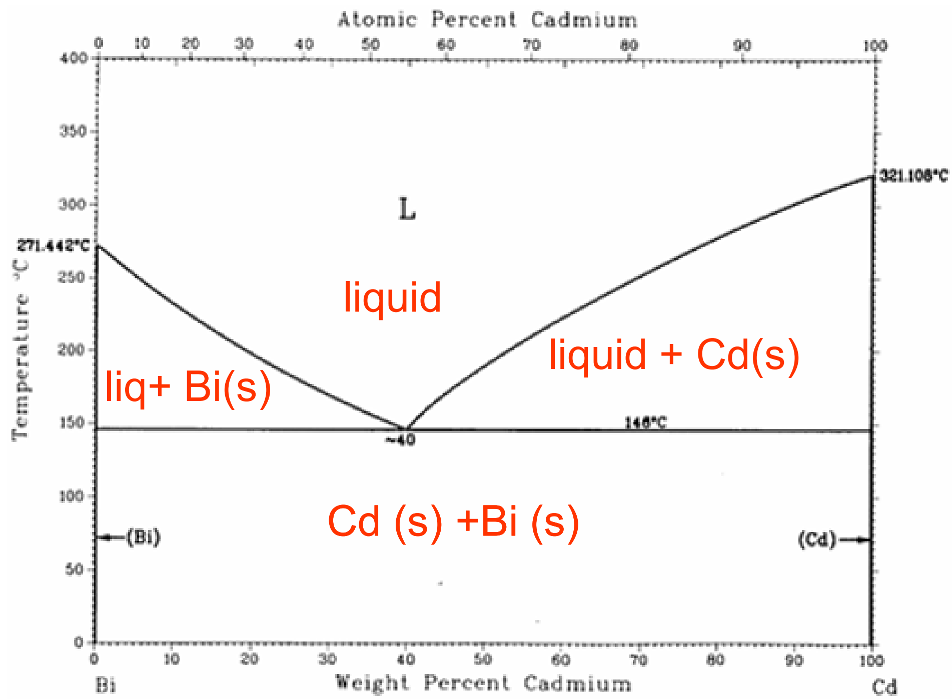
- *f = total variables – total restrictions*

  T,P $\quad$ $X_i^{(\phi)}$ $\quad$ $\mu_i^{(\alpha)} = \mu_i^{(\beta)} \ldots$
- **$f = 2 + (c-1)\,p - c\,(p-1) = \boxed{2 + c - p}$**

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

P= 1 atm

T↑



"χ^{ℓ}_{Cd} "→

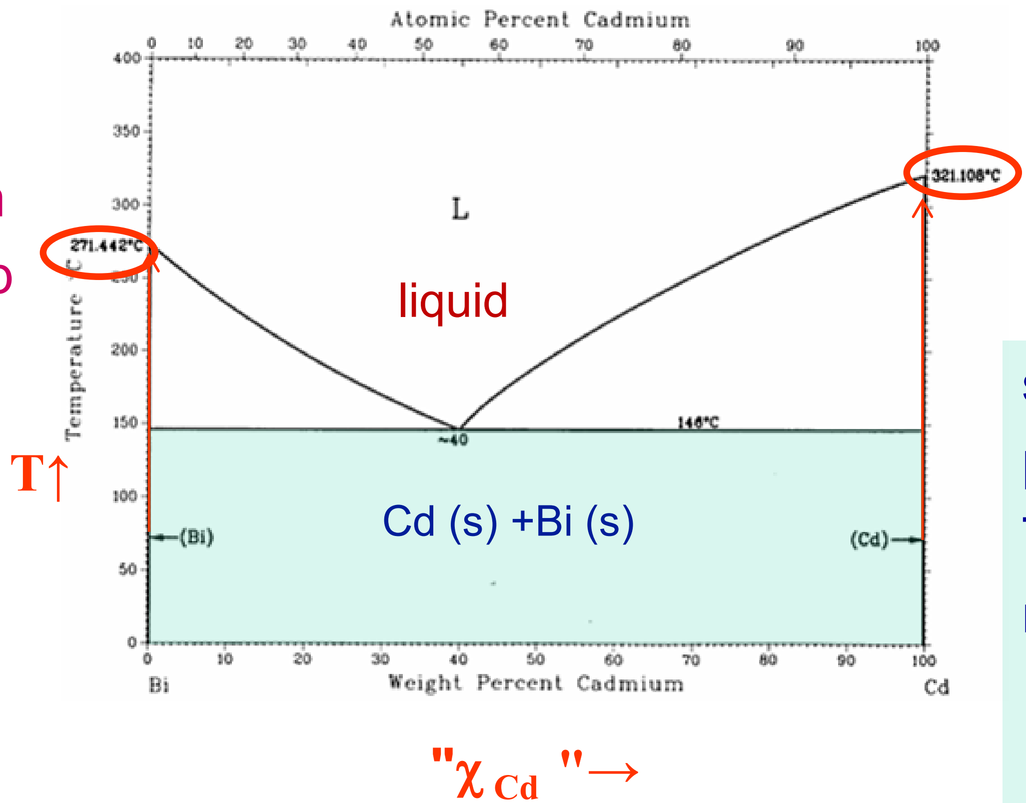
UNDERSTAND THE FOLLOWING DISCUSSION OF THE PHASE RULE AND THIS BINARY COMPONENT PHASE DIAGRAM

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=1atm
- $f_{remaining}$=3-p
- variables: T, χ^{ℓ}_{Cd}



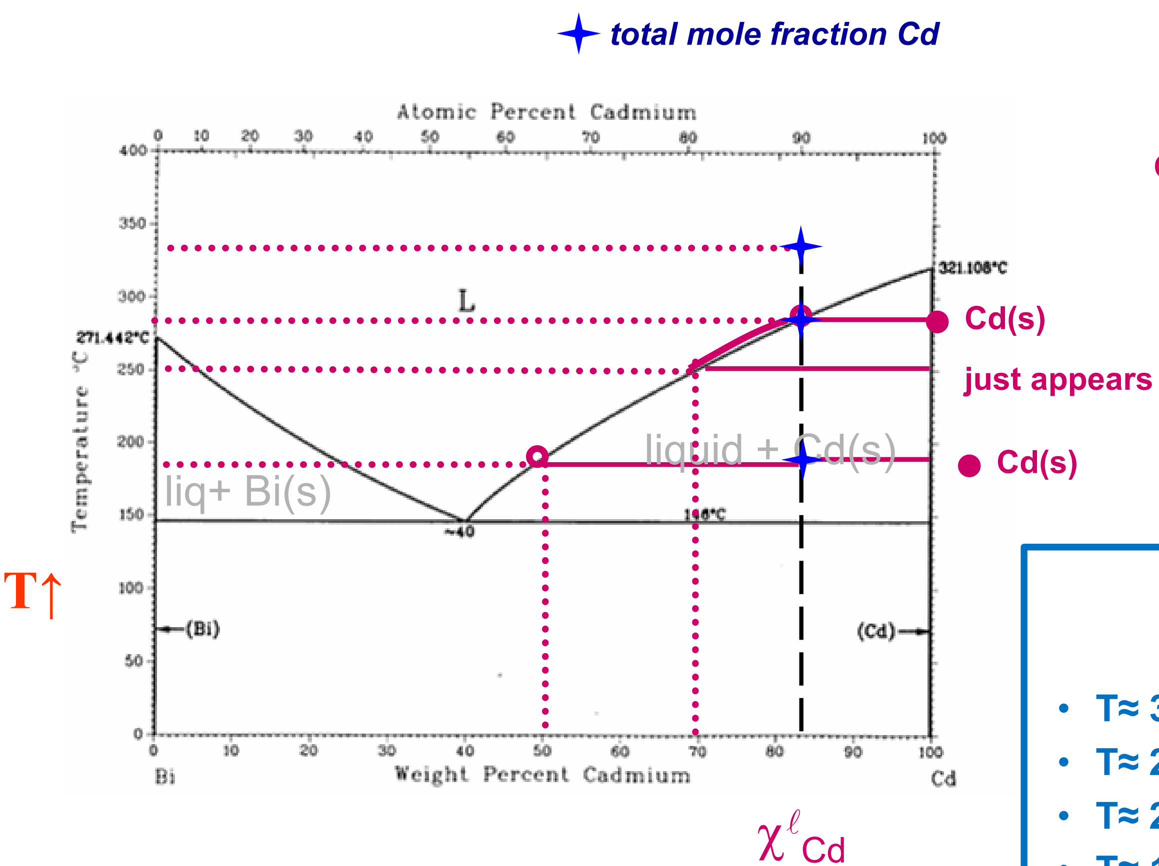
liquid,
p=1, f=2
T, χ^{ℓ}_{cd} can vary

solid < 146° C,
p=2, f=1
T can vary
note: Cd(s) and Bi(s) are pure solids,
not solution (alloy),
χ^{s}_{cd}=1 χ^{s}_{Bi}=1

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)

- $f_{remaining}$=3-p
- variables: T, χ^{ℓ}_{Cd}



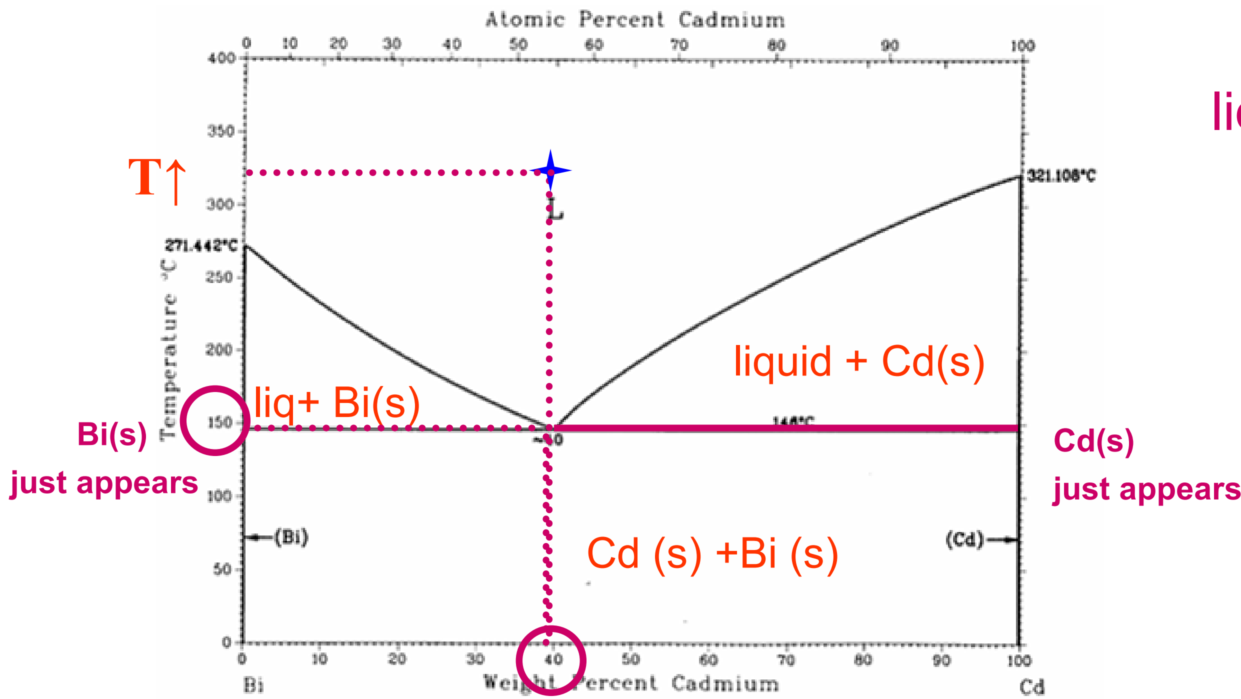
T < 280°C
liquid + Cd(s),
p=2, f=1
only T or χ^{ℓ}_{cd} can independently vary (i.e. T and χ^{ℓ}_{cd} covary)

lower T χ^{total}_{Cd} fixed

- **T≈ 340°C [liquid $X_{Cd}^{(\ell)}=X_{Cd}^{(total)}$]**
- **T≈ 280°C [liquid +Cd(s) begins to appear]**
- **T≈ 250°C [$X_{Cd}^{(\ell)}$ decreases, as more Cd(s)]**
- **T≈ 185 °C [$X_{Cd}^{(\ell)}$ decreases, more Cd(s)]**

phase rule and Cd-Bi phase diagram (eutectic)

$f_{remaining}$=3-p



liquid +Cd(s) + Bi(s)

p=3, f=0

T and χ^{ℓ}_{cd}

fixed

T=146° C,

χ^{ℓ}_{Cd}=0.55

=0.39 wt%

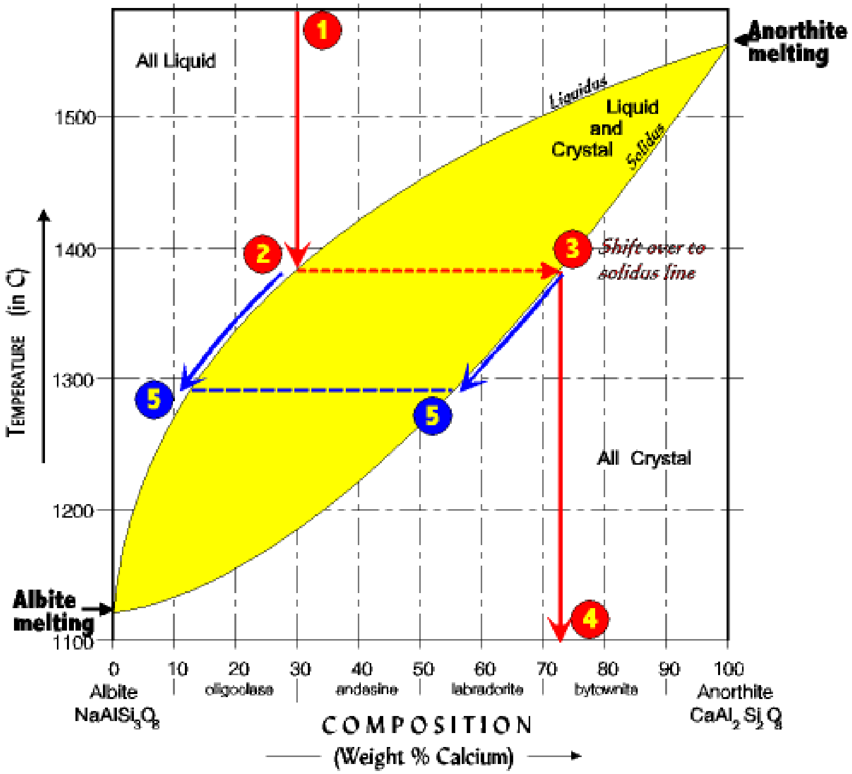
"χ^{ℓ}_{Cd} "→

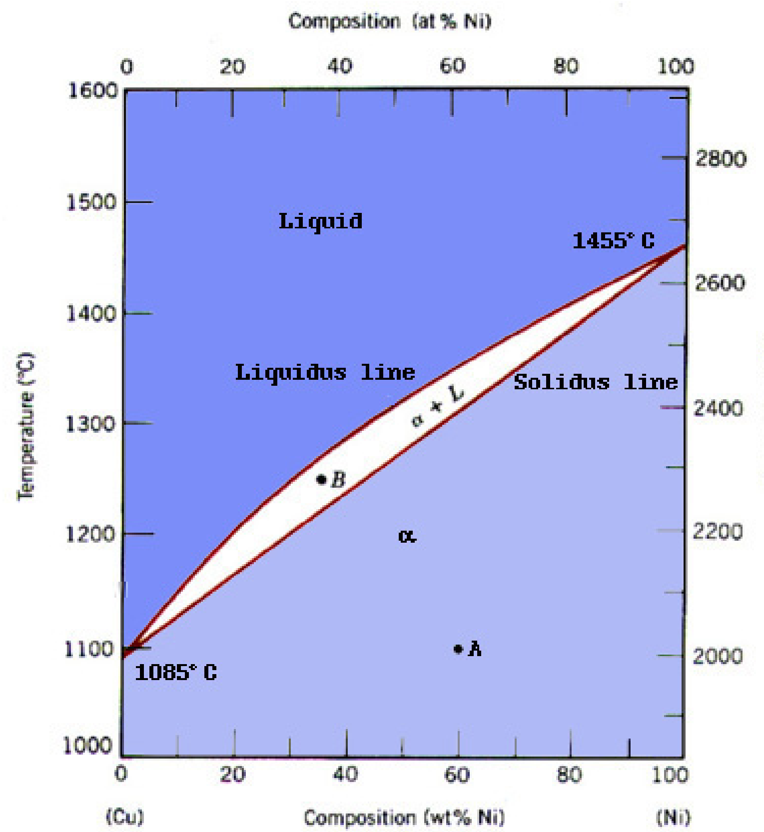
eutectic=constant freezing composition (mixture)

not all solid-solid mixtures form eutectics

$NaAlSi_3O_8$ + $CaAl_2Si_2O_8$

Cu + Ni

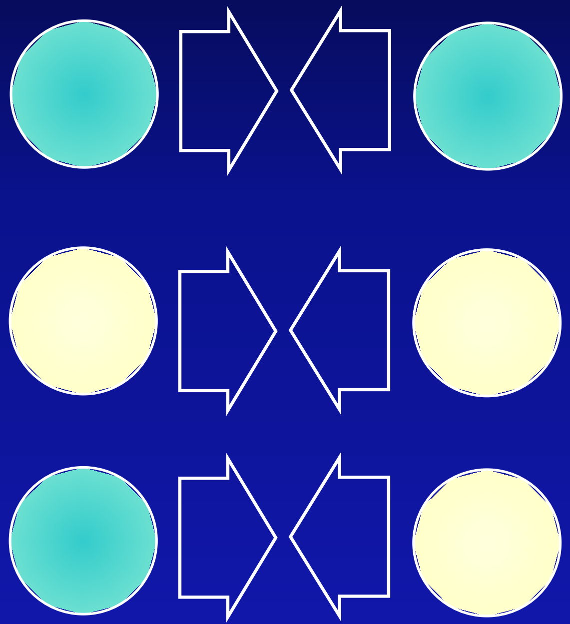




Ideal Solutions

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.
- $\Delta H_{mixing} = 0$ **means that all three interactions are of equal strength**.



http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt

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

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

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

$$P_{total} = P_A^{(v)} + P_B^{(v)} = X_A^{(\ell)} P_A^{\bullet} + X_B^{(\ell)} P_B^{\bullet}$$

$$= X_A^{(\ell)} P_A^{\bullet} + \left(1 - X_A^{(\ell)}\right) P_B^{\bullet}$$

$$= X_A^{(\ell)} \left(P_A^{\bullet} - P_B^{\bullet}\right) + P_B^{\bullet}$$

linear P_{total} vs $X_A^{(\ell)}$

correction for non-ideality
activity
HW #7 prob 55

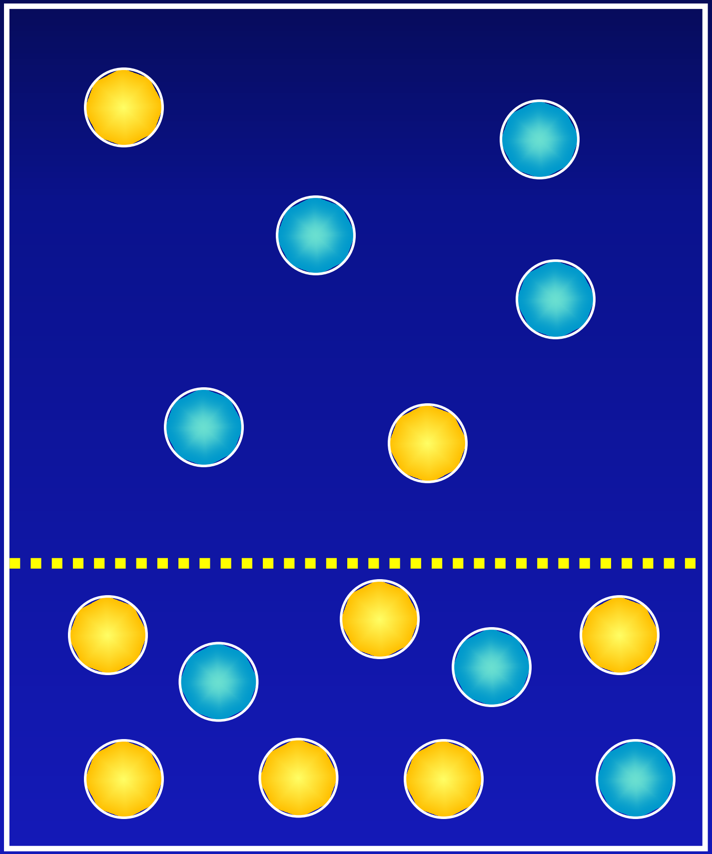
$$P_i^{(v)} = a_i^{(\ell)} P_i^{\bullet}$$

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

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

liq ↔ vap Eq. in Binary Mixtures

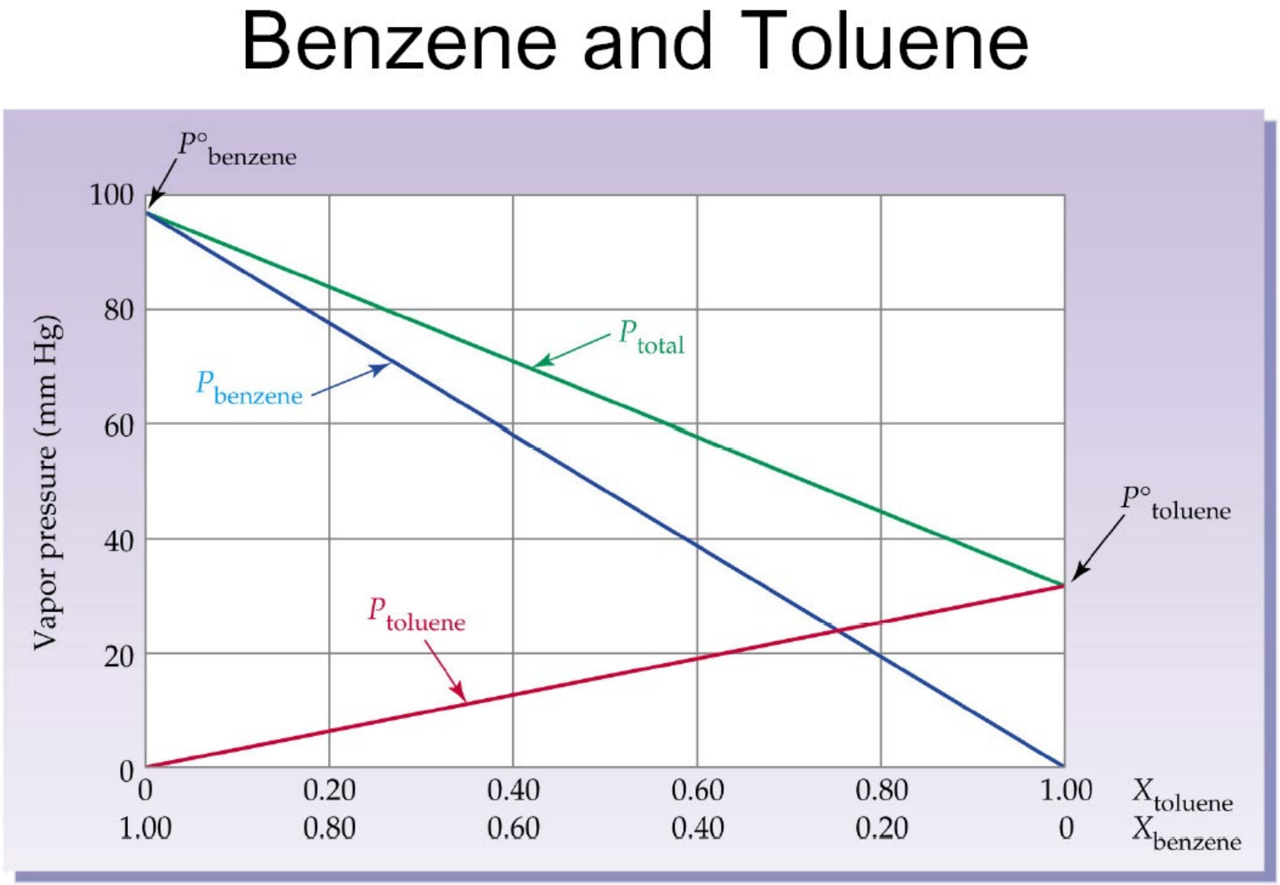
- Both the liquid and the vapor phase are binary mixtures of A and B.
- x_A, x_B are the mole fractions in the liquid.
- y_A, y_B are the mole fractions in the vapor.
- p_A, p_B are the partial pressures in the vapor.



http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt

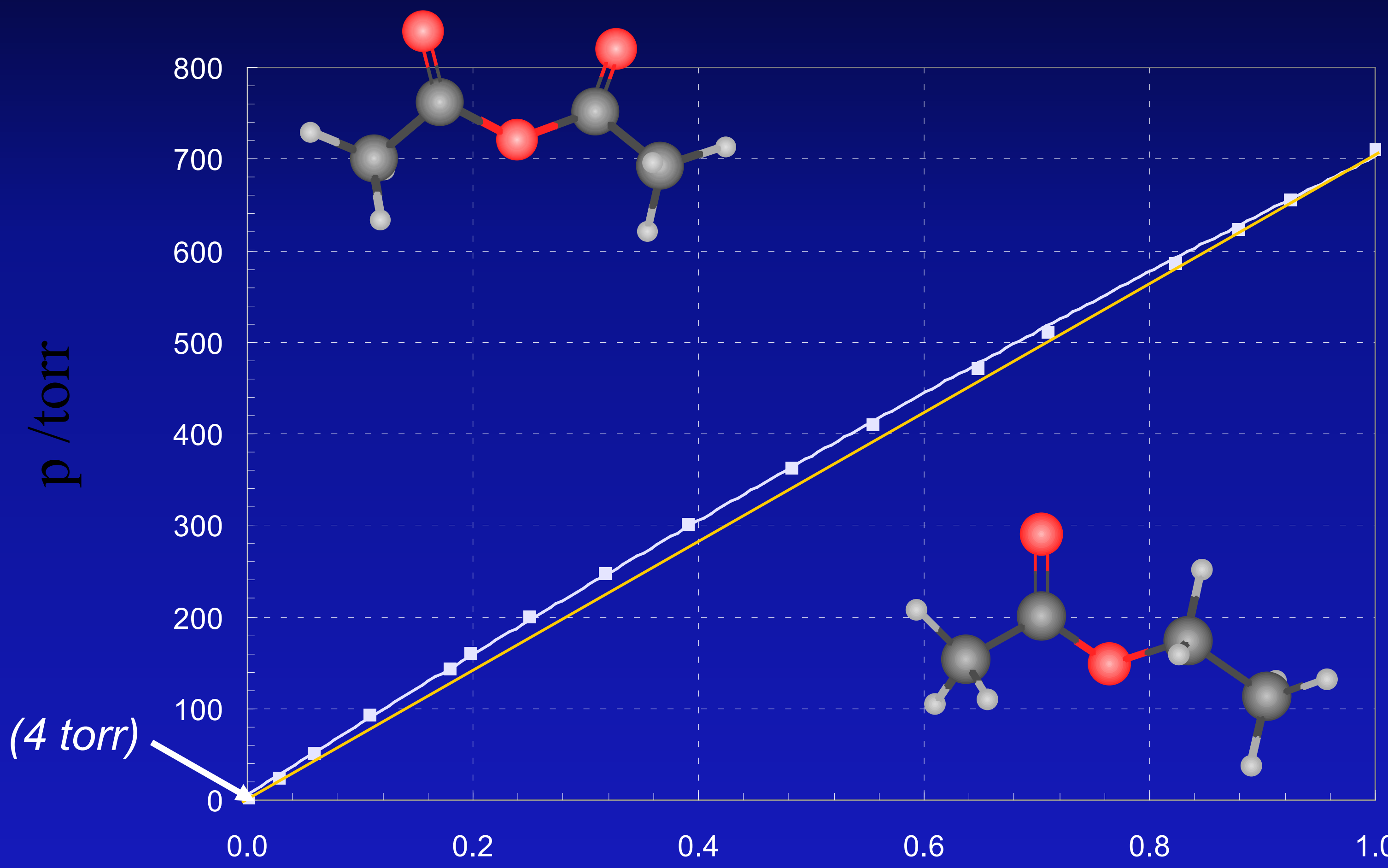
benzene-toluene, quite ideal (similar to Fig 9.2 E&R4th) !!

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



http://www.chem.ucsb.edu/coursepages/06fall/1C-Watts/dl/Lecture_Notes/Lecture16.%2011-8-06Colligative%20Properties%20Solutions.pdf

Ethyl Acetate/Acetic Anhydride



http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt

$X^{(\ell)}$ vs $X^{(v)}$ (notation conventions)

conventions :

mole fraction liquid component A:

$X_A^{(\ell)}$ 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***

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

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

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

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

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

HW#7 probs 50, 55 use E&R's y_i

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

$$\mu_i^{(\ell)} = \mu_i^{(v)} \text{ for each component i in mixture}$$

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{\circ(v)}(T) + RT\,ln(\underbrace{\gamma_i^{(v)} P_i^{(v)}(T)}_{f_i} / 1\ bar)$$

$$\mu_i = \mu_i^0 + RT \ln\left(\frac{P_i}{1\ bar}\right) \text{ old stuff !!}$$

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

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \underbrace{\mu_i^{\circ(v)}(T) + RT\,ln(\gamma_i^{(v)} P_i^{\bullet(v)}(T) / 1\ bar)}_{\mu_i^{\bullet(v)}(T,P_i^{\bullet})} + RT\,ln(\gamma_i^{(\ell)} X_i^{(\ell)})$$

chemical potential of pure component i

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

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

$$\mu_i^{(v)}(T,P,X_i^{(\ell)}) = \mu_i^{\bullet(v)}(T,P_i^{\bullet}) + RT\ ln(X_i^{(\ell)}) \quad \text{ideal soln } \gamma_i^{(\ell)} = 1$$

solution ⇄ vapor components in equilibrium at T

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

pure liquid ⇄ 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

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

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

Ideal Solutions

from: https://switkes.chemistry.ucsc.edu/teaching/CHEM163B/HANDOUTS/ideal_soln_thermo.pdf

Handout #50

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

$$\overline{V}_i = \overline{V}_i^{\bullet\ell} \qquad V = \sum_i n_i \overline{V}_i$$

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

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

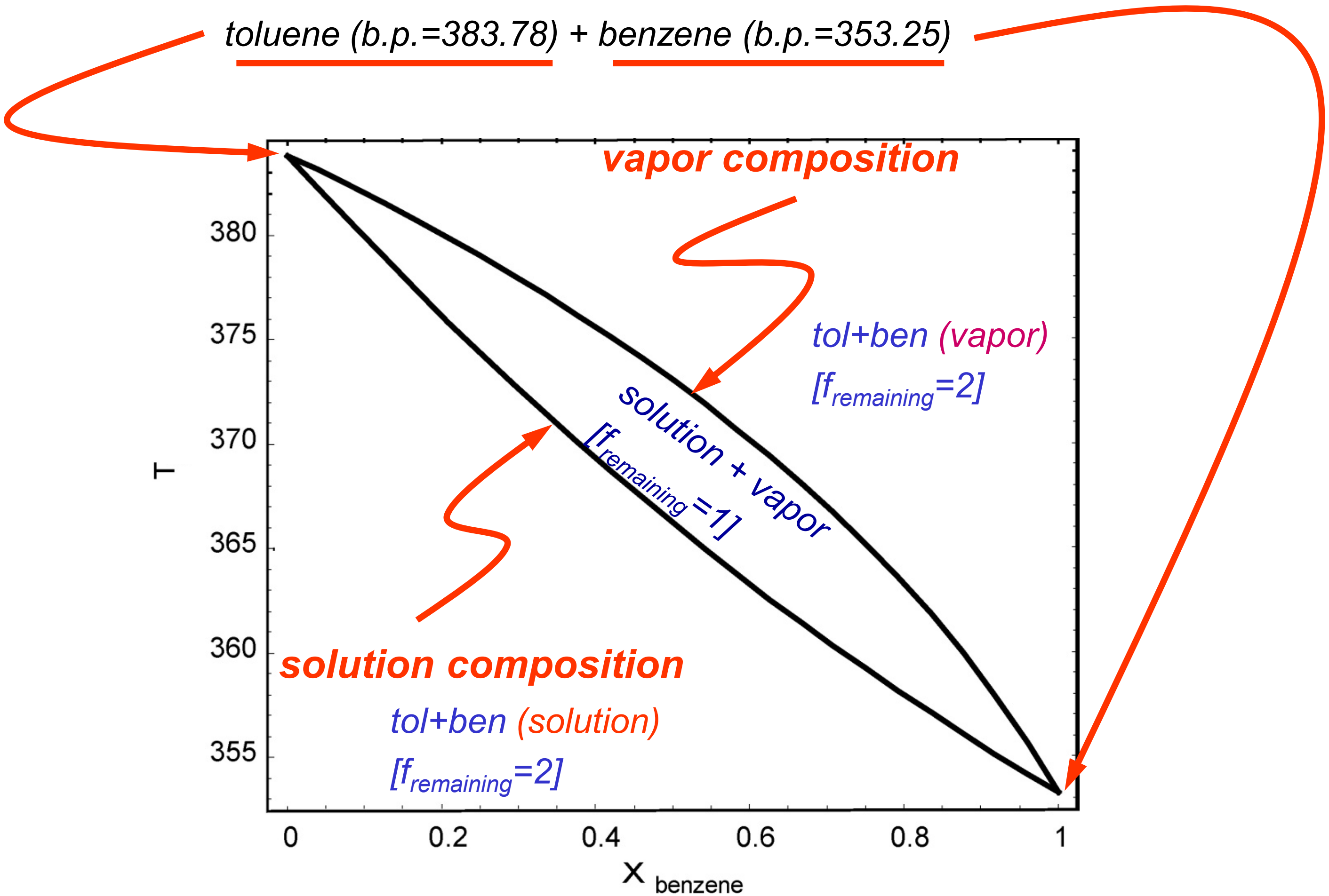
IV. The entropy of mixing is: $\Delta S_{mix} = \dfrac{\Delta H_{mix} - \Delta G_{mix}}{T} = -\sum_k n_k R \ln X_k^\ell$

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

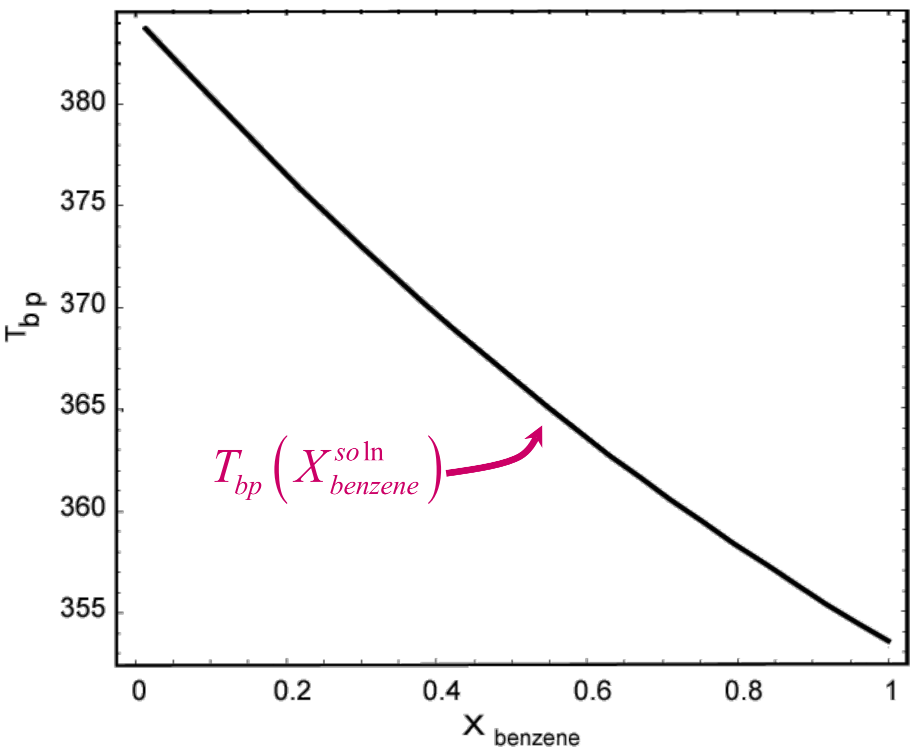
it may be very good for your future

happiness

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



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



- $\ln\left(\frac{P^{\bullet}_{benzene}(T)}{1\text{ atm}}\right)=-\frac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\frac{1}{T}-\frac{1}{(T^{\bullet}_{bp})_{ben}}\right]$
- $\frac{P^{\bullet}_{benzene}(T)}{1\text{ atm}}=e^{-\frac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\frac{1}{T}-\frac{1}{(T^{\bullet}_{bp})_{ben}}\right]}$ **vapor pressure of benzene at T**
- $\frac{P^{\bullet}_{toluene}(T)}{1\text{ atm}}=e^{-\frac{(\Delta\bar{H}_{vap})_{tol}}{R}\left[\frac{1}{T}-\frac{1}{(T^{\bullet}_{bp})_{tol}}\right]}$ **vapor pressure of toluene at T**
- **in ideal solution**

  $P_{benzene}(T)=X^{solution}_{benzene}P^{\bullet}_{benzene}(T)$ and $P_{toluene}(T)=X^{solution}_{toluene}P^{\bullet}_{toluene}(T)$

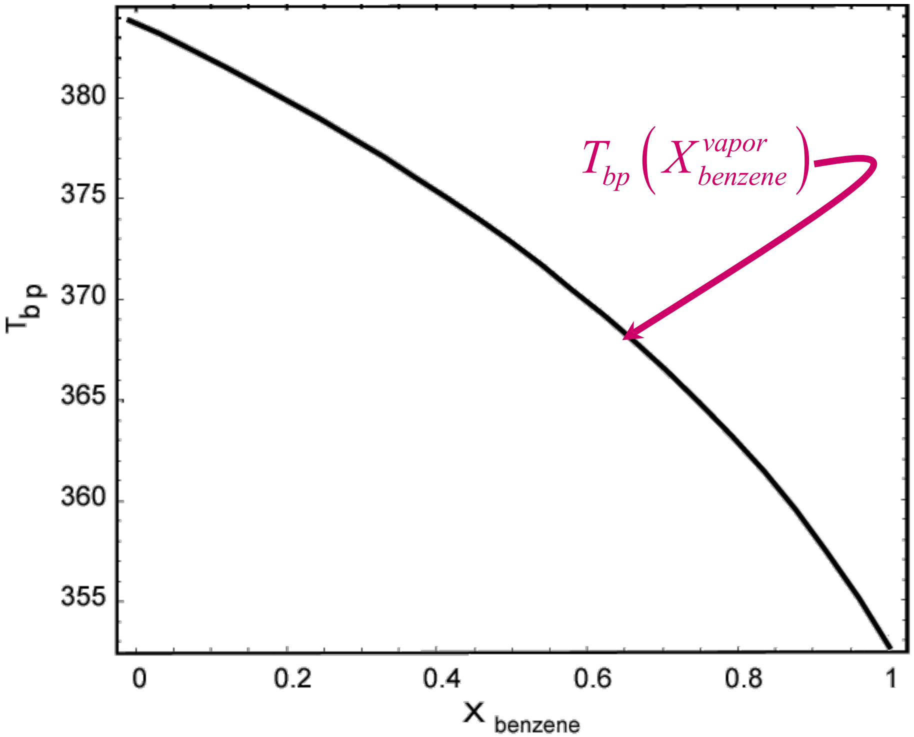
- **at boiling** $\Rightarrow$ $P_{benzene}+P_{toluene}=1\text{ atm}$

  $1\text{ atm}=X^{solution}_{benzene}P^{\bullet}_{benzene}(T^{solution}_{bp})+(1-X^{solution}_{benzene})P^{\bullet}_{toluene}(T^{solution}_{bp})$

- **for a given** $X^{solution}_{benzene}$ **solve for** $T^{solution}_{bp}$

  (or better have Mathematica solve equations see handout #51)

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



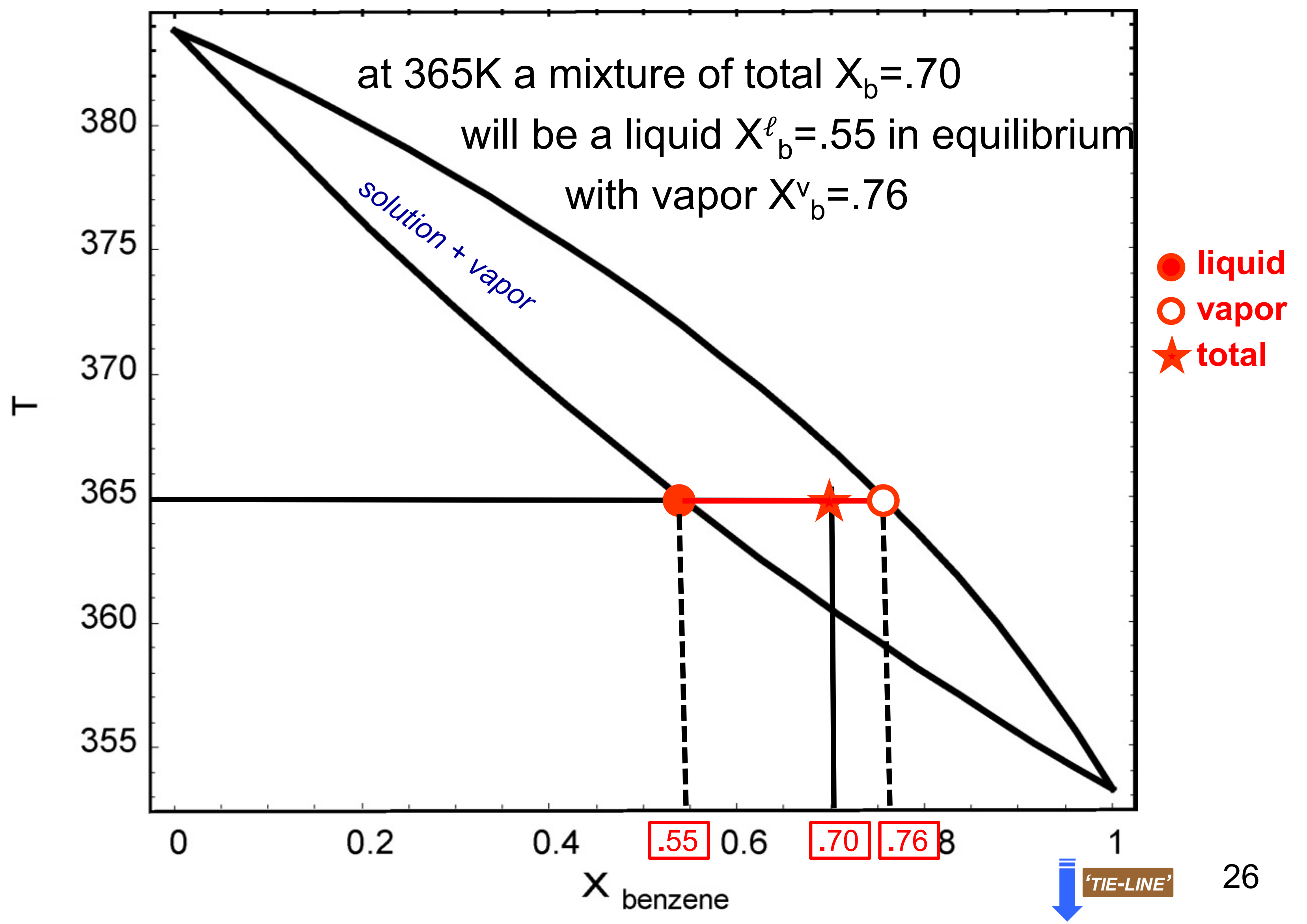
$$X_{benzene}^{vapor} = \frac{P_{benzene}}{P_{total}} = \frac{X_{ben}^{so\ln} P_{ben}^{\bullet}(T_{bp}^{solution})}{P_{total}}$$

$$X_{benzene}^{vapor} = X_{ben}^{so\ln} P_{ben}^{\bullet}(T_{bp}^{solution})$$

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

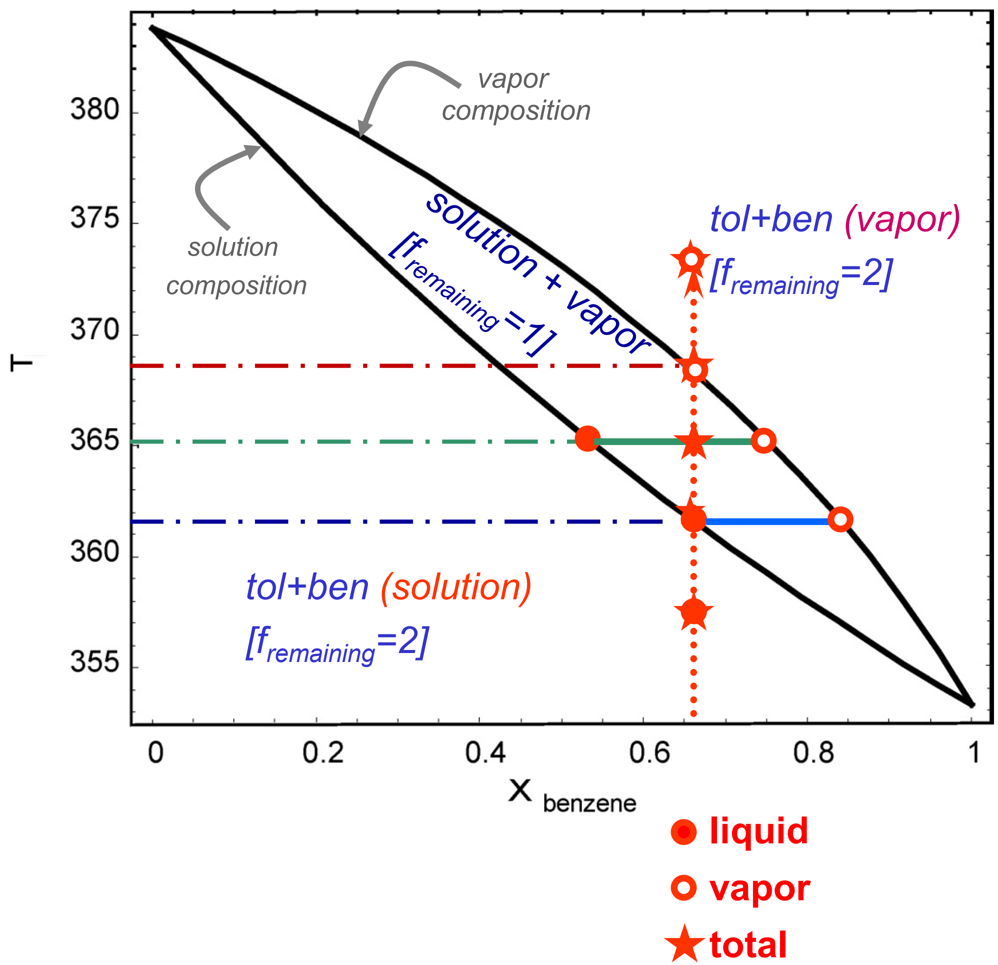
get $T_{bp}^{solution}$ *from equations on previous slide*

two-phase region (P=1 atm) TOLUENE + BENZENE ($\ell \rightleftarrows v$)



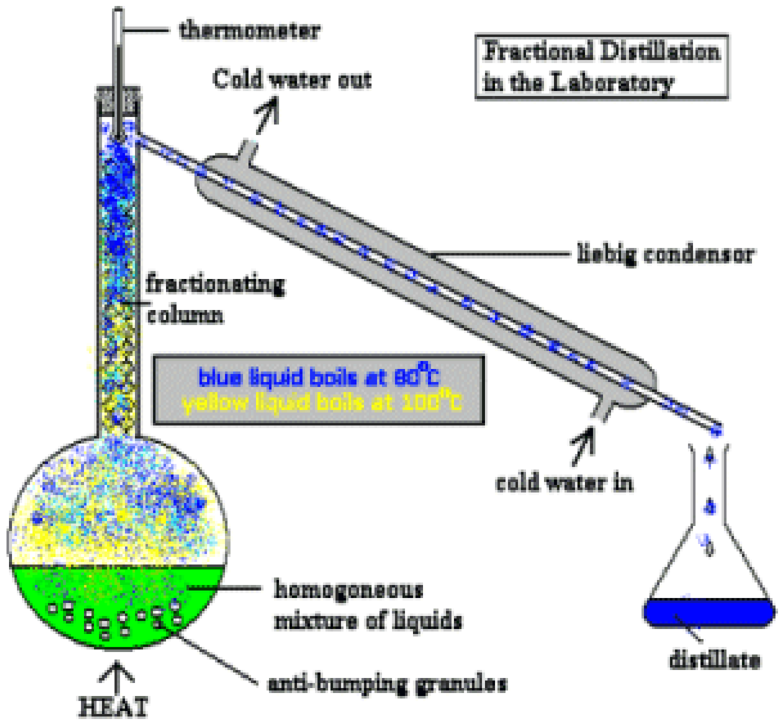
T vs X (P=1 atm) for solution-vapor equilibrium TOLUENE + BENZENE

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



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

- **a solution of $X_{benz}^{(\ell)} \approx 0.65$ at T=357K is a liquid**
- **that boils at ~362K (P_{total}=1atm)**
- **at T ~362K the soluton 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 $X_{benz}^{(\ell)}$=0.53 and $X_{benz}^{(v)}$=0.74**
- above T=369.8K the system is all vapor with $X_{benz}^{(v)} = 0.65$



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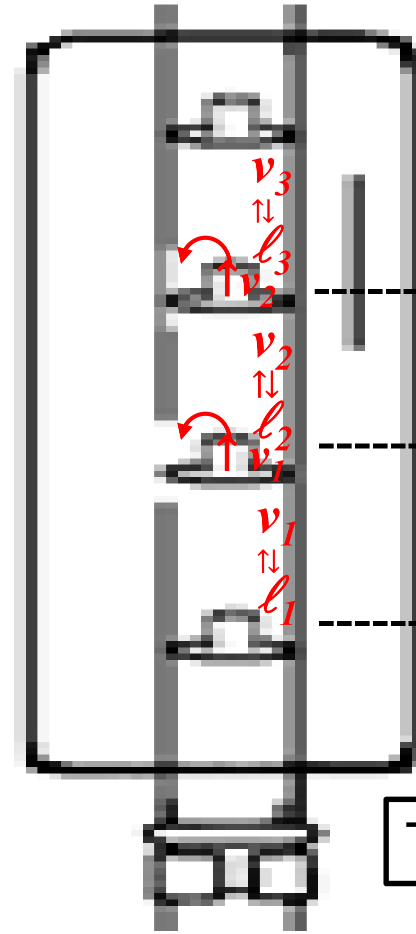


etc !!

T_3 $X_3^{(\ell)} = X_2^{(v)}$

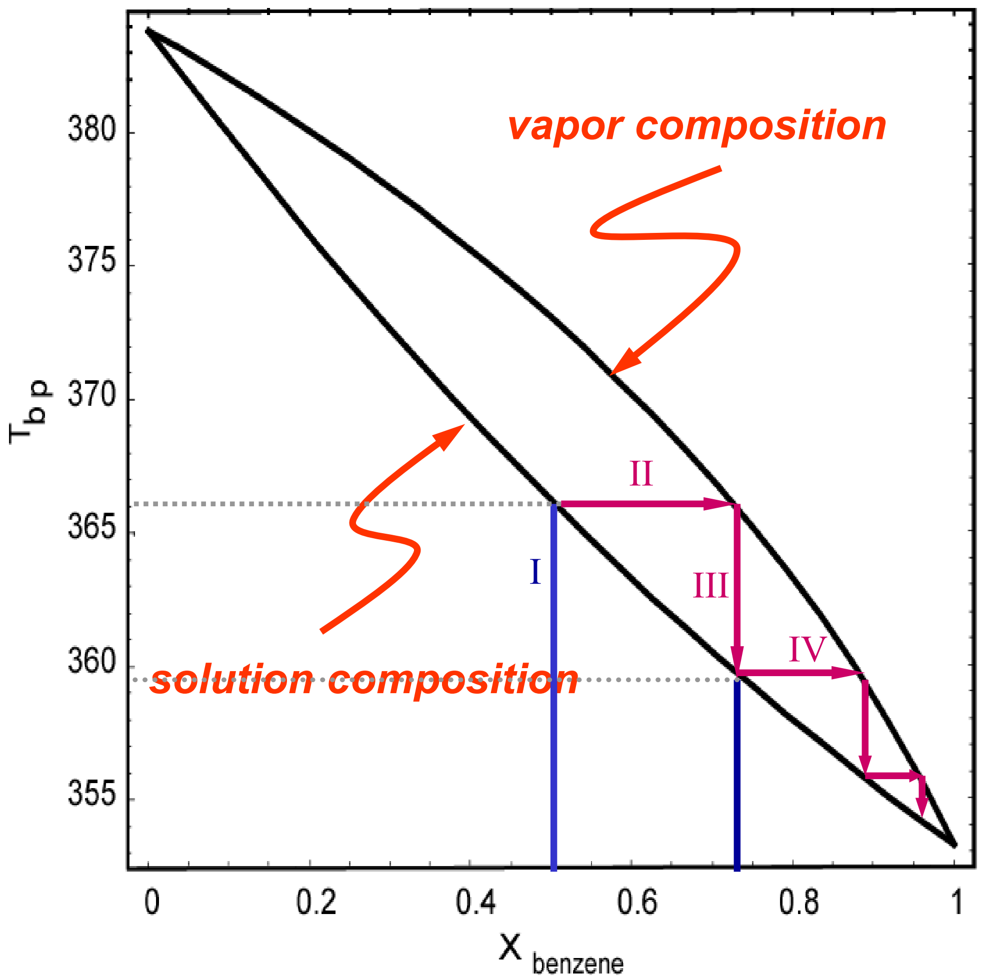
T_2 $X_2^{(\ell)} = X_1^{(v)}$

T_1

$T_1 > T_2 > T_3$

fractional distilation

toluene (b.p.=383.78) + benzene (b.p.=353.25)
benzene more "volatile" than toluene



top of column (cooler)

VI. approaches $X_{benzene}=1$

V. etc, ...

IV.
- evaporate
  - vapor $X^{v}_{benzene} \approx .88$

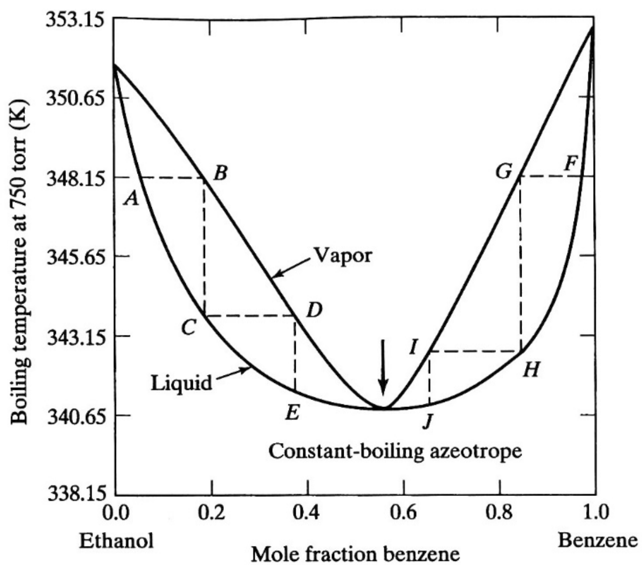
III.
- condense $X^{soln}_{benzene} \approx .72$
- $T_{bp} \approx 359.5$

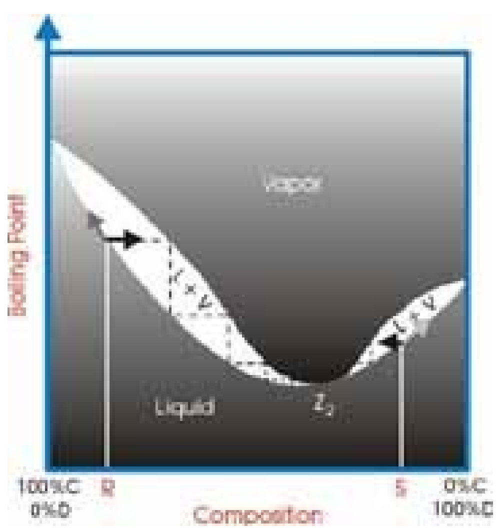
II.
- vapor $X^{v}_{benzene} \approx .72$

I.
- start with 50-50 mixture
- $T_{bp} \approx 366$

bottom of column (warmer)

azeotrope (non-ideal solution)





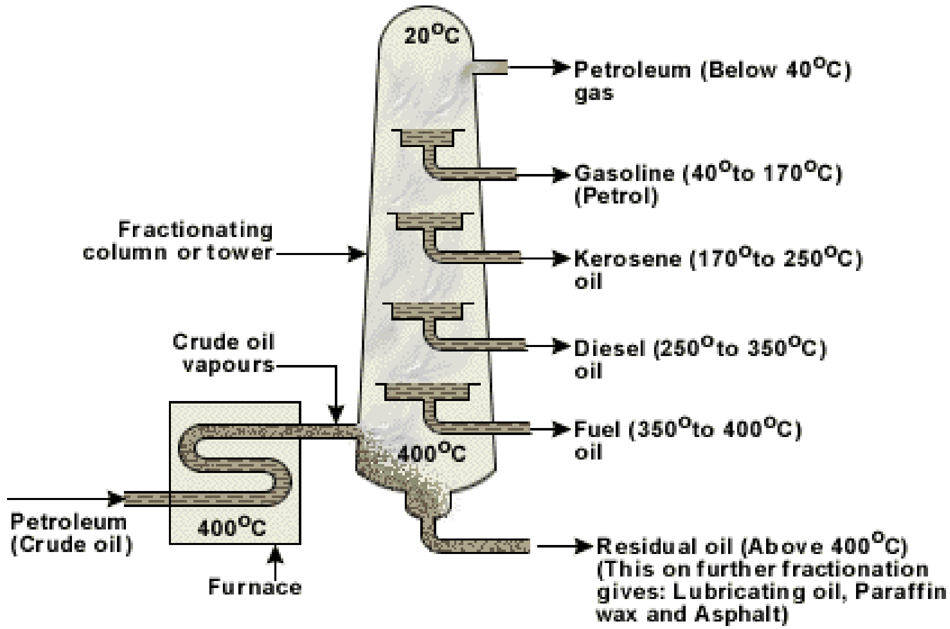
• fractional distillation leads to constant boiling azeotrope in vapor

•*and (in pot after azeotrope boils off)*

- $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
- $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B

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

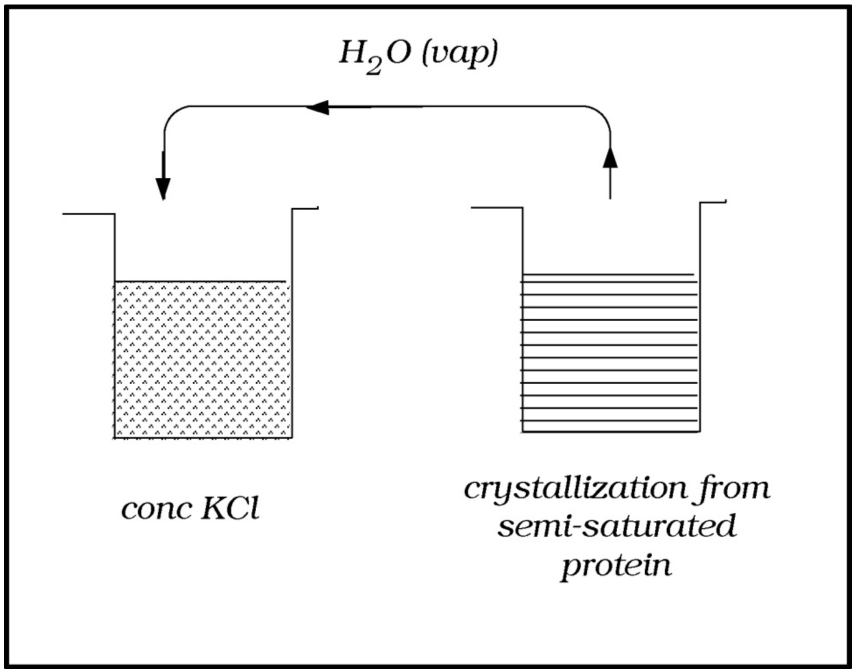
fractional distillation



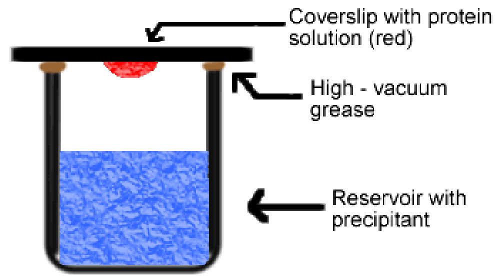
Fractional distillation of petroleum.

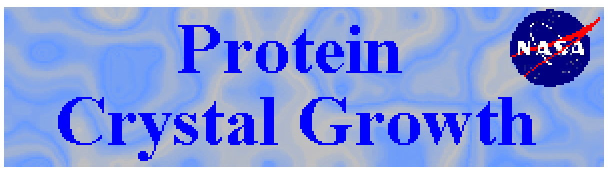
http://home.att.net/~cat6a/images/fuels_06.gif

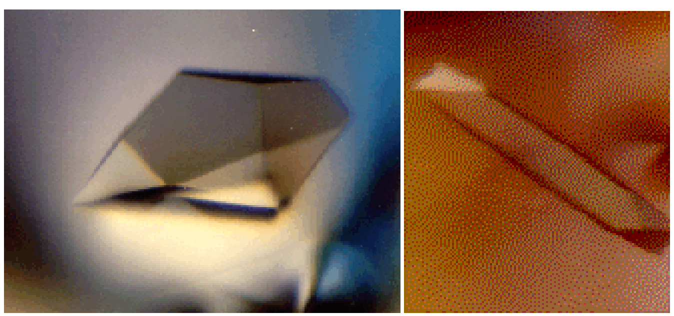
vapor diffusion crystal growth



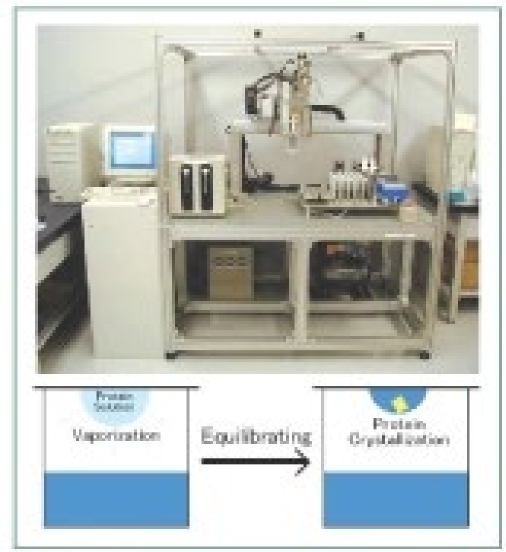
Vapor Diffusion Crystal Growth







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



End of Lecture 20-21

$\mu_i^{(\ell)} = \mu_i^{(v)}$ for each component i

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^{th} phase

i^{th} component

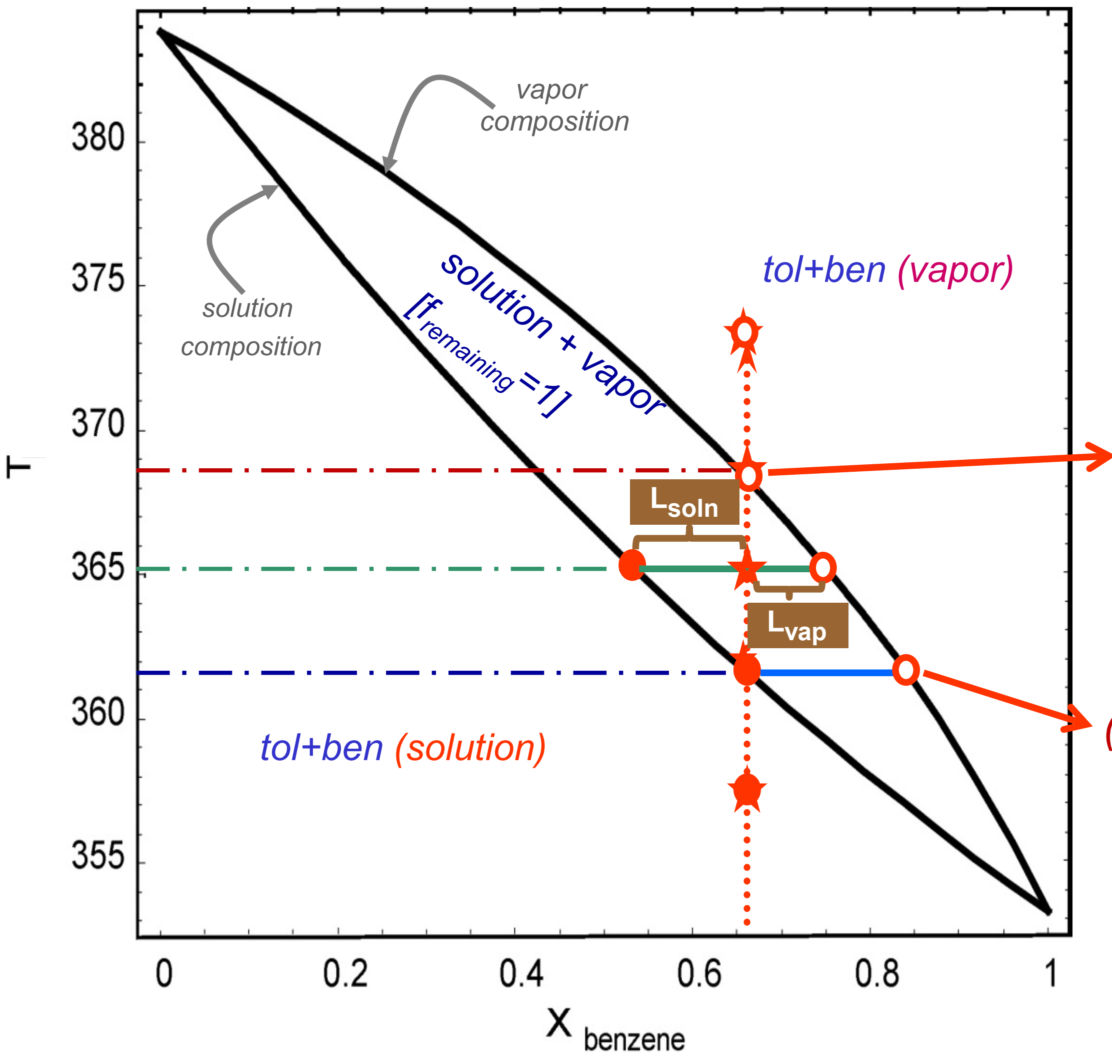
at equilibrium

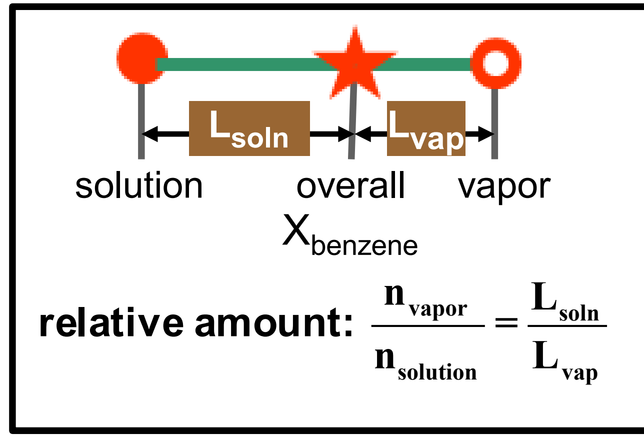
$$dG_{T,P} = 0 = \sum_{i,\omega} \mu_i^{(\omega)} dn_i^{(\omega)}$$

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

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

relative amounts of components in two-phase region

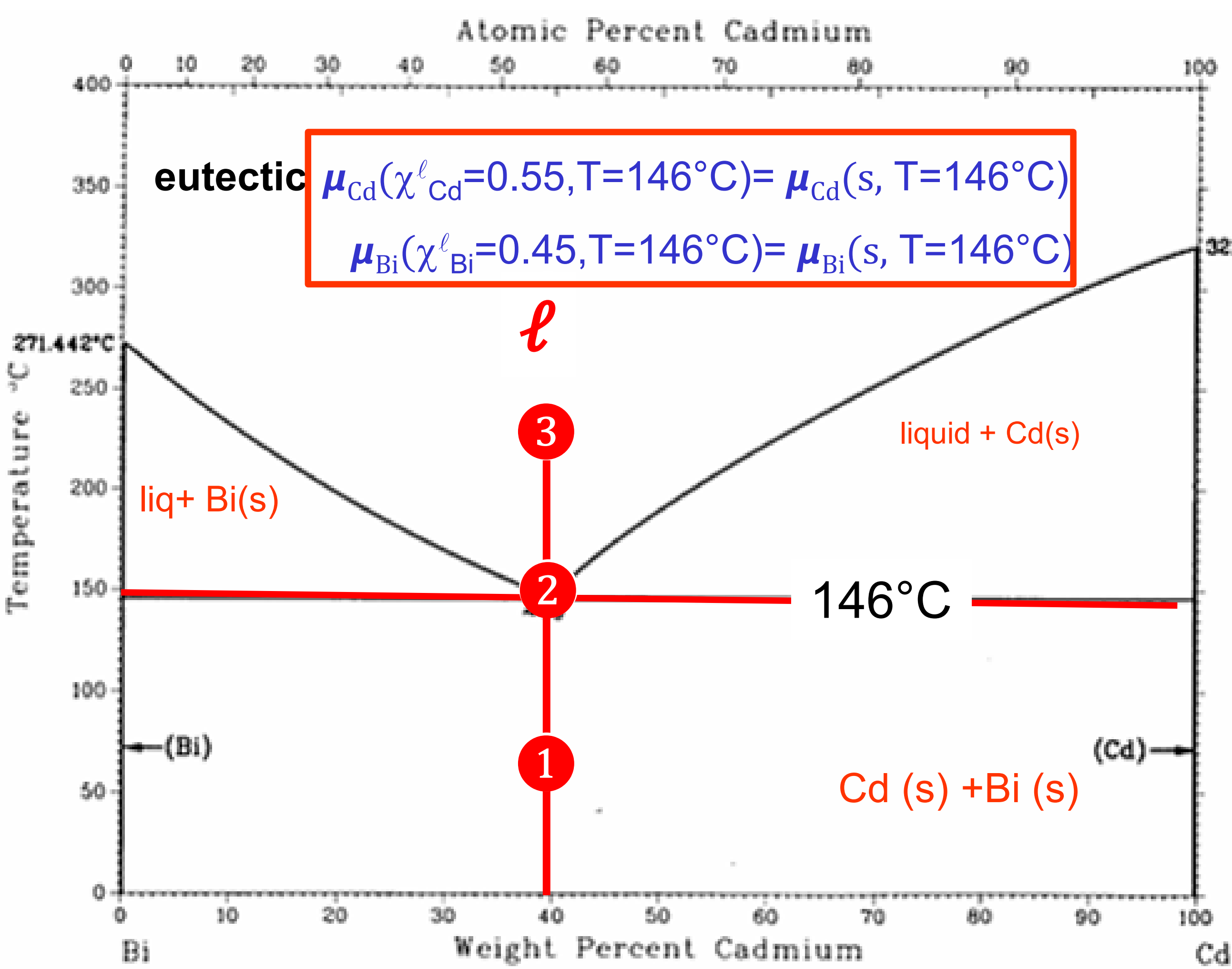




(L_{vap}=0) all vapor $\frac{n_{solution}}{n_{vapor}} = \frac{L_{vap}}{L_{soln}}$

(L_{soln}=0) all solution $\frac{n_{vapor}}{n_{solution}} = \frac{L_{soln}}{L_{vap}}$

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄*liquid is straight line T=146°C*



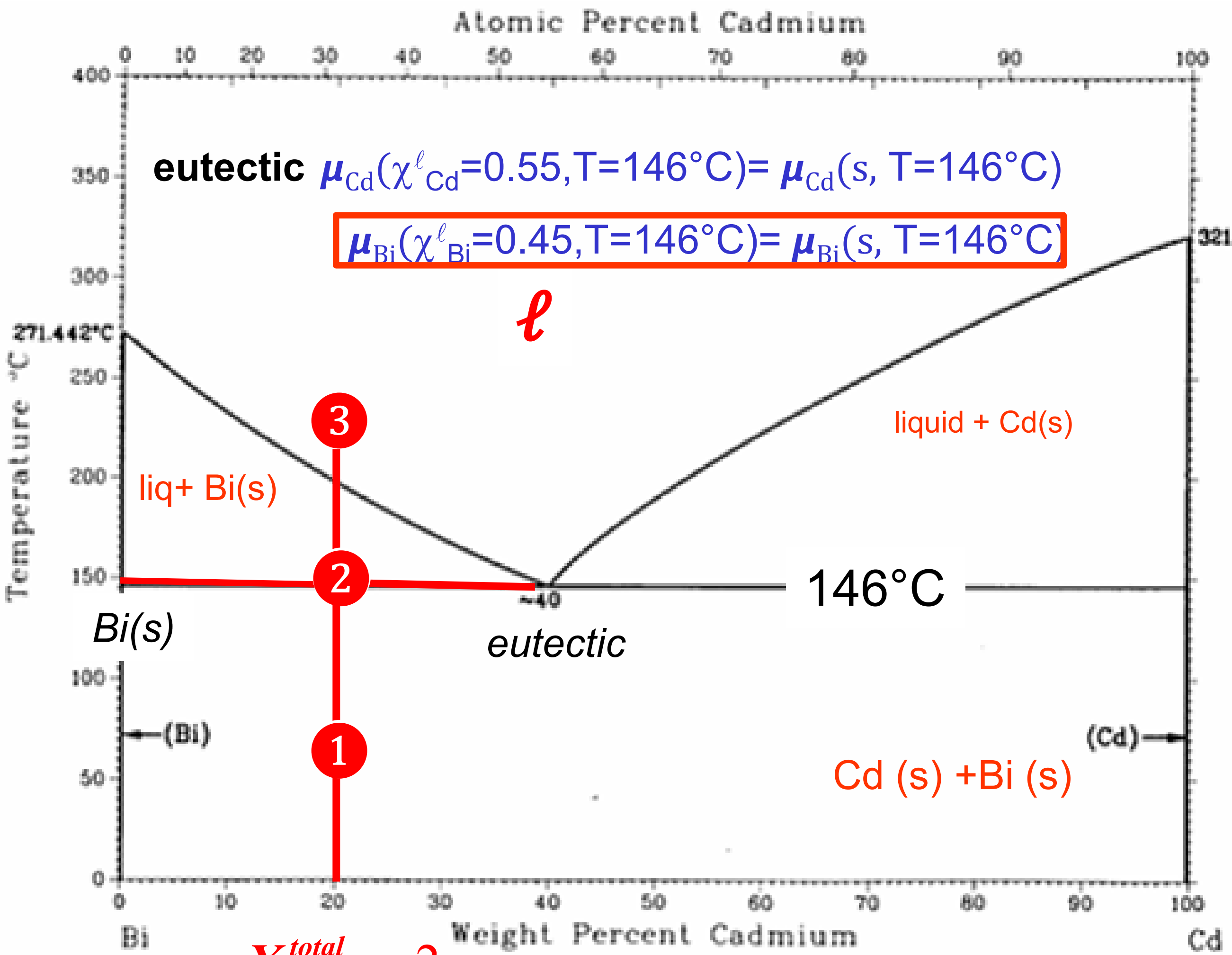
❸ T>146C°
Cd-Bi (X_{Cd})=.55

❷ T=146C°
Cd (s) +Bi (s)
↑↓
Cd-Bi (X_{Cd})=.55

❶ T<146C°
Cd (s) +Bi (s)

"χ^{ℓ}_{Cd}"→ $X_{Cd}^{total} = .55$

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄*liquid is straight line T=146°C*



3 T>≈225°C
Cd-Bi (X_{Cd})=.2

2 T=146°C (first liquid)
Bi (s) *remaining Bi(s)*
↑↓
Cd-Bi (X_{Bi})=.45
all of Cd, some of Bi

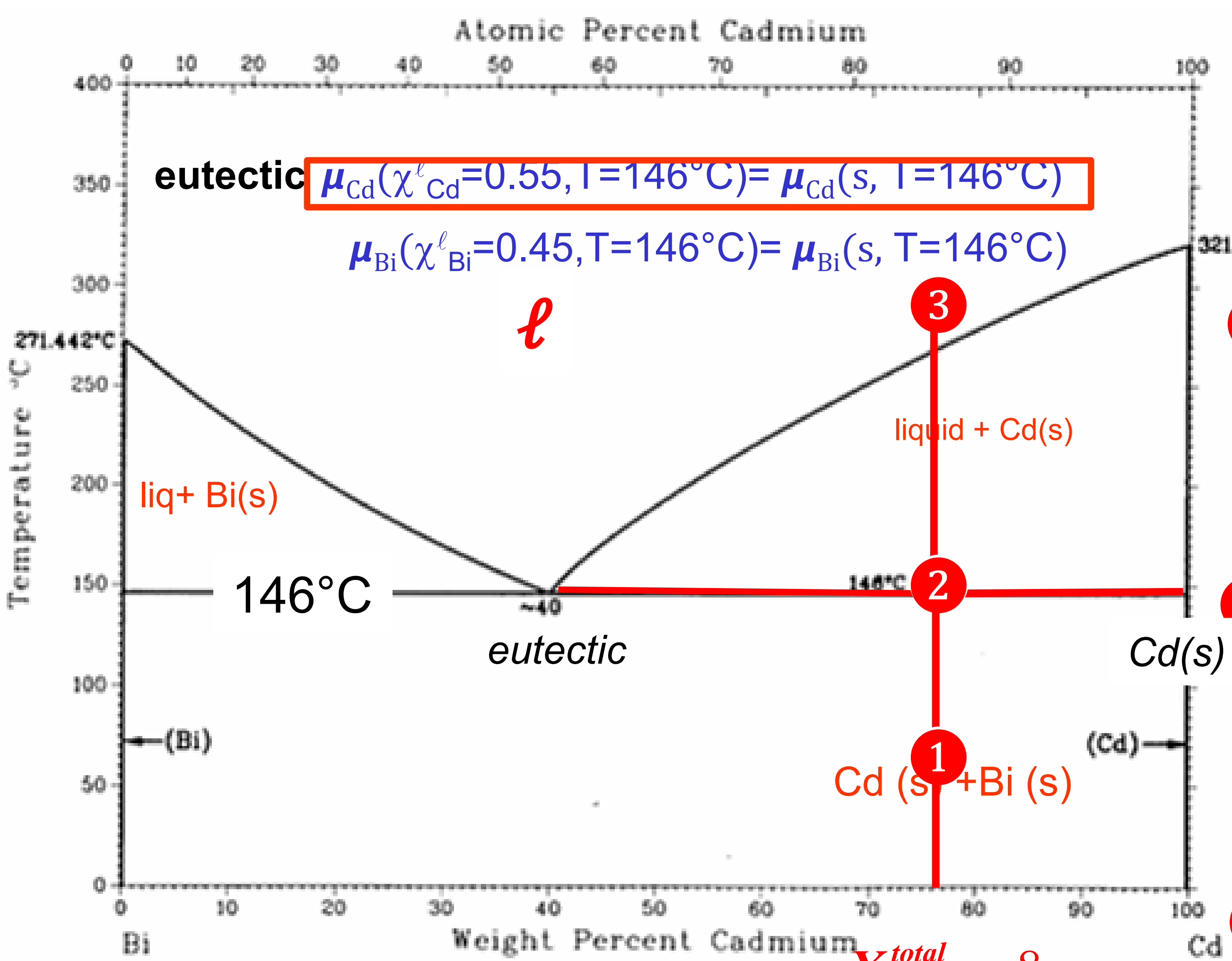
1 T<146°C
Cd (s) +Bi (s)

$X_{Cd}^{total} = .2$

$X_{Bi}^{total} = .8$

"χ^{ℓ}_{Cd} "→

Cd-Bi phase diagram (eutectic) Cd(s)+Bi(s)⇄liquid is straight line T=146°C



❸ T>≈280°C
Cd-Bi (X_{Cd})=.8

❷ T=146°C (first liquid)
Cd (s) *remaining Cd(s)*
↑↓
Cd-Bi (X_{Cd})=.55
all of Bi, some of Cd

❶ T<146°C
Cd (s) +Bi (s)

$X_{Cd}^{total} = .8$

$X_{Bi}^{total} = .2$

"χ^{ℓ}_{Cd} "→