Chemistry 163B, Winter 2013

Lectures 20-21 Multicomponent Phase Rule, Solution Behavior

α
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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]

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

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

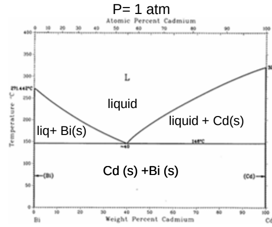
- *f = total variables – total restrictions*
- *f = 2 + (c-1) p - c (p-1) = 2 + c - p*

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

P= 1 atm



"χ^{ℓ}_{Cd} "→

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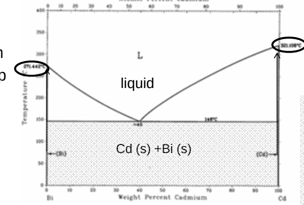
phase rule and Cd-Bi phase diagram (P=1 atm)

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



"χ_{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= 271.4ºC
m.p. of pure Cd= 321.1ºC

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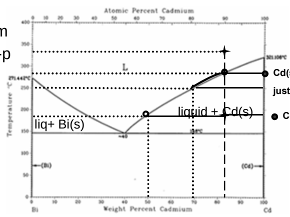
phase rule and Cd-Bi phase diagram (P=1 atm)

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

✚ *total mole fraction 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}

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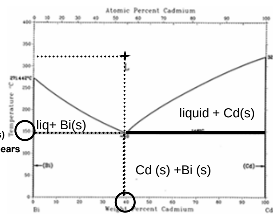
phase rule and Cd-Bi phase diagram (eutectic)

$f_{remaining}$=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%

"χ^{ℓ}_{Cd} "→

eutectic=constant freezing composition (mixture)

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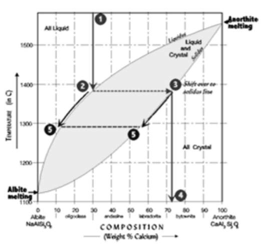
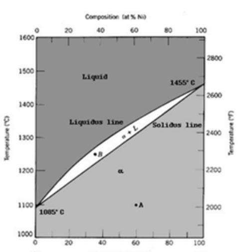
not all solid-solid mixtures form eutectics

$NaAlSi_3O_8$ + $CaAl_2Si_2O_8$

Cu + Ni





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Ideal Solutions

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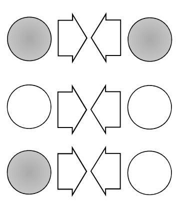
Molecular Basis for Ideal Sol'ns.

- 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.
- ΔH_{mixing}= 0 **means that all three interactions are of equal strength**.



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

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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

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

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

$$P_{total} = P_A^{(v)} + P_B^{(v)} = X_A^{(\ell)} P_A^* + X_B^{(\ell)} P_B^*$$
$$= X_A^{(\ell)} P_A^* + \left(1 - X_A^{(\ell)}\right) P_B^*$$
$$= X_A^{(\ell)} \left(P_A^* - P_B^*\right) + P_B^*$$ ← *linear P_{total} vs $X_A^{(\ell)}$*

correction for non-ideality activity HW #8 prob 55

$$P_i^{(v)} = a_i^{(\ell)} P_i^*$$
$$ideal \; a_i^{(\ell)} = X_i^{(\ell)}$$
$$non-ideal \; a_i^{(\ell)} = \gamma_i^{(\ell)} X_i^{(\ell)}$$

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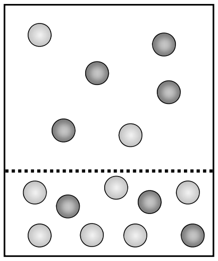
liq ↔ vap Eq. in Binary Mixtures

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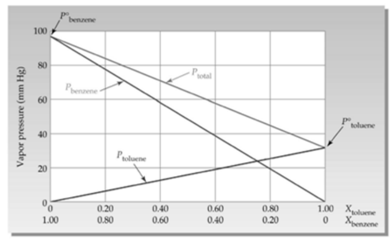
benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

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

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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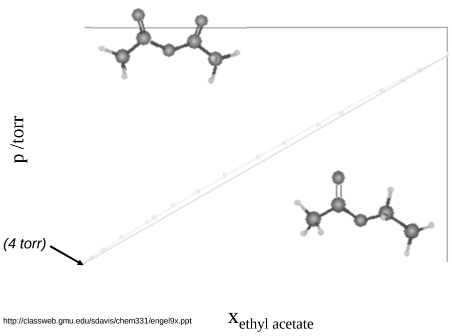
Ethyl Acetate/Acetic Anhydride



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

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

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

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

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

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

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

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

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

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

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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)*

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

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

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

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

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

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

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

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

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

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

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Listen up!!!

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

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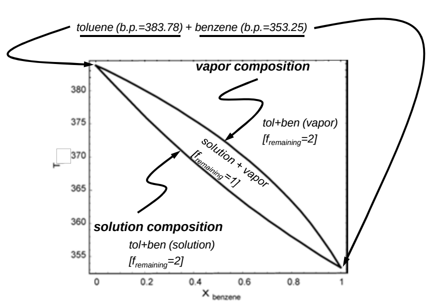
T vs X (P=1 atm) for solution-vapor equilibrium **TOLUENE + BENZENE**



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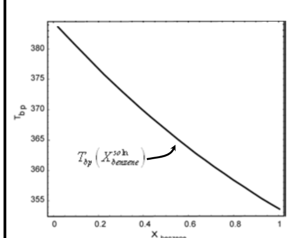
fractional distillation [T_{bp} vs $(X_{benzene})^{solution}$]



- $\ln\left(\dfrac{P^\bullet_{benzene}(T)}{1\text{ atm}}\right) = -\dfrac{(\Delta H_{vap})_{ben}}{R}\left[\dfrac{1}{T} - \dfrac{1}{(T^\bullet_{bp})_{ben}}\right]$
- $\dfrac{P^\bullet_{benzene}(T)}{1\text{ atm}} = e^{-\frac{(\Delta H_{vap})_{ben}}{R}\left[\frac{1}{T} - \frac{1}{(T^\bullet_{bp})_{ben}}\right]}$ vapor pressure of benzene at T
- $\dfrac{P^\bullet_{toluene}(T)}{1\text{ atm}} = e^{-\frac{(\Delta H_{vap})_{tol}}{R}\left[\frac{1}{T} - \frac{1}{(T^\bullet_{bp})_{tol}}\right]}$ 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)

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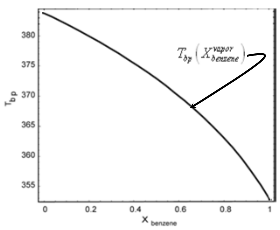
fractional distillation [T_{bp} vs $(X_{benzene})^{vapor}$]



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

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

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

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

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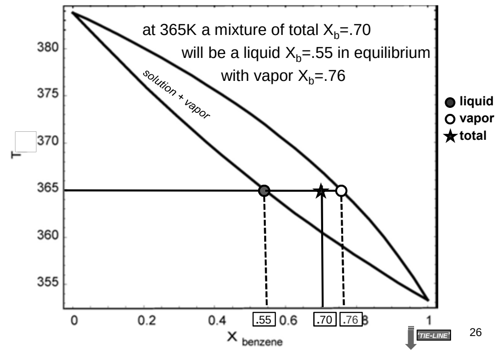
two-phase region (P=1 atm) TOLUENE + BENZENE ($\ell \rightleftarrows$ v)



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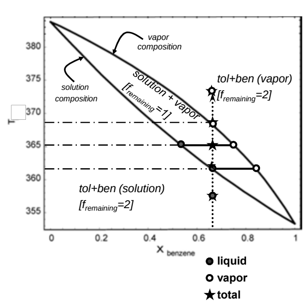
T vs X (P=1 atm) for solution-vapor equilibrium TOLUENE + BENZENE

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 $X^{(v)}_{benz} = 0.65$

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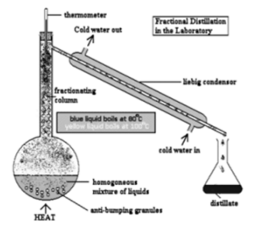
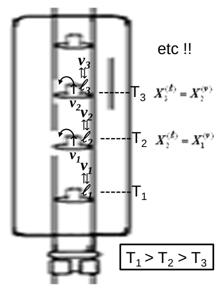
fractional distillation



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



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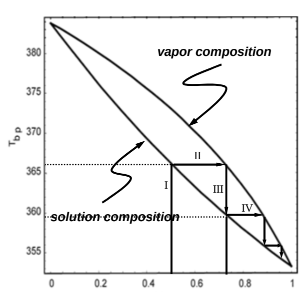
Fractional Distilation



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)

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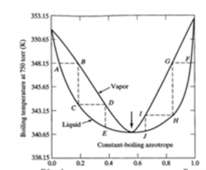
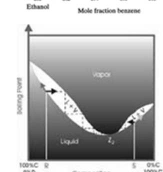
azeotrope (non-ideal solution)



- 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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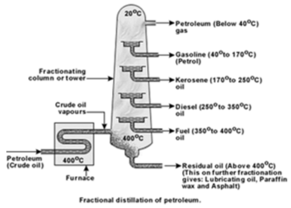
fractional distillation



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

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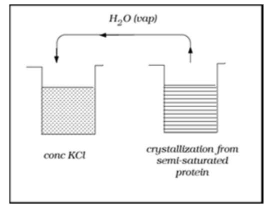
Vapor Diffusion Crystal Growth



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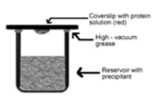
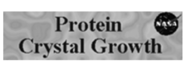
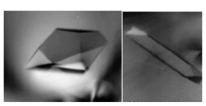
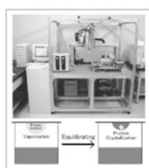
Vapor Diffusion Crystal Growth









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

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End of Lecture

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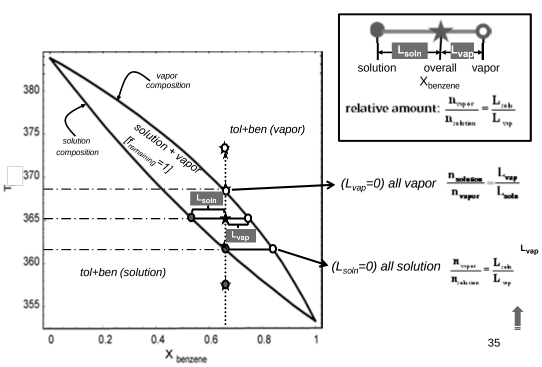
relative amounts of components in two-phase region



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

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

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

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