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

1

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

2

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phase rule (lectures 18-19)

1 component   P

$$f = 3-p$$
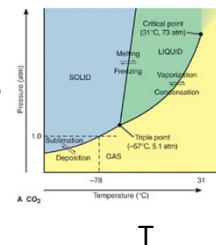
T

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

3

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

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

- *f = total variables – total restrictions*
        T,P   **$X_i^{(\emptyset)}$**   **$\mu_i^{(\alpha)} = \mu_i^{(\beta)}$ ...**
- **$f = 2 + (c-1) p - c (p-1) = \boxed{2 + c - p}$**   4

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

P= 1 atm

- 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

$T\uparrow$

L

liquid

liquid + Cd(s)

liq+ Bi(s)

Cd (s) +Bi (s)

$"\chi^{\ell}_{Cd}"\rightarrow$
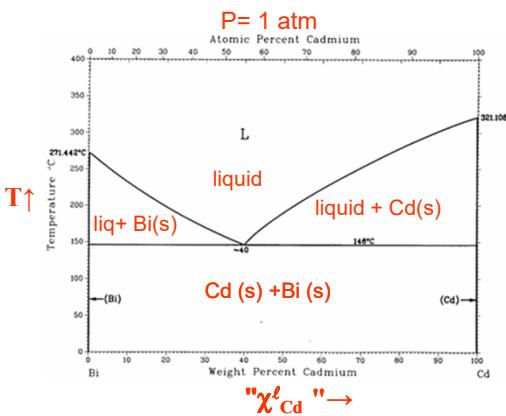
5

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**

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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}

T↑

"χ_{Cd}" →

m.p. of pure Bi= 271.4°C
m.p. of pure Cd= 321.1°C
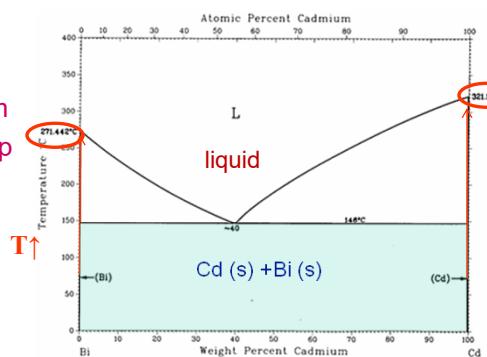
liquid,
p=1, f=2
T, χ^{ℓ}_{cd} can vary

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

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

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

total mole fraction Cd

T↑

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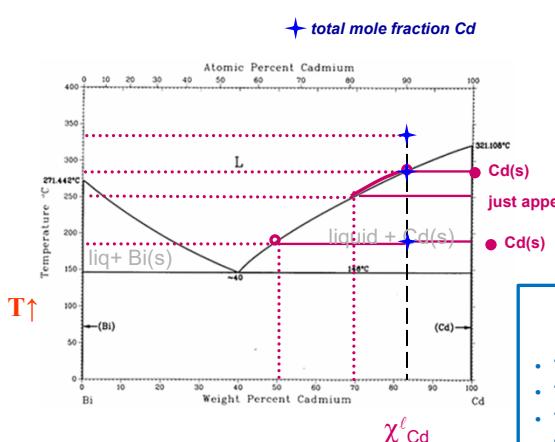
T < 280°C
liquid + Cd(s),
p=2, f=1
only T or χ^{ℓ}_{cd} can independently
vary (i.e. T and χ^{ℓ}_{cd} covary)

Cd(s)
just appears

Cd(s)

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)]

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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%

T↑

liquid + Cd(s)

liq+ Bi(s)

Bi(s)
just appears

Cd(s)
just appears

(Bi)

Cd (s) +Bi (s)

(Cd)
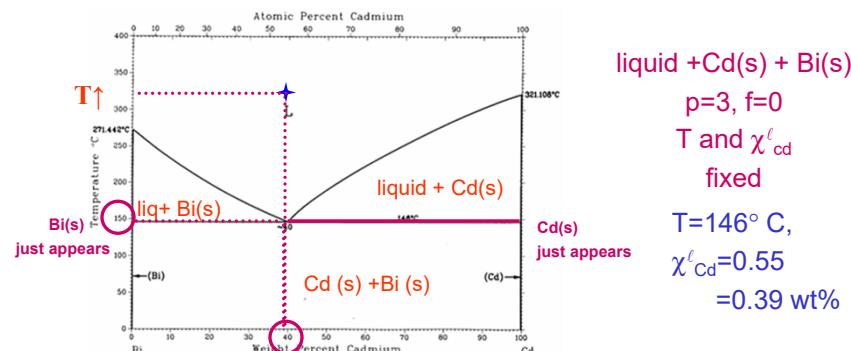
"χ^{ℓ}_{Cd} "→

eutectic=constant freezing composition (mixture)

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not all solid-solid mixtures form eutectics

$NaAlSi_3O_8$ + $CaAl_2Si_2O_8$ Cu   +   Ni

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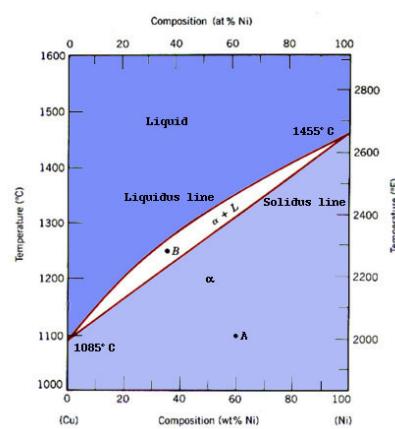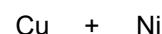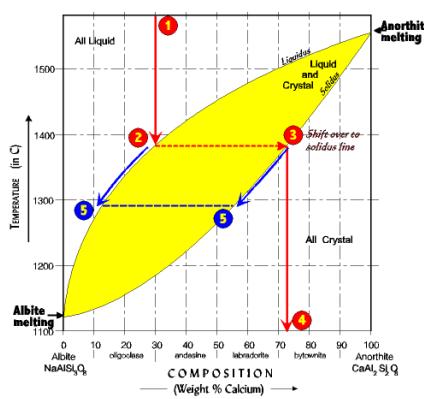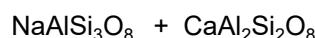
Ideal Solutions

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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**.
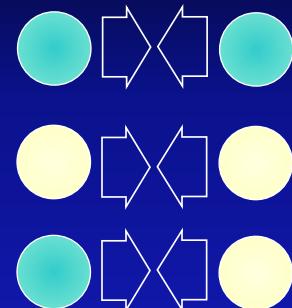
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ideal solutions

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 ⟶

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

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

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

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

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

correction for non-ideality activity

HW #7 prob 55

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

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

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

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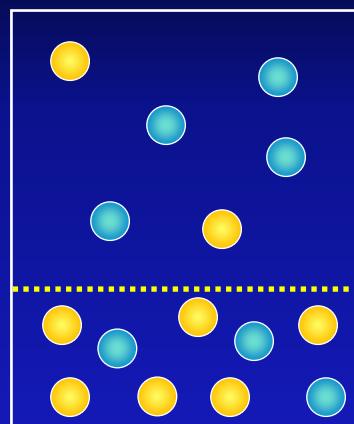
http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt

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

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

Benzene and Toluene

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

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Ethyl Acetate/Acetic Anhydride

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

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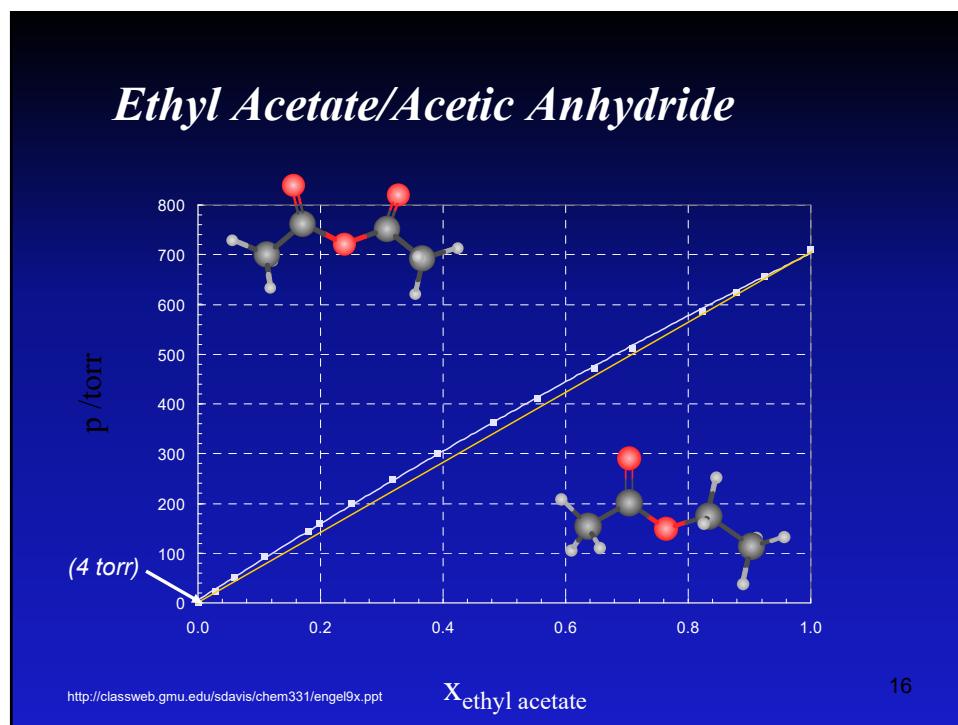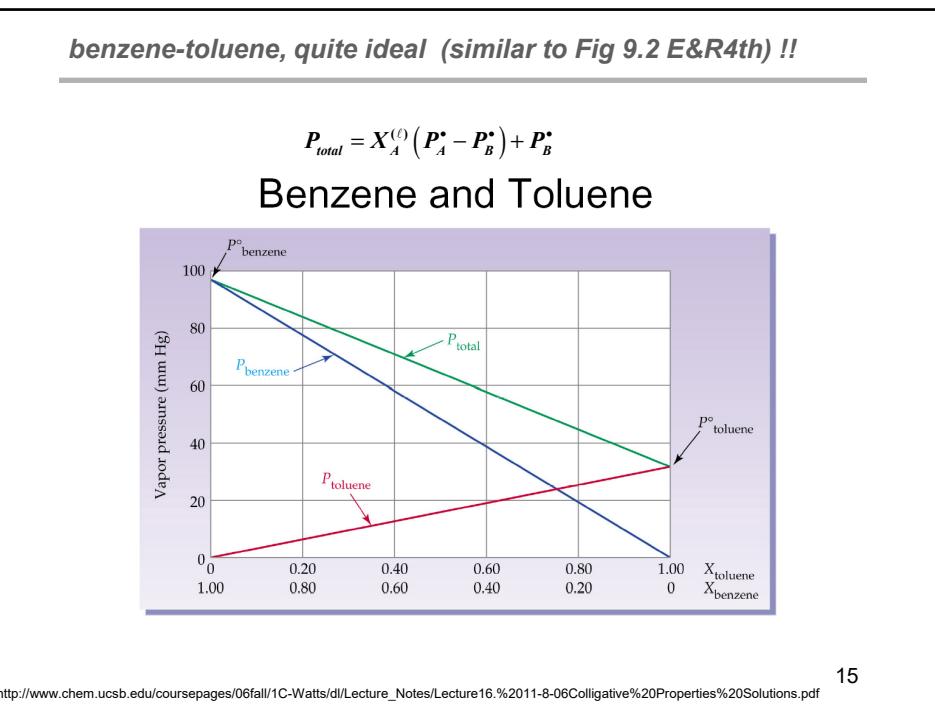
X$^{(\ell)}$ vs X$^{(v)}$ (notation conventions)

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]

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

chemical potential of pure component i

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

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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 $\rightleftarrows$ vapor components in equilibrium at T

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

pure liquid $\rightleftarrows$ 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

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

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

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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**

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

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:** $\Delta S_{mix} = \dfrac{\Delta H_{mix} - \Delta G_{mix}}{T} = -\sum_k n_k R \ln X_k^{\ell}$

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it may be very good for your future   **happiness**

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11

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

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

vapor composition

tol+ben (vapor)
$[f_{remaining}=2]$

solution + vapor
$[f_{remaining}=1]$

solution composition

tol+ben (solution)
$[f_{remaining}=2]$
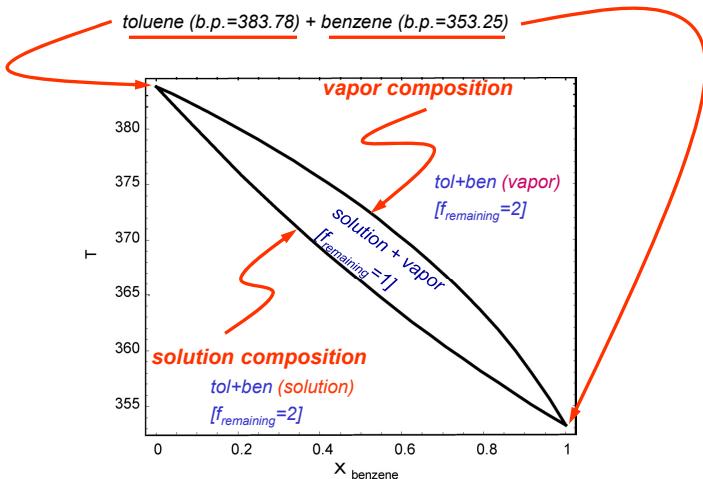
23

fractional distillation $[T_{bp}$ *vs* $(X_{benzene})^{solution}]$
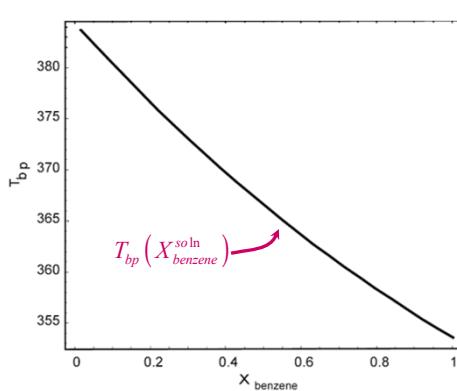
$T_{bp}\left(X_{benzene}^{soln}\right)$

- $\ln\left(\dfrac{P_{benzene}^{\bullet}(T)}{1\ atm}\right)=-\dfrac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\dfrac{1}{T}-\dfrac{1}{(T_{bp}^{\bullet})_{ben}}\right]$

- $\dfrac{P_{benzene}^{\bullet}(T)}{1\ atm}=e^{-\frac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\frac{1}{T}-\frac{1}{(T_{bp}^{\bullet})_{ben}}\right]}$ vapor pressure of benzene at T

- $\dfrac{P_{toluene}^{\bullet}(T)}{1\ atm}=e^{-\frac{(\Delta\bar{H}_{vap})_{tol}}{R}\left[\frac{1}{T}-\frac{1}{(T_{bp}^{\bullet})_{tol}}\right]}$ vapor pressure of toluene at T

- in ideal solution
  $P_{benzene}(T)=X_{benzene}^{solution}P_{benzene}^{\bullet}(T)$ and $P_{toluene}(T)=X_{toluene}^{solution}P_{toluene}^{\bullet}(T)$

- at boiling $\Rightarrow$ $P_{benzene}$ + $P_{toluene}$ = 1 atm
  $1\ atm=X_{benzene}^{solution}P_{benzene}^{\bullet}(T_{bp}^{solution})+(1-X_{benzene}^{solution})P_{toluene}^{\bullet}(T_{bp}^{solution})$

- for a given $X_{benzene}^{solution}$ solve for $T_{bp}^{solution}$
  (or better have Mathematica solve equations
   see handout #51)

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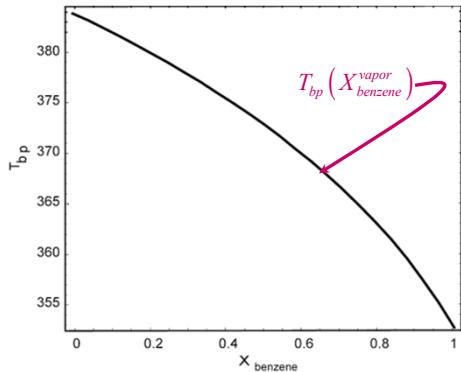
$T_{bp}\left(X_{benzene}^{vapor}\right)$

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

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

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

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

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

at 365K a mixture of total X_b=.70

will be a liquid X^{ℓ}_b=.55 in equilibrium

with vapor X^v_b=.76

solution + vapor

● **liquid**
○ **vapor**
★ **total**

.55   .70   .76
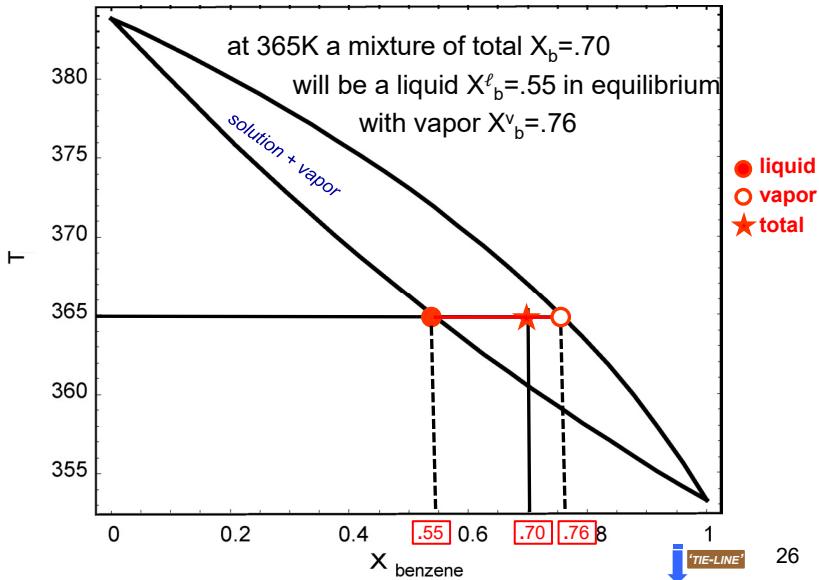
'TIE-LINE'   26

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

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

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

- 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 $X_{benz}^{(v)} = 0.65$

● liquid
○ vapor
★ total

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fractional distillation

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

etc !!

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

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

T_1

$T_1 > T_2 > T_3$

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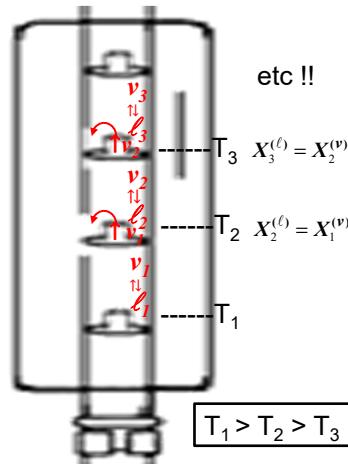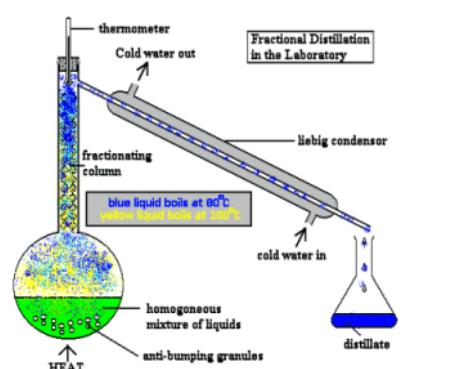
fractional distilation

toluene (b.p.=383.78) + benzene (b.p.=353.25)
benzene more "volatile" than toluene
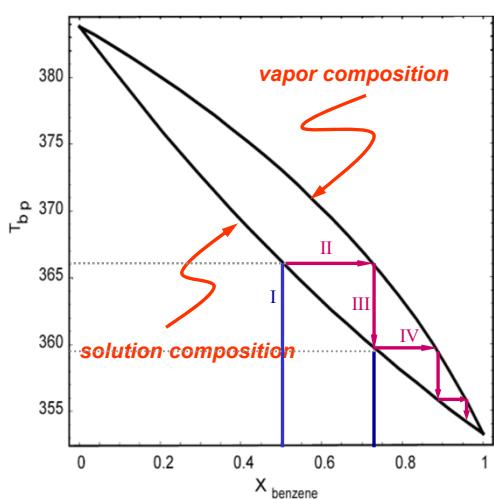
top of column (cooler)

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)

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azeotrope (non-ideal solution)
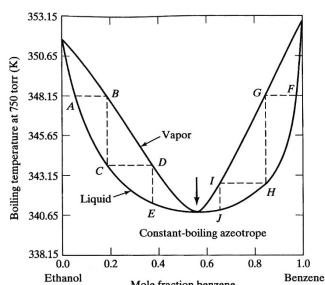
• fractional distillation leads to constant boiling azeotrope in vapor

•*and (in pot after azeotrope boils off)*
    • $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
    • $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B
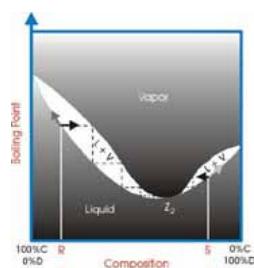
http://www.solvent--recycling.com/azeotrope_1.html

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fractional distillation

Fractional distillation of petroleum.
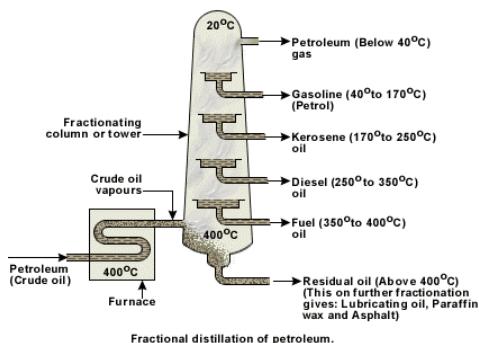
http://home.att.net/~cat6a/images/fuels_06.gif

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vapor diffusion crystal growth
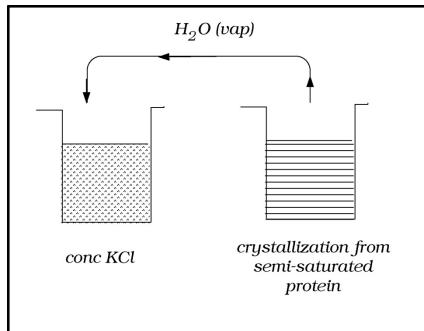
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$H_2O\ (vap)$

conc KCl

crystallization from
semi-saturated
protein

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Vapor Diffusion Crystal Growth

Coverslip with protein solution (red)

High - vacuum grease

Reservoir with precipitant

Protein Crystal Growth

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

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End of Lecture 20-21

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17
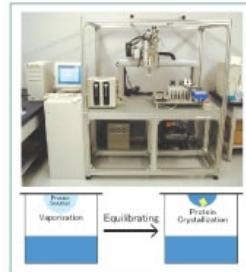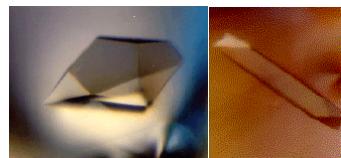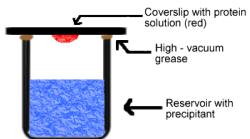
$\mu_i^{(\ell)} = \mu_i^{(v)}$ **for each component i**

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*

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relative amounts of components in two-phase region

L_{soln} L_{vap}

solution   overall   vapor

$X_{benzene}$

relative amount: $\dfrac{n_{vapor}}{n_{solution}} = \dfrac{L_{soln}}{L_{vap}}$

vapor composition

solution composition

solution + vapor
[f_{remaining} = 1]

tol+ben (vapor)

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

L_{soln}

L_{vap}

tol+ben (solution)

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

T

380
375
370
365
360
355

0   0.2   0.4   0.6   0.8   1

$X_{benzene}$

36

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

eutectic $\mu_{Cd}(\chi^{\ell}_{Cd}=0.55,T=146°C)= \mu_{Cd}(s, T=146°C)$
$\mu_{Bi}(\chi^{\ell}_{Bi}=0.45,T=146°C)= \mu_{Bi}(s, T=146°C)$

ℓ

liq+ Bi(s)

146°C

liquid + Cd(s)

Cd (s) +Bi (s)

(Bi)   (Cd)

③ T>146C°
Cd-Bi (X_{Cd})=.55

② T=146C°
Cd (s) +Bi (s)
↑↓
Cd-Bi (X_{Cd})=.55

① T<146C°
Cd (s) +Bi (s)

$"\chi^{\ell}_{Cd}"\rightarrow$ $X^{total}_{Cd} = .55$

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

eutectic $\mu_{Cd}(\chi^{\ell}_{Cd}=0.55,T=146°C)= \mu_{Cd}(s, T=146°C)$
$\mu_{Bi}(\chi^{\ell}_{Bi}=0.45,T=146°C)= \mu_{Bi}(s, T=146°C)$

ℓ

liq+ Bi(s)

Bi(s)

146°C

eutectic

liquid + Cd(s)

(Bi)   (Cd)

Cd (s) +Bi (s)

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)

$X^{total}_{Cd} = .2$
$X^{total}_{Bi} = .8$ $"\chi^{\ell}_{Cd}"\rightarrow$

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

eutectic $\mu_{Cd}(\chi^{\ell}_{Cd}=0.55,T=146°C)=\mu_{Cd}(s,T=146°C)$

$\mu_{Bi}(\chi^{\ell}_{Bi}=0.45,T=146°C)=\mu_{Bi}(s,T=146°C)$

ℓ

146°C

eutectic

Cd(s)

T>≈280°C
3 Cd-Bi (X$_{Cd}$)=.8

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

T<146°C
1 Cd (s) +Bi (s)

liquid + Cd(s)

liq+ Bi(s)

Cd (s) +Bi (s)

$X^{total}_{Cd}=.8$

$X^{total}_{Bi}=.2$

"χ^{ℓ}_{Cd}" →

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