

## 2. Phase Equilibrium

### 2.1 Review of relations for gaseous mixtures:

Partial Pressure: ( $P_i$ ) <sup>→ for a component i</sup>

الضغط الجزئي هو الضغط الذي يمارسه الغاز في الخليط  
system

In a mixture of different gases the molecules of each gas are distributed throughout the available space and their motion contributes to the total pressure of the system.

The partial pressure of a component gas that is present in the mixture is the pressure that would be exerted by that component if it were present alone in the same volume and at the same temperature as the mixture.

For an ideal gas:

$$P_i = n_i \frac{RT}{V} ; \quad V : \text{total volume}$$

Pure component volume:  $V_i$

The pure component volume of a component gas that is present in a mixture of gases is the volume that would be occupied by that component if it were present alone at the same temperature and pressure as the mixture.

For an ideal Gas

$$V_i = n_i \frac{RT}{P} ; \quad P : \text{total pressure}$$

Relation between Partial pressure, pure component volume and mole fraction:

$$\frac{P_i}{V_i} = \frac{n_i(RT/V)}{n_i(RT/P)} \Rightarrow \frac{P_i}{P} = \frac{V_i}{V}$$

$$\frac{P_i}{P} = \frac{n_i(RT/V)}{n(RT/V)} \Rightarrow \frac{P_i}{P} = \frac{n_i}{n}$$

$$\Rightarrow \frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n} = y_i$$

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### Dalton's Law of Partial Pressures:

The total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of the components present in the mixture:

$$P = \sum P_i$$
$$n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + \dots = P$$
$$\frac{RT}{V} (n_1 + n_2 + n_3 + \dots) = P$$
$$\frac{RT}{V} \sum_{i=1}^n n_i = P = \sum p_i$$

### Amagats Law:

The total volume occupied by a gaseous mixture is equal to the sum of the pure component volumes.

$$V = \sum V_i$$

Vapor pressure: as the temperature ↑ the collision ↑ vapor pressure ↑

A vapor is a gas below its critical point. Vapor pressure is the pressure at which the liquid and vapor phases of a pure substance may exist at equilibrium at a certain temperature.

### Change of vapor pressure with temperature:

**Antoine Equation:** (predictions of vapor pressures)

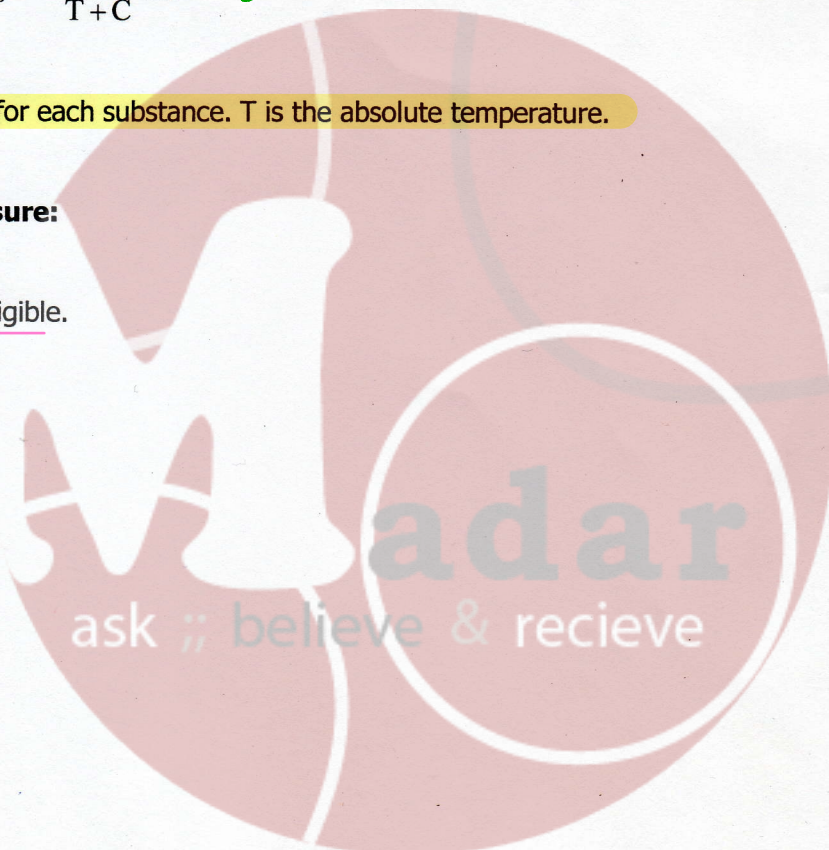
$$\ln(P) = -\frac{A}{T+C} + B$$

→ No n linear

A, B and C are constants specific for each substance. T is the absolute temperature.

### Change of vapor pressure with pressure:

Under normal conditions it is negligible.





Bubble point or Boiling point (B.P)  
 B.P for pure component  
 Bubble point for mixtures

## Boiling point:

It is the temperature at which the vapor pressure of a pure liquid becomes equal to the external pressure.

## Saturation:

A+B+C	g
A+B+C	L

$$P_A = P_A(\text{vapor pressure})$$

A gaseous mixture in contact with a pure liquid is said to be saturated when the partial pressure of the liquid vapor in the mixture is equal to the vapor pressure of the liquid at a certain temperature. The vapor and liquid are at equilibrium.

## Phase Rule:

For a nonchemically reactive system at heterogeneous equilibrium.

$$F = C - P + 2 \Rightarrow \text{state equation}$$

- C = Number of components (chemical species)
- P = Number of phases
- F = Number of degrees of freedom (variance)
- = Number of intensive properties (independent variables) that must be specified to completely fix the state of the system [In this course the intensive properties are T, P and concentration].

### Ex:

For a pure gas  $F = 2 \Rightarrow T$  and  $P$  can be changed by small amounts without changing the state of the gas [no change in phase].

At Triple Point  $P = 3 \Rightarrow F = 0$

It is therefore impossible to have solid / liquid / vapor at equilibrium at conditions other than the triple point.

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## 2.2 Vapor Liquid Equilibrium

most cases be a two component one of them is more volatile than the other one.

### 2.2.1 Binary Vapor Liquid Equilibrium

**System:** vapor – Liquid mixture of components A and B.

**Phase Rule:**  $C = 2$   $P = 2 \Rightarrow F = 2$

**Independent variables:** T, P and the concentration of one of the components in the vapor (y) and in the liquid (x).

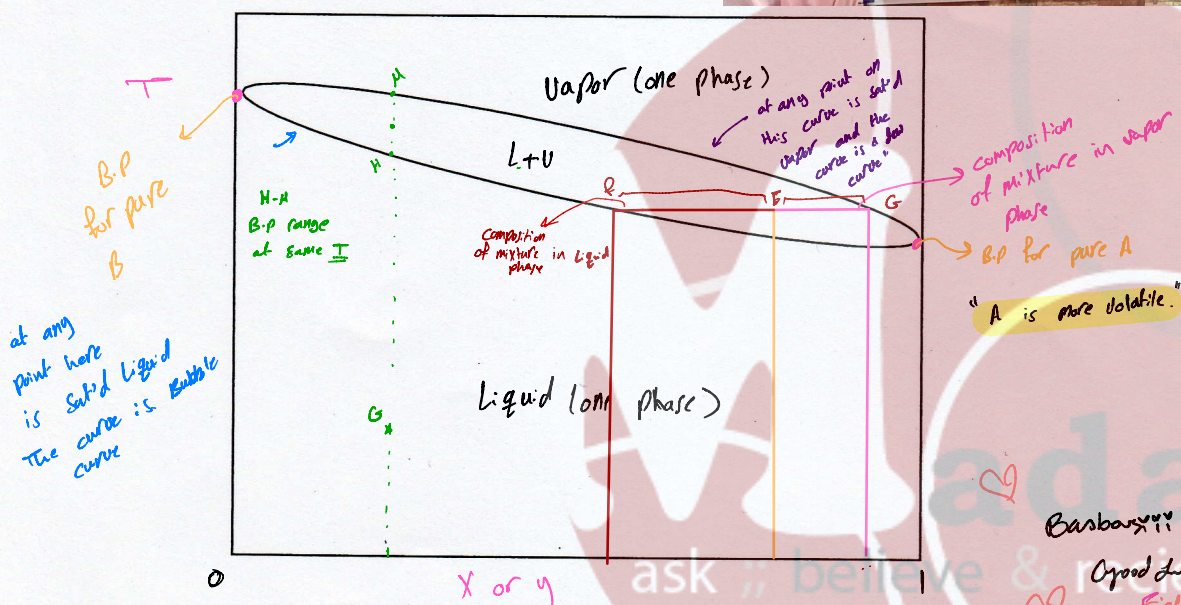
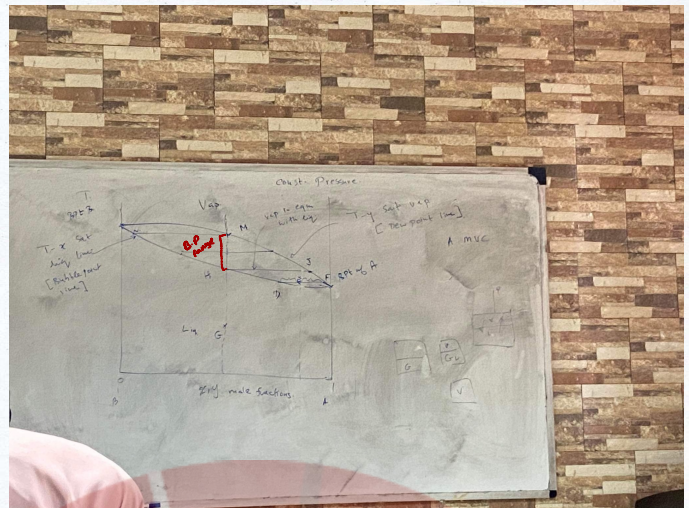
#### 2.2.1.1 Phase equilibrium diagrams:

- Usually pressure is specified (fixed)  $\Rightarrow$  one independent variable remains to be fixed.
- At constant pressure four isobaric phase equilibrium diagrams involving the variables T, x and y can be constructed:

• T-x • T-y • T-x-y • x-y

#### Constant Pressure Equilibrium:

• T-x • T-y • T-x-y diagrams:



Barbaray!! Nave

Oyod Juch!!

Fighting!!

-R.  
xxx



- **Liquid and vapor mixtures at equilibrium are at the same temperature and pressure and a horizontal line called a tie line joins their respective compositions.**
- A mixture between two equilibrium curves such as E is a two phase mixture consisting of a liquid with composition at D and a vapor with composition at F.

**The relative amounts of equilibrium phases are given by the lever rule**

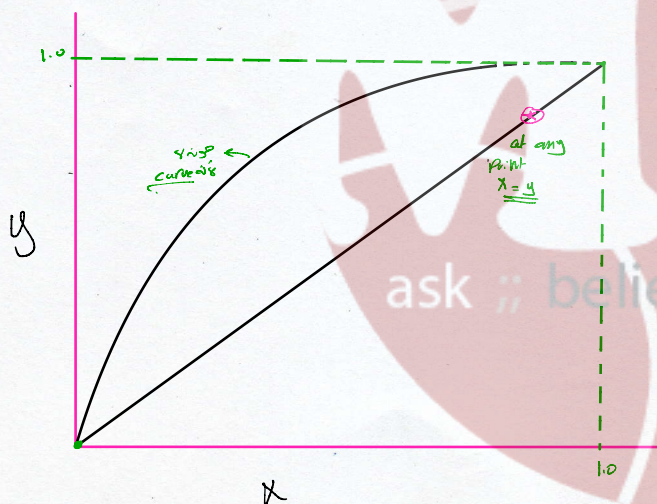
$$\frac{\text{Moles } D}{\text{Moles } F} = \frac{\overline{EF}}{\overline{DE}} \Rightarrow \begin{matrix} L+V=1 \\ Lx_1 + Vy_1 = z_1 \end{matrix} \quad \begin{matrix} \text{rearrange} \\ \text{these} \\ \text{two equations} \\ \text{to get } L, V \\ \text{expressed on} \end{matrix}$$

- Heating a liquid mixture composition (G):

**Closed system with constant pressure.** If the liquid is heated, the first bubble of vapor forms at (H) with vapor composition at (J) richer in the more volatile component (mvc). As more mixture is vaporized more vapor forms at the expense of liquid but the entire mass composition is still the same. **The last drop of liquid mixture vaporizes at M and has composition at N.** The boiling range of the mixture is HM.

**Open system:** If a solution is boiled in an open vessel, the vapor is richer in the more volatile component. As vaporization proceeds the liquid becomes leaner. The temperature and composition of saturated liquid move along HN as vaporization (distillation) proceeds.

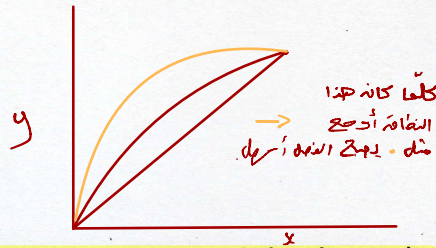
**x vs. y diagram:**



این نمودار را می‌توانیم برای تعیین ترکیب بخار و مایع در تعادل استفاده کنیم. فرض کنیم ما یک مخلوطی داریم که ترکیب آن  $x$  است. اگر ما این مخلوط را گرم کنیم، اولین حباب بخار در نقطه  $H$  تشکیل می‌شود. ترکیب این بخار  $y$  خواهد بود. اگر ما بیشتر مخلوط را بخار کنیم، بخار بیشتری تشکیل می‌شود و مایع باقی‌مانده فقیرتر می‌شود. این فرآیند تا زمانی که آخرین قطره مایع بخار شود ادامه می‌یابد. محدوده جوش این مخلوط از  $H$  تا  $M$  است. در یک سیستم باز، بخار غنی‌تر از مایع خواهد بود و مایع فقیرتر می‌شود. این فرآیند در یک سیستم باز مانند تقطیر اتفاق می‌افتد.



### 2.2.1.2 Relative volatility



The greater the distance between the equilibrium curve and the diagonal, the greater the difference in VL composition and the easier the separation.

Relative volatility is a measure of the difference between vapor and liquid composition at equilibrium. It is called separation factor.

$$\alpha = \frac{(\text{moles A / moles B}) \text{ in vapor}}{(\text{moles A / moles B}) \text{ in liquid}}$$

$$= \frac{y_A / (1 - y_A)}{x_A / (1 - x_A)} = \frac{\frac{y_A}{x_A} \cdot \frac{(1 - x_A)}{(1 - y_A)}}{\frac{y_B}{x_B} \cdot \frac{(1 - x_B)}{(1 - y_B)}} = \frac{\frac{y_A}{x_A} \cdot \frac{(1 - x_A)}{(1 - y_A)}}{\frac{y_B}{x_B} \cdot \frac{(1 - x_B)}{(1 - y_B)}}$$

or  $\alpha = \frac{K_A}{K_B}$

$\alpha = 1$

no separation

$\alpha > 1$

separable mixture

$\alpha < 1$

Also separable mixture but B would be more volatile B



### 2.2.1.3 VLE for ideal solutions:

#### Characteristics of ideal solutions:

- Average inter molecular forces in the solution are unchanged upon mixing.
- No heat will be absorbed or released upon mixing.
- Volume of solution varies linearly with composition [i.e. Total solution volume equals the sum of pure component volumes].
- The total vapor pressure of solution varies linearly with composition.

Ideal solutions do not exist in reality. However, many solutions approach ideality. For example: adjacent members of homologous series of organic compounds. e.g. benzene in toluene.   
  $\rightarrow$  same structure

#### Raoult's Law:

When the gas mixture in equilibrium with an ideal liquid solution also follows ideal gas law, the partial pressure of a solute gas is linearly proportional to its

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mole fraction in the liquid phase. The constant of proportionality being the vapor pressure of the pure species at the system temperature.

$$P_i = \overset{\text{slope}}{P_i^s} x_i \rightarrow \text{Solute property}$$

Equilibrium partial pressure      vapor pressure      mole fraction in liquid

It is seen that the solubility of a certain gas in an ideal solution is independent of the nature of the solvent.

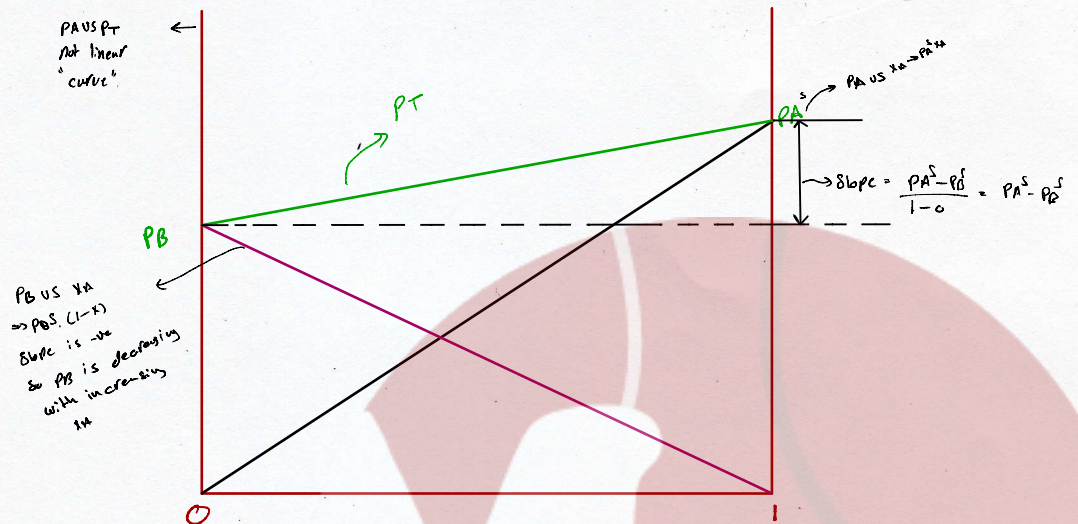
For a binary mixture we have:

$$P_A = P_A^s x_A \Rightarrow \bullet \quad P_B = P_B^s (1 - x_A) \Rightarrow \bullet$$

$$P_t = P_A + P_B \\ = P_A^s x_A + P_B^s (1 - x_A)$$

$$P_t = (P_A^s - P_B^s) \cdot x_A + P_B^s \Rightarrow \bullet$$

At constant temperature these are linear since  $P_A^s$  and  $P_B^s$  are constant.



For ideal solutions it is possible to calculate the vapor liquid equilibria from vapor pressure data of pure substances.



For Binary mixture: At a given temperature:

$$x_A + x_B = 1.0$$

$$; \quad y_A + y_B = 1.0$$

$$x_A = \frac{(P_t - P_B^S)}{(P_A^S - P_B^S)}$$

$$y_A = \frac{P_A}{P_t} \Rightarrow$$

$$y_A = \left( \frac{P_A^S}{P_t} \right) x_A$$

Relative volatility:

$$\alpha_{AB} = \frac{y_A (1 - x_A)}{x_A (1 - y_A)}$$

$$= \frac{P_A^S x_A (1 - x_A)}{P_t x_A \frac{P_B^S}{P_t} (1 - x_A)}$$

$$\therefore \alpha_{AB} = \frac{P_A^S}{P_B^S} \text{ function in } T$$

$$x_A = \frac{P_t - P_B}{P_A - P_B}$$

$$y_A = \frac{P_A}{P_t} \cdot x_A$$

$$\alpha = \frac{P_A^S}{P_B^S} = \frac{\frac{y_A}{(1 - y_A)}}{\frac{x_A}{(1 - x_A)}}$$

ex. Compute the vapor liquid equilibria at constant pressure of 1 std atm for mixtures of n-heptane and n-octane.

Solution:

We need to establish t-x,y diagram at 1 atm in the temperature range between boiling points of the pure components.

At 1 atm BP<sub>t</sub>n-C<sub>7</sub> = 98.4 °C

BP<sub>t</sub>n-C<sub>8</sub> = 125.6 °C

$$x_A = \frac{P_t - P_B^S}{P_A^S - P_B^S}$$

$$y_A = \frac{P_A^S}{P_t} x_A$$

Sample calculation

At 110 °C

$$P_A^S = 1050 \text{ mm Hg}$$

$$P_B^S = 484 \text{ mm Hg}$$

$$P_t = 760 \text{ mm Hg}$$

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$T(^{\circ}\text{C}) \propto \log_{10} \left( \frac{P_A^S}{P_B^S} \right)$  exd cald  $\left( \frac{A+B+C}{3} \right)^{\frac{1}{n}}$   
 exd cald  $\frac{P_A^S}{P_B^S}$  exd cald

$$x = \frac{760 - 484}{1050 - 484} = 0.487$$

$$y = \frac{1050}{760} \times 0.487 = 0.674$$

$\left( \frac{A+B+C}{3} \right)^{\frac{1}{n}}$

$\alpha_{AB}$ : at  $110^{\circ}\text{C}$

$$\alpha_{AB} = \frac{P_A^S}{P_B^S} = \frac{1050}{484} = 2.17$$

Temp. $^{\circ}\text{C}$	$P_A^S$ mm Hg	$P_B^S$ mm Hg	$X_A$	$Y_A$	$\alpha_{AB}$
98.4					2.28
105.0					2.25
110.0	1050	484	.487	.674	2.17
115.0					2.14
120.0					2.08
125.0					2.02

Note:  $\alpha$  for ideal solutions does not vary considerably. An average value of  $\alpha$  can be calculated and used.  $\Rightarrow (\alpha_1, \alpha_2, \dots, \alpha_n)^{\frac{1}{n}}$

$$\alpha_{AB} = \frac{y_A (1 - x_A)}{x_A (1 - y_A)} \Rightarrow y_A = \alpha_{AB} x_A \frac{(1 - y_A)}{(1 - x_A)}$$

$$X_A = \frac{P_T - \frac{P_A^S}{\alpha_{AB}}}{\frac{P_B^S}{\alpha_{AB}} - \frac{P_A^S}{\alpha_{AB}}}$$

$$y_A [(1 - x_A) + \alpha_{AB} x_A] = \alpha_{AB} x_A \leftarrow y_A (1 - x_A) = \alpha_{AB} x_A (1 - y_A)$$

$\Rightarrow$  A relative to B

$$y_A = \frac{\alpha_{AB} x_A}{1 + x_A (\alpha_{AB} - 1)}$$

Notes:

1. Raoult's Law can generally be applied to a component whose mole fraction in the liquid phase approaches unity or to solutions of components quite similar in chemical nature.  $\Rightarrow$  Such as benzene and toluene.
2. Equilibrium constant or an equilibrium distribution coefficient can be defined.

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$$P_i = P_i^s \cdot x_i \Rightarrow \text{liquid + vapor}$$

$$P_i = y_i \cdot P_t \Rightarrow \text{vapor only}$$

$\Downarrow$

$$K_{i, \text{Raoult}} = \frac{y_i}{x_i} = \frac{P_i^s}{P_t}$$

$\Rightarrow$  distribution coefficient depends on T and composition of the components at given T and pressure.

In general VLE data may be represented by:

$$y_i = K_i x_i$$

$$K_i = f(T, P, \text{composition})$$

It can be seen that

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{y_i}{y_j} \cdot \frac{x_j}{x_i} = \frac{y_i (1 - x_i)}{x_i (1 - y_i)}$$

#### 2.2.1.4 Actual solutions:

##### Miscible binary mixtures:

Few binary miscible systems obey Raoult's law throughout the complete range of concentrations. Most systems deviate from Raoult's law to a greater or lesser extent.

For real mixtures

$$P_i \neq P_i^s \cdot x_i \Rightarrow \text{for ideal solutions.}$$

but instead

$$P_i = \gamma_i P_i^s x_i$$

$\gamma_i$  = activity coefficient

$$= \frac{\text{real eqm partial pressure}}{\text{ideal eqm partial pressure}} = \frac{P_i \text{ real}}{P_i^s \cdot x_i}$$

therefore  $\gamma$  is a measure of the deviation from ideality

$$\gamma = 1 \Rightarrow \text{ideal solution}$$

$$\gamma > 1 \Rightarrow + \text{ve deviation}$$

$$K_F = \frac{P_A}{P_T}$$

$$K_L = \frac{P_B}{P_T}$$

$$\alpha = \frac{P_A^s}{P_B^s}$$

$$P_A = \gamma_A P_A^s \cdot x_A$$

$$\Rightarrow \gamma_A = \frac{y_A \cdot P_T}{x_A P_A^s}$$

$$x_A = \frac{P_T - P_B^s}{P_A^s - P_B^s}$$

$$\gamma_A = \frac{P_A}{P_T} \cdot x_A$$

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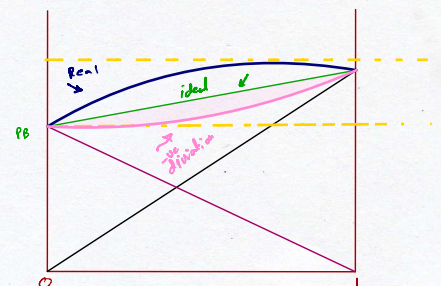


$\gamma < 1 \Rightarrow$  - ve deviation

All miscible pairs can be classified into three general types:

**Type I:** systems whose total vapor pressure is intermediate between those of pure components.

Ex.  $\text{CCl}_4$  - cyclohexane  $p_i^A < p_T < p_i$   
 $\text{CCl}_4$  - benzene  
 Benzene - toluene  
 Water - methyl alcohol.

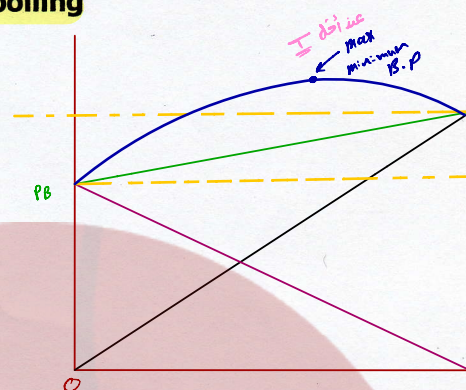


**Type II:** systems exhibiting a **maximum** in the total vapor pressure curve. They exhibit positive deviation from ideality and they form **minimum boiling point** mixtures.

Ex. Carbon disulfide - acetone, benzene - cyclohexane, water - ethyl alcohol.

**Type III:** systems exhibiting a minimum in the total vapor pressure curve. They exhibit negative deviation from ideality and they form **maximum boiling point** mixtures.

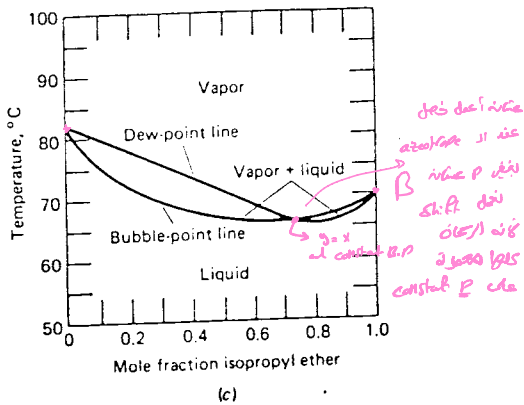
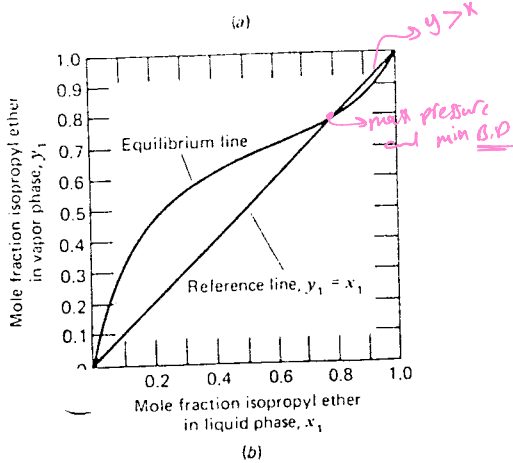
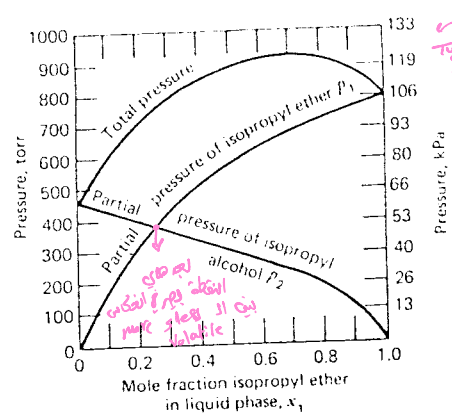
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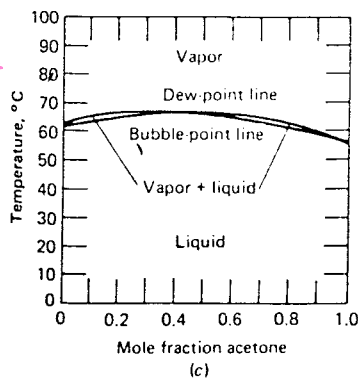
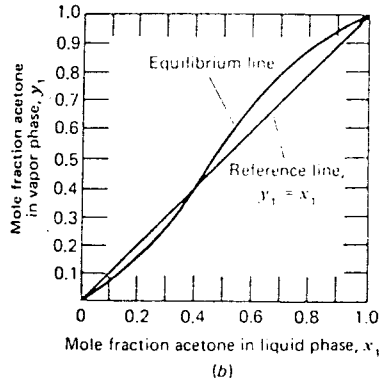
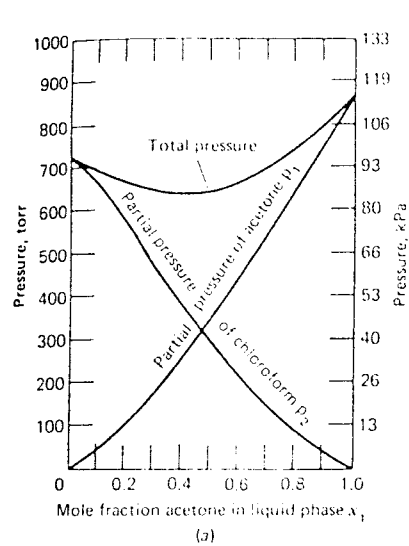
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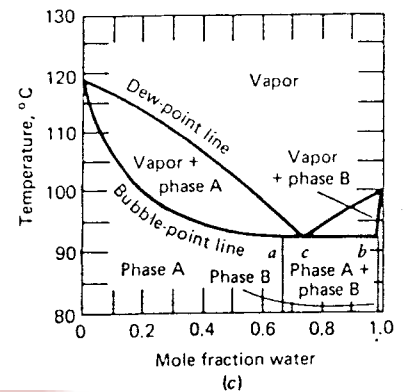
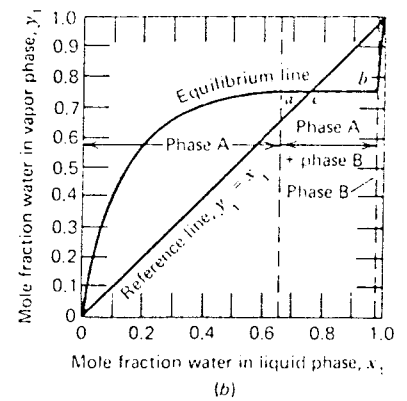
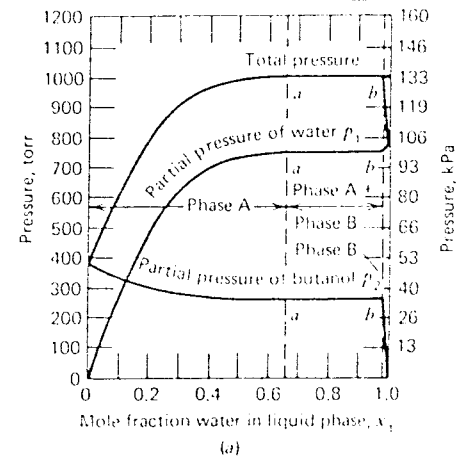




**Figure 3.5. Minimum-boiling-point azeotrope, isopropyl ether–isopropyl alcohol system.** (a) Partial and total pressures at 70°C. (b) Vapor–liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N. Y. © (1959).]



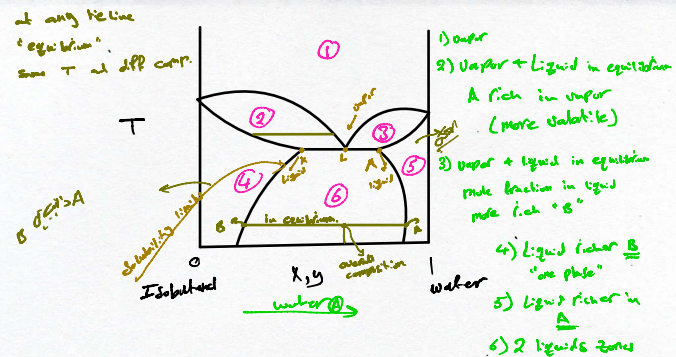
**Figure 3.6. Maximum-boiling-point azeotrope, acetone–chloroform system.** (a) Partial and total pressures at 60°C. (b) Vapor–liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N. Y. © (1959).]



**Figure 3.7. Minimum-boiling-point (two liquid phases) water–n-butanol system.** (a) Partial and total pressures at 100°C. (b) Vapor–liquid equilibria at 101 kPa. (c) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N.Y. © (1959).]



$K > 1$  liquid rich in B  
 $M > 1$  liquid rich in A  
 $L > 1$  vapor  
 $KML > 1$  equilibrium



## Partially Miscible Binary Mixtures:

→ 2 phase not completely soluble.

Some systems do not dissolve completely in all proportions. They exhibit large positive deviations (minimum boiling) [Forces of repulsion → 2  $\phi$ ]



### I. Zones:

1. all vapor
2. vapor and liquid in equilibrium with vapor richer in A
3. vapor and liquid in equilibrium with vapor richer in B
4. Liquid solution richer in B (solution of A in B)
5. Liquid solution richer in A (solution of B in A)
6. Two-phase mixtures. Each phase represents a solution of one component in the other. At constant temperature the composition of each phase is constant; however the proportions of phases are different.

II. For homogeneous liquids (zones 4 and 5), the vapor-liquid equilibrium phenomena are normal.

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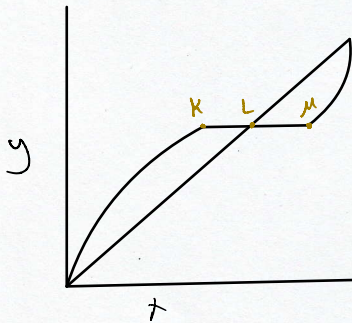
III. Two phase mixtures within the range KM will boil at the temperature of line KM, and they all give rise to the same vapor of composition L in equilibrium with two liquids at K and M which are also in equilibrium with each other.

IV. A two-phase mixture of average composition L which produces a vapor of the same composition is sometimes called a **heteroazeotrope**.

V. Phase rule for systems at temperature KM:

$$C = 2 \quad P = 3 \quad F = C - P + 2 \Rightarrow F = 1$$

∴ If pressure is set, everything else is specified.



### IMMISCIBLE BINARY MIXTURES (heterogeneous solutions)

Immiscible liquids are mutually insoluble – addition of one liquid to the other does not affect the properties of either liquid. Each will behave independently and will exert its own vapor pressure corresponding to the pure liquid at a given temperature.

$$P_t = P_A^s + P_B^s \Rightarrow \text{B.P. of the mixture is less than either of the B.P. of each liquid.}$$

The mixture will boil at a certain temperature when the sum of the vapor pressures equals the external pressure. The vapor composition is:

$$y_A = \frac{P_A^s}{P_t}$$

$$x_A = \frac{n_A}{n_T}$$

Partial pressure  $\equiv$  vapor pressure.

Handwritten notes: "B.P. of mixture is less than either of the B.P. of each liquid." and "B.P. of mixture is less than either of the B.P. of each liquid."

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Notes:

1. The boiling point of any mixture of two immiscible liquids is less than the boiling point of either of the two liquids.
2. Boiling point of all possible mixtures of two immiscible liquids is the same (no change in vapor pressure with composition).
3. At any boiling point, the vapor composition remains constant and is independent of overall liquid composition.

### 2.2.2 VLE for multi-component systems:

- Graphical presentation of more than three component systems is extremely complex.
- Many of the multi-component systems of industrial importance can be considered nearly ideal solutions. Raoult's law can be applied and vapor liquid equilibrium data can be calculated from pure component data.
- Sometimes equilibrium data can be calculated from binary mixtures data.

For multi-component systems, equilibrium data is represented by means of distribution coefficients.

For any component i

$$y_i = k_i x_i$$

For ideal solutions at moderate pressures,  $k_i$  is independent of composition. It depends only on temperature and total pressure.

At equilibrium:

$$k_i = \frac{y_i}{x_i} = \frac{P_i / P_t}{P_i^s / P_i^s} = \frac{P_i^s}{P_t}$$

It is also customary to choose a convenient reference component (in many cases heaviest component) to which data can be referred:

→ the heaviest (high BP, less volatile)

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At equilibrium:

$$\alpha_{ij} = \frac{(y_i/x_i)}{(y_j/x_j)} = \frac{k_i}{k_j} \Rightarrow \text{high BP}$$

$$\alpha_{ij} = \frac{P_i^s/P_t}{P_j^s/P_t} = \frac{P_i^s}{P_j^s}$$

**VLE** For a given vapor-liquid system at equilibrium:

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j}$$

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j}$$

$$y_i = \frac{\alpha_{ij} \cdot x_i}{(x_j/y_j)}$$

$$x_i = \frac{y_i/\alpha_{ij}}{(y_j/x_j)}$$

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \frac{\alpha_{ij} \cdot x_i}{(x_j/y_j)} = 1$$

$$\sum x_i = \sum \frac{y_i/\alpha_{ij}}{y_j/x_j} = 1.0$$

$$\left( \frac{x_j}{y_j} \right) = \sum_{i=1}^n \alpha_{ij} \cdot x_i$$

$$\frac{y_j}{x_j} = \frac{1}{\sum \alpha_{ij} \cdot x_i}$$

$$\left( \frac{y_j}{x_j} \right) = \sum y_i / \alpha_{ij}$$

substitute for  $\frac{y_j}{x_j} = \frac{y_i}{\alpha_{ij} \cdot x_i}$

$$y_i = \frac{\alpha_{ij} \cdot x_i}{\sum \alpha_{ij} \cdot x_i}$$

useful for Bubble  
point calculation

$$x_i = \frac{y_i / \alpha_{ij}}{\sum y_i / \alpha_{ij}}$$

useful for Dew  
point calculation

ask :: believe & recieve



### 2.2.3 Enthalpy concentration diagrams:

Binary VLE data can also be represented by enthalpy concentration diagrams [useful in showing energy changes as well as composition changes].

State → State  
enthalpy concentration  
energy

#### Calculation of Enthalpy contents:

##### Liquids:

For a liquid solution:

$H_L$  = sensible heat and heat of mixing

$$H_L = C_L (t_L - t_0) M_{av} + \Delta H_S \Rightarrow H_L = C_L (\Delta T) M_{av} + \Delta H_S$$

$C_L$ : heat capacity of solution. For ideal solution it is the weighted average of the pure components heat capacities. (energy / mass. deg.).

$M_{av}$ : average molecular weight.

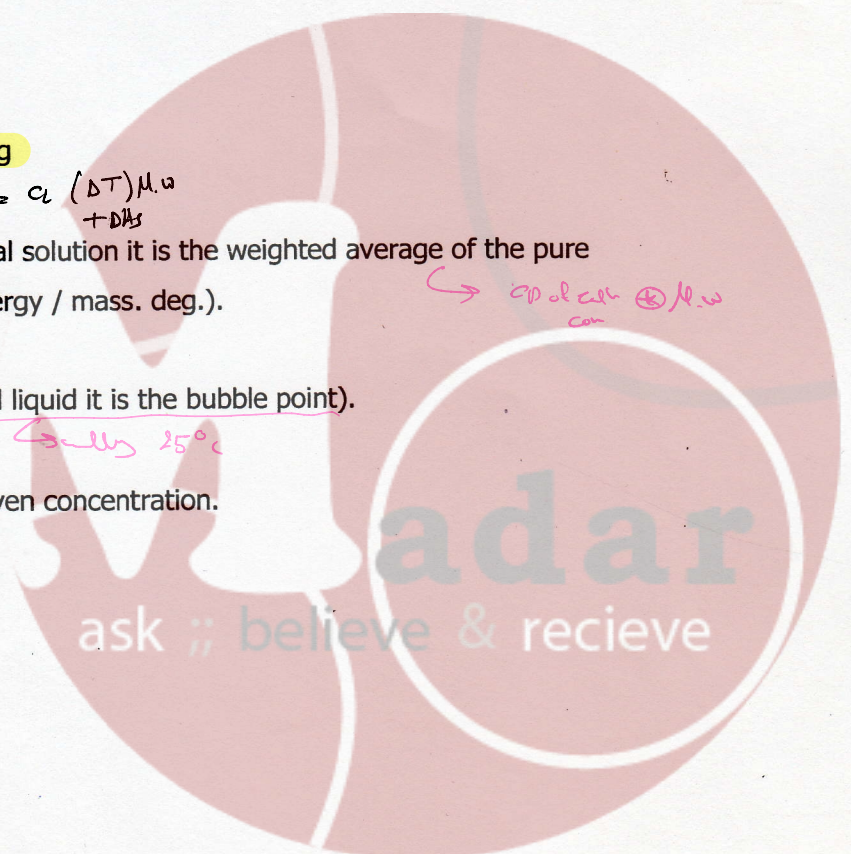
$t_L$ : liquid temperature (for a saturated liquid it is the bubble point).

$T_0$ : reference temperature.

$\Delta H_S$  = heat of solution at  $T_0$  for the given concentration.

→  $\Delta H \Rightarrow -$   
we evolved  
 $\Rightarrow +$   
we added  
 $\Rightarrow$  ; dissol  
sol.

→ cp of each @  $M_{av}$   
con





## Saturated vapor:

We can assume pure liquids are heated separately to the dew point  $t_v$ , each vaporized at this point and vapors are mixed.

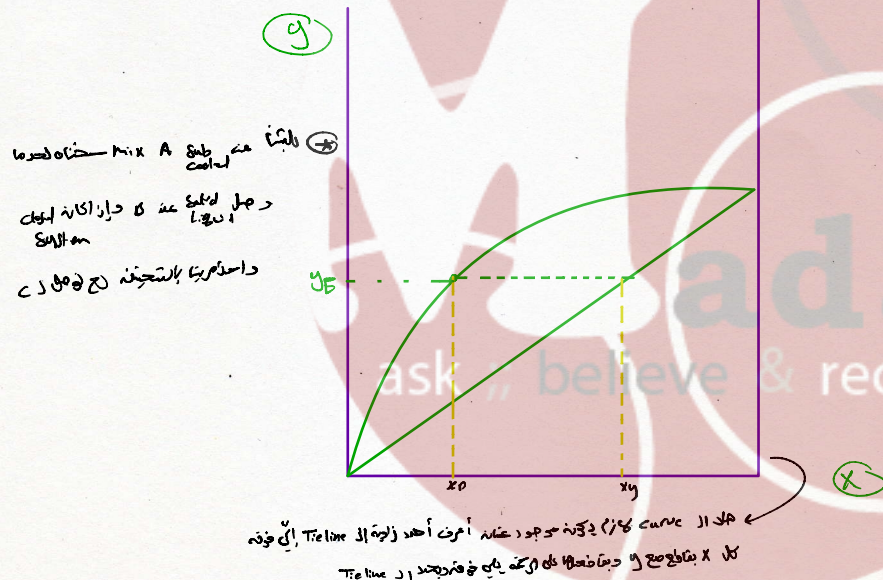
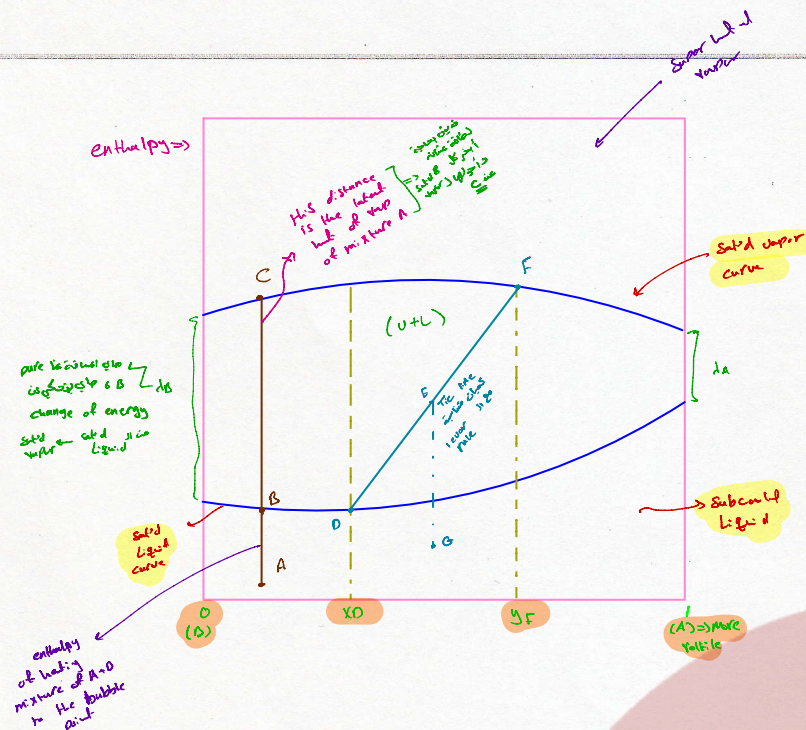
$$H_v = y_A [C_{L,A} \Delta T \cdot M_A + \lambda_A \cdot M_A] + y_B [C_{L,B} \Delta T \cdot M_B + \lambda_B \cdot M_B]$$

$H_v$  = Enthalpy of Vap A + Enthalpy of Vap B.

$$H_v = y [C_{L,A} (t_v - t_0) M_A + \lambda_A \cdot M_A] + (1-y) [C_{L,B} (t_v - t_0) M_B + \lambda_B]$$

$\lambda$ : latent heat of vaporization of pure substances at  $t_v$  [energy/mass]

$C_L$ : heat capacity of pure liquid energy/mass deg.





## 2.3 Gas – Liquid systems, Henry's Law

*dilute  
gas  
L=2*

$$y = K_A x$$

**System:** Gaseous mixture A+B

A to be absorbed by liquid S

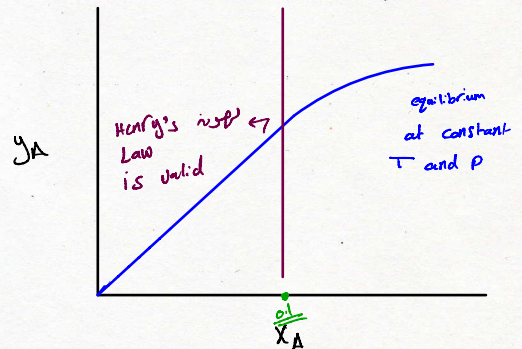
B carrier gas.

**Thermodynamics variables:**  $P, T, x_A, x_B, x_y, y_A, y_B, y_s$

**Degrees of freedom:**  $C = 3 \quad P = 2 \Rightarrow F = 3 - 2 + 2 = 3$

Therefore if three variables are specified, all other variables are determined. If B is insoluble in S, and S has negligible vapor pressure, then the remaining variables are:  $P, T, x_A$  and  $y_A$

*if S is insoluble in B  
so  $x_s, y_s = 0$*



For gases whose mole fraction in the liquid phase approaches zero, a linear equilibrium relationship may be assumed with reasonable accuracy.

### Henry's Law:

$$P_A = k_h \cdot x_A$$

Partial pressure of A
Henry's law constant
mole fraction of A in liquid

*\* Way bal*

almost all liquids will deviate above mole fractions of 0.1.

*because it is only valid at dilute systems.*

Equilibrium constant:

$$K_A = \frac{y_A}{x_A} = \frac{k_h}{P_i}$$

adar  
ask :: believe & recieve