

Chemistry 163B, Winter 2020
Lectures 20-21 Multicomponent Phase Rule, Solution Behavior

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

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le menu

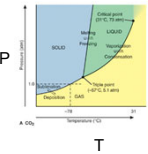
- phase rule for multicomponent systems
- solid A-solid B phase diagram
- ideal solutions
- solution-vapor phase diagrams
- fractional distillation and vapor diffusion crystal growth

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phase rule (lectures 18-19)

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

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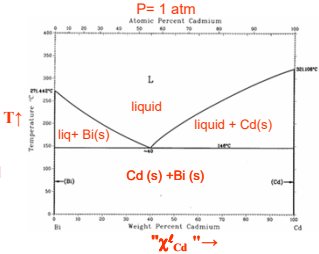
multi-component phase rule $f = 2 + c - p$ $f=3-p$ for $c=1$

- 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 $\mu_i^{(\alpha)} = \mu_i^{(\beta)} = \dots = \mu_i^{(\gamma)}$ ($p-1$ restrictions for each component)
- $c(p-1)$ total restrictions for c components
- $f = \text{total variables} - \text{total restrictions}$
T,P $X_i^{(\alpha)}$ $\mu_i^{(\alpha)} = \mu_i^{(\beta)} \dots$
- $f = 2 + (c-1)p - c(p-1) = 2 + c - p$

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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, X_{Cd} in liquid




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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

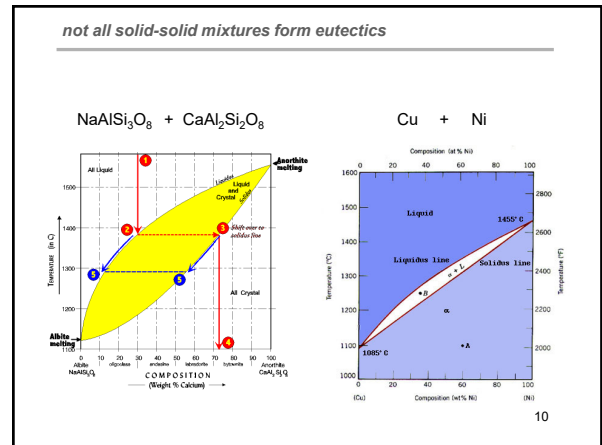
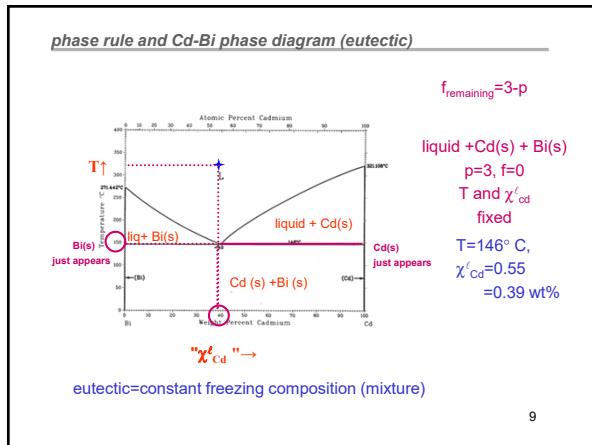
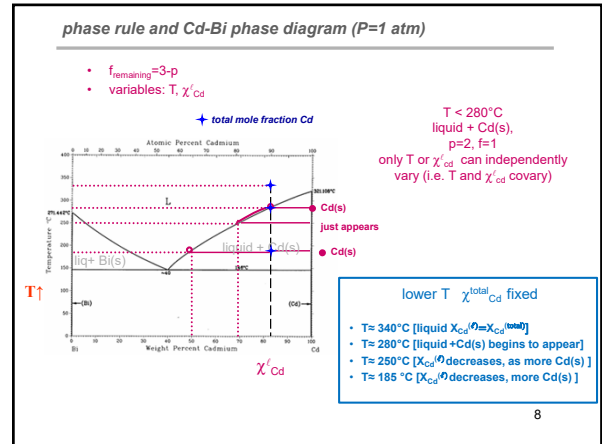
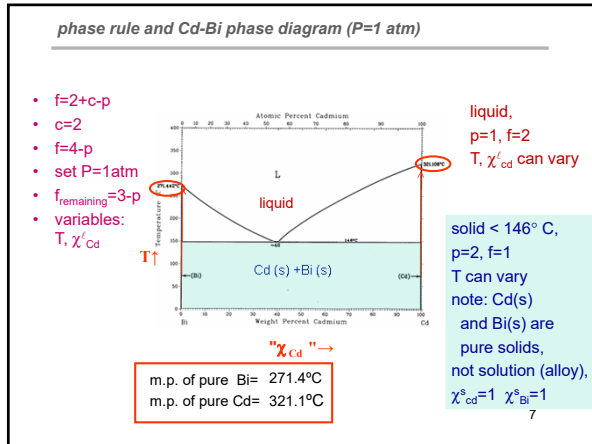


happiness

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Ideal Solutions

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Molecular Basis for Ideal Sol'n's.

- 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.

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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 \rightarrow

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

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

$$P_{total} = P_A^{(v)} + P_B^{(v)} = X_A^{(l)} P_A^* + X_B^{(l)} P_B^*$$

$$= X_A^{(l)} P_A^* + (1 - X_A^{(l)}) P_B^*$$

$$= X_A^{(l)} (P_A^* - P_B^*) + P_B^* \leftarrow \text{linear } P_{total} \text{ vs } X_A^{(l)}$$

correction for non-ideality activity
HW#7 prob 55

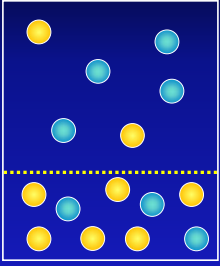
$$P_i^{(v)} = a_i^{(l)} P_i^*$$

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

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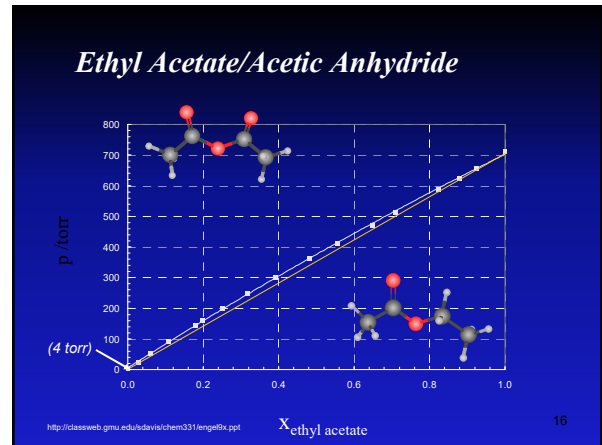
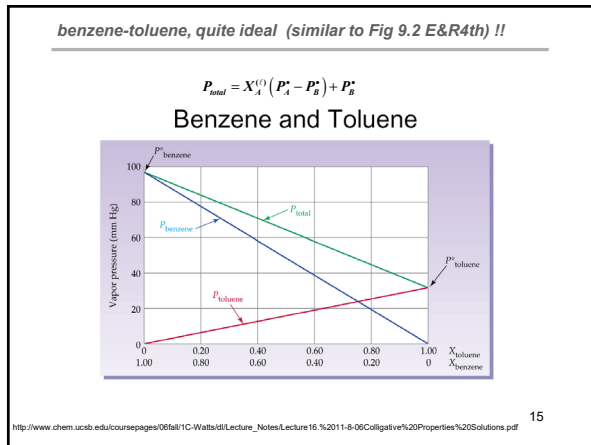
liq \leftrightarrow vap Eq. in Binary Mixtures

- 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.



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

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$X^{(l)}$ 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_A (E & R)

mole fraction gas (vapor) component A:
 $X_A^{(v)}$ most descriptive;
but also y_A (E & R) [not very descriptive and weird??;
but note for E&R HW probs]

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

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

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

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

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

$$P_A = X_A^{(l)} P_A^* \quad \text{or} \quad P_A = \gamma_A X_A^{(l)} P_A^*$$

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

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

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

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

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

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

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

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

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

chemical potential of pure component i

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

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

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

solution \rightleftharpoons vapor components in equilibrium at T

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

pure liquid \rightleftharpoons pure vapor components in equilibrium at T

$$\mu_i^{(l)}(T, P_i^*) = \mu_i^{(v)}(T, P_i^*)$$

we get

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

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

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Ideal Solutions

from: https://swilkes.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

$$\bar{V}_i = \bar{V}_i^* \quad V = \sum_i n_i \bar{V}_i$$
- II. The enthalpy of mixing is zero: $\Delta H_{\text{mix}} = 0$
- III. The free energy of mixing is: $\Delta G_{\text{mix}} = \sum_i n_i RT \ln X_i^l$
- IV. The entropy of mixing is: $\Delta S_{\text{mix}} = \frac{\Delta H_{\text{mix}} - \Delta G_{\text{mix}}}{T} = -\sum_i n_i R \ln X_i^l$

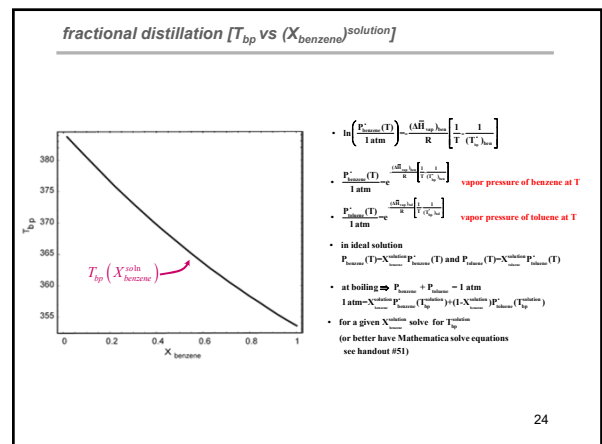
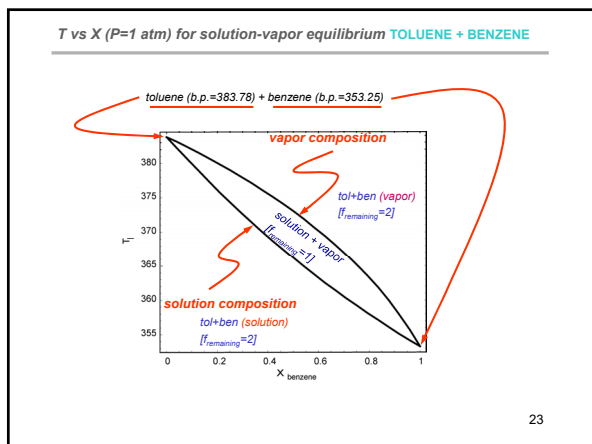
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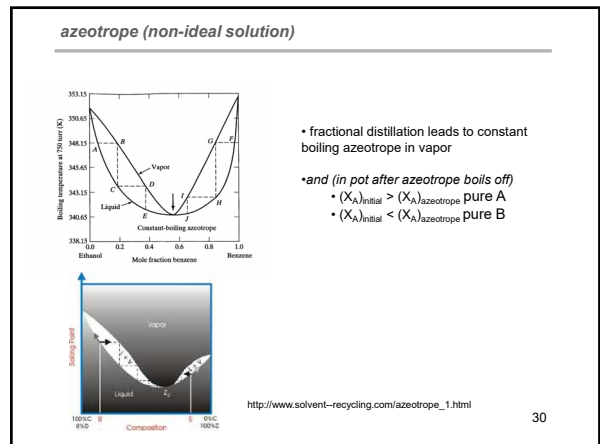
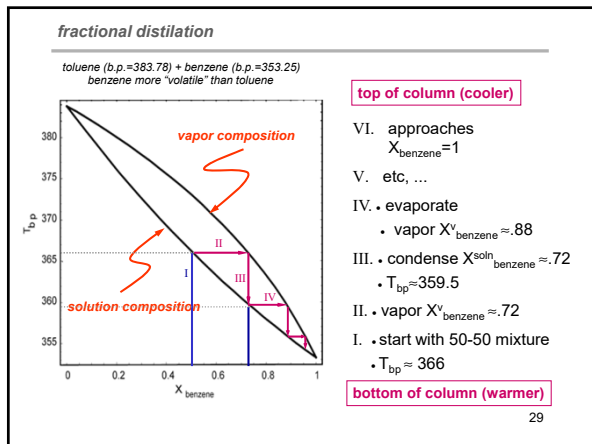
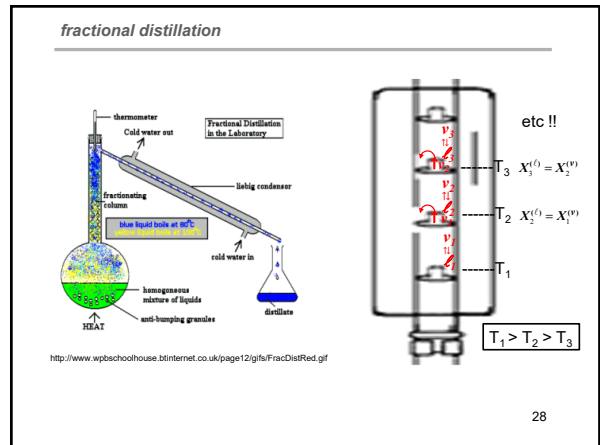
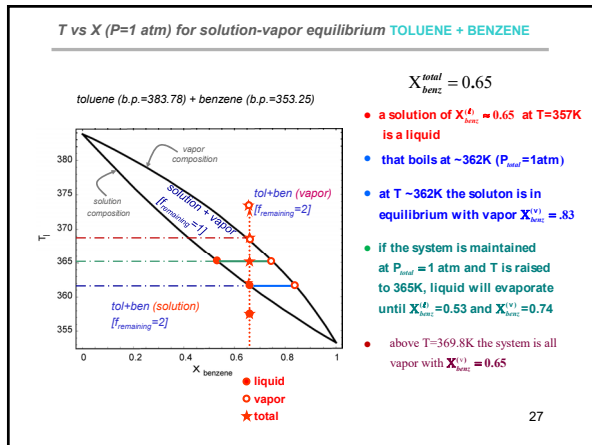
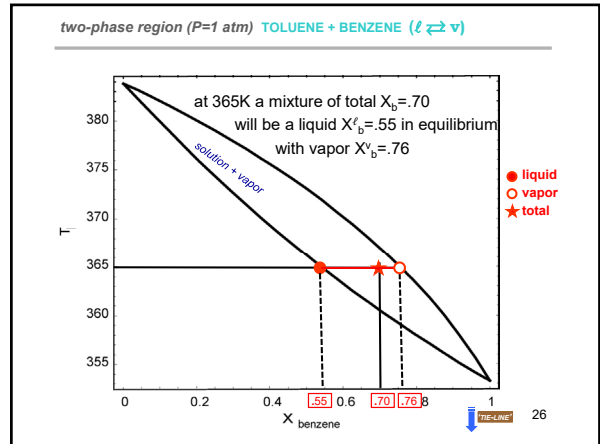
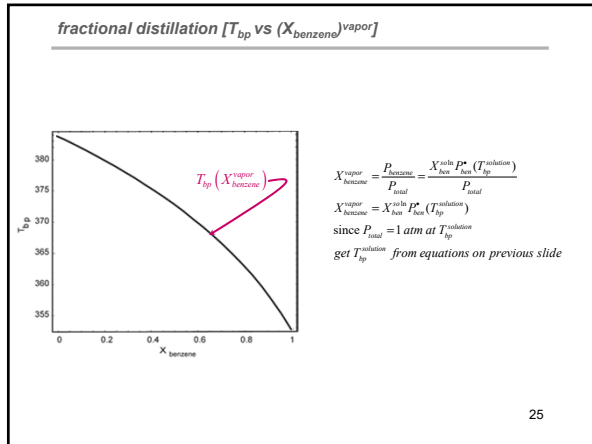
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it may be very good for your future happiness

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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 20-21

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

have proven $\mu_A^{(l)} = \mu_A^{(v)}$ 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 $i \quad \ell \rightleftharpoons v \quad dn_i^{(v)} = -dn_i^{(l)}$

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

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relative amounts of components in two-phase region

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

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

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

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