Chemistry 163B, Winter 2013
Lectures 20-21 Multicomponent Phase Rule, Solution Behavior

Chemistry 163B
Multicomponent Phase Rule
Solution Behavior
Handout

1

---

phase rule

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

2

---

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]

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

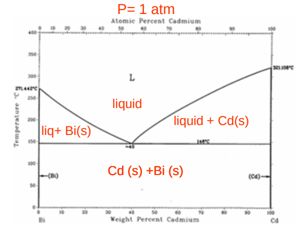
- *f = total variables – total restrictions*
- *f = 2 + (c-1) p - c (p-1) = 2 + c - p*

3

---

phase rule and Cd-Bi phase diagram (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



4

Listen up!!!

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

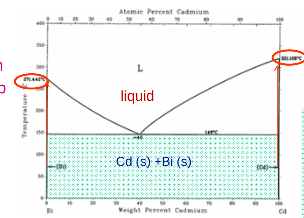
it may be very good for your future  **happiness**

5

---

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

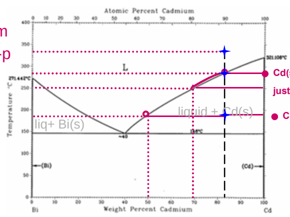
solid < 146° C,
p=2, f=1
T can vary
note: Cd(s) and Bi(s) are pure solids, not solution (alloy),
χ^{s}_{cd}=1 χ^{s}_{Bi}=1

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

6

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

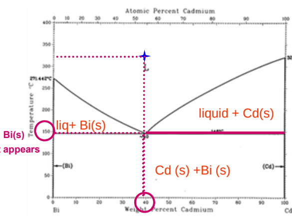
lower T
χ^{total}_{Cd} fixed

χ^{ℓ}_{Cd}

7

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%

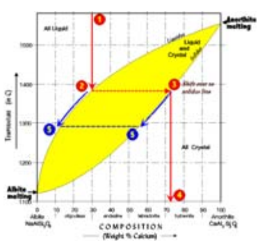
"χ^{ℓ}_{Cd} "→

eutectic=constant freezing composition (mixture)

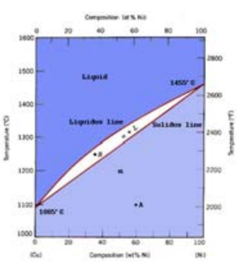
8

not all solid-solid mixtures form eutectics

$NaAlSi_3O_8$ + $CaAl_2Si_2O_8$



Cu + Ni



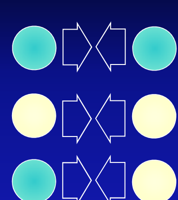
9

Ideal Solutions

10

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

11

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

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

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

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

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

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

correction for non-ideality activity HW #8 prob 55

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

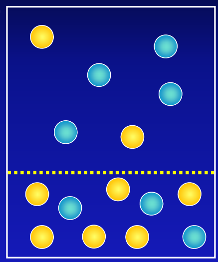
$$\textbf{ideal } a_i^{(\ell)} = X_i^{(\ell)}$$

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

12

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.

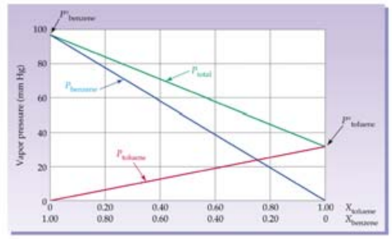


http://classweb.gmu.edu/sdavis/chem331/engel9x.ppt

13

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

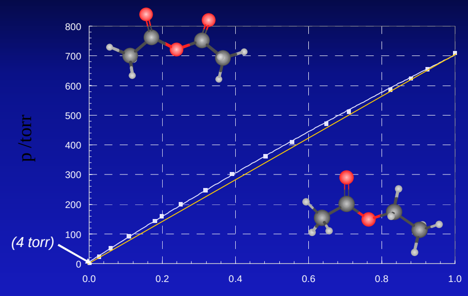
$$P_{total} = X_A^{(\ell)}\left(P_A^{\bullet} - P_B^{\bullet}\right) + P_B^{\bullet}$$



14

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

15

$X^{(\ell)}$ 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]

16

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

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

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

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

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

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

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

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

17

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 $\quad \ell \rightleftarrows v \quad dn_i^{(v)} = -dn_i^{(\ell)}$

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

18

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

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

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

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

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

19

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 ⇄ 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

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

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

20

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***

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

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

21

Listen up!!!

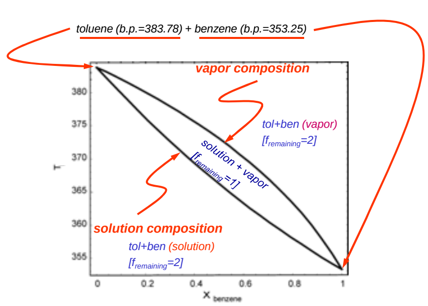
UNDERSTAND THE FOLLOWING DISCUSSION OF THE PHASE RULE AND THIS BINARY COMPONENT PHASE DIAGRAM

it may be very good for your future

happiness

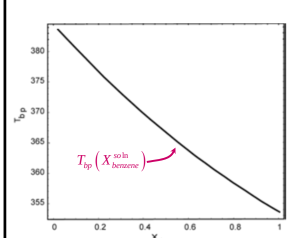
22

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



23

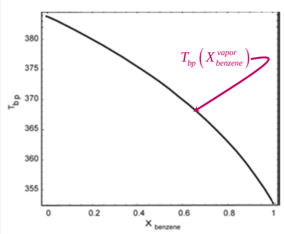
fractional distillation [T_{bp} vs $(X_{benzene})^{solution}$]



- $\ln\left(\dfrac{P^{\bullet}_{benzene}(T)}{1\text{ atm}}\right) = -\dfrac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\dfrac{1}{T} - \dfrac{1}{(T^{\bullet}_{bp})_{ben}}\right]$
- $\dfrac{P^{\bullet}_{benzene}(T)}{1\text{ atm}} = e^{-\frac{(\Delta\bar{H}_{vap})_{ben}}{R}\left[\frac{1}{T} - \frac{1}{(T^{\bullet}_{bp})_{ben}}\right]}$ **vapor pressure of benzene at T**
- $\dfrac{P^{\bullet}_{toluene}(T)}{1\text{ atm}} = e^{-\frac{(\Delta\bar{H}_{vap})_{tol}}{R}\left[\frac{1}{T} - \frac{1}{(T^{\bullet}_{bp})_{tol}}\right]}$ **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** ⇒ $P_{benzene} + P_{toluene} = 1$ 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 #54)

24

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



$$X^{vapor}_{benzene} = \frac{P_{benzene}}{P_{total}} = \frac{X^{soln}_{ben} P^{\bullet}_{ben}(T^{solution}_{bp})}{P_{total}}$$

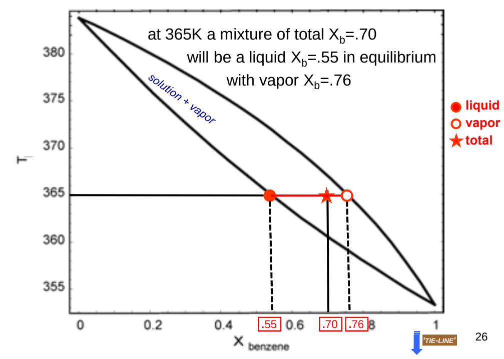
$$X^{vapor}_{benzene} = X^{soln}_{ben} P^{\bullet}_{ben}(T^{solution}_{bp})$$

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

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

25

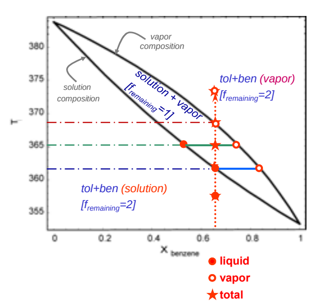
two-phase region (P=1 atm) TOLUENE + BENZENE ($\ell \rightleftarrows$ v)



26

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

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

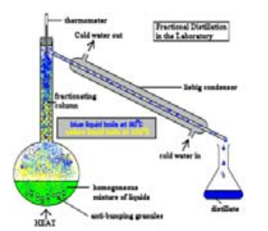


$$X^{total}_{benz} = 0.65$$

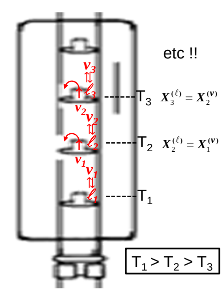
- a solution of $X^{(\ell)}_{benz} \approx 0.65$ at T=357K is a liquid
- that boils at ~362K (P_{total}=1atm)
- at T ~362K the soluton is in equilibrium with vapor $X^{(v)}_{benz}$ = .83
- if the system is maintained at P_{total} = 1 atm and T is raised to 365K, liquid will evaporate until $X^{(\ell)}_{benz}$=0.53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

27

fractional distillation

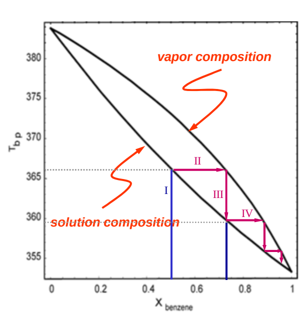


http://www.wpbschoolhouse.btinternet.co.uk/page12/gifs/FracDistRed.gif



28

Fractional Distilation



top of column (cooler)

VI. approaches $X_{benzene}$=1

V. etc, ...

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

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

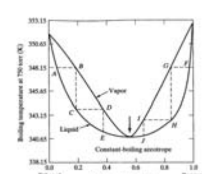
II. • vapor $X^{v}_{benzene} \approx .72$

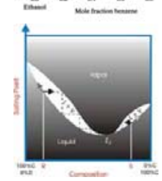
I. • start with 50-50 mixture
- $T_{bp} \approx 366$

bottom of column (warmer)

29

azeotrope (non-ideal solution)





- fractional distillation leads to constant boiling azeotrope in vapor

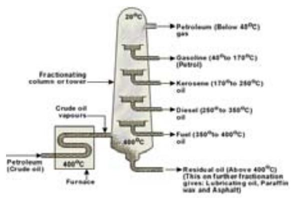
•*and (in pot after azeotrope boils off)*
- $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
- $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B

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

30

Chemistry 163B, Winter 2013
Lectures 20-21 Multicomponent Phase Rule, Solution Behavior

fractional distillation

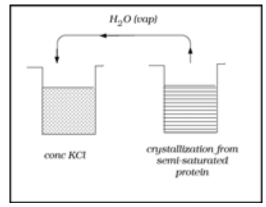


Fractional distillation of petroleum.

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

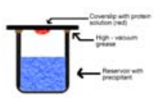
31

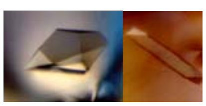
Vapor Diffusion Crystal Growth



32

Vapor Diffusion Crystal Growth



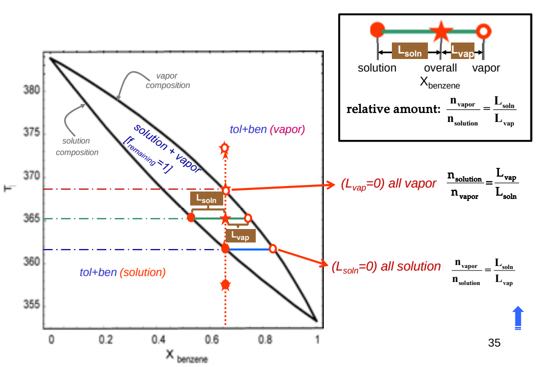

http://science.nasa.gov/ssl/msad/pcg/#HARDWARE

33

End of Lecture

34

relative amounts of components in two-phase region



35