

Subject:

* Measuring ~

* Estimation & Correlations

① Clapeyron Equation :

$$\frac{dP^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_L)}$$

① From measuring

P^* : Vapor pressure

T : absolute temp (K, °R)

$\Delta \hat{H}_v$: Latent heat of Vaporization

$\hat{V}_g$: specific molar volume of Gas ($\frac{\text{Volume}}{\text{mole}}$)

$\hat{V}_L$: Liquid

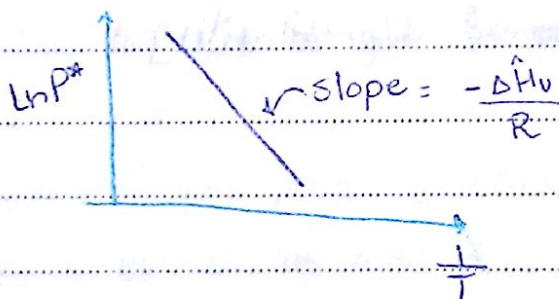
~ at low to moderate pressure

$$\hat{V}_g \gg \hat{V}_L \Rightarrow \hat{V}_g - \hat{V}_L = \hat{V}_g$$

Ideal Gas law $\Rightarrow \hat{V} = \frac{RT}{P^*}$ $\Rightarrow \frac{RT}{P^*} = \hat{V}_g - \hat{V}_L$

$$\frac{dP^*}{dT} = \frac{\Delta \hat{H}_v}{T \cdot \frac{RT}{P^*}} \Rightarrow \frac{d(\ln P^*)}{d(1/T)} = \frac{-\Delta \hat{H}_v}{R} \quad \text{②}$$

to get this $\uparrow$ derive this



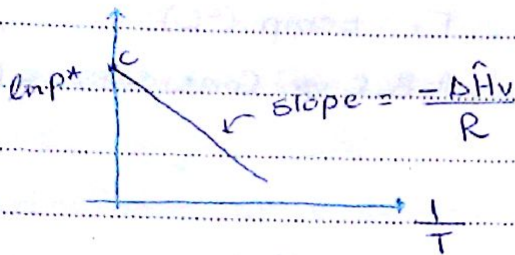
Subject:

* Suppose that $\Delta \hat{H}_v \neq f(T)$

Integrate eq. ②

$$\boxed{\ln P^* = \frac{-\Delta \hat{H}_v}{RT} + C} \quad \text{Clausius - Clapeyron Equ.}$$

$C \rightarrow$ Const. depends on substance



① if you have single pt (P^*, T) & $\Delta \hat{H}_v$

$\rightarrow$ intercept $\rightarrow C$

② if you have set of $P^* \text{ vs } T$

$\Rightarrow$ slope $\Rightarrow \Delta \hat{H}_v$

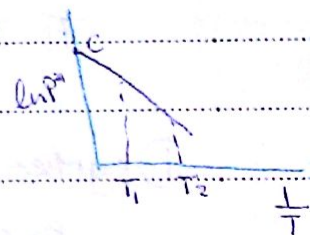
$\Rightarrow$ intercept $\Rightarrow C$

Ex $\rightarrow$ 6.1-1 $\rightarrow$ at $T_1 = 7.6^\circ\text{C} \rightarrow P^* = 40 \text{ mmHg}$

$\rightarrow T_2 = 15.4^\circ\text{C} \rightarrow P^* = 60 \text{ mmHg}$

a) $\rightarrow \Delta \hat{H}_v$ & B

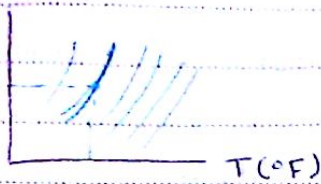
b) $T_2 = 42.2^\circ\text{C} \rightarrow P^* = ??$



vapor pressure (P^*)

Cox Chart Fig. 6-1-4 P-247

$$po = \frac{P^*}{14.7}$$



+ Antoine Equation

$$\log_{10} P^* = A - \frac{B}{T+C}$$

 P^* = vapor pressure (mmHg) T = Temp ($^{\circ}\text{C}$) $A, B, C \Rightarrow$ Constants $\Rightarrow$ Table B.4Sec 6.2 $\rightarrow$ Gibbs Phase Rule

Equilibrium between 2- Phases

T, P & composition in each phase no longer changes with time.

T	Phase II
a	P
b	Composition
c	
T	Phase I
a	P
b	Composition
c	

Variables

Intensive

do not depend on size
of system

 $T, P, \hat{V}, \mu, x, y$

Extensive

do depend on size
of system

 m, U

Degrees of Freedom $\rightarrow$ # of intensive variables that must be specified for a system at equ before the remaining intensive variables can be calculated.

$$DF = 2 + C - R$$

(non-reactive)

 C = # of components R = # of phases

$$DF = 2 + C - \pi - r \quad , \quad r = \# \text{ of rxns occur}$$

Ex. 6.2-1 $\rightarrow$ 1. $DF = 2 + C - \pi$

$$2 + 1 - 1 = 2$$

2. $DF = 2 + 1 - 3 = 0$

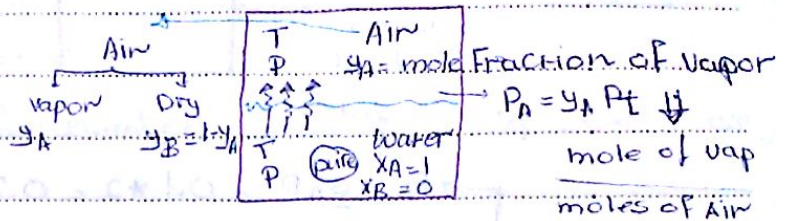
3. $DF = 2 + 2 - 2 = 2$

Sec 6.3 Gas-Liquid Systems - One Condensable Component.

Boiling $\rightarrow$ Saturation = Equilibrium

$$DF = 2 + C - \pi$$

$$= 2 + 2 - 2 = 2$$



• Raoult's Law $\sim$ water

$$P_A = y_A P = P_A^*(T)$$

- Gas-Liquid System
- Saturated Vapor (at equilibrium)
- One condensable component

'the vapor is the only species that would condense'

Ex. 6.3-1

$$DF = 2 + 2 - 2 = 2$$

$$y_A P = P_A^*(T)$$

$$y_A = \frac{P_A^*(T)}{P}$$

Air
$T = 75^\circ\text{C}$
$P_t = 760 \text{ mmHg}$
Water

Table
B.3

$$= \frac{P_A^*(75^\circ\text{C})}{P_t} = \frac{229}{760} = 0.38 \leftarrow y_A$$

$$y_{DA} = 1 - y_A$$

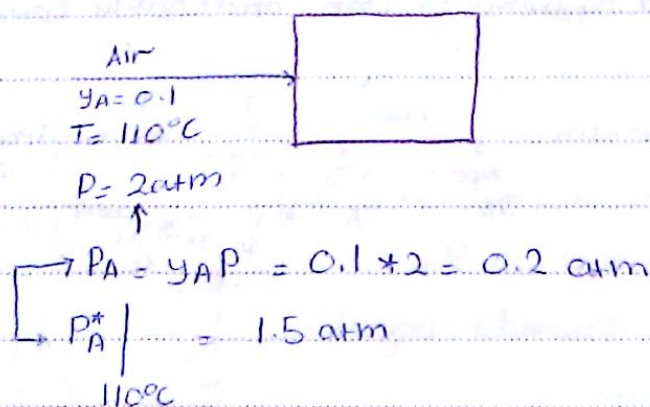
* If $P_i = y_i P = P_i^* \Rightarrow$ the vapor is sat.

P_i cannot exceed P_i^*

* If $P_i < P_i^* \Rightarrow$ the vapor is superheated vapor
cooling ($T \downarrow$) at const. P (isobarically)

or $P \uparrow$ at const T (isothermally)

* Degrees of Superheat = $T - T_{sat}$



$$P_i < P_i^*$$

dew point
 $\uparrow$

$$P_i = 0.2 \text{ atm} = P_i^* (T_{sat})$$

$$\log P_A^* = A - \frac{B}{T + C}$$

$$T = 80^\circ\text{C}$$

$$\text{Degree} = 110 - 80 = 30^\circ\text{C}$$

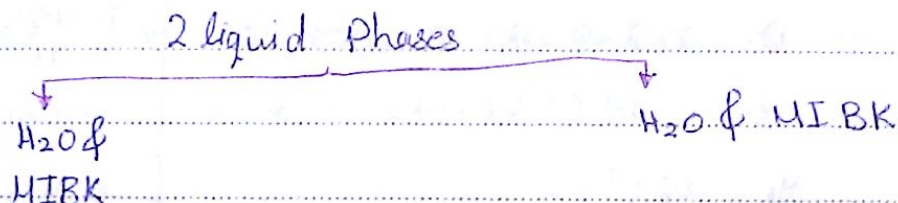
* Ex 6.3-2 / P (251) * Very impor

6.6 Equilibrium between two liquid Phases.

6.6.1

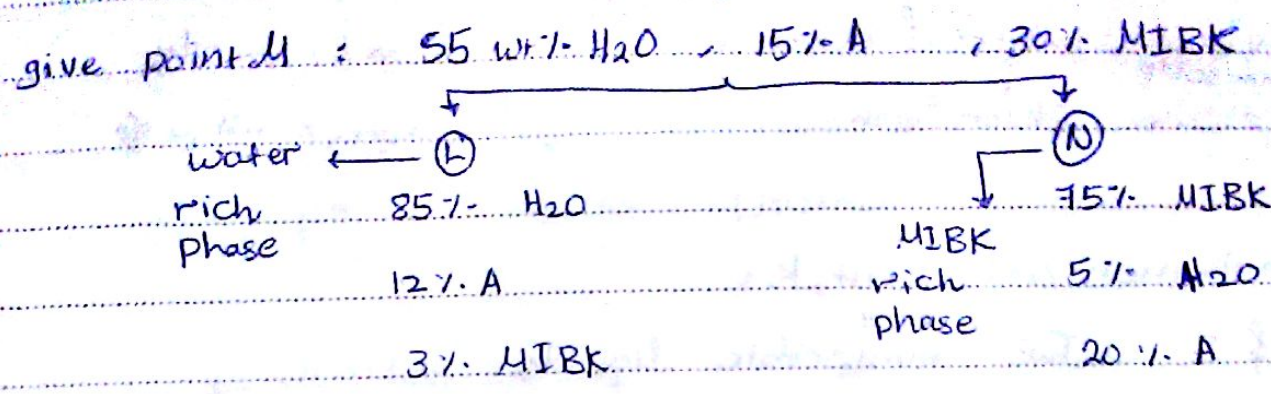
دانشگاه

① Partially miscible $\rightarrow$ water & MIBK



Subject:

give $\sim$ 80% Acetone , 10% H_2O , 10% MIBK] $\rightarrow$ azeotropic mix



tie line $\rightarrow$ connects phases at equilibrium

6.4] Multi Components Gas-Liq. System.

6.4a] $\rightarrow$ Vapor-Liquid Equilibrium Data (VLE Data)

Perry's Chemical Engineering handbook.

6.46] Raoult's law & Henry's law

Distribution of components between phases

↓
mole fraction

Gas-liq at equilibrium $\Rightarrow T, P$

x_A : mole Fraction of A in liq. phase

y_A : " " " " ~~8~~ 5 gas phase

P_A : partial pressure of A in gas phase

A hand-drawn phase diagram for a binary system. The diagram is enclosed in a rectangular box. A horizontal line divides the box into two regions. The top region is labeled "Gas" in the upper right corner. Inside this region, the chemical formulas Y_A , Y_B , and Y_C are written vertically in the center. The bottom region is labeled "liq" (liquid) in the lower right corner. Inside this region, the chemical formulas X_A , X_B , and X_C are written vertically in the center.

Raoult's law $\Rightarrow P_A = y_A P = x_A P^*(T)$

$P_A^*(T)$: Vapor pressure of pure A at T

Valid when ϵ

① $x_A \sim 1 \Rightarrow$ the liquid phase is almost pure of A

$x_A \sim 1 \Rightarrow$ pure liquid of A

↳ one condensable comp.

② Similar compounds:-

toulene & benzene

Subject:

Henry's law:-

$$P_A = y_A P = x_A H_A(T)$$

$H_A(T)$: Henry's law constant for A in a specific solvent.

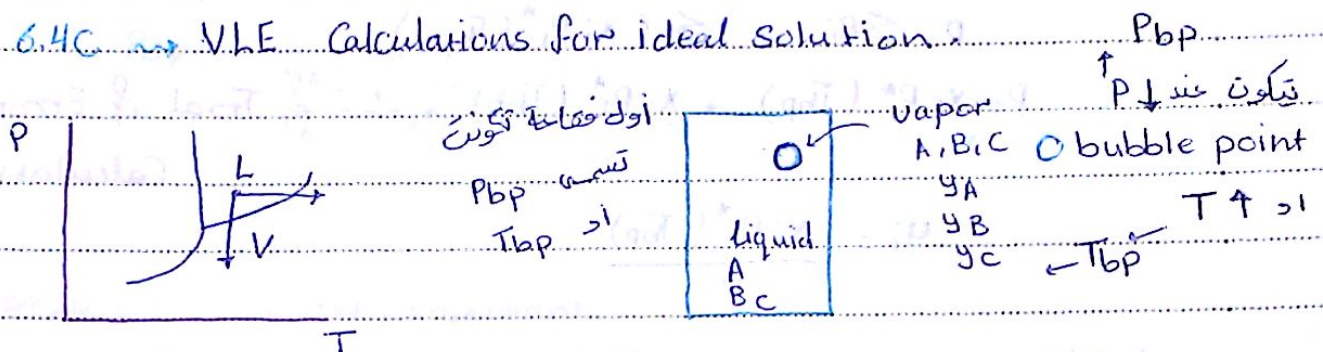
valid when:-

$x_A \sim 0 \rightarrow$ the solution is diluted.

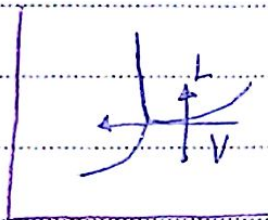
Ideal solution is a solution for which Raoult's law or Henry's law is obeyed for all species at all solution composition.

Example 6.4-2 is very important.

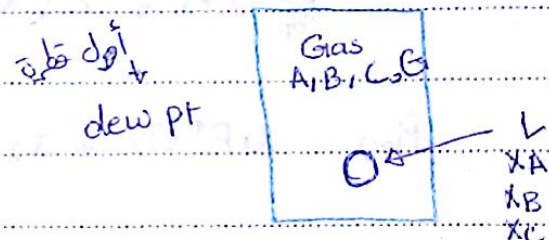
6.4C is VLE Calculations for ideal solution.



isobaric decomposition at const. T
L $\rightarrow$ V OR heating at const. P



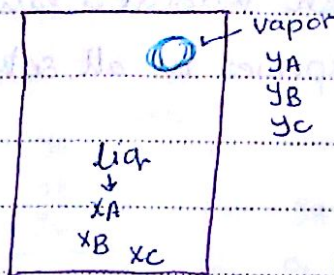
isobaric compression at const. T
V $\rightarrow$ L OR cooling at const. P



Def :-

Bubble pt. T_{bp} $\rightarrow$ the temp at which the 1st vapor bubble forms when a liq is heated slowly at const P.

Bubble pt. pressure $\rightarrow$ the temp at which the 1st vapor bubble forms when a liq decompressed at const T



bubble point temp calculations.

$$T_{bp} \rightarrow y_A = y_B = y_C$$

the liq. $\rightarrow$ ideal solnthe gas $\rightarrow$ ideal GasRaoult's law $\rightarrow$

$$P_i = y_i P = x_i P_i^* (T_{bp})$$

$$P = \sum P_i = \sum (x_i P_i^* (T_{bp}))$$

$$P = x_1 P_1^* (T_{bp}) + x_2 P_2^* (T_{bp}) + \dots \text{ Trial \& Error}$$

Calculation

$$y_i = \frac{x_i P_i^* (T_{bp})}{P}$$

bubble point pressure calculation $\rightarrow T_v$

$$\text{Raoult's law} \rightarrow P_i = y_i P = x_i P_i^* (T)$$

$$P_{bp} = \sum P_i = \sum (x_i P_i^* (T))$$

$$P_{bp} = x_1 P_1^* (T) + x_2 P_2^* (T) + \dots$$

$$y_i = \frac{x_i P_i^* (T)}{P_{bp}}$$

Subject:

dew point Calculation (temp) (T_{dp})

Suppose a gas mixture contains A, B, C,
& noncondensable G, at const P.

Raoult's Law $\Rightarrow x_i = \frac{y_i P}{P_i^*(T_{dp})}$



$$\sum x_i = 1 \Rightarrow \sum \frac{y_i P}{P_i^*(T_{dp})} = 1$$

$$\frac{y_1 P}{P_1^*(T_{dp})} + \frac{y_2 P}{P_2^*(T_{dp})} + \dots = 1 \quad \text{~ Trial \& Error Calculation}$$

* dew point pressure at const T

$$x_i = \frac{y_i P_{dp}}{P_i^*(T)}$$

$$P_{dp} = \frac{1}{\frac{y_A}{P_A^*} + \frac{y_B}{P_B^*} + \dots}$$

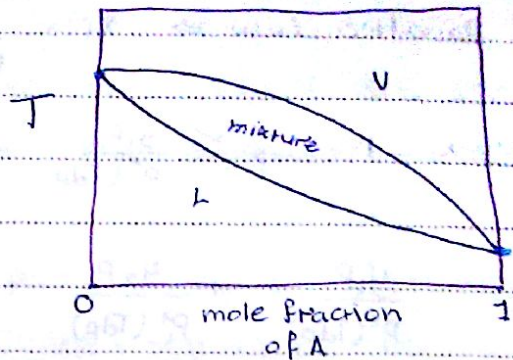
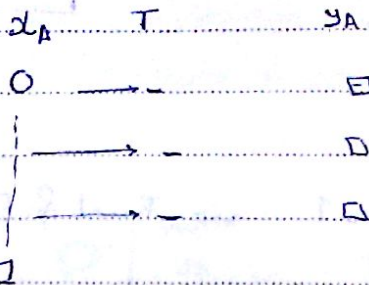
Example 6.4-3 ~ very important.

Subject:

6.4.d Graphical Representations of Vapor-Liquid Equilibrium

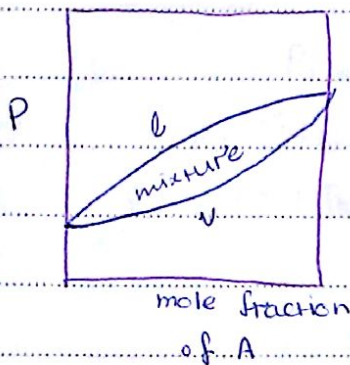
T_{xy} & P_{xy} $\rightarrow$ VLE representations for binary system
2-components

$T_{xy} \rightarrow P = 1 \text{ atm}$



$P = 1 \text{ atm}$

P_{xy} x_A P_{dp} $y_A \Rightarrow \text{const. } T = 100^\circ\text{C}$

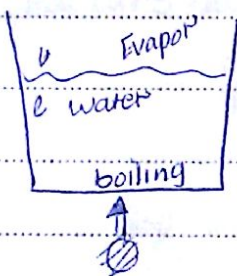


$T = 100^\circ\text{C}$

L is $\leftarrow$ bubble point

V is $\leftarrow$ dew point

* Boiling Point of a mixture



between 2 phases $\rightarrow$ Evaporation

between phases of 1 $\rightarrow$ Boiling

$\rightarrow$ boiling point $\rightarrow T_{bp} \rightarrow$ boiling point

$$P = x_A (P_A^*(T_{bp})) + x_B P_B^*(T_{bp})$$

Subject:

6.7. Adsorption on solid surfaces.

↳ attraction of chemical species in gases or liquids to the surfaces of solid.

* adsorbent

↓
solid

adsorbate

↓
solute

* adsorption Isotherm → adsorbate eq. data on a specific adsorbent taken @ cert. T

adsorbent → activated carbon

adsorbate → CCl_4

@ low adsorbate partial pressure/conc

linear $\Rightarrow x_i^* = K C_i f_i$

or $K P_i$

For higher conc $\Rightarrow$ Langmuir

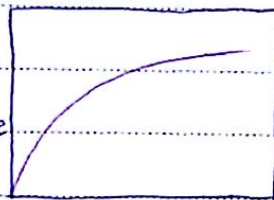
Isotherm

$$x_i^* = \frac{a K_L P_i}{1 + K_L P_i} \quad \text{or} \quad x_i^* = \frac{a K'_L C_i}{1 + K'_L C_i}$$

max mass
of adsorbate
↓
(i)

* can be held

by unit



P_i or C_i

↳ Concentration

mass of adsorbent