



# *PRINCIPLES* 1

**DR.** LINDA ALHMOUD



unit and dimensions.

→ any measured quantity has a  $\left\{ \begin{array}{l} \text{numerical (value)} \\ \text{unit} \end{array} \right.$

→ dimension a property that can be measured such as length, mass, time.

(or) can be calculated such as dividing the measured dimensions or multiplying or both of them.

\* the units must be the same to use mathematical operators (+, -)

such as

$$10 \text{ cm} - 7 \text{ cm} = 3 \text{ cm}$$

the same as  $3x - x = 2x$

but,

$$10 \text{ cm} - 7 \text{ mm} = ?$$

the same as  $3x - y = ?$

the unit and its corresponding one can be used for dividing/multiplying.

$$\frac{10 \text{ km}}{2 \text{ hour}} \div \frac{2 \text{ m} \cdot 3 \text{ m}}{6 \text{ m}^2} \div \frac{7 \text{ hour}}{\text{km}} \cdot \text{km} = 7 \text{ hour}$$





## Force and weight

**Newton's second law** :- Force is proportional to mass and acceleration (length/(time)<sup>2</sup>)

|       | multiple unit                                   | derived unit                                           |
|-------|-------------------------------------------------|--------------------------------------------------------|
| Force | $\frac{\text{kg} \cdot \text{m}}{\text{s}^2}$   | Newton                                                 |
|       | $\frac{\text{g} \cdot \text{cm}}{\text{s}^2}$   | dyne                                                   |
|       | $\frac{\text{lbm} \cdot \text{ft}}{\text{s}^2}$ | lbf                                                    |
|       |                                                 | 32.174 $\frac{\text{lbm} \cdot \text{ft}}{\text{s}^2}$ |

**weight** :- Force exerted on the object by gravitational attraction

$$W = mg \quad \text{where } g = \begin{cases} 9.8066 \text{ m/s}^2 \\ 980.66 \text{ cm/s}^2 \\ 32.174 \text{ ft/s}^2 \end{cases}$$

**Scientific Notation** :- a number is expressed as the product of another number (usually) between 1 and 10 and a power of 10.

$$\begin{aligned} 123000000 &= 1.23 \times 10^8 \quad \text{or} \quad 0.123 \times 10^9 \\ 0.000028 &= 2.8 \times 10^{-5} \quad \text{or} \quad 0.28 \times 10^{-4} \end{aligned}$$



## Significant figures:-

$$\bullet 2300 \text{ or } 2.3 \times 10^3 \rightarrow 2 \text{ s.f.}$$

$$\bullet 2300. \text{ or } 2.300 \times 10^3 \rightarrow 4 \text{ s.f.}$$

$$\bullet 2300.0 \text{ or } 2.3000 \times 10^3 \rightarrow 5 \text{ s.f.}$$

$$\bullet 23040 \text{ or } 2.3040 \times 10^4 \rightarrow 5 \text{ s.f.}$$

$$\bullet 0.035 \text{ or } 3.5 \times 10^{-2} \rightarrow 2 \text{ s.f.}$$

$$\bullet 0.03500 \text{ or } 3.500 \times 10^{-2} \rightarrow 4 \text{ s.f.}$$

## Chemical Engineering

### Round and Dimension

Roundling "أبداً هو الـ"

$$1) 1.35$$

$$\rightarrow 1.25$$

Round them to 3 s.f.

$$2) 1.35$$

$$\rightarrow 1.25$$

### Solution

$$1) 1.40$$

$$\rightarrow 1.30$$

$$2) 1.40$$

$$\rightarrow 1.20$$

why?

إذا كان العدد خمسة موجود عند التحويل إذا كان من  
أدنى إلى أعلى فهو

أما لو كان من أعلى فهو  
أنه لا يؤثر





## Dimensional Homogeneity

### example 2.6-2

consider the following equation of motion:

$$D(Pt) = 3t(s) + 4$$

كل ما يكون له وحدة  $D$  التي هي (س، م)  
فإنه لا يمكن أن يكون إلا  $Pt$  (س، م)

$$\begin{array}{l} t \Rightarrow s \\ 3 \Rightarrow Pt/s \\ 4 \Rightarrow Pt \end{array} \Rightarrow \begin{array}{l} 3 * t(s) + 4 \\ Pt * s + Pt \end{array} \begin{array}{l} ? \\ = Pt \\ ? Pt \end{array}$$

$$Pt + Pt = Pt$$

$$Pt \neq Pt \quad \#$$

\* to derive from  $Pt \rightarrow m$  and  $s \rightarrow min$

$$D(Pt) = D'(m) = D\left(\frac{3.2808 Pt}{1 m}\right) = 3.2808 D'$$

$$t(s) = t'(min) = t \left( \frac{60 s}{1 min} \right) = 60 t'$$

$$\text{So } \Rightarrow D(Pt) = 3t(s) + 4$$

$$\begin{aligned} 3.2808 D' &= 3 * 60 t'(min) + 4 \quad / 3.2808 \\ &= D'(m) = 55 t'(min) + 1.22 \quad \# \end{aligned}$$

## operation units : Addition and Subtraction

The numerical values of two or more quantities can be added/subtracted only if the units of the quantities are the same

- $10 \text{ kg} + 3 \text{ m} = \text{No physical meaning}$
- $10 \text{ m} + 20 \text{ ft} = \text{has a physical meaning}$
- $3 \text{ ft} + 10 \text{ ft} = 13 \text{ ft}$

## operation units : Multiplications and Division

Multiplications and division can be done on quantities with unlike units, but the units can only be cancelled or merged if they are identical

- $5 \text{ kg} \cdot 3 \text{ m} = 15 \text{ kg} \cdot \text{m}$
- $3 \text{ m}^2 / 60 \text{ cm} = 0.05 \text{ m}^2 \text{ cm}$
- $3 \text{ m}^2 / 0.6 \text{ m} = 5 \text{ m}$

## Dimensionless Quantities

Reynolds numbers  $\frac{\rho D u}{\mu}$

Where:-

$\rho$  fluid density ( $\text{kg/m}^3$ )

$D$  pipe diameter (m)

$u$  fluid mean velocity (m/s)

$\mu$  fluid dynamic viscosity ( $\text{kg/m} \cdot \text{s}$ )

\* The net of Reynolds numbers = 1 dimensionless \*



\* Importance of the dimensionless quantities  
 used arguments of special functions such as  
 exponential, logarithmic, trigonometric functions

$e^{10}$  is ok  $e^{(10 \text{ K})}$  NO  
 $\cos(10)$  is ok  $\cos(10 \text{ K})$  NO

example | what is the unit of  $R$  in this eq.

$$K = A e^{\left(\frac{E}{RT}\right)}$$

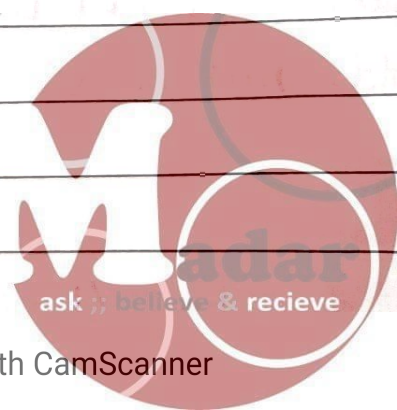
where  $E$  in (cal/mol)  
 $T$  in (K)

Solution

$e$  is an exp function & its dimensionless

$$\frac{\text{cal}}{\text{mol}} \bigg| R \bigg| \frac{1}{\text{K}} = 1$$

$$\text{So } R = \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$



## Process Data Representation and analysis

### Experiment:-

Collection of measurements data, each represented by numbers which give us information about quantity being determined.

- Some of numbers occur only once, other are repeated several times.
  - This due to variability of measurements arising from inaccuracies  $\Rightarrow$  Error

we display measurements as: frequency distribution.

\* To know the true value between some of measurements we find its average =  $\frac{\text{sum of measures}}{\text{number of measures}}$ .

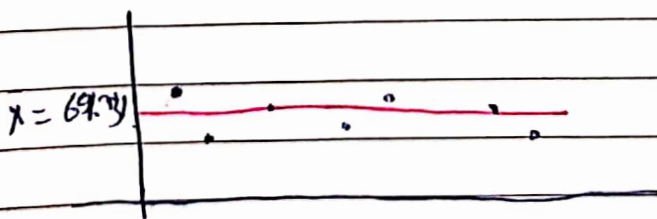
ways to estimate values

of  $x$

- Sample mean (Average) ( $\bar{x}$ )

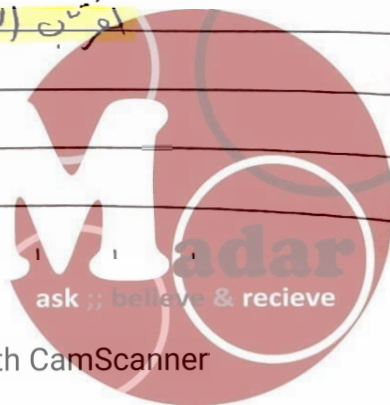
$$\bar{x} = \frac{x_1 + x_2 + x_3 + \dots + x_n}{n}$$

in Graphically way Suppose that  $\bar{x} = 69.34$ .



if  $\bar{x}$  is 69.34

\*  $\bar{x}$  is 69.34





## \* Sample Variance of Scattered data

$$\text{Range} = X_{\max} - X_{\min}$$

↳ The crudest measure of scatter

\* يعني ما بدفعه مني مقيا بين هو بغير مدى التناثر، القيم مني أكثر مني، إذا كانت القيم غريبة من المقياس.

$$\text{Sample Variance } S_x^2 = \frac{1}{N-1} [(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \dots + (X_N - \bar{X})^2]$$

مقيا ما أدفعه مني مقيا، التناثر، القيمة ولكن مقيا ترتيب

$$\text{Sample Standard deviation } \sqrt{S_x^2} = S_x$$

↳ To determine - errors :-

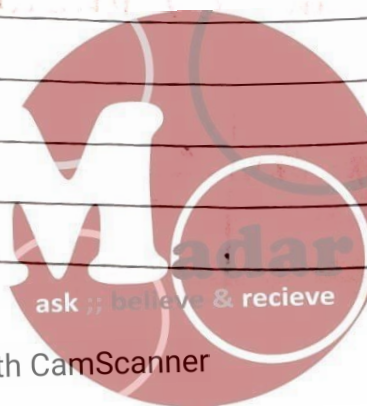
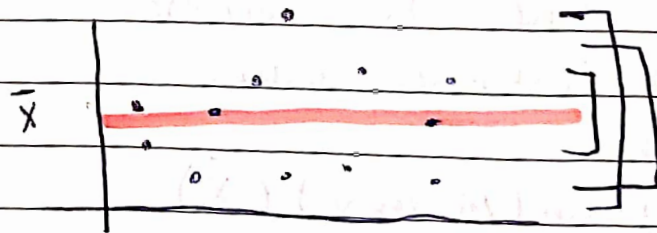
$$1) \bar{X} \pm S_x \Rightarrow \text{Maximum}$$

$$2) \bar{X} \pm 2S_x$$

$$3) \bar{X} \pm 3S_x \Rightarrow \text{Maximum}$$

س<sub>x</sub> ← لسان في السؤال كس

يريد



⇒ to find slope  $(x_1, y_1)$   $(x_2, y_2)$

$$[ S = \frac{y_2 - y_1}{x_2 - x_1} ]$$

⇒ to find intercept  $(x_1, y_1)$

$$[ I = x_1 - S y_1 ]$$

The line eq.

$$y - y_1 = S (x - x_1)$$

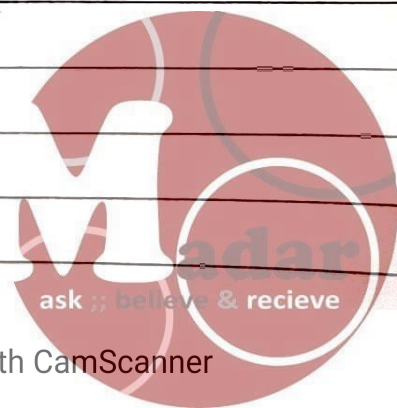
$$y - y_1 = Sx - Sx_1$$

$$y = \underset{\substack{\downarrow \\ \text{Slope}}}{S} x + \underset{\substack{\downarrow \\ \text{Intercept}}}{y - Sx_1}$$

another methods :-

$$1) \text{ slope} = \frac{n(Sxy) - (SxSy)}{n(Sxx) - (Sx)^2}$$

$$b = \frac{Sy - \text{Slope} \times Sx}{n}$$





## Chapter 3

### Processes and Process Variables

#### • Process

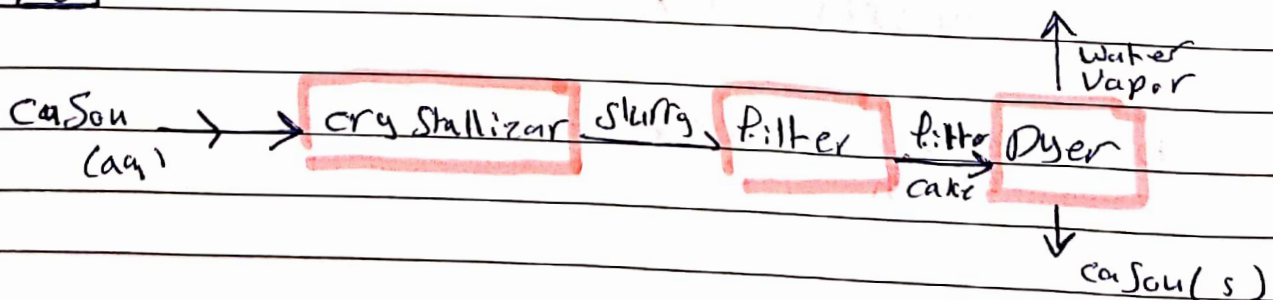
is any operation or series of operation by which a particular objective is accomplished

#### • Chemical process

is any series of operations by which a particular product is produced from raw materials



#### Example



## process streams

What we want to know about these streams?

Temperature, pressure, mass flow, volumetric flow, chemical composition

- Some of these variables are given

- other we measure.

- but many we have to calculate

- and, what happens in the boxing, designing, sizing and costing unit operation (Rest of the curriculum)

## What is chemical process variables?

Any measurements used to characterize or describe a chemical process

→ Some of measurements we quantify a material or specify a chemical composition

Mass, volume, mole

→ and some of measurements used to specify process conditions.

pressure, Temperature.





## Density

$$\rho = \frac{\text{mass}}{V}$$

→ used as a conversion factor between mass and volume and mass rate flow and volumetric rate flow

→ liquid and solid densities vary slightly with temperature because they are incompressible

→ Density of gas depends heavily on temperature and pressure

$$\text{Specific Volume (Density inverse)} = \frac{1}{\text{density}}$$

## Specific gravity

$$S_g = \frac{\rho}{\rho_{\text{water at } 4^\circ\text{C and 1 atm}}}$$

$\rho_{\text{water at } 4^\circ\text{C and 1 atm}}$

$$\rightarrow \text{because } = 1 \text{ g/cm}^3 = 1000 \text{ kg/m}^3 = 62.43 \text{ lbm/ft}^3$$

$S_g$  is given at particular temperature.

remember  $1 \text{ ml} = 1 \text{ cm}^3$



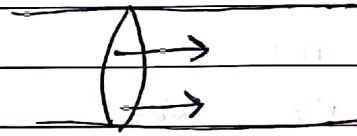
Note] density of a liquid in  $(\text{gm}/\text{cm}^3) = \text{sg}$   
(in numerically way)

because density of water =  $1 \text{ gm}/\text{cm}^3$ .

⇒ Flow rate:-

Rate of which a material is transported through a process line

Such as mass and Volumetric  
flow rate.



[mass flow rate] =  $\text{g}/\text{s}$

[volumetric flow rate]  $\text{cm}^3/\text{s}$

$$\left[ \rho = \frac{m}{V} \right]$$

⇒ flow meter:-

a device mounted in a process line that provides a continuous reading of flow rate in the line

Such as:-

Rotameters, Orifice, Meter





## Non additivity Volume water

Suppose :-

$$\begin{array}{|c|c|} \hline m_A \\ \hline n_A \quad V_A \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline m_B \\ \hline n_B \quad V_B \\ \hline \end{array} = \begin{array}{|c|c|} \hline m_T \\ \hline n_T \quad V_T \\ \hline \end{array}$$

$$m_A + m_B = m_T$$

$$n_A + n_B = n_T$$

$$V_A + V_B \neq V_T \quad \text{Why?}$$

$\Rightarrow$  molecules between each other become more close  
So the Volume will change.

إذا لم يتركز الجزيئات في الخليط، فإن الحجم لا يتغير.

## chemical composition

We need chemical composition because:-

- 1) Most Materials encountered in nature in chemical process systems are mixtures of various species
- 2) The physical properties of a mixture depend strongly on the mixture composition



## • Moles and molecular weight

**Atomic weight of an element**:- Refers to the mass of an atom on a scale that assigns to the carbon atom of exactly 12.

**Molecular weight of a compound**:- Sum of Atomic weights of the atoms constitute a molecule of the compound

**Mole**:- Amount of species whose mass is numerically equal to its molecular weight

• Gram-mole or g-mole in SI units

• lb mole in American Engineering units

Ex)  $1 \text{ g-mole } \text{CH}_3\text{OH} = 32.0 \text{ g } \text{CH}_3\text{OH} = 6.02 \times 10^{23} \text{ molecules of } \text{CH}_3\text{OH}$

$1 \text{ lb mole of } \text{CH}_3\text{OH} = 32.04 \text{ lbm } \text{CH}_3\text{OH}$

$1 \text{ kg mole of } \text{CH}_3\text{OH} = 32.04 \text{ kg } \text{CH}_3\text{OH} = 1000 \text{ mole } \text{CH}_3\text{OH}$





## Conversion between Mass and Mole

To convert the number of Moles to mass, we make use of (m.w)

$$m.w = \frac{\text{mass}}{\text{mole}} \left( \frac{g}{mol}, \frac{kg}{kmol}, \frac{lbm}{lbmol} \right)$$

الوزن الجزيئي هو النسبة بين الكتلة والعدد المولي

## Mass Fraction and Mole Fraction

For a mixture of two or more components, the composition can be expressed as

A) Mass fraction  $X_A = \frac{\text{mass of A}}{\text{total mass}}$

$$\left( \frac{g_A}{g_{\text{total}}}, \frac{kg_A}{kg_{\text{total}}}, \frac{lbm_A}{lbm_{\text{total}}} \right)$$

B) Mole fraction  $y_A = \frac{\text{moles of A}}{\text{total moles}}$

$$\left( \frac{g\text{-mole } A}{g\text{-mole total}}, \frac{kg\text{-mole } A}{kg\text{-mole total}}, \frac{lbm\text{-mole } A}{lbm\text{-mole total}} \right)$$



## Notes

1) m.w in g/mol, kg/kmol & lbm/lbmole are the same and equals!!

$$12 \text{ g/mol} = 12 \text{ kg/kmol} = 12 \text{ lbm/lbmole} \#$$

2) to convert from g-mol to lb-mol

$$1 \text{ lb-mol} = 454 \text{ g-mol}$$

یہ گائیڈ بی ایس اسٹن میں غلطی دیا ہوتا ہے (ملاحظہ کیجیے)

$$[1 \text{ lb-mole} \neq 1 \text{ g-mol}]$$

$$1 \text{ g-mol} = 10^{-3} \text{ kg-mol} \quad \text{and so on.}$$

**NOTE** Numerical Value of a mass or mole fraction does not depend on the numerator or denominator as long as these units are the same

**example** if mass fraction of benzene is 0.25 then:-

$$x_{\text{C}_6\text{H}_6} = \frac{0.25 \text{ kg C}_6\text{H}_6}{2 \text{ kg total}}$$

$$= \frac{0.25 \text{ g C}_6\text{H}_6}{1 \text{ g total}}$$

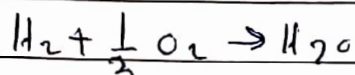
$$= \frac{0.25 \text{ lbm C}_6\text{H}_6}{1 \text{ lbm total}}$$





## Conversion by Mole to a Mass composition

- Most instruments measure the mole fraction
- Balances are done on mass fraction
- Moles are not always conserved
- Mass is conserved



1.5 mole          1 mole

↓  
1 mole H<sub>2</sub>O

⊕  
 $\frac{1}{2}$  H<sub>2</sub>O<sub>2</sub>

## to convert from Mole fraction to the mass fraction

• Basis :- 100 moles of mixture

25% H<sub>2</sub>O, 75% H<sub>2</sub>

2.25 g H<sub>2</sub>O, 17.75 g H<sub>2</sub>

2) Calculate number of moles of each species

3) Find mws

4) Calculate mass of each species

5) Normalize to find mass fractions



## How to convert from mass fraction to mole fraction

1) Basis 100 grams

2) compute mass of each species

3) divide by  $MW_i$  to get moles

4) sum of number of moles (to get total moles)

5) compute mole fraction

## \* Average M.W. of a mixture

↳ ratio of the mass fraction of the mixture ( $M$ ) to the total number of moles of all species

units:  $\text{kg/kmol}$ ,  $\text{lb/lb-moles}$  etc

$y_i$  = Mole fraction of  $i^{\text{th}}$  component

$x_i$  = Mass fraction of  $i^{\text{th}}$  component

$M_i$  = M.W. of  $i^{\text{th}}$  component

$$\bar{M} = y_1 M_1 + y_2 M_2 + \dots$$

$$\frac{1}{\bar{M}} = \frac{x_1}{M_1} + \frac{x_2}{M_2} + \frac{x_3}{M_3} + \dots$$



also,  $M = \frac{m_t}{n_t}$

## Concentration

**Mass concentration** of a component of a mixture or solution is the mass of this component per unit volume of mixture ( $\text{g/cm}^3$ ,  $\text{kg/m}^3$ )

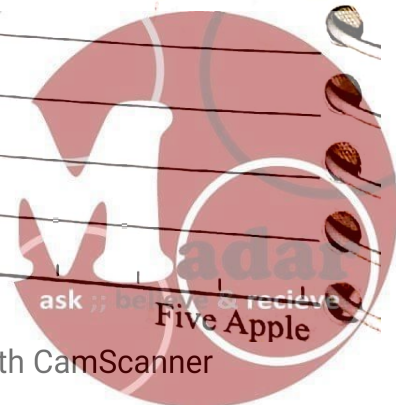
**Molar concentration** is the number of moles of the component per unit volume

Special

**Molarity** Value of Molar concentration of the solute in g-moles solute/liter sol. (M)

2 Molar Solution of A  $\rightarrow$  2 g-mol A Solution  
2 liter

used as a conversion factor to relate the mass (moles) of a component in a sample of the mixture to the sample value



### Example

0.02 Molar solution of NaOH

means that 1

0.02 Moles of NaOH

2 liter solution

but if we have 5 L of sol. how many moles do we have in NaOH?

$$\frac{0.02 \text{ Moles NaOH}}{2 \text{ liter sol}} \cdot 5 \text{ L sol} = 0.1 \text{ Moles NaOH}$$

### Example

in a stream of solution at a rate 2L/min the Molar flow rate of NaOH

$$\frac{0.02 \text{ Mole of NaOH}}{2 \text{ liter solution}} \cdot \frac{2 \text{ L}}{\text{min}} = 0.04 \text{ mol NaOH/min.}$$





## Relative and Absolute Temperature Scales

### Temperature

→ The average kinetic energy possessed by the substance

### \* Relative Temperature Scale

"Celsius and Fahrenheit"

The zero value is preset at some arbitrarily defined level

$$\begin{aligned} T(^{\circ}\text{F}) &= 1.8 T(^{\circ}\text{C}) + 32 \\ T(^{\circ}\text{C}) &= \frac{1}{1.8} (T(^{\circ}\text{F}) - 32) \end{aligned}$$

### absolute Temperature Scale

"Kelvin and Rankin"

A temperature scale at which reading of zero coincides with theoretical absolute zero (zero entropy configuration)

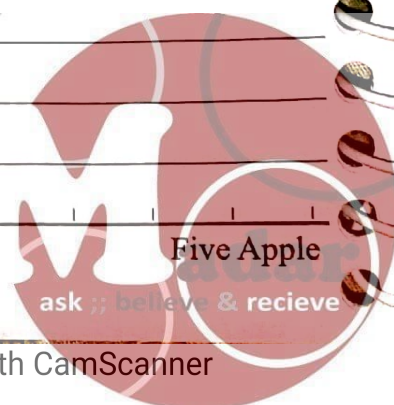
$$\begin{aligned} T(\text{K}) &= T(^{\circ}\text{C}) + 273.15 \\ T(^{\circ}\text{R}) &= T(^{\circ}\text{F}) + 459.67 \end{aligned}$$

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

$$T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$$

$$T(\text{K}) = 1.8 T(^{\circ}\text{C})$$

$$T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$$



## Unit Temperature difference

When temperature is used as a unit difference, then the following relationship is used:

$$\Delta C^{\circ} = \Delta K$$

كلاهما الفرق بين نقطتين موقوع

$$\Delta F^{\circ} = \Delta R^{\circ}$$

كلاهما الفرق بين نقطتين موقوع

$$\Delta C^{\circ} = 1.8 \Delta F^{\circ}$$

كلاهما الفرق بين نقطتين موقوع

$$\Delta K = 1.8 \Delta R^{\circ}$$

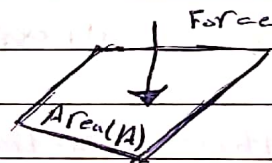
## pressure

pressure is defined as Normal force per unit area

$$P = \frac{F}{A}$$

$$\text{units} = \frac{N}{m^2} = \frac{lb.f}{in^2} \text{ (psi)}$$

Pascal

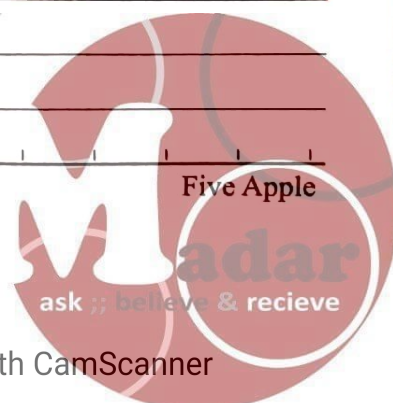


## Types of pressure

### A) Atmospheric pressure

The pressure of surrounding air or the local pressure of the atmosphere

- the pressure @ the base of column air
- it decreased with increase the elevation





### B) Absolute pressure ( $p_{abs}$ )

pressure measured relative to a fixed reference point of zero

pressure (vacuum, no molecules present) e.g. pressure relative to a perfect vacuum

### C) Gauge pressure ( $p_g$ )

The pressure relative to atmospheric pressure.

$$p_{abs} = p_g + p_{atmospheric}$$

$p_{psig} = 1 \text{ bar/in}^2$  gauge pressure

$p_{psia} =$  absolute pressure

we use the absolute pressure when:-

1)  $pV = nRT$  ideal gas

2) you can use  $p_g$  when we take difference in pressure

$$\Delta p_g = \Delta p_{absolute}$$

3) taking ratio of pressure



## Atmospheric pressure (Barometric pressure)

can vary with location, weather, conditions and other factor. Usually determined from barometer (Barometric pressure)

The standard atmospheric pressure:-

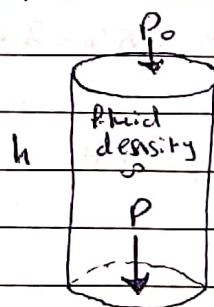
$$\begin{aligned} P_{\text{atm}} &= 1.01 \text{ atm} && \leftarrow \text{at sea level} \\ &= 760 \text{ mmHg} \\ &= 101.3 \text{ kPa} \\ &= 29.92 \text{ in Hg} \\ &= 33.91 \text{ ft H}_2\text{O} \\ &= 14.7 \text{ psi (lbf/in}^2\text{)} \end{aligned}$$

## Hydrostatic pressure

The pressure at the bottom of static (non-moving) column of water

\* Relationship between pressure at top ( $P_0$ ) and pressure at the bottom ( $P$ )

$$P = P_0 + \rho gh$$



where :-

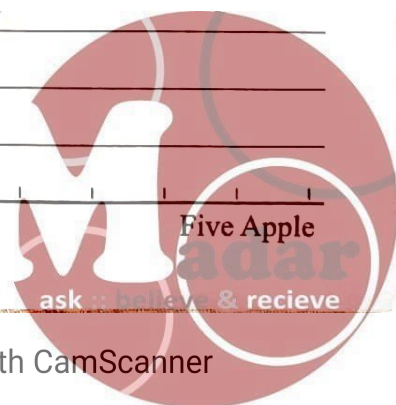
$P$ :- pressure at bottom

$P_0$ :- pressure at top

$\rho$ :- fluid density

$g$ :- acceleration due to gravity

$h$ :- height of fluid





$$\Rightarrow \frac{F}{A} = \frac{F_0}{A} + \frac{w}{A}$$

$$\frac{F}{A} = \frac{F_0}{A} + \frac{mg}{A}$$

$$m = \rho \times V$$

$$\frac{F}{A} = \frac{F_0}{A} + \frac{\rho V g}{A}$$

$$V = A \times h$$

$$\frac{F}{A} = \frac{F_0}{A} + \frac{\rho A h g}{A}$$

$$P = P_0 + \rho g h$$

ways to express the pressure:

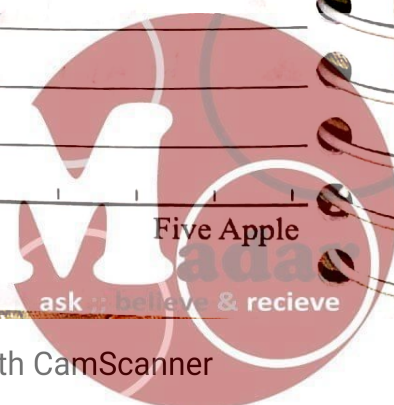
if we have a -20 mmHg of gauge pressure at a point has a atmospheric pressure = 755 mmHg

So 1) -20 mmHg gauge pressure

2) 20 mmHg vacuum

3)  $755 - 20 = 735$  mmHg abs

\*  $P_H = P_0 + H$  (H has the same unit)  
and same fluid.

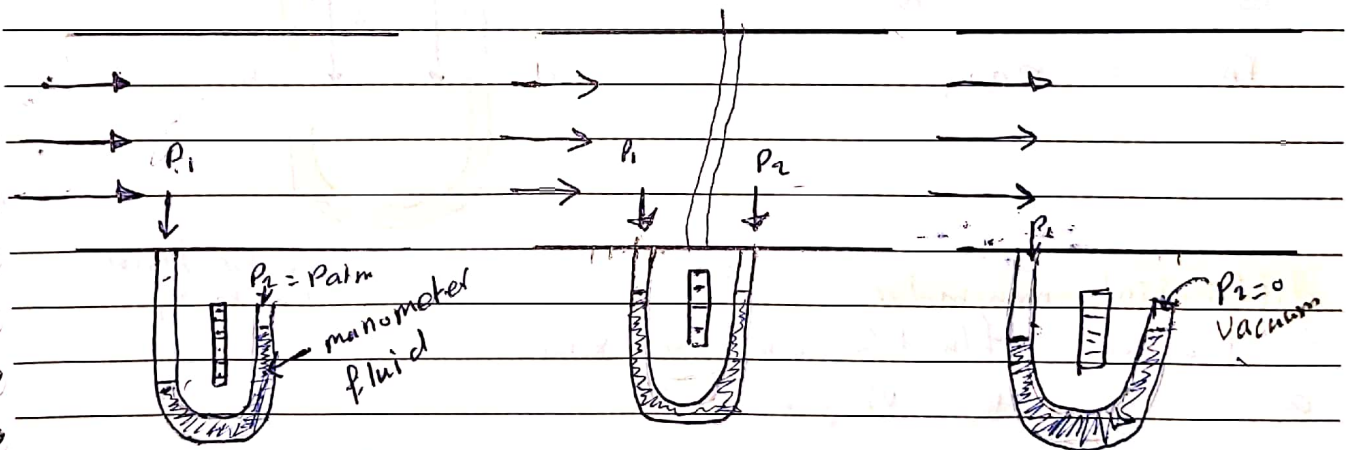


## Pressure Measurements

### Bourdon Gauge (gives a gauge pressure)

- A hollow tube closed @ one end and bent into a C configuration
- The open end of tube is exposed to the fluid whose pressure is to be measured.
- As the pressure increases, the tube tends to straighten causing a pointer attached to the tube to rotate.
- The position of the pointer on a calibrated dial gives the gauge pressure to the fluid.

### Manometer



(a) open end  
gives gauge pressure

گاہ بگاہ 2' الی 3' الی  
المنسوب الی

(b) differential

(c) sealed end  
Barometer

گاہ بگاہ 1' الی 2' الی  
المنسوب الی  
gives absolute pressure  
directly

Five Apple

adar  
ask :: believe & recieve



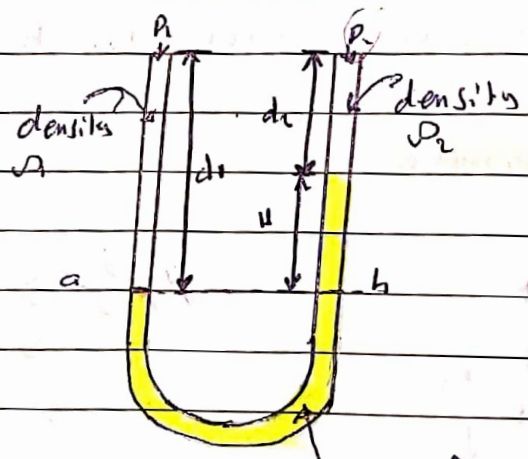
manometer is used for measurements of pressures below 3 atm

- U shaped tube partially filled with fluid of known density
- Both end of the tube are exposed to different pressure causing differences of the manometer fluid in both arms.
- The differences between pressures can be calculated from the difference between the fluid of each level arm (h)

#### General manometer equation

$$P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_p g h$$

$$P_A = P_B$$

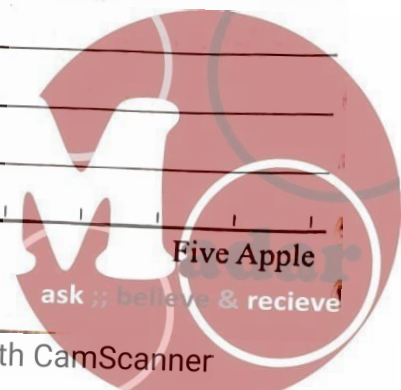


#### differential manometer

fluid 1 and fluid 2 are the same and consequently  $\rho_1 = \rho_2 = \rho$ .

So

$$\Delta P = P_1 - P_2 = (\rho_p - \rho) g h$$



• if the fluid process is gas

$$\rho \ll \rho_f$$

So  $p_1 - p_2 = \rho_f gH$  why?

کے ذریعہ کان ہوا اس سے اس طرح کی سی

الغہ کثرتاً حسب س.ف



الرقم كثيرًا حسب S.P.

## Chapter Four

### Fundamental of Material Balances

• in chemical engineering

The process is "a series of operations involving the physical and chemical or biological transformation of an input material for the purpose of achieving a desired product material"

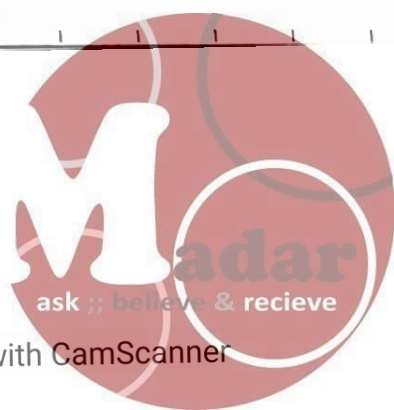
#### Types of Process

##### 1) Batch Process

All materials are added at the start of process

Then the process is allowed to proceed and the products are withdrawn after completion of process

\* في عملية الإنتاج يتم إدخال المواد الخام في وقت واحد في العملية  
والتحويل يتم في وقت لاحق بعد اكتمال العملية



## 2) Continuous process

There is continuous supply of feed and there is continuous withdrawal of products

\* Input / Output  
Reactor : Inputs :  $\rightarrow$  outputs

## 3) Semi-continuous (Semi-batch) process

There is a continuous supply of feed but the products withdrawn only at the end of the process.

\* Input / Output  
Reactor : Inputs :  $\rightarrow$  outputs  
In process :  $\rightarrow$  outputs  
Feed :  $\rightarrow$  outputs  
Outputs :  $\rightarrow$  outputs

\* Accumulation  $\Rightarrow$  التراكم

\* Accumulation  $\Rightarrow$  التراكم

\* Accumulation  $\Rightarrow$  التراكم





## \* System and Boundary

portion of a process which contains fluid or a mixture in question has a boundaries (physical boundary or imaginary (control volume))

## Examples

- System city :- which contain people, city boundaries
- System tank :- which contain water  $\Rightarrow$  tank boundary walls

- open system (Continuous process)  $\Rightarrow$  mass crosses system boundaries
- closed system (Batch process) mass crosses system boundaries.

## \* Balance equation

\* Balance on a (conserved quantity)  $\Rightarrow$  total mass, mass of a particular substance, momentum, energy in a system (single process unit, a collection of units, or an entire process) can be written as:

|                                                                                                   |                                                         |                                                                                                    |                                                     |                                                                                                |
|---------------------------------------------------------------------------------------------------|---------------------------------------------------------|----------------------------------------------------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------------------------------------------------|
| input<br>into<br>the<br>system<br>through<br>the boundaries<br>(surrounding $\Rightarrow$ system) | $\oplus$ generation<br>produced<br>within the<br>system | $-$ output<br>leaves the<br>system through<br>the boundaries<br>(system $\Rightarrow$ surrounding) | $-$ consumption<br>consumed<br>within<br>the system | $=$ Accumulation<br>(depletion)<br>build up or<br>depletion<br>within<br>system<br>boundaries. |
|---------------------------------------------------------------------------------------------------|---------------------------------------------------------|----------------------------------------------------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------------------------------------------------|

if a conserved quantity (total mass or non reactive substance) "inert" so generation = 0  
consumption = 0  $\Rightarrow$

\* depletion  $\Rightarrow$  نقصان المادة  $\leftarrow$

• if there no chemical rxn i.e (There is no means for a material to be consumed or generated) Then

$$\text{Consumption} = 0 \quad \text{generation} = 0$$

$$\boxed{\text{in} + \text{out} - \text{accumulation}}$$

أو

• if there is a (steady-state) conditions:-

1) Accumulation = 0

2) depletion material within system so

$$\boxed{\text{input} = \text{output}} \quad (\text{steady state with no chemical rxn})$$

**NO CHANGE WITH TIME**

\* **Steady-State**

All values of all variables (mass, chemical composition, temperature & pressure ...) in the process do not change with time. other wise it is unsteady-state or transient state process

$$\boxed{\frac{dx}{dt} = 0}$$

x = process variable

Accumulation or depletion = 0

$$\boxed{\text{input} + \text{generation} - \text{output} - \text{consumption} = 0}$$

أو  $\text{input} + \text{gen} - \text{output} - \text{cons} = 0$



## Types of Balances

### A) Differential Balances

indicates what is happening in a system at an instant of time

Each term of Balance equation is a rate (rate of input, rate of generation —) and has a unit that is a quantity unit divided by time i.e. people/year, song/s —

This type applied on continuous process

### B) Integral balances

indicates and describe what happens at two instant of time

Each term of Balance is an amount of the balanced quantity and has corresponding unit (people, song —)

This type applied on Batch process

with two instants of time being the moment after input takes place and the moment before the product is withdrawn

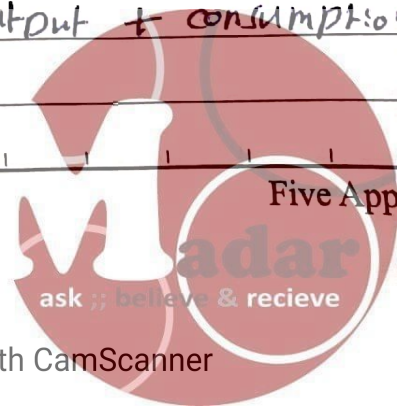
دالة التفاضل في العمليات المستمرة

دالة التكامل في العمليات الدفعية

- Differential Balance of steady state and continuous process  
[Input + generation = output + consumption]

Integral Balance of batch process

[Initial input + generation = final output + consumption]



### • Volume Balance :-

it should be converted to mass or moles before we do Balance on the Volume why?

because we can do it without conversion when  $P$  is constant and it is not gas — and there is a steady state

لا نحتاج تحويل في الحالة الثابتة

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{\text{mass}}{\text{mw}} RT$$

$$\text{So } P = \frac{P \cdot \text{mw}}{RT}$$

تقاس الضغط في الحالة الثابتة

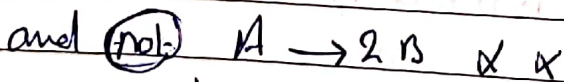
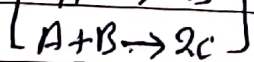
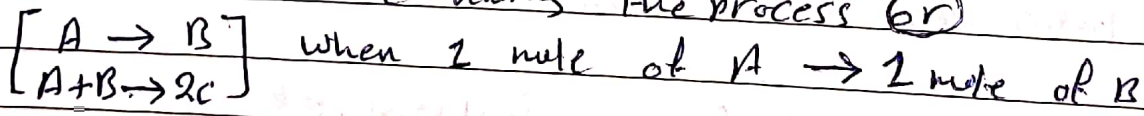
الضغط في الحالة الثابتة

Balance قبل إجراء الأجراء

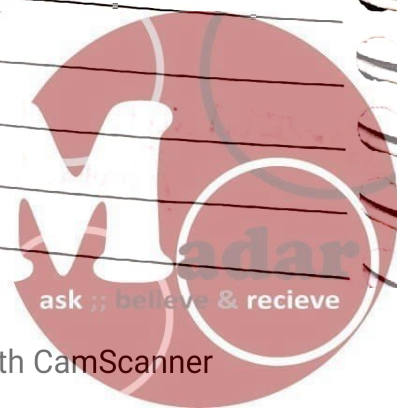
Note) total moles when input = output

when accumulation = 0 @ steady state

and no rxn occur during the process (or)

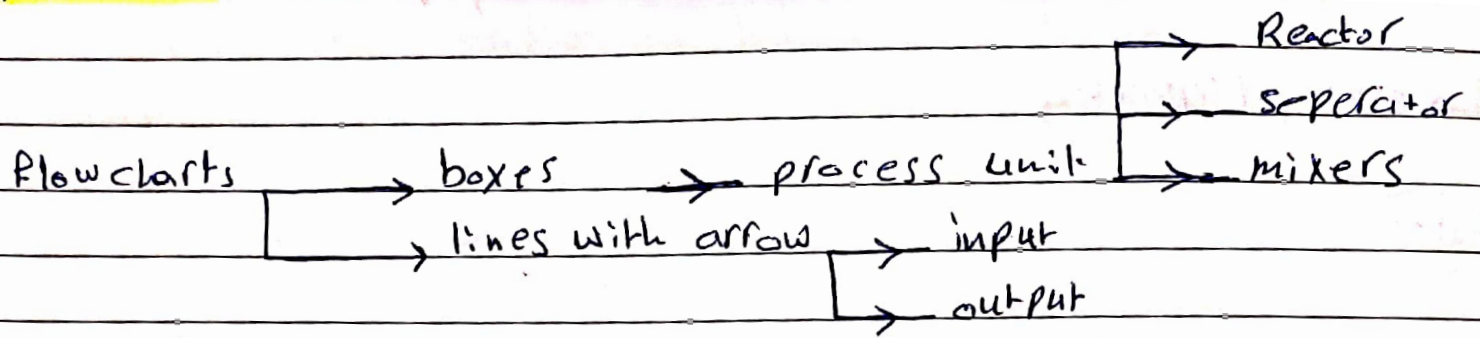


here input  $\neq$  output.





## Flowchart



Flow chart labeling

- values → For known process variables
- symbols → For unknown variables

## How to make flowchart:-

- 1) write the values and units of all known streams variables at the location of the stream on the chart.

$400 \text{ mol/h}$   
 $0.21 \text{ O}_2/\text{mol}$   
 $0.79 \text{ N}_2/\text{mol}$   
 $T = 360^\circ\text{C}, P = 1.4 \text{ atm}$

قوة المدخل 400 مول/ساعة  
0.21 أكسجين  
0.79 نيتروجين  
درجة الحرارة 360°س  
الضغط 1.4 atm

- 2) Assign algebraic symbols to unknown streams variables and write these variables name and their associated units on the charts

$n_i (\text{mol/h})$   
 $0.21 \text{ mol O}_2/\text{mol}$   
 $0.79 \text{ mol N}_2/\text{mol}$   
 $360^\circ\text{C}, P_i = 1.4 \text{ atm}$

or  $400 \text{ mol/hr}$   
 $y (\text{mol O}_2/\text{mol})$   
 $(1-y) (\text{mol N}_2/\text{mol})$   
 $360^\circ\text{C}, P_i = 1 \text{ atm}$

Five Apple

ask :: believe & recieve

## Solving Material balance for non reacting processes

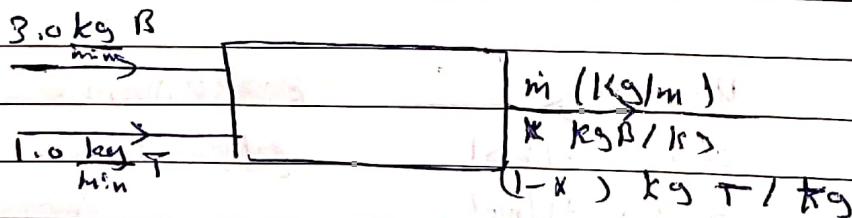
→ Mixing / Separating

### Rules

1. Maximum # of independent equations that can be derived by writing balances on a non reactive system = # of chemical species in the input and output streams.

المعادلات المستقلة التي يمكن اشتقاقها من موازنات الكتلة على نظام غير متفاعل = عدد الأنواع الكيميائية في التيارات الداخلة والخارجة

2. Write balances first that involve the fewest unknown variable/s





## Degree of freedom

used to determine whether you have enough information to solve a given problem.

to perform DOF Analysis:-

Draw and completely label flowchart

Count unknown variables on the chart (unknown)

Count No. of independent eq. relating them (indep. eq.)

Calculate DOF by  $= n_{\text{unknown}} - n_{\text{indep. eq.}}$

## How to find independent equations?

1) independent balance equations

2) Stoichiometric relation based on chemical ~~process~~ rxn

3) physical constraints on some variables ( $\sum y_i = 1$ ) e.g. (mole/mass frac)

4) process of specifications (degrees of freedom)

5) physical properties and law (density —)

6) energy balance equations  $\Rightarrow$  principles II

if  $DOF \Rightarrow d > 0$  المعلومات غير كافية

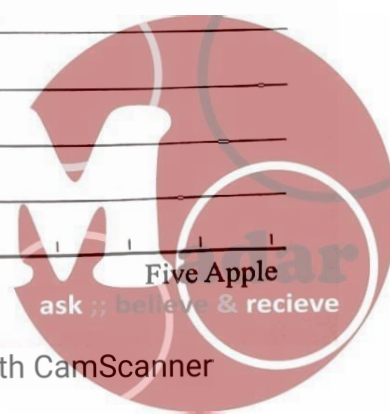
معلومات إضافية مطلوبة

البرهان يتخذ شكل

المعلومات كافية

يمكن حل النظام بسهولة

Flowchart كافي؟



## Balance of Multiple-unit process

⇒ System is any portion of a process that can be enclosed within a hypothetical box (boundary)

How to draw a boundary?

1) The entire process

2) an interconnected combination of some of the process unit

3) a single unit

4) a point at which two or more process streams come together or one stream split into branches

⇒ input and outputs to a system are the boundaries intersect the system boundary

## How to solve Multiple unit process

1) choose the basis of calculation an amount or flow rate of one of the process streams.

از اولا يك مقدار (flowchart) تعريف كنيد.

8.5 گرم بكونه موجود في السؤال و افترض ان "ا" عليه انتر مدد است



2) draw the flowchart

3) express what the problem statement asks you to determine in terms of labeled variables

4) if you are given mass mixed and mole units convert all in one unit (mass  $\leftrightarrow$  mole)

5) Do DOF Analysis

problem 4.28

How? unit 1

# unknowns  $\Rightarrow 2$

# species  $\Rightarrow 2$

# independent equations  $\Rightarrow 2 + 0 = 2$

# DOF =  $n_{\text{unknown}} - n_{\text{indp eq}} = 0$

# is there process specification or physical constraint?

For each unit  
DOF = 0

How? unit 2

# unknowns  $\Rightarrow 7$

# species  $\Rightarrow 3$

# Independent species  $\Rightarrow 3 + 1 = 4$

# is there process specifications or physical constraint ( $x + y + z = 1$ )

# DOF =  $n_{\text{unknown}} - n_{\text{indp eq}} = 7 - 4 = 3$



How? mixing point

# unknowns :- 5

# species :- 3

# independent equations ~~and (the number of) species (the number of) not~~

# physical constraint  $\downarrow$  3

# DoF = unknown - independent eq.  $5 - 3 = 2$

How? over all process

# unknowns = 4  $\Rightarrow$  why? ~~the number of~~  $\downarrow$

# species = 3

# physical = 1 ( $X + Y + Z = 1$ )

# Independent eq. = 4

# DoF = 0

How? unit 1 + mixing point

# unknowns. 3

# species. 3

# Independent eq. = 3

# physical constraint 0

# DoF = 0

How? unit 2 + mixing

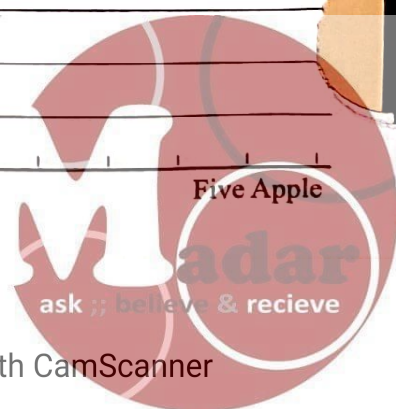
# unknowns. 6

# species. 3

# physical constraint - 1 ( $X + Y + Z = 1$ )

# independent eq. 4

# DoF:  $6 - 4 = 2$





6) Write equations and start with  $\boxed{DOF=0}$

## Stoichiometry



1) What information can we get from this equation?

→ A chemical eq. provides both qualitative and quantitative informations

2) What do you call the number that precedes each chemical formula?

Stoichiometric coefficient

3) How to interpret those numbers?

The stoichiometric coefficient may be interpreted as moles of molecular.

So the stoichiometric coefficient tell us the relationships (stoichiometric ratios) of the compounds participating the reaction

So from the eq. above

1 mol  $C_7H_{16}$  react with 11 mol  $O_2$

to yield

7 mol  $CO_2$  and 8 mol  $H_2O$



\* 1 mole =  $6.022 \times 10^{23}$  atoms or molecules.

\* Values of stoichiometric coefficient may be

Positive

or

Negative

↓

↓

Products

Reactants

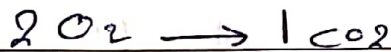


$$V_{\text{CH}_4} = -1, V_{\text{O}_2} = -2, V_{\text{CO}_2} = +1, V_{\text{H}_2\text{O}} = +2$$

Stoichiometric ratio between  $\text{O}_2$ ,  $\text{CO}_2$  =  $\frac{2 \text{ moles O}_2 \text{ consumed}}{1 \text{ mole CO}_2 \text{ produced}} = 2:1$

If we have 16 kg  $\text{CO}_2$  How many kg in  $\text{O}_2$

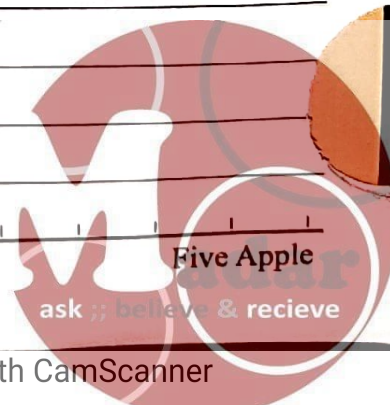
$$\text{First} \Rightarrow 16 \text{ kg} \cdot \frac{1 \text{ kmol}}{38.1 \text{ kg}} = 0.263 \text{ kmol} \Rightarrow 263 \text{ mole}$$



$$\text{So } n_{\text{O}_2} = 526 \text{ moles} \cdot 32 \text{ g} = 16832 \text{ g} \Rightarrow 16.8 \text{ kg}$$

~~32 g moles~~

16.8 kg



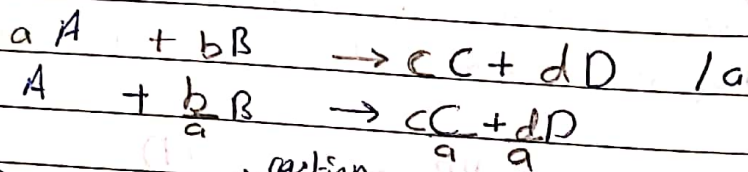




Fractional excess A =  $\frac{n(A)_{\text{feed}} - n(A)_{\text{stoich}}}{(nA)_{\text{stoich}}}$

فقدان المواد

Fractional conversion:  $P = \frac{\text{moles reacted}}{\text{moles fed}} = \frac{n_{\text{in}} - n_{\text{out}}}{n_{\text{in}}}$



المواد المتفاعلة  
\* L.R. لا يدخل

Reaction  
 $P_A = \frac{nA_0 - nA}{nA_0} \Rightarrow nA = nA_0(1 - P_A)$

Feed

We can calculate the amount of the rest (B, C, D)  
for example (C)

$n_C = n_{C_0} + \frac{c}{a} nA_0 P_A \Rightarrow \oplus$  because its product

$n_B = n_{B_0} - \frac{b}{a} nA_0 P_A$

\* The extent of the reaction (C, C')

The amount of moles that converted in a given rxn  
normalized to stoichiometric eq

$n_{\text{species out}} = n_{\text{species feed}} + \nu_i C$

Extent of rxn: number of moles reacted or the reactants  
that have stoichiometric coefficient = 1





## Chemical equilibrium

The final composition of the reaction mixture is determined by chemical thermodynamics.

and, The time needed for a system to reach specific state (start of equilibrium) is determined by chemical kinetics.

\* It depends on Temperature  $aA + bB \rightleftharpoons cC + dD$

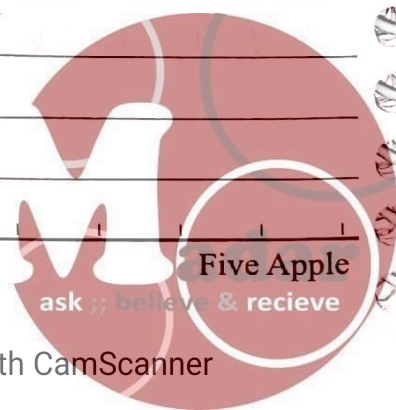
\* Equilibrium composition (K)  $K(T) = \frac{y_C y_D}{y_A y_B} = f(T)$

\* Yield =  $\frac{\text{moles of desired product formed}}{\text{moles at 100\% conversion with no side reaction}}$

\* Selectivity =  $\frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}}$

\* Extent of reaction for multiple reactions:-  
( $c_1, c_2, c_3$ )

$$n_i \pm n_{i0} + \sum \nu_i c_i$$



## \* Balances on Reactive Process

### \* Independent species

|                                       |  |                                            |
|---------------------------------------|--|--------------------------------------------|
| $n_1 (\text{mol O}_2/\text{s})$       |  | $n_3 (\text{O}_2)$                         |
| $7.76 n_1 (\text{N}_2)$               |  | $3.76 n_3 (\text{mole N}_2/\text{s})$      |
|                                       |  | $n_4 (\text{C}_2\text{H}_4)/\text{s}$      |
| $n_2 (\text{C}_2\text{H}_4/\text{s})$ |  | $n_5 (\text{mole C}_2\text{H}_4/\text{s})$ |

If two species have the same ratio we can do (one) ind equation

For example:

N and O we can't do two ind eq:

#### N Balance

$$3.76 n_1 = 3.76 n_3$$

$$n_1 = n_3$$

#### O<sub>2</sub> Balance!

$$2 n_1 = 2 n_3$$

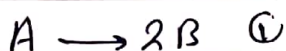
$$n_1 = n_3$$

The same we can do only one

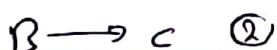
\* Chemical reactions are also independent equations:

For example:

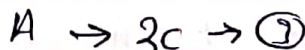
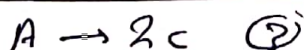
How many indp equations here?



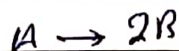
2, why??



if we substitute (B → C) in (1)



So there is two indp eq.



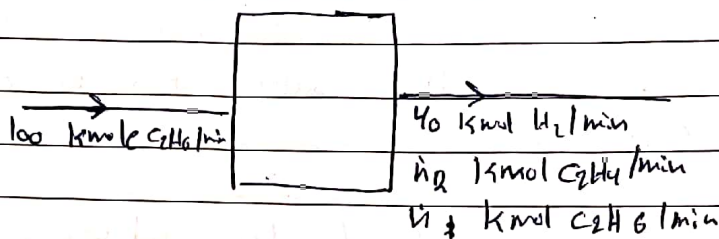


⇒ how to make balance on reactor system

\* Possible Balances

- 1) Mass balance  $\Rightarrow \dot{m}_{in} = \dot{m}_{out}$   $\alpha \alpha \alpha$
- 2) Molecular balance  $\Rightarrow C_2H_6, C_2H_4$  and  $H_2$  with consumption and generation
- 3) Atomic balance on C and H with  $\dot{m}_{in} = \dot{m}_{out}$

Example



1) Molecular balance:-

- A. 40 kmol/min  $H_2$  has been generated
- B.  $n_2$  kmol/min  $C_2H_4$  has been generated
- C. 100 - consumption  $C_2H_6 = \dot{n}_1$

~~100 - consumption~~

2) Atomic Balance:-

C - Balance:-

$$100 \times 2 = 2\dot{n}_2 + 2\dot{n}_1 \quad /2$$

$$100 = \dot{n}_2 + \dot{n}_1 \quad -$$

H - Balance:-

$$6 \times 100 = 2 \times 40 + 4 \times \dot{n}_2 + 6\dot{n}_1 \quad /2$$

$$300 = 40 + 2\dot{n}_2 + 3\dot{n}_1$$

$$\text{Then } \dot{n}_1 = 40 \text{ kmol} \quad \dot{n}_2 = 40 \text{ kmol}$$



## To Solve Material Balance by 2 methods:-

1) Molecular species Balance  $\Rightarrow$  مولی نوعی توازن  
ایک نوعی کے لیے

2) Atomic species Balances  $\Rightarrow$  ایٹمی توازن  
ایٹم کے لیے

3) extent of reaction  $\Rightarrow$  suits for 3 chemical reaction.

### 1) Molecular species Balance

General equation:-

$$\text{In} + \text{generation} = \text{out} + \text{consumption}$$

\* The DOF:

+ Unknown labeled variables

+ Indp chemical reaction

- Indp Molecular species balance

- other equation relating unknown variables

\* The degree of freedom

For previous example DOF

+ 2 \* generation  $H_2 = 40$

+ 1 \* generation of  $C_2H_4 = 40$  \* 1 = 40

- 3 \* consumption of  $C_2H_6 = 100 - \text{consump} = n_1$

- 0  $40 * 1 = 40$

$100 - 40 = n_1$

$60 = n_1$



## Atomic Balance

General equation

$$\text{Input} = \text{output}$$

\* DoP:

+ unknown labeled variables

+ Indp Atomic species balance

- molecular species on indp non reactive species

- other equations



0

## extract of reaction

General equation

$$n_i = n_{i0} + \nu_i C$$

# DoF  $\Rightarrow$  The same of molecular





## \* Recycle and purging

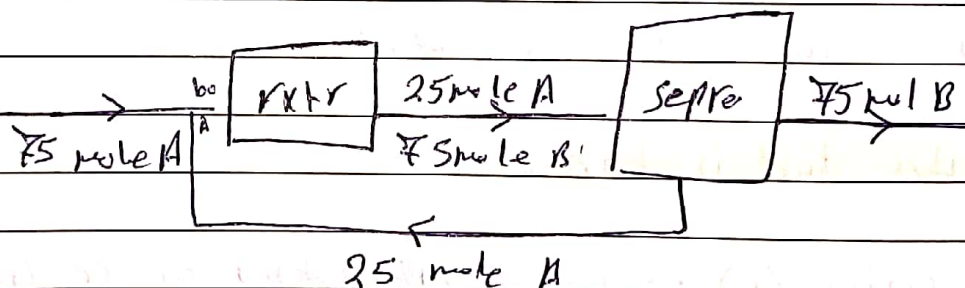
Product Separation and recycle we use them of unconsumed of reacted

$$\text{Overall conversion} = \frac{\text{reactant input} - \text{reactant output}}{\text{reactant input process}}$$

$$\text{Single pass conversion} = \frac{\text{reactant input to reactor} - \text{output from reactor}}{\text{reactant input to reactor}}$$

overall conversion > single pass conversion

why? because when we use the recycle we increase the overall conversion



$$\text{overall} = \frac{75 - 0}{75} \times 100\% = 100\%$$

$$\text{single pass} = \frac{75 - 25}{75} \times 100\% = 66.67\%$$

### \* Purging

We use it to decrease the amount of inert!!

Feed of inert = feed of inert in purge stream!  
(in fresh feed)

Stoichiometric ratio  
نسبة المول  
نسبة المول

### \* Combustion

→ rapid rxn of fuel and ox

common fuel

- 1) Solid e.g. coal
- 2) liquid e.g. gasoline, diesel oil, fuel oil
- 3) gaseous fuel e.g. natural gas

### \* When fuel is burned

Carbon (C)  $\Rightarrow$  CO<sub>2</sub> (complete comb) or CO (partial comb)

Hydrogen (H<sub>2</sub>)  $\Rightarrow$  H<sub>2</sub>O

Sulfur (S)  $\Rightarrow$  SO<sub>2</sub>

N forms  $\Rightarrow$  NO<sub>x</sub> above (1800°C)

\* Assume Air  $\Rightarrow$  0.79 N<sub>2</sub>, 0.21 O<sub>2</sub> (mole)

\* Stack gas, flue gas  $\Rightarrow$  mixture of



Wet basis  $\Rightarrow$  water will include in mole fraction

Dry basis  $\Rightarrow$  S will not

### \* Theoretical and excess Air

less expensive reactant commonly fed excess also, to make sure that  $\text{CO}_2$  is formed (complete combustion)

Theoretical  $\text{O}_2$  (stoichiometric amount)  $T_{\text{O}_2}$

$$\text{Theoretical air} = \frac{T_{\text{O}_2}}{0.21}$$

$$\text{Excess air} = \frac{\text{Feed} - \text{Theoretical}}{\text{Theoretical}} = \frac{\text{Air in} - \text{Stoichiometric}}{\text{Stoichiometric}}$$

### \* Material Balance for on combustion of rxn

1. Draw flow chart and label the outlet stream

A. unreacted fuel

b. unreacted  $\text{O}_2$

c. water and  $\text{CO}_2$  (and  $\text{CO}$  if combustion is incomplete)

d.  $\text{N}_2$  (if air is used instead of pure  $\text{O}_2$ )

2. calculate  $\text{O}_2$  feed from the specified excess air

3. in Multiple rxn, do Atomic balance instead of the rest because it is more simple than the other.



## Chapter (5) Single phase systems

### 5.1 liquid and densities

density  $\Rightarrow \frac{\text{mass}}{\text{Volume}}$

For solid and liquid the pressure doesn't cause a change  
So they are incompressible

To calculate density of mixture,

$$\left[ \frac{1}{\bar{\rho}} = \sum \frac{x_i}{\rho_i} \right] \quad \text{Mass Fraction}$$

This is used for ideal mixtures (Now for them are Almost equal)

Example: propane and butane

Also,  $\bar{\rho} = \sum x_i \rho_i$  No general rule



## Ideal gas

gases are strongly affected by temperature and pressure.

(\*) An equation of state relates the molar quantity and volume of gas to temperature and pressure.

The equation of ideal gas state :-

$$PV = nRT, \quad P = \frac{nRT}{V}$$

↳ condition that must be in the gas to be an ideal ones.

- 1) have a low amount of pressure (below 5 atm)
- 2) high temperature (above  $0^\circ\text{C}$ )

STP  $\Rightarrow$  1 mol of an ideal gas @  $0^\circ\text{C}$  and 1 atm.

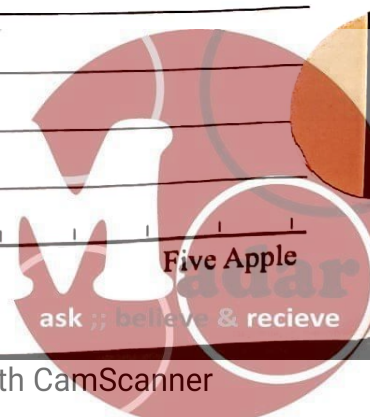
occupies 22.415 L

$$R \Rightarrow 8.314 \text{ J/mol}\cdot\text{K} = 0.082 \text{ L}\cdot\text{atm/mol}\cdot\text{K} = 10.73 \text{ ft}^3\cdot\text{psi/lb-mol}\cdot\text{R}^\circ$$

pressure  $\Rightarrow$  abs //  $T \Rightarrow$  Kelvin (or) Rankine.

## Standard temperature & pressure

$$\frac{PV}{P_S V_S} = n \cdot \frac{T}{T_S} \Rightarrow P_S = 1 \text{ atm}, \quad V_S = 22.415$$
$$T_S = 273 \text{ K}$$



For natural gas, usually described by:-

Volumetric flow rate of 20 SCFM = 20 ft<sup>3</sup>/min at 0° and 1 atm (STP)

$$20 \text{ SCFM} = 20 \text{ m}^3/\text{min} @ 0^\circ \text{ and } 1 \text{ atm}$$

• Partial pressure of A ( $p_A$ ) :- The pressure that would exerted by ( $n_A$ ) moles of (A) alone in the SAME total volume  $V$  at the same temperature.

• Dalton's law  $\Rightarrow p_A = y_A P$

$$P_{\text{Total}} = p_A + p_B + p_C + \dots = (y_A + y_B + y_C + \dots) P$$

• pure component volume of A ( $V_A$ )

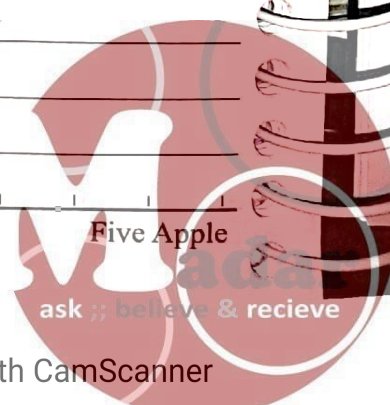
$$V_{\text{Total}} = V_A + V_B + V_C + \dots$$

and

$$\left[ \frac{V_A}{V_{\text{Total}}} = \frac{n_A}{n_{\text{Total}}} = y_A \right] \quad \underline{\underline{\text{Eq. 1}}}$$

Amagat's law

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2} \quad @ \text{ Constant } (n)$$





## equations of state for nonideal gases

• More complex, but more accurate for single species.

1) Virial eq      2) Van der Waals eq      3) Soave Redlich Kwong eq

\* critical temperature and pressure.

@ 100°C for water it is on equilibrium (two phases co-exist: vapor and liquid) at 1 atm.

@  $T_c$  and  $p_c$  there is no liquid of species!! (can't be liquidized)

$p_u = p_l$  There is no way to condense.

### • Vapor vs gas

Vapor below  $(T_c, p_c)$  gas above  $(T_c, p_c)$

↳ you can't condense vapor but gas not

• Super critical fluids  $\Rightarrow$  ~~transformation~~ the substance for liquid is above their  $T_c, p_c$

### • Virial equations

$\left[ \frac{p\hat{V}}{RT} = 1 + B \right] \Rightarrow$  We can't use it for polar compounds.  
Such as water.

The procedure to estimate  $\hat{V}$  or  $p$

1) look up for  $T_c, p_c$  of species

2) look up for Pitzer factor ( $w$ ) as it is the parameter reflects the geometry and polarity of molecules

(5.3.1)

3) Calculate reduced temperature ( $T_r$ )

$$T_r = \frac{T}{T_c}$$

4) Estimate ( $B$ ) by  $\Rightarrow$

$$B = \frac{R T_c}{P_c} (B_0 + W B_1)$$

to find  $B_0$  and  $B_1$ :

$$B_0 = 0.083 - \frac{0.422}{(T_r)^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

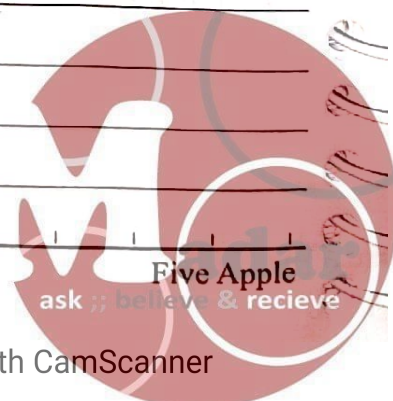
5) Then substitute  $B$  value in  $\frac{P\hat{V}}{RT} = 1 + B$

if we want to calculate ( $P$ ) then the solution is straight forward

(but, if  $\hat{V}$  is to be determined the eq can be rearranged into quadratic and there is two solutions!!

$\hookrightarrow$  if the 1st solution is negative and the other is positive. of course we'll choose the positive

$\hookrightarrow$  if the both of them is positive we have to estimate  $\hat{V}$  from ideal gas eq, the closest value to it we'll choose it..





## Cubic Equations of State

Vander Waals eq.:-

$$p = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \quad \text{where } \frac{a}{\hat{V}^2} \text{ accounts for attractive}$$

molecules force between each other

and  $b$  is correction accounting for volume occupied by the molecules themselves.

$$\text{to find } a: \quad a = \frac{27 R^2 T_c^2}{64 P_c}$$

$$b = \frac{RT_c}{8 P_c}$$

Soave Redlich Kwong (SRK) eq.:-

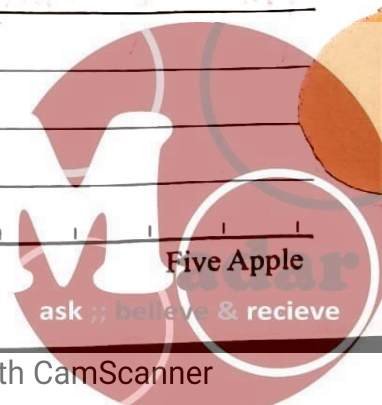
$$p = \frac{RT}{\hat{V} - b} + \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$

$$a = 0.42747 \frac{(R T_c)^2}{P_c}$$

$$b = 0.08664 \frac{R T_c}{P_c}$$

$$\alpha = \left[ 1 + m \left( \sqrt{1 - \sqrt{T_c}} \right)^2 \right]$$

$$m = 0.48508 + 1.55171 \omega - 0.1561 \omega^2$$



## • The compressibility factor ( $z$ )

$z = \frac{p\hat{V}}{RT}$  in ideal gas is equal to 1

to find  $z$  we have to calculate  $T_r, p_r, V_r^{\text{ideal}}$

$$T_r = \frac{T}{T_c} \quad / \quad p_r = \frac{p}{p_c} \quad / \quad V_r^{\text{ideal}} = \frac{p_c \hat{V}}{R T_c}$$

→ if the gas is  $H_2, He$  we have to calculate  $T_c, p_c$  by:

$$T_c^a = T_c + 8K$$

$$p_c^a = p_c + 8 \text{ atm}$$

$$V = \frac{z n R T}{P}$$

\* Pressure and temp must be absolute.

## • non ideal mixtures

Mixture's rule == Kay's rule

- pseudocritical temperature  $T'_c = \sum y_i T_{c,i}$
- pressure  $p'_c = \sum y_i p_{c,i}$

then  $T'_r = \frac{T}{T'_c} \quad / \quad p'_r = \frac{p}{p'_c}$

$$\left[ \hat{V} = \frac{z_{\text{mixture}} R T}{P} \right]$$

$$\left[ \dot{m} = \frac{\dot{V}}{v} \cdot m_{\text{MW}} \right]$$



## Chapter 6

### Multiple Systems

- Materials is transformed into one phase into another

All phases operations

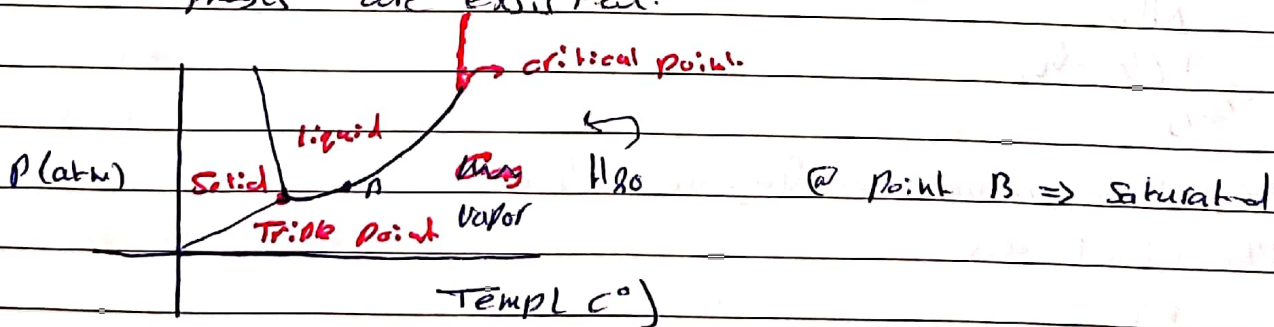
- Freezing  $\rightarrow$  Solid
- Melting
- Evaporating
- Condensation

Most separation and purification

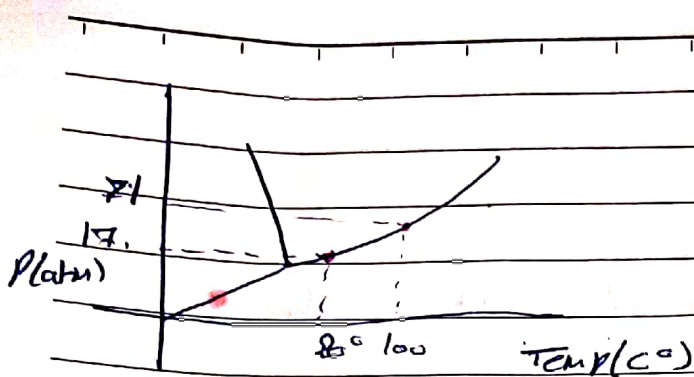
- Leaching
- Absorption / scrubbing
- Distillation
- Liquid extraction
- Adsorption
- Crystallization

### Single phase

- At certain temperature and pressures two and even three phases are existed.



After critical point  $\Rightarrow$  Gas can't be liquid.



Water  $\Rightarrow$  vapor pressure @ b.p. =  $20^\circ\text{C}$

Normal b.p.  $\Rightarrow$  atm @  $100^\circ\text{C}$

Sublimation point (S  $\rightarrow$  Vapor)

### estimation of vapor pressures

Volatility  $\Rightarrow$  of a species is the degree @ which the species tends to transfer from liquid or solid to the vapor state

Vapor pressure  $\uparrow$  Volatility  $\uparrow$

### clapeyron eq

$\rightarrow$  energy need to vaporize one unit of certain species

$$\frac{dp^*}{dt} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)}$$

$\Delta \hat{H}_v$

(EPP)

in very high pressure  $\Rightarrow \hat{V}_g - \hat{V}_l = \hat{V}_g$

by apply ideal gas

$$\hat{V}_g = \frac{RT}{p^*}$$

$$\text{So } \boxed{\frac{d(\ln p^*)}{d(\frac{1}{T})} = - \frac{\Delta \hat{H}_v}{R}}$$



$$B = \ln p_i - \frac{a}{T}$$

Kelvin

$$a = \frac{\ln(p_2^*/p_1^*)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

Clausius-Clapeyron eq  $\Rightarrow$

$$\ln(p^*) = \frac{a}{T} + b$$

$$\ln(p^*) = \frac{-\Delta H_v}{RT} + B$$

$\rightarrow$  B is a constant that varies from one substance to another.

Antoine eq.

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

$T$  in  $^{\circ}\text{C}$   
 $p^*$  (mmHg)

Cox chart

$p^* \Rightarrow p^{\text{Si}}$   
 $T(^{\circ}\text{C}) \Rightarrow P$

The Gibbs phase rule

to reach to equilibrium the species become change

@ equilibrium

|   |   |
|---|---|
| A | B |
| C |   |
| A | C |
| B | C |

- 1) Temp and pressure of both phases are the same
- 2) The composition of each phase no longer change with time

So, to describe the system

- 1) The system temperature and pressure
- 2) The masses of each phase
- 3) Two mass or mole fraction for each phase

intensive variables

independent to  
size of system

temp, pressure, density  
specific volume, mass  
and mole fractions

Extensive variables

dependent to  
size of system

total mass and molar  
flow rate, number of  
moles, volume  
and volumetric flow  
rate

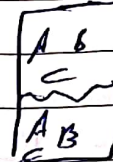
## The Gibbs rule

The number of intensive variables that can be specified independently for a system @ equilibrium is called the DoF of system

→ number of chemical species

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

↙ number of phases



DoF for this system

$$\pi = 2$$

$$DoF = 2 + 9 - 2$$

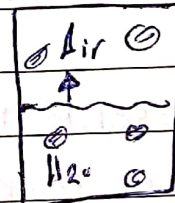
$$C = 3$$

$$DoF = +8$$

→ Temp, pressure, mole fraction, etc.

## Gas-liquid Systems: one condensable component

\* if a gas contains  $T, P$  contains a saturated vapor ( $H_2O$ ) whose mole fraction ( $y_i$ ) (mol/vapor / mol total gas) and if the vapor is the only species that would condense if the temperature were slightly lowered



$$T = 75^\circ C$$

$$P = 760 \text{ mmHg}$$

then  $P_i^*(T) = y_i P_{\text{total}}$

→ Raoult's law single condensable species



• A gas in equilibrium with liquid must be saturated with volatile components of that liquid

• if  $p_i = p_i^*$  the vapor is saturated if we increase  $p_i$  by adding more vapor to the gas phase (or) by increasing the  $P_t$  @ constant temperature must lead to condensation.

• A Vapor present in a gas in less than saturation amount is referred to as a superheated vapor (e.g. dry steam)

$$p_i = y_i P < p_i^*(T)$$

• to Achieve condensation in a system containing superheated vapor

• dew point ( $T_{dp}$ )  $\Rightarrow$  when  $p_i^*(T_{dp}) = y_i P$

$\hookrightarrow$  if a gas containing single condensible superheated vapor is cooled at constant pressure, the temperature at which vapor becomes saturated

of the gas

• degrees of super heat is the difference between temperature and the dew point

So using Raoult's law

and eq, graph to find  $p_i^*$  @ certain T

We can find  $y_i, p_i^*, T$

## Quantities commonly used to describe a gas containing condensable vapor

"Saturation"  $\leftrightarrow$  any gas + combination<sup>vapor</sup>

"humidity"  $\leftrightarrow$  air + water system

$\rightarrow$  if gas  $\Rightarrow$  air      vapor  $\Rightarrow$  water

$$p_i = y_i + p_{i,sat}$$

\* Relative Saturation (humidity) =  $SR(Air) = \frac{p_i}{p_i^*} \times 100\%$

$\rightarrow$  For system

\* Molal Saturation (humidity)  $\phi = \frac{p_i}{p_{tot} - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry gas)}}$

\* Absolute Saturation  $Sa(ha) = \frac{p_i M_i}{(p - p_i) M_{dry}}$        $M \Rightarrow \text{mass}$

\* Percentage Saturation  $SP = \frac{S_m}{S_m^*} = \frac{(p_i)/(p - p_i)}{p_i^*/(p - p_i^*)} \times 100\%$



## Multi Component Gas-liquid Systems

→ mole fraction in liquid phase

$$P_{\text{Henry's law}} = y_A P = P_A = x_A H_A(T)$$

↳ Henry's law constant.  
For a specific solvent

when the liquid is almost pure A:  $x_A \rightarrow 1$

Raoult's law is applied

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

$$x_A = 1$$

and mole fraction for similar components (Almost same m.w.)

and Henry's law

is used which  $x_A$  is close to zero (diluted solution of A)

provided that A does not

1) dissociate

2) Ionize

3) react in liquid phase

and it is applied for non condensible gases, such as ( $O_2$ )

• if we can apply Raoult's law or Henry's law 'Ideal sol'  
@ equilibrium.

$$P_A = y_A P = x_A P_A^*(T_A)$$

\* in multicomponent we call B.P  $\Rightarrow$  Bubble point temp

\* dew-point temp  $\Rightarrow$  Vapour point temp

(Vapour point temp)

to calculate dew point, Bubble point @ equilibrium

$$p_i = x_i p_i^*(T_{bp})$$

$$P = x_A p_A^*(T_{bp})_A + x_B p_B^*(T_{bp})_B \text{ ---}$$

↳ Bubble point pressure

dew point

$$P_{dp} =$$

$$\frac{y_A}{p_A^*(T)} + \frac{y_B}{p_B^*(T)} + \frac{y_C}{p_C^*(T)} \text{ ---}$$

$$x_i = \frac{y_i P}{p_i^*(T_{dp})} \quad i = A, B, C \text{ ---}$$