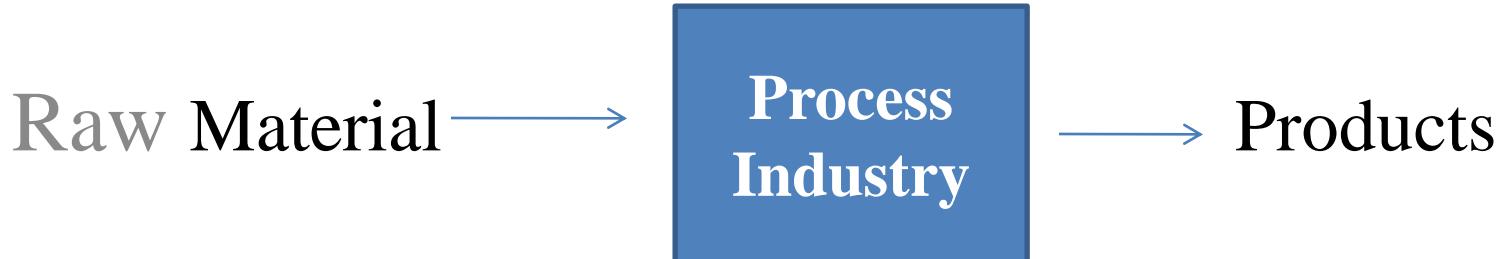


# Material and Energy Balances

# Books

1. Basic Principles and Calculations in Chemical Engineering: David M. Himmelblau, James B. Riggs; PHI Learning Pvt. Ltd.
  2. Elementary Principles of Chemical Processes: Richard M. Felder, Ronald W. Rousseau; Third Ed., John Wiley & Sons Inc.
- Stoichiometry: B.I. Bhatt, S. M. Vora; 4<sup>th</sup> Ed.; Tata McGraw-Hill Publishing Company Ltd.



- Crude oil to gasoline, petrol, diesel, kerosene etc. (Middle Distillates), Lubricants
- Wood to paper (Pulp & Paper)
- Salt to  $\text{Cl}_2$
- Sulphur to  $\text{H}_2\text{SO}_4$  (DCDA Process)
- Textile, Fertilizer, Cement, Metallurgical
- Pharmaceutical, Food, Chlor Alkali, Speciality Chemicals
- Role of Chemical Engineers: design, operation, control, trouble shooting, research (products, processes), process intensification
- Solution to the problems about the amount of raw materials, products, energy requirements

# Units and Dimensions

- ‘Take care of your units and they will take care of you’
- Check the consistency of units in solving the equations
- Physical quantity : product of number (value) and unit- 5 kilogram, 10 meter, 30 seconds
- Dimension: Concept of measurement such as length, time, temperature, mass;

# Units and Dimensions

- Fundamental (dimension/unit): that can be measured independently; Length (L), Mass (M), Time, Temperature.
- Derived Dimension: property that can be measured or obtained by multiplying or dividing other dimensions e.g. velocity = length/time; volume = length x length x length; density = mass/ (length x length x length), Force, Pressure, Energy
- Unit: means of expressing the dimensions; feet or cm. for length, second or hour for time

# Units and Dimensions (contd.)

- ✓ Fundamental quantities represented by a system of units.
- ✓ Systems of units: fps, mks, SI.

- fps: Based on foot, pound and second as standard measurement for length, mass and time respectively.
- mks: Developed in France (1791). Introduced in India in 1957.
- CGS system( subsidiary system): Derived from mks system.
- SI: international system of units, meter, kilogram, Second, Ampere (electric current), Kelvin, Candela (luminous intensity)
- Two supplementary units: Radians & Steradians
- 1971: Mole was introduced.

# Fundamental quantity

	SI	Metric	fps`
Length	Meter	Meter	Foot
Mass	Kilogram	Kilogram	Pound
Temperature	Kelvin	Celsius	Fahrenheit
Electric current	Ampere	Ampere	Ampere
Amount of substance	Mole		
Luminous intensity	Candela		
Time	Second	Second	Second

$$\text{Degree Kelvin (K)} = {}^{\circ}\text{C} + 273.15$$
$$\text{Degree Rankin (}{}^{\circ}\text{R)} = {}^{\circ}\text{F} + 459.67$$

Derived SI units : unit which is derived from basic or supplementary units or both.

Quantity	Symbol	Unit	Symbol of unit	Equivalence
Force	F	Newton	N	$\text{kg m/s}^2, \text{J/m}$
Energy	E	Joule	J	$\text{kg m}^2/\text{s}^2, \text{Nm}$
Power	P	Watt	W	$\text{kg m}^2/\text{s}^3, \text{J/s}$
Pressure	P	Pascal	Pa	$\text{N/m}^2, \text{Pa}$
Quantity of heat	Q	Joule	J	Nm
Work	W	Joule	J	Nm

## ■ Conversion factors

Conversion of a quantity (any number & its physical quantity) from one set of units to another- multiply by the conversion factor

$$(55 \text{ g}) \times (1\text{kg}/1000 \text{ g}) = 0.055 \text{ kg}$$

## ■ Units of time

60 sec/min, 60 min/hr, 3600 sec /hr

## ■ Units of length

2.54 cm/ in, 100 cm/m, 1000 mm/m, 12 in/ft,  
 $10^6 \mu\text{m}$ (micron),  $10^{10} \text{ A/m}$  (Angstrom)

## ■ Units of mass

454 gm/ lb, 1000 gm/ kg

# Exercise

- The speed of the bullet train is 90 miles/h.  
What is its speed in ft/s.
- Convert  $10 \text{ cm}^3/\text{min}$  to  $\text{in}^3/\text{day}$ .
- Convert  $100 \text{ km/day}^2$  to  $\text{cm/s}^2$ .

1. The speed of bullet train is 90 miles/h. What is its speed in ft/s.

$$1 \text{ mile} = 5280 \text{ ft}$$

$$\frac{90 \text{ miles}}{\text{h}} \left| \begin{array}{c} 5280 \text{ ft} \\ \hline 1 \text{ mile} \end{array} \right| \frac{1 \text{ h}}{3600 \text{ s}} = 132 \frac{\text{ft}}{\text{s}}$$

$$\frac{\text{m}}{\text{h}} \quad \frac{\text{ft}}{\text{h}}$$

$$1 \text{ mile} = 1.61 \text{ km}$$

$$\frac{90 \text{ miles}}{\text{h}} \left| \begin{array}{c} 1.61 \text{ km} \\ \hline 1 \text{ mile} \end{array} \right| \frac{10^3 \text{ m}}{1 \text{ km}} \left| \begin{array}{c} 10^2 \text{ cm} \\ \hline 1 \text{ m} \end{array} \right| \frac{1 \text{ in}}{2.54 \text{ cm}} \left| \begin{array}{c} 1 \text{ ft} \\ \hline 12 \text{ in} \end{array} \right| \frac{1 \text{ h}}{3600 \text{ s}}$$

$$\frac{\text{miles}}{\text{h}} \quad \frac{\text{km}}{\text{h}} \quad \frac{\text{m}}{\text{h}} \quad \frac{\text{cm}}{\text{h}} \quad \frac{\text{in}}{\text{h}} \quad \frac{\text{ft}}{\text{h}}$$

$$= 132.05 \frac{\text{ft}}{\text{s}}$$

2.  $10 \text{ cm}^3/\text{min}$  to  $\text{in}^3/\text{day}$

$$\frac{10 \frac{\text{cm}^3}{\text{min}}}{\text{min}} \left| \begin{array}{c} (1 \text{ in})^3 \\ 2.54 \text{ cm} \end{array} \right| \frac{1440 \text{ min}}{1 \text{ day}} = 878.74 \frac{\text{in}^3}{\text{day}}$$

Ans.

2

3.  $100 \frac{\text{km}}{\text{day}^2}$  to  $\text{cm}/\text{s}^2$

$$\begin{aligned}
 & 100 \frac{\text{km}}{\text{day}^2} \left| \frac{10 \text{ cm}}{1 \text{ km}} \right| \left( \frac{1 \text{ day}}{24 \text{ hr}} \right)^2 \left| \left( \frac{1 \text{ hr}}{3600 \text{ s}} \right)^2 \right. \\
 & = 1.34 \times 10^{-3} \frac{\text{cm}}{\text{s}^2}
 \end{aligned}$$

# SI Prefixes

$10^9$	giga	G	$10^{12}$	tera	T
$10^6$	mega	M	$10^{15}$	peta	P
$10^3$	kilo	k	$10^{18}$	exa	E
$10^2$	hecto	h	$10^{21}$	zetta	Z
$10^1$	deka	da	$10^{24}$	yotta	Y
$10^{-1}$	deci	d	$10^{-12}$	pico	p
$10^{-2}$	centi	c	$10^{-15}$	femto	f
$10^{-3}$	milli	m	$10^{-18}$	atto	a
$10^{-6}$	micro	$\mu$	$10^{-21}$	zepto	z
$10^{-9}$	nano	n	$10^{-24}$	yocto	y

Numerical quantities can be added, subtracted or equated only if the units of the quantities are same.

**Dimensional consistency** : equations must be dimensionally consistent. Each term in an equation must have the same dimensions and units as every other term to which it is added or subtracted or equated.

$$(P + a/V^2) (V - b) = RT$$

- ❖ Unit symbols do not change in plural.
- ❖ Unit symbols are not followed by a full stop except at the end of sentence.
- ❖ Compound prefixes formed by juxtaposition of two or more SI prefixes are not to be used.
- ❖ A prefix should never be used alone.
- ❖ SI prefix not to be used with  ${}^0\text{C}$
- ❖ If magnitude of a number is less than unity the decimal sign should preferably be proceeded by zero.

- Pound mass and Pound force

- Newton's Law

Force = (Const.)( mass). (acceleration)

- SI system of units: unit of force is Newton

Newton is the force which when applied to a body having a mass of one kg gives it an acceleration of 1 meter per second per second.

$$1 \text{ Newton (N)} = 1 \text{ kg. m/s}^2$$

The force in Newton required to accelerate a mass of 10 kg at a rate of 5 m/s<sup>2</sup>

$$F = 10 \text{ kg. } 5 \text{ m/s}^2. 1 \text{ N } / (1 \text{ kg.m/s}^2) = 50 \text{ N}$$

AE system of units: numerical value of force and mass be same at earth surface; Pound force (lbf)- product of a unit mass ( 1 lbm) and the acceleration of gravity at sea level and  $45^0$  latitude,  $32.174 \text{ ft/s}^2$

$g_c$  is a conversion factor;  
 $32.174 \text{ (ft. lbm)/(lbf.s}^2\text{)}$

$$1 \text{ kg}_f = 9.81 \text{ N}, 1 \text{ lb}_f = 32.174 \text{ poundals}$$

The force required to accelerate a mass of 10 lbm at  $5 \text{ ft/s}^2$

$$F = 10 \text{ lbm. } (5 \text{ ft/s}^2). \{ \text{lbf.s}^2 / (32.174 \text{ lbm. ft}) \} = 1.55 \text{ lbf}$$

Two quantities  $g$  &  $g_c$  are not the same. The numerical value of a pound mass is also that of a pound force if the numerical value of the ratio  $g/g_c$  is equal to unity.

**Ex.** Sixty pounds of water is flowing through a pipe at the rate of 5 ft/s. What is the kinetic energy of this water in (ft)(lb<sub>f</sub>)

**Ex.** What is the potential energy in (ft)(lb<sub>f</sub>) of a 10 lb drum hanging 100 ft above the surface of the earth.

**Ex.** The density of water is 62.4 lbm/ft<sup>3</sup>. What is the weight of 10 ft<sup>3</sup> of water at sea level.

E<sub>x</sub>.

$$\text{Flow Rate} = 5 \text{ ft/s}$$

$$\text{Mass} = 60 \text{ lbm}$$

$$K.E. = \frac{1}{2} \cdot m \cdot v^2$$

$$= \frac{1}{2} \cdot 60 \text{ lbm} \cdot \left(5 \frac{\text{ft}}{\text{s}}\right)^2 \cdot \frac{(\text{lbf})(\text{s}^2)}{32.174(\text{ft})(\text{lbf})}$$

$$= 2138 \text{ ft-lbf}$$

Ex -

$$\text{Mass} = 10 \text{ lb}$$

$$\text{height} = 100 \text{ ft.}$$

$$\text{P.E.} = m \cdot g \cdot h.$$

$$= (10 \text{ lbm}) \cdot (32.174 \frac{\text{ft}}{\text{s}^2}) (100 \text{ ft}) \cdot \frac{1 \text{ lb}}{32.174 \text{ lb}}$$

$$= 1000 (\text{lbf})(\text{ft})$$

Ex.

$$\text{Mass of water} = \left( 62.4 \frac{\text{lbm}}{\text{ft}^3} \right) (10 \text{ ft}^3)$$

$$= 624 \text{ lbm}$$

Weight of water

$$W = (624 \text{ lbm}) g \left( \frac{\text{ft}}{\text{s}^2} \right) \left( \frac{1}{32.174} \frac{\text{lbf}}{\text{lbm}} \right)$$

$$= 624 \text{ lbf}$$

Weight of an object is the force

exerted on the object by gravitational attraction

Suppose that an object of mass  $m$  is subjected to a gravitational force  $W$  ( $W$  by definition is the weight of the object) and if this object were falling freely its acceleration would be  $g$

$$(W = mg)$$

- Mole : the amount of substance that contains as many elementary entities as there are atoms in 0.012 kg of  $^{12}\text{C}$ .
- In SI, mole is composed of  $6.02 \times 10^{23}$  molecules
- Pound mole (lb mole  $6.02 \times 10^{23} \times 453.6$  molecules)
- kilo mole, kmole, kg mol, 1000 moles
- To convert number of moles to mass
- gmol = mass in g / molecular weight
- lb mol = mass in lb / molecular weight

- Density: ratio of mass per unit volume; Specific volume is the inverse of density (volume/mass)
- Specific Gravity: Ratio of two densities- that of the substance of interest A, to that of a reference substance.

$$sp.gr = \frac{\left(\frac{lb}{ft^3}\right)_A}{\left(\frac{lb}{ft^3}\right)_{ref}} = \frac{\left(\frac{g}{cm^3}\right)_A}{\left(\frac{g}{cm^3}\right)_{ref}} = \frac{\left(\frac{kg}{m^3}\right)_A}{\left(\frac{kg}{m^3}\right)_{ref}}$$

- The reference substance for liquids and solids is normally water. Gases frequently referred to air as reference . State the temperature at which each density is chosen.

$$sp.gr = 0.5 (20^0/4^0)$$

- In case temperature for which sp. gravity is stated are unknown, assume ambient temp for the substance and 4°C for water respectively.

Petroleum industry

API Gravity

- Mole fraction and Mass (weight) Fraction

$$\text{mole fraction of } A = \frac{\text{moles of } A}{\text{total moles}}$$

$$\text{mass(weight) fraction of } A = \frac{\text{mass (weight) of } A}{\text{total mass (weight)}}$$

# Exercise

- A mixture of gases has the following composition by mass:

CO                    2 %

CO<sub>2</sub>                14 %

N<sub>2</sub>                70 %

O<sub>2</sub>                14 %

Determine the molar composition of the mixture of gases.

# Exercise-Calculation of Average Molecular Weight

- Calculate the average atomic weight of air assuming its molar composition of 79 % nitrogen and 21 % oxygen.
- Air contains small amounts of carbon dioxide, argon and other gases which have been neglected.

# Exercise

- Calculate the average molecular weight of air from its approximate mass composition of 76.7% nitrogen and 23.3% oxygen.

# Concentration

- Concentration: refers to the quantity of substance per unit volume
- Mass per unit volume ( $\text{kg of solute}/\text{m}^3$ )
- Moles per unit volume ( $\text{gmol of solute}/\text{L}$ )
- ppm, ppb: concentration of extremely dilute solutions; mass (weight) fraction for solids and liquids; mole fraction for gases

# Temperature

- Relative scale: degrees Fahrenheit ( $^{\circ}\text{F}$ ) and Celsius ( $^{\circ}\text{C}$ ); based on specified reference temperature ( $32^{\circ}\text{F}$  or  $0^{\circ}\text{C}$ )
- Absolute scale: degree Rankine ( $^{\circ}\text{R}$ ) and kelvin (K); have their zero point at the lowest possible temperature that can exist (ideal gas law)

- Temp:  $\Delta^0\text{F} = \Delta^0\text{R}$      $\Delta^0\text{C} = 1.8^0\text{F}$   
 $\Delta^0\text{C} = \Delta^0\text{K}$         $\Delta\text{K} = 1.8^0\text{R}$

Unit Temperature Difference

Size of one unit

Temperature Scales

Convert  $200^0\text{C}$  to  $^0\text{F}$ ,  $^0\text{R}$ ,  $\text{K}$

Convert  $100 \text{ Btu/h.ft}^2.(^0\text{F}/\text{ft})$  to

$\text{Btu/h.ft}^2.( \text{ K}/\text{ft})$

$$100^{\circ}\text{C} = (100 + 273)^{\circ}\text{C} \frac{1\Delta K}{1\Delta C} = 373\text{K}$$

$$100^{\circ}\text{C} \left( \frac{1.8\Delta F}{1\Delta C} \right) + 32^{\circ}\text{F} = 212^{\circ}\text{F}$$

$$(212 + 460)^{\circ}\text{F} \frac{1\Delta R}{1\Delta F} = 672^{\circ}\text{R}$$

or

$$(373\text{K}) \frac{1.8\Delta R}{1\Delta K} = 672^{\circ}\text{R}$$

$$\frac{100 \text{ Btu}}{\text{h} \cdot \text{ft}^2 (\text{F}/\text{ft})}$$

$$\frac{100 \text{ Btu}}{\text{h} \cdot \text{ft}^2 \left( \frac{1\Delta K}{1.8\Delta F} \right) \text{ft}}$$

$$= 118 \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 (\text{K}/\text{ft})}$$

# Exercise

- Vapor pressure of benzene in the temperature range of 280.65 K to 377.15 K can be calculated using the following Antoine equation:
- $\log_{10}P = 6.9057 - 1211/(t + 220.8)$   
where P is vapor pressure in torr (mm.Hg) and t is temperature in  $^{\circ}\text{C}$ .
- Convert the above equation in SI units

$$8. \log_{10} P = 6.9057 - \frac{1211}{T+220.8}$$

$P$  = Vap. Pr. in mm. Hg

${}^{\circ}\text{C}$  = Temp.

SI Units       $P$ ,  $\mu$  in Pa  
 $T$ ,  $\mu$  in K.

$$[1 \text{ mm. Hg} = 133.32 \text{ Pa}]$$

$$\log_{10} \left( \frac{P^*}{133.32} \right) = 6.9057 - \frac{1211}{T^* - 273 + 220.8}$$

$P^*$     in Pa  
 $T^*$     in K }

$$\log_{10} \left( \frac{P^*}{133.32} \right) = 6.9057 - \frac{1211}{T^* - 52.2}$$

$$\log_{10} P^* = 6.9057 + \log_{10}(133.32) - \frac{1211}{T^* - 52.2}$$

$$= 6.9057 + 2.125 - \frac{1211}{T^* - 52.2}$$

$$\log_{10} P^* = 9.0307 - \frac{1211}{T^* - 52.2}$$

# Exercise

- $C_P \text{ (J/gmol. } ^\circ\text{C)} = 55 + 1.25 \times 10^{-1} T \text{ (} ^\circ\text{C)}$
- Convert  $C_P$  into  $(\text{Btu/lbmol.}^\circ\text{R})$  and  $T$  in  ${}^\circ\text{R}$

# Pressure

## Absolute pressure

## Relative pressure

- Measuring against a complete vacuum or against ‘no pressure’.
- Absolute pressure based on complete vacuum; fixed reference point, unchanged regardless of location, temperature, weather or other factors.

- Zero point of an absolute pressure scale corresponds to perfect vacuum.
- Zero point for a relative pressure scale usually corresponds to pressure of air surrounding us; reference point or zero point for the relative pressure scales is not constant.

$$\text{Absolute pressure} = \text{Gauge pressure} + \text{Barometer pressure}$$

- Standard atmosphere means pressure ( in a standard gravitational field) equivalent to 1 atm or 760 mm Hg

$$1\text{ atm} = 101325 \text{ Pa}$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.986923 \text{ atm}$$

Do not confuse between standard atmosphere and atmospheric pressure

Psia, psig

- Vacuum refers to substance atmosphere pressure.

$$\text{Absolute pressure} = \text{atmosphere pressure} - \text{vacuum.}$$

# Negative Pressure

- Negative gauge pressures (absolute pressures less than atmospheric) are generally referred as positive amounts of vacuum. A gauge pressure of – 10 cm Hg (66 cm Hg absolute if atmospheric pressure is 76 cm Hg) may be referred as 10 cm of vacuum.

Standard atmosphere is equal to

1	atm
33.91	feet of water (ft H <sub>2</sub> O)
29.92	inches of mercury (in. Hg)
14.7 (psia)	pounds per square inch absolute
760	Millimeters of mercury (mm Hg)
$1.013 \times 10^5$ Pa	Pascal (Pa) or Newton per square meter (N/m <sup>2</sup> )

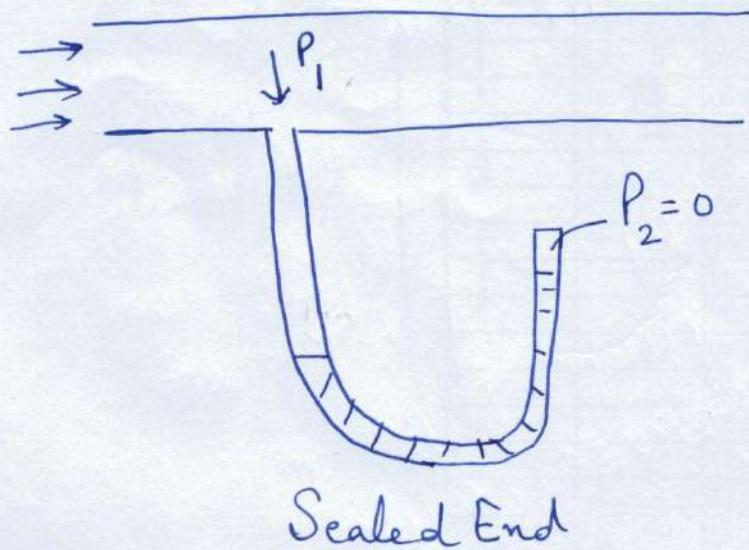
# Fluid Pressure Measurement

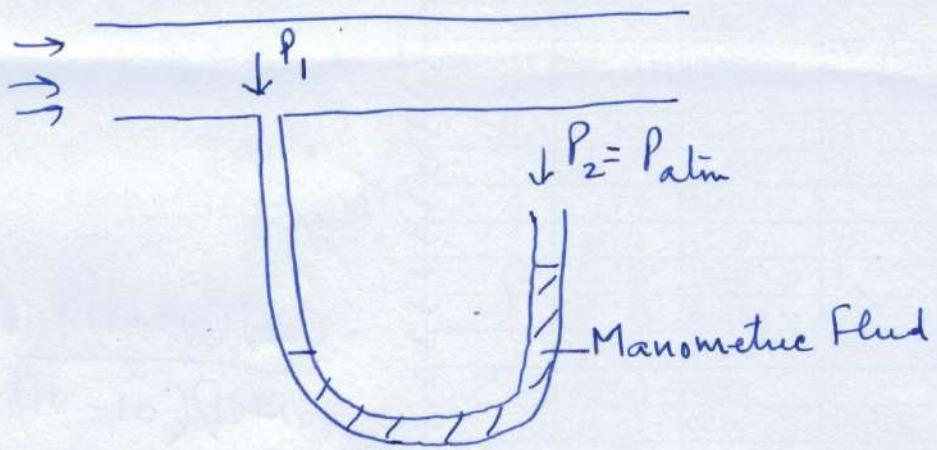
- Bourdon gauge: hollow tube closed at one end; the open end of tube is exposed to fluid whose pressure is to be measured; gauge pressure of the fluid
- Manometer : U-shaped tube partially filled with a liquid of known density(called manometer fluid, mercury)

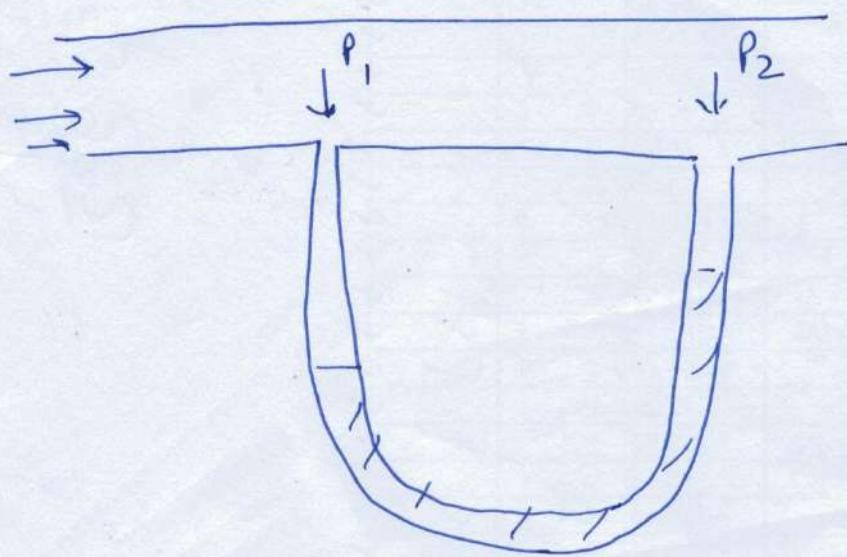
# Fluid Pressure Measurement

- Open-end manometer: one end is exposed to fluid whose pressure is to be measured and the other end to atmosphere
- Sealed-end manometer
- Differential manometer

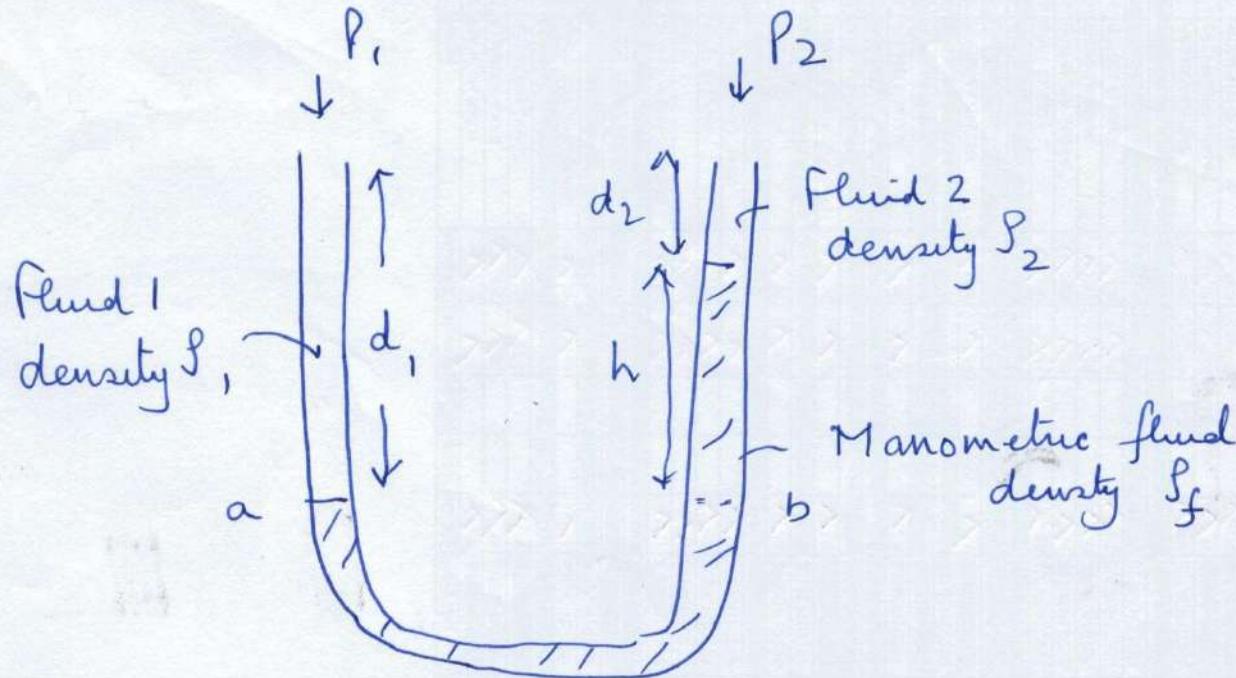
$$P_{\text{Absolute}} = P_{\text{Gauge}} + P_{\text{Atmosphere}}$$







Differential Manometer



Manometer

Fluid pressure must be same at any two points at the same height in a continuous fluid.

Manometer Eqn :

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

Fluid pressure must be same at any two points at the same height in a continuous fluid.

Manometer Eqn :  $P_1 + \rho_1 gd_1 = P_2 + \rho_2 gd_2 + \rho_f gh$

Differential Manometer

$$P_1 - P_2 = (\rho_f - \rho)gh$$

$\rho_1$  &  $\rho_2$  are same

$$\begin{aligned} P_1 - P_2 &= \rho g(d_2 - d_1) + \rho_f gh \\ &= \rho g(-h) + \rho_f gh \\ &= (\rho_f - \rho)gh \\ &\approx \rho_f gh \end{aligned}$$

# **Thank you**

# Material and Energy Balances

# Processes-Batch Reactor

- There is neither inflow nor outflow of reactants or products during the period of reaction.  
Reactants are fed into the reactor and products are withdrawn from the reactor after the completion of the reaction
- Used for production of relatively small quantities
- Unsteady-state operation where composition changes with time; however, at any instant the composition throughout the reactor is uniform.

# Batch Reactor

- Used for testing new processes that have not been fully developed
- Used for the manufacture of expensive products
- Higher conversions by providing more reaction time
- High labor cost per unit product

# Continuous Process

- The reactants and products flow continuously throughout the duration of the process
- Used for large production rates
- Steady-state operation

# Semi-batch reactor

- One of the reactants is continuous; Generally used for two-phase reactions in which gas is continuously bubbled through liquid
- Provides good temperature control
- Reduces the unwanted side reactions by maintaining low concentration of one of the reactants; helpful in exothermic reactions

# Material balances

- Application of the conservation of law for mass: mass can be neither created nor destroyed
- Accounting for material.
- Improve the efficiency and maintain control of the process
- Reduce the losses
- System: Any portion of or whole of process set out specifically for analysis. Reactor, refinery,
- System boundary- defines the limits of the system

# Closed and Open System

- Closed System: material neither enters nor leaves the system i.e. no material crosses the system boundary.
- There is no exchange of mass from the system with the surroundings but changes can take place inside the system.
- Open System : Flow system; there is exchange of mass with the surroundings, material crosses the system boundary.

# Steady and Unsteady-state Systems

- Steady-state system: The process parameters (temperature, pressure, flow rates etc.) do not change with time.
- Unsteady-state system: All the process parameters remain constant with time.

# Material Balance

- Single Component System

Accumulation of Material in the System = Flow of Material into the System – Flow of Material out of the System

Negative Accumulation: When flow of material out of the system is more than the flow of material into the system

At steady state conditions, accumulation term is equal to zero.

## Multi-component System: Component Balance



Not concerned with internal details of system,  
passage of material across system.

*[Accumulation within the system]*

$$\begin{aligned} &= [\text{input through system boundaries}] \\ &- [\text{output through system boundaries}] \\ &+ [\text{generation within the system}] \\ &- [\text{consumption within the system}]. \end{aligned}$$

- Total mass, total moles, mass of a chemical compound, mass of an atomic species, moles of a chemical compound, moles of an atomic species, volume?
  - Accumulation refers to change in mass or moles ( plus or minus) within the system with respect to time.
  - Steady state: The values of the variables within the system do not change with time.
  - Accumulation term is zero.
  - Generation & consumption terms are omitted from consideration, material balance reduces to
- $[mass/mole\ input\ through\ system\ boundaries]$   
 $= [mass/mole\ output\ through\ system\ boundaries]$

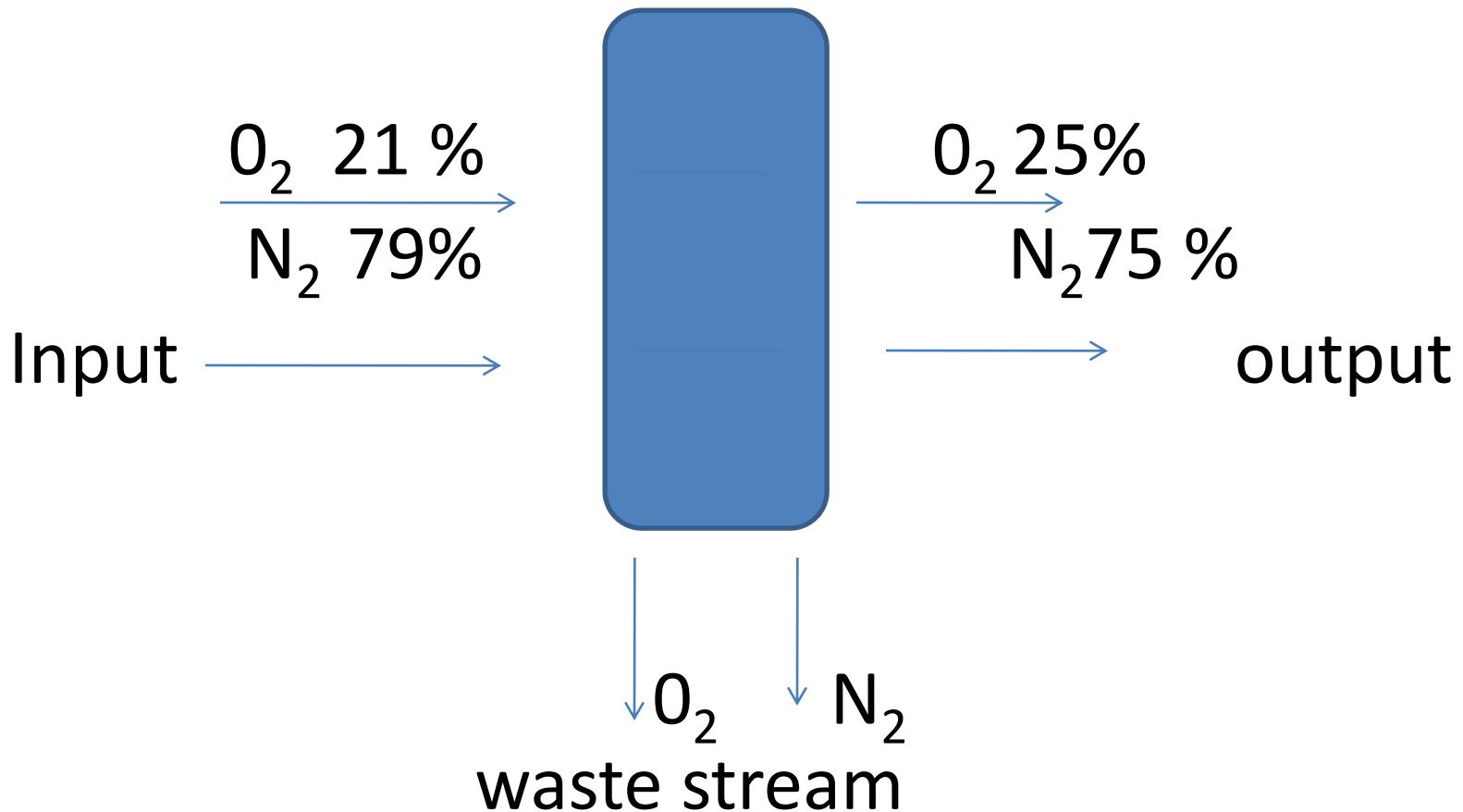
- Solution to a material balance problem
  - No solution, unique solution, multiple solutions
- The number of variables whose values are unknown equals the number of independent equations.
  1. Read the problem carefully
  2. Draw a sketch of the process (simple box or circle). Draw arrows for flows.
  3. Label with symbols the flow of each stream and its composition.
  4. Put all known values of compositions and stream flows on the figure
  5. Select a basis.
  6. List symbols for variables whose values are unknown and count them.

7. Write down independent equations.
8. Count them
9. Solve the equations.
10. Check your answers by introducing them into any redundant material balances.

# Membrane

H.P. Side

L. P. Side



- What is the composition of waste stream if the stream amounts to 80 % of input.
- Steady-state process without chemical reaction.
- Accumulation term, generation, consumption are zero.
- System: membrane
- $x_{O_2}$  mole fraction of  $O_2$
- $x_{N_2}$  mole fraction of  $N_2$
- $n_{O_2}, n_{N_2}$  moles of  $O_2, N_2$

	$F \text{ (g mol)}$		$P \text{ (g mol)}$	
	mol fr		mole fr.	
•	$O_2 \ 0.21$		$O_2 \ 0.25$	
•	$N_2 \ 0.79$		$N_2 \ 0.75$	
		↓		
		$W \text{ (gmol)}$		
			mole fr.	Mole
			$X_{O_2}$	$n_{O_2}$
			$X_{N_2}$	$n_{N_2}$

- Basis : 100 g mol F
- $W = 0.80(100) = 80 \text{ mol}$
- Three unknowns exist  $P, x_{O_2}, x_{N_2}$   
 $P, n_{O_2}, n_{N_2}$
- Independent equations are  
 $O_2$  balance,  $N_2$  balance,  $x_{O_2} + x_{N_2} = 1$   
 $n_{O_2} + n_{N_2} = 80$

input	output	
$O_2: 0.21(100)$	$= 0.25P + x_{O_2}(80)$ or $0.21(100) = 0.25P + n_{O_2}$	
$N_2: 0.79(100)$	$= 0.75P + x_{N_2}(80)$	$0.79(100) = 0.75P + n_{N_2}$
$1.00$	$= x_{O_2} + x_{N_2}$	$n_{O_2} + n_{N_2} = 80$

$$x_{O_2} = 0.20 \quad x_{N_2} = 0.80 \quad P = 20 \text{ g mol}$$

- A double effect evaporator system concentrates weak liquor containing 4 % (by mass) caustic soda to produce a lye containing 25 % solids (by mass). Calculate the evaporation of water per 100 kg feed in the evaporator.
- Basis: 100 kg weak liquor contains 4kg caustic soda  
Let quantity of lye =  $x$  kg  
caustic soda in lye =  $0.25x$   
Caustic soda does not take part in evaporation

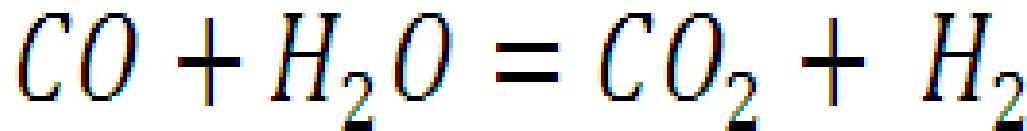
$$0.25 x = 4$$

$$x = 16 \text{ kg}$$

$$\text{Evaporation} = 100 - 16 = 84 \text{ kg.}$$

## Material balances involving chemical reactions.

- Law of conversion of mass holds good; convenient to work with moles rather than with mass, particularly gaseous systems.
- In chemical reactions, total mass of input remains constant, but total moles may or may not remain constant.



1 mole      1 mole      1 mole      1 mole



1 mole    3 moles    2 moles

- Limiting reactant : One which decides the conversion in the reaction.
- Excess reactant: Which is in excess amount over stoichiometric requirement of the reactant.
- Conversion: Ratio of the reacting amount of a component to its initial amount.
- Extent of Reaction

# Limiting Reactant

- ❖ Two reactants A and B are said to be present in stoichiometric proportions if the ratio (moles A present)/ (moles B present) equals the stoichiometric ratio (ratio of coefficients in the stoichiometric equation) obtained from the balanced reaction equation.  
For the reactants in the reaction



to be present in stoichiometric proportion, there must be 2 moles of  $SO_2$  for every mole of  $O_2$ .

- ❖ 200 moles of  $SO_2$ , 100 moles of  $O_2$ ; when proceeds to completion and  $SO_2$  &  $O_2$  would disappear at the same instant.

# Limiting Reactant

- ❖ Less than 200 moles of  $\text{SO}_2$  & 100 moles  $\text{O}_2$ .
- ❖ The reactant that would run out if a reaction proceeded to completion is called limiting reactant & other reactants are termed excess reactants.
- ❖ A reactant is limiting if it is present in less than its stoichiometric proportion relative to every other reactant.

$$\textit{Fractional excess of } A = \frac{(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}}{(n_A)_{\text{stoich}}}$$

- ❖ Percentage excess of A is 100 times the fractional excess.

# Example

- Hydrogenation of acetylene to form ethane



20 kmol/h acetylene, 50 kmol/h hydrogen fed to the reactor

Stoichiometric ratio of hydrogen to acetylene is 2: 1; ratio in the feed is 2.5:1; hydrogen is fed in more than the stoichiometric proportion; acetylene is the limiting reactant

# Example (contd.)

- Fractional excess of  $H_2$  =  
$$[(50 - 40) \text{ kmol/h}] / 40 \text{ kmol/h} = 0.25$$
or 25 % excess of hydrogen in the feed

# Exercise

- The oxidation of ethylene to produce ethylene oxide takes place in a reactor and the feed to the reactor contains 100 kmol  $\text{C}_2\text{H}_4$  and 100 kmol  $\text{O}_2$ 
  - a. Which reactant is limiting
  - b. what is the percentage excess of the other reactant.

- C. if the reaction proceeds to completion, how much of the excess reactant will be left; how much  $C_2H_4O$  will be formed; what is the extent of reaction
- D. if the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50 %, how much of each reactant and product is present at the end; what is the extent of reaction

- Flue or stack gas: All the gases resulting from a combustion process including water vapor, sometimes known as wet basis.
- Orsat analysis or dry basis: All the gases resulting from a combustion process not including water vapor.
- Theoretical air ( or theoretical oxygen): Amount of air ( or oxygen) required to be brought into process for complete combustion.
- Excess air ( or oxygen): Air (or oxygen) in excess of that required for complete combustion; Does not depend on how much material is actually burned but what can be burned.

$$\% \text{ excess air} = 100 \frac{\text{excess air}}{\text{required air}} = 100 \frac{\text{excess } O_2/0.21}{\text{required } O_2/0.21}$$

$$\% \text{ excess air} = 100 \frac{O_2 \text{ entering process} - O_2 \text{ required}}{O_2 \text{ required}}$$

$$\% \text{ excess air} = 100 \frac{\text{excess } O_2}{O_2 \text{ entering} - \text{excess } O_2}$$

Ex: 20 kg of C<sub>3</sub>H<sub>8</sub> is burned with 400 kg of air to produce 44 kg of CO<sub>2</sub> and 12 kg of CO. What is % excess air?



- Basis : 20 kg C<sub>3</sub>H<sub>8</sub>
- Excess air is based on complete combustion

$$20 \text{ kg C}_3\text{H}_8 \mid 1 \text{ k mol C}_3\text{H}_8 / 44.09 \text{ kg C}_3\text{H}_8$$

$$5 \text{ k mol O}_2 / 1 \text{ k mol C}_3\text{H}_8 = 2.27 \text{ k mol O}_2$$

Entering O<sub>2</sub> is

$$400 \text{ kg air} \mid 1 \text{ k mol air} / 29 \text{ kg air} \mid 21 \text{ k mol O}_2 / 100 \text{ k mol air}$$

$$= 2.90 \text{ k mol O}_2$$

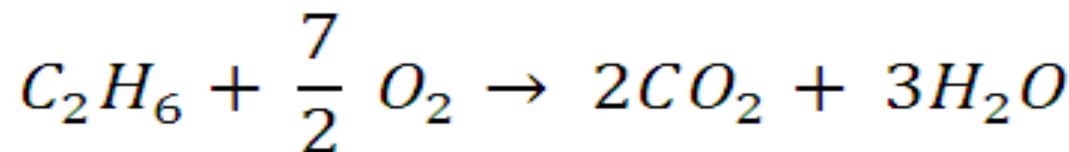
% excess air is

$$100 * \frac{\text{excess O}_2}{\text{required O}_2} = 100 * \frac{\text{entering O}_2 - \text{required O}_2}{\text{required O}_2}$$

$$\frac{2.90 \text{ kmol } O_2 - 2.27 \text{ kmol } O_2}{2.27 \text{ kmol } O_2} * 100$$

= 28%.

A gas containing 80 % C<sub>2</sub>H<sub>6</sub> and 20 % O<sub>2</sub> is burned in an engine with 200 % excess air. 80 % of ethane goes to CO<sub>2</sub>, 10% goes to CO and 10% remained unburned. What is the amount of excess air per 100 moles of the gas.



- 80 moles of  $\text{C}_2\text{H}_6$  require  $3.5(80) = 280$  moles of  $\text{O}_2$  for complete combustion. The gas contains 20 moles of  $\text{O}_2$  so  $280-20 = 260$  moles of  $\text{O}_2$  are needed in entering air for complete combustion; 260 moles of  $\text{O}_2$  are required and calculation of 200% excess  $\text{O}_2$  is based on 260, not 280 moles of  $\text{O}_2$

Entering with air	Moles $\text{O}_2$
Required $\text{O}_2$	260
Excess $\text{O}_2 (2)(260)$	520
Total	780



➤ Material balance for  $O_2$  in moles

$O_2$  : Acccmn in out Gen Con

$$0 = 1 - 0 + 0 - 1$$

➤ Mole balance on C and O elements

$$C: 0 = 1 - 1 + 0 - 0$$

$$O: 0 = 2 - 2 + 0 - 0$$

➤ Mass balance for elements

$$\text{C : } 0 = 12 - 12 + 0 - 0$$

$$\text{O: } 0 = 32 - 32 + 0 - 0$$

➤ You can avoid generation & consumption term by using element balance.

# Exercise

- Ethane is burned with 50 % excess air. The percentage conversion of the ethane is 90 %; of the ethane burned, 25 % reacts to form CO and the balance reacts to form  $\text{CO}_2$ . Calculate the molar composition of the stack gas on a dry basis and the mole ratio of water to dry stack gas.

# Exercise

- A hydrocarbon gas is burned with air. The dry-basis product gas composition is 1.5 mol %, 6 % CO<sub>2</sub>, 8.2 % O<sub>2</sub> and 84.3 % N<sub>2</sub>. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate on what the fuel might be. Then calculate the % excess air fed to reactor.

# Exercise

- A stack gas contains 60 mol % nitrogen, 15 % carbon dioxide, 10 % oxygen and the balance water. Calculate the molar composition of the gas on a dry basis.

# Exercise

- An Orsat analysis yields the following dry composition:
- Nitrogen 65 %, carbon dioxide 14 %, carbon monoxide 11 % and oxygen 10 %.
- A humidity measurement shows that the mole fraction of water in the stack gas is 0.07. calculate the stack gas composition on a wet basis.

# Multiple Units

- Flowsheet (flowchart)
- Block diagram
- Subsystem
- Mixer
- Separator
- splitter

Ex. A stack gas contains 60 mole%  $N_2$ , 15%  $CO_2$ , 10%  $O_2$  and the balance  $H_2O$ . Calculate the molar composition of the gas on dry basis ①

Basis: 100 mole Wet gas

$$\begin{array}{r} 60 \text{ mole } N_2 \\ 15 \text{ mole } CO_2 \\ 10 \text{ mole } O_2 \\ \hline 85 \text{ mole dry gas} \end{array}$$

$$\frac{60}{85} = 0.706 \frac{\text{mol } N_2}{\text{mol dry gas}}$$

$$\frac{15}{85} = 0.176 \frac{\text{mol } CO_2}{\text{mol dry gas}}$$

$$\frac{10}{85} = 0.118 \frac{\text{mol } O_2}{\text{mol dry gas}}$$

85

moles of  $\text{O}_2$ )

Ex. An Orsat analysis yields the following dry basis composition:

$\text{N}_2$  65%

$\text{CO}_2$  14%

$\text{CO}$  11%

$\text{O}_2$  10%

A humidity measurement shows that the mole fraction of  $\text{H}_2\text{O}$  in the stack gas is 0.07. Calculate the stack gas composition on wet basis.

Basis: 100 moles dry gas

Mole fraction of  $H_2O$  in stack gas is 0.07.

$$\Rightarrow 0.07 \frac{\text{mole } H_2O}{\text{mole wet gas}} \text{ or } 0.93 \frac{\text{mol dry gas}}{\text{mol wet gas}}$$

$$\frac{0.07 \text{ mol } H_2O / \text{mol wet gas}}{0.93 \text{ mol dry gas} / \text{mol wet gas}} = 0.0753 \frac{\text{mol } H_2O}{\text{mol dry gas}}$$

$$100 \text{ mole dry gas} \left| \frac{0.0753 \text{ mol } H_2O}{\text{mol dry gas}} \right. = 7.53 \text{ mole } H_2O$$

$$\begin{aligned}
 100 \text{ mole dry gas} & \left| \frac{0.65 \text{ mole H}_2\text{O}}{\text{mole dry gas}} \right. = 65 \text{ mole N}_2 \\
 & = 14 \text{ mole CO}_2 \\
 & = 11 \text{ mole CO} \quad \Rightarrow \\
 & = 10 \text{ mole O}_2 \\
 & \hline
 & 107.53 \text{ mole wet gas}
 \end{aligned}$$

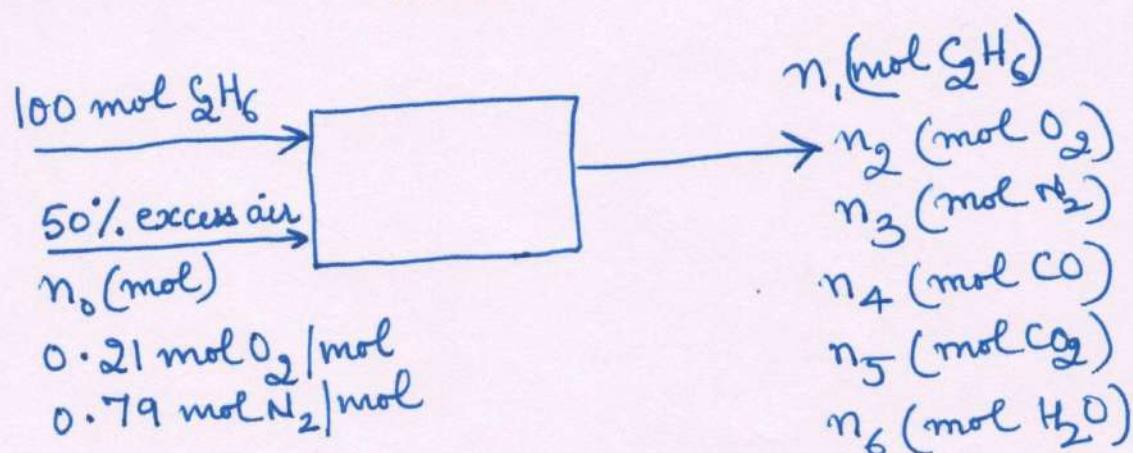
Mole fraction of each species can be calculated.

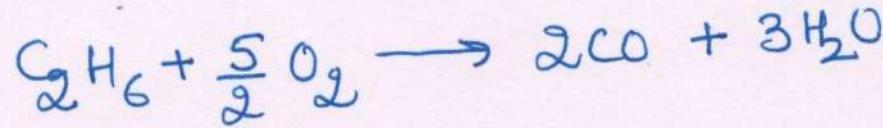
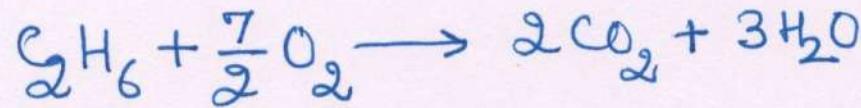
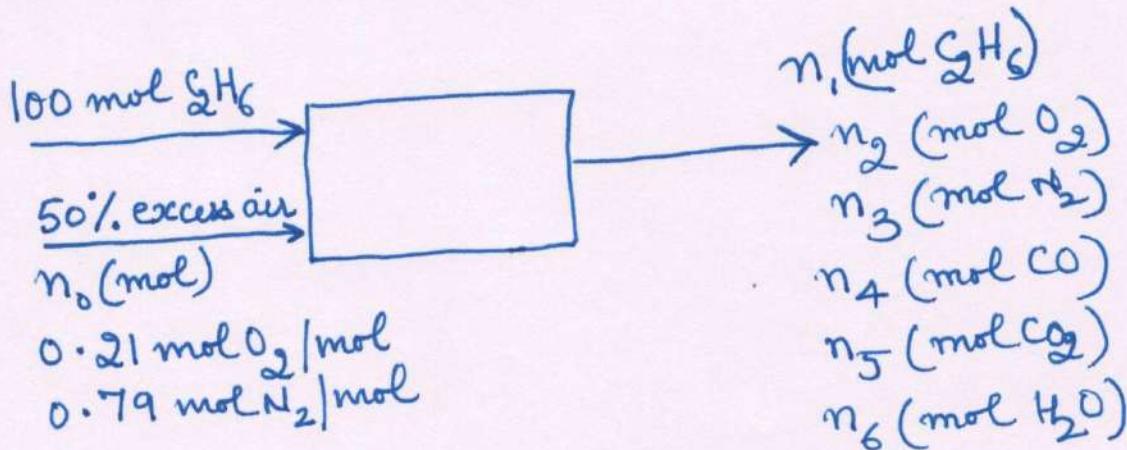
$$\text{Mole fraction H}_2\text{O} = \frac{7.53 \text{ mole H}_2\text{O}}{107.53 \text{ mole wet gas}} = 0.07 \frac{\text{mole H}_2\text{O}}{\text{mole wet gas}}$$

(3)

Ex. Ethane is burned with 50% excess air. The percentage conversion of ethane is 90%; of the ethane burned, 25% reacts to form CO and the balance to form  $\text{CO}_2$ . Calculate the molar composition of the stack gas on a dry basis and the molar ratios of water to dry stack gas.

Basis: 100 mol  $\text{C}_2\text{H}_6$





- 7 unknown variables  $n_0, n_1, \dots, n_6$
- 3 atomic balances (C, H, O)
- 1  $\text{N}_2$  balance
- 1 excess air specification (relates  $n_0$  to the quantity)
- 1 ethane conversion specification of fuel
- 1 CO/CO<sub>2</sub> ratio specification

(4)

50% Excess Air

$$(n_{O_2})_{\text{theoretical}} = \frac{100 \text{ mol } C_2H_6}{1 \text{ mole } C_2H_6} \left| \frac{3.5 \text{ mole } O_2}{2} \right.$$

$$= 350 \text{ mol } O_2$$

$$0.21 n_0 = 1.5 (350 \text{ mol } O_2) \Rightarrow n_0 = 2500 \text{ mol air fed}$$

90% Ethane Conversion  $\Rightarrow$  10% Unreacted

$$n_1 = 0.1 (100 \text{ mol } C_2H_6 \text{ fed}) = 10 \text{ mol } C_2H_6$$

25% Conversion to CO

$$n_4 = (0.25 \times 90) \text{ mol react to form CO} \left| \begin{array}{l} \text{2 mol CO formed} \\ \text{1 mol } C_2H_6 \text{ reacted} \end{array} \right.$$

$$= 45 \text{ mol CO}$$

Nitrogen Balance: Input = Output  
 $n_1 = 0.79(2500 \text{ mol}) = 1975 \text{ mol N}_2$

Atomic Carbon Balance: Input = Output

$$100 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 2 \text{ mol C} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = n_1 (\text{mol C}_2\text{H}_6) \left| \begin{array}{l} 2 \text{ mol C} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right.$$

$$+ n_4 (\text{mol CO}) \left| \begin{array}{l} 1 \text{ mol C} \\ \hline 1 \text{ mol CO} \end{array} \right.$$

$$+ n_5 (\text{mol CO}_2) \left| \begin{array}{l} 1 \text{ mol C} \\ \hline 1 \text{ mol CO}_2 \end{array} \right.$$

Since  $n_1 = 10 \text{ mol}$ ;  $n_4 = 45 \text{ mol}$

$$n_5 = 135 \text{ mol CO}_2$$

Atomic Hydrogen Balance: Input = Output

$$100 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 6 \text{ mol H} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = 10 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 6 \text{ mol H} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right.$$

$$+ n_6 (\text{mol H}_2\text{O}) \left| \begin{array}{l} 2 \text{ mol H} \\ \hline 1 \text{ mol H}_2\text{O} \end{array} \right.$$

$$\rightarrow n_6 = 270 \text{ mol H}_2\text{O}$$

⑤

Atomic Oxygen Balance: Input = Output

$$525 \text{ mol O}_2 \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. = n_2 (\text{mol O}_2) \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right.$$

$$+ 45 \text{ mol CO} \left| \frac{1 \text{ mol O}}{1 \text{ mol CO}} \right.$$

$$+ 135 \text{ mol CO}_2 \left| \frac{2 \text{ mol O}}{1 \text{ mol CO}_2} \right.$$

$$+ 270 \text{ mol H}_2\text{O} \left| \frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}} \right.$$

$$n_2 = 232 \text{ mol O}_2$$

Composition

$$n_1 = 10 \text{ mol C}_2\text{H}_6$$

$$10/2396 = 0.00417 \frac{\text{mol C}_2\text{H}_6}{\text{mol}}$$

$$n_2 = 232 \text{ mol O}_2$$

$$232/2396 = 0.097 \frac{\text{mol O}_2}{\text{mol}}$$

$$n_3 = 1974 \text{ mol N}_2$$

$$= 0.824 \frac{\text{mol N}_2}{\text{mol}}$$

$$n_4 = 45 \text{ mol CO}$$

$$= 0.019 \text{ mol CO/mol}$$

$$\underline{n_5 = 135 \text{ mol CO}_2}$$

$$= 0.0563 \text{ mol CO}_2/\text{mol}$$

2396 mol dry gas

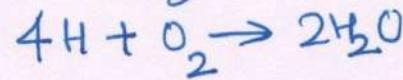
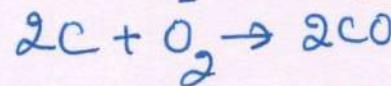
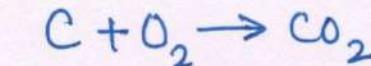
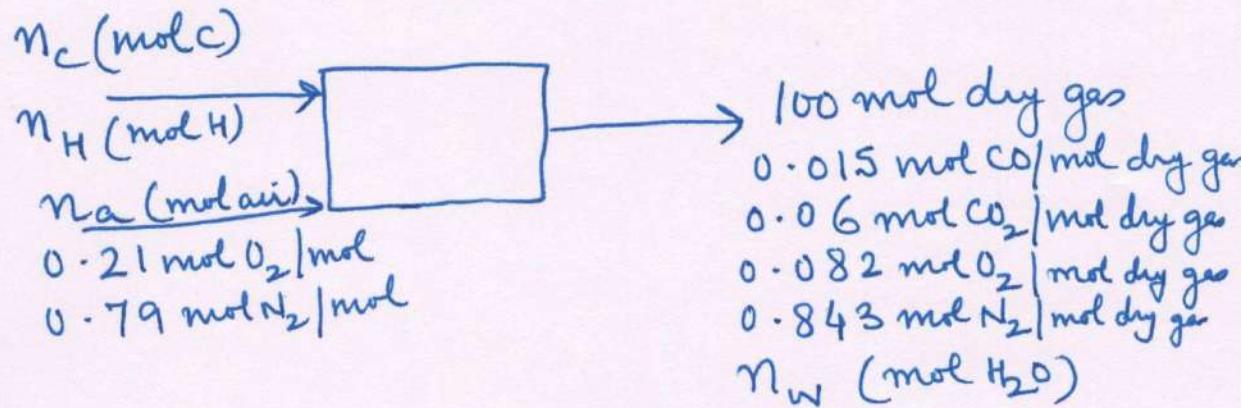
$$n_6 = 270 \text{ mol H}_2\text{O}$$

Mole ratio of water to dry stack gas

$$\frac{270 \text{ mol H}_2\text{O}}{2396 \text{ mol dry stack gas}} = 0.113 \frac{\text{mol H}_2\text{O}}{\text{mol dry stack gas}}$$

Ex. A hydrocarbon gas is burned with air. The dry basis product gas composition is 1.5 mole% CO<sub>2</sub>, 6% CO, 8.2% O<sub>2</sub> and 84.3% N<sub>2</sub>. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate what the fuel might be. Then calculate the percent excess air fed to reactor.

Basis: 100 mol Product gas



4 Variables ( $n_c, n_H, n_a, n_w$ )

3 Independent Atomic Balances (C, H, O)

1  $N_2$  Balance

$$N_2 \text{ Balance: } 0.79 n_a = 100 (0.843) \text{ mol } N_2 \Rightarrow n_a = 106.7 \text{ mol air}$$

$$\text{Atomic C Balance: } n_c = \frac{100 \text{ mol}}{\frac{0.015 \text{ mol CO}}{\text{mol}}} \left| \begin{array}{c} 1 \text{ mol C} \\ 1 \text{ mol CO} \end{array} \right.$$
$$+ (100)(0.06)(1) \text{ mol C}$$

$$\Rightarrow n_c = 7.5 \text{ mol C}$$

CO

$$\text{Atomic O Balance: } 0.21 n_a(2) = n_w(1) + 100 [0.015(1) + (0.06)(2) + (0.082)(2)]_{\text{H}_2\text{O}}$$

$$\text{Since } n_a = 106.7 \text{ mol}$$

$$\Rightarrow n_w = 14.9 \text{ mol H}_2\text{O}$$

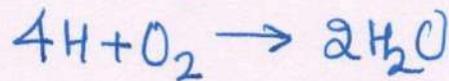
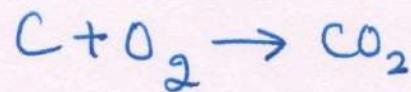
$$\text{Atomic H Balance: } n_H = n_w(2) \xrightarrow[n_w=14.9]{\text{H}_2\text{O}} n_H = 29.8 \text{ mol H}$$

$$\text{C/H ratio in the fuel} = \frac{n_H}{n_c} = \frac{29.8 \text{ mol H}}{7.5 \text{ mol C}} = 3.97 \frac{\text{mol H}}{\text{mol C}}$$

$(\text{CH}_{3.97})_n$

$\text{C.H}_n$

## Percent Excess Air



$$(n_{O_2})_{\text{theoretical}} = \frac{7.5 \text{ mol C}}{\frac{1 \text{ mol } O_2}{1 \text{ mol C}}} + \frac{29.8 \text{ mol H}}{\frac{1 \text{ mol } O_2}{4 \text{ mol H}}} \\ = 14.95 \text{ mol } O_2$$

$$(n_{O_2})_{\text{fed}} = 0.21 (106.7 \text{ mol air}) = 22.4 \text{ mol } O_2$$

$$\% \text{ Excess Air} = \frac{(n_{O_2})_{\text{fed}} - (n_{O_2})_{\text{theoretical}}}{(n_{O_2})_{\text{theoretical}}} \times 100$$

$$= \frac{(22.4 - 14.95) \text{ mol } O_2}{14.95 \text{ mol } O_2} \times 100\%$$

$$= 49.8\%$$

# Thank Q

## Material Balance Involving Multiple Units

Process Flowsheet : Graphical representation of a process.

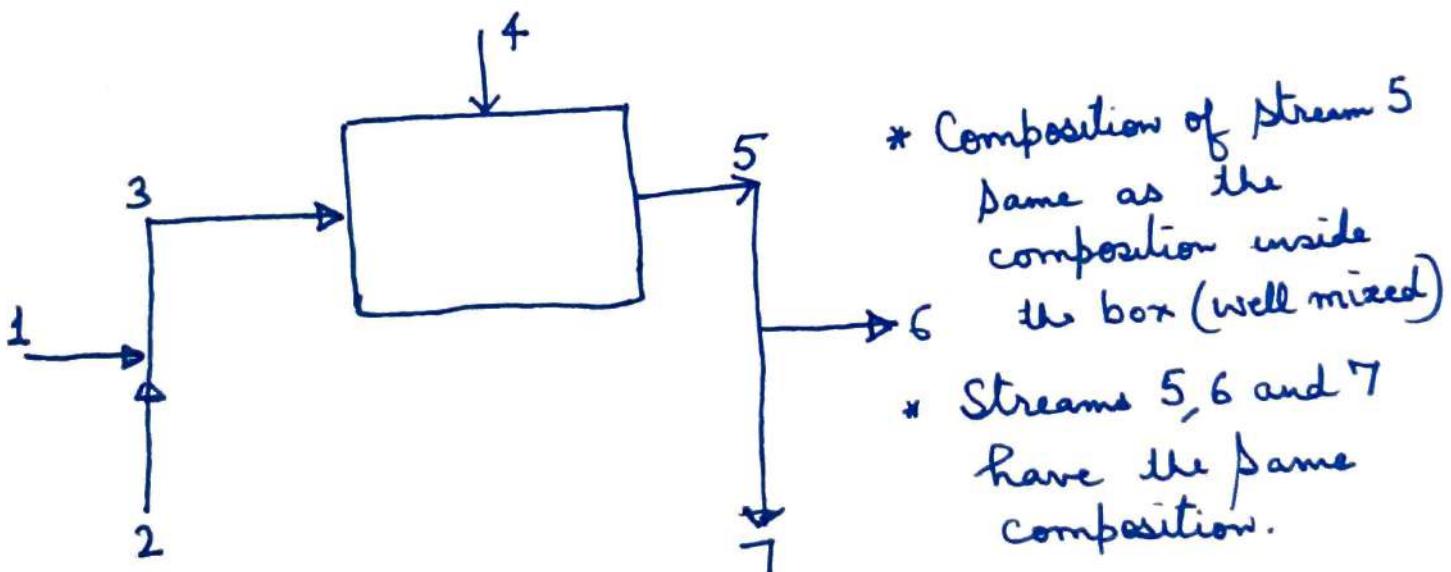
Large number of interconnected processing units

Block Diagram; Subsystems

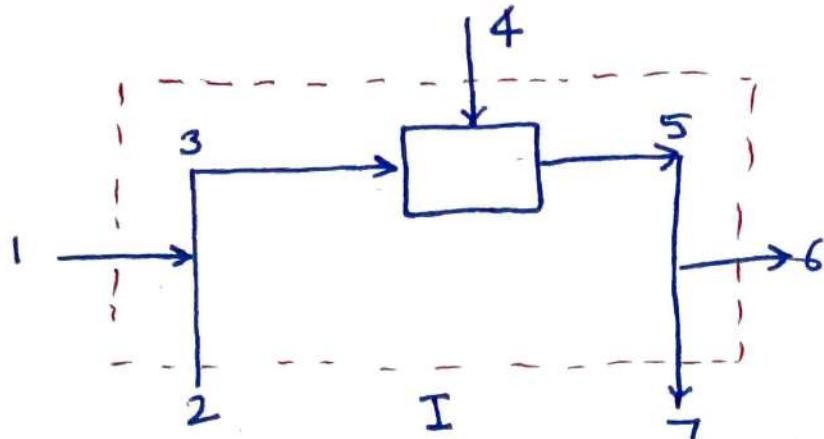
Mixer: Two or more streams (entering) of different compositions are combined.

Splitter: Two or more streams exit, all have the same composition

Separator: Exit streams can be of different compositions.



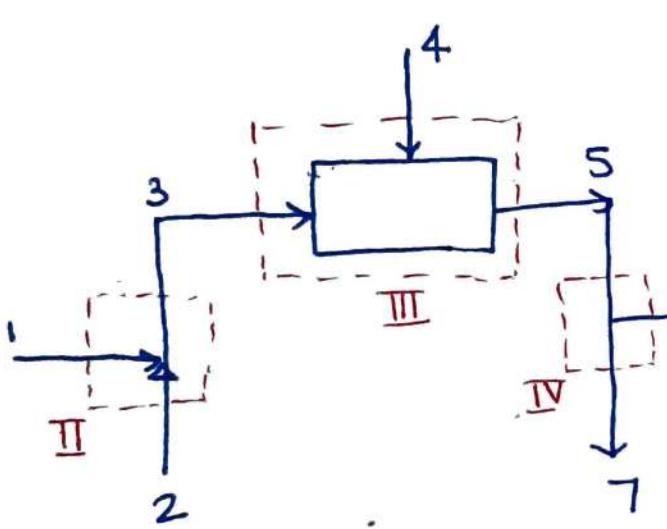
## Overall Material Balance



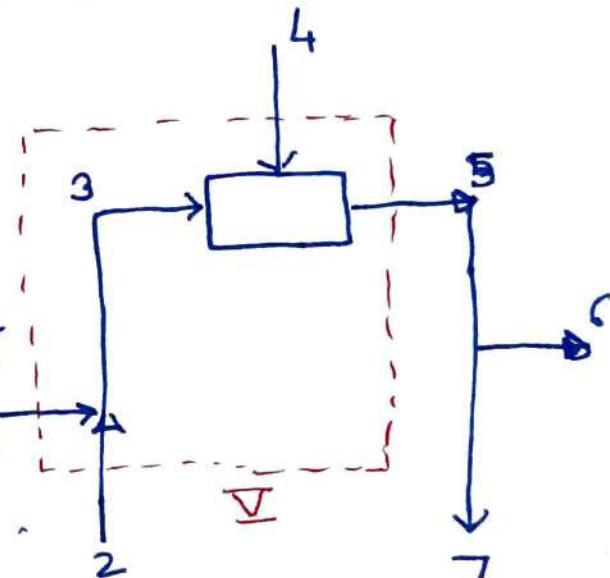
I: Overall Material Balance

Balance on a system that includes all of the units within the boundary denoted by dashed lines

You can make balances on each of the three units that make the overall process.  
(Dashed lines II, III, IV)



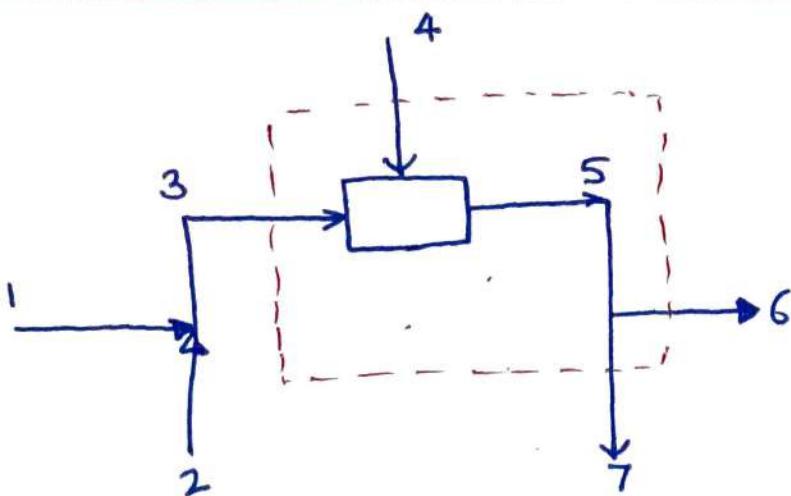
Material Balances around each of the individual units comprising the overall process



Material Balances around a system comprised of the mixing point plus the unit shown by box.

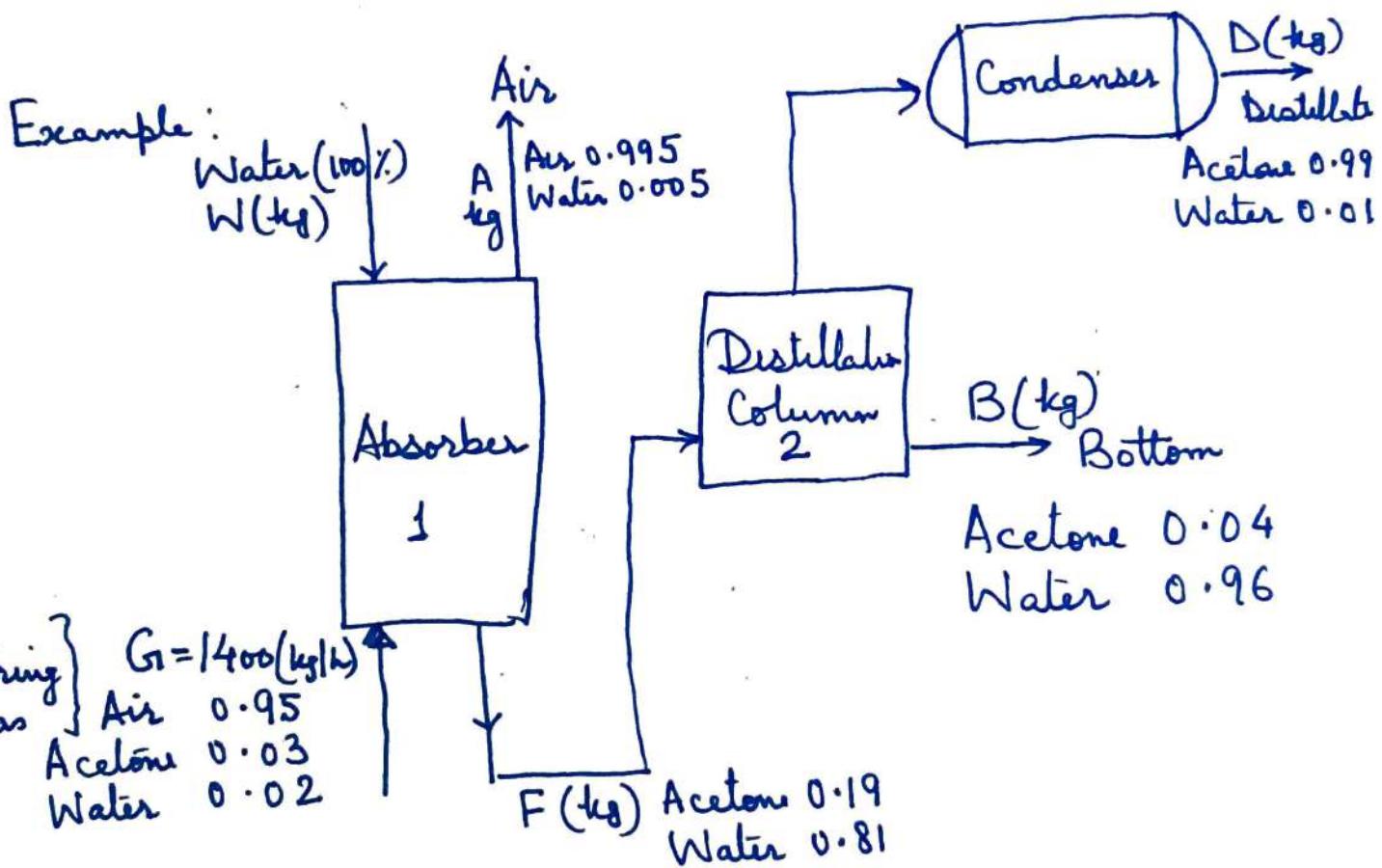
You can write an independent material balance equation for each component present in each unit or subsystem except for Splitters.

For Splitters, only one independent mass balance eqn. can be written regardless of the number of components present in stream.



Material Balances about a system comprised of the unit represented by box and the splitter

- \* Material Balance for the Overall Process ignoring information about internal connections.



- All concentrations for both gases & liquids are in weight percent.
- Calculate A, F, W, B and D per hour
- $G_1 = 1400 \text{ kg/h}$

(D)

Open System

Steady - State Process without Chemical Reaction  
Three subsystems.

Basis : 1 Hour

$$G = 1400 \text{ kg}$$

Unit I

16 variables

W, G, F, A, Mass Fraction in each stream = 4

In

Out

$$\text{Air} : 1400(0.95) = A(0.995)$$

$$\text{Acetone} : 1400(0.03) = F(0.19)$$

$$\text{Water} : 1400(0.02) + W(1) = F(0.81) + A(0.005)$$

$$A = 1336.7 \text{ kg/h}$$

$$(F) B = 221.05 \text{ kg/h}$$

$$(W) C = 157.7 \text{ kg/h}$$

Check: Use Total Balance

$$G + W = A + F$$

$$\begin{aligned} 1400 + 157.7 &= 1336.7 + 221.05 \\ &= 1557.7 \end{aligned}$$

(E)

## Mass Balance for combined Units 2 plus 3

$$\text{Acetone: } 221.05(0.19) = D(0.99) + B(0.04)$$

$$\text{Water : } 221.05(0.81) = D(0.01) + B(0.96)$$

$$D = 34.9 \text{ kg/h}$$

$$B = 186.1 \text{ kg/h}$$

$$\text{Check: } F = D + B$$

$$221.05 \quad 34.9 + 186.1 \\ = 221$$

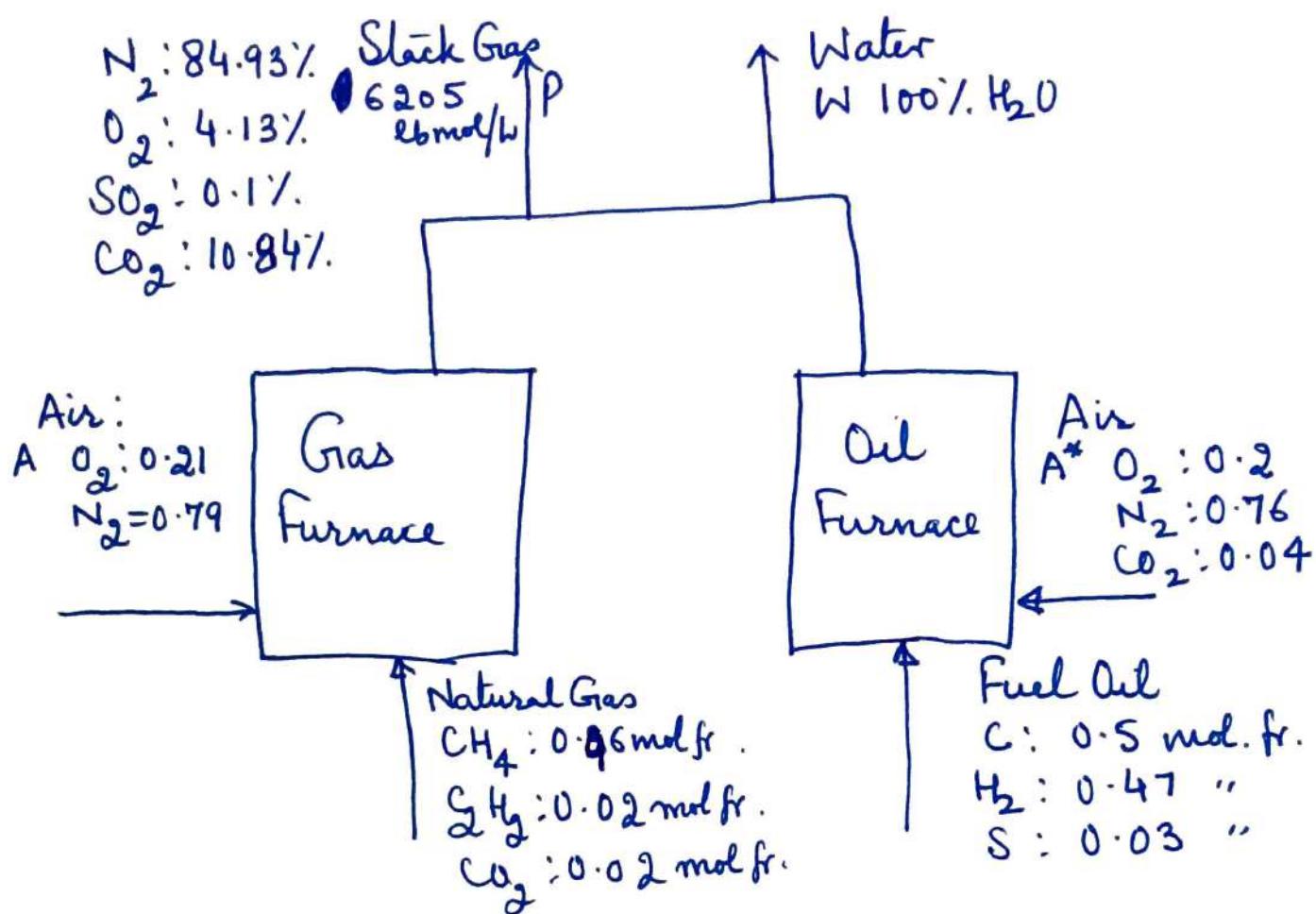
Alternately

Overall Balance

	In	Out
Total	$G_1 + W$	$= A + D + B$
Air	$G(0.95)$	$= A(0.995)$
Acetone	$G(0.03)$	$= D(0.99) + B(0.04)$
Water	$G(0.2) + W$	$= A(0.005) + D(0.01) + B(0.96)$

(F)

# Material Balance Involving Multiple Units & Rxns.



Reserve of Fuel Oil: 560 bbl

How many hours could the company operate before shutting down.

Mol. wt. of Fuel Oil 7.91  $\frac{\text{lb}}{\text{lbmol}}$

Density of Fuel Oil 7.578  $\frac{\text{lb}}{\text{gal}}$ .

(G)

## Open System

Steady-State Process with Chem. Reactions

Two Subsystems

Basis: 1 Hour

$$P = 6205 \text{ lbmol}$$

Five Variables A, G, F, A\*, W

Five Elements H, N, O, S, C

Overall Balances for the elements (in lbmol)

	In	Out
2H:	$G(1.94) + F(0.47)$	$= W(1)$
2N:	$A(0.79) + A^*(0.76)$	$= 6205(0.8493)$
2O:	$A(0.21) + A^*(0.2 + 0.04)$ + $G(0.02)$	$= 6205(0.0413 + 0.001$ $+ 0.1084)$ $+ W(0.5)$

$$S: F(0.03) = 6205(0.001)$$

$$C: G(0.96) + (2)(0.02) + 0.02 + F(0.5) + 0.04A^* = 6205(0.1084)$$

$$F = 207 \text{ lbmol/h}$$

$$G = 499 \text{ lbmol/h}$$

The fuel oil consumption is

$$207 \frac{\text{lb mol}}{\text{h}} \left| \frac{7.91 \text{ lb}}{\text{lb mol}} \right| \frac{\text{gal}}{7.578 \text{ lb}} \left| \frac{\text{bbl}}{42 \text{ gal}} \right.$$
$$= 5.14 \text{ bbl/h}$$

Fuel Oil Reserve 560 bbl

$$\frac{560 \text{ bbl}}{5.14 \text{ bbl/h}} = 109 \text{ h}$$

(A)

**Limiting Reactant**: The species in a chemical reaction that would theoretically run out first (would be completely consumed) if the reaction were to proceed to completion according to the chemical equation - even if the reaction does not proceed to completion. All other reactants are called excess reactants.



1 gmol of  $C_7H_{16}$ ; 12 gmol of  $O_2$  are fed

Limiting reactant  $C_7H_{16}$

Excess reactant  $O_2$

If the ~~excess~~ rxn goes to completion, the amount of product formed would be controlled by limiting reactant.

Determine  $\zeta_p^{\max}$  (maximum extent of reaction) for each reactant based on complete reaction of the reactant. The reactant with the smallest maximum extent of reaction is the limiting reactant.

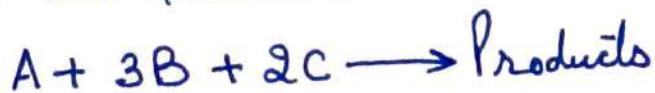
$$\zeta_p^{\max} (\text{based on } O_2) = \frac{0 \text{ gmol } O_2 - 12 \text{ gmol } O_2}{-11 \text{ gmol } O_2 / \text{moles reacted}} = 1.09 \text{ moles reacted}$$

$$\zeta_p^{\max} (\text{based on } C_7H_{16}) = \frac{0 - 1}{-1} = 1 \text{ moles reacted}$$

Heptane is the limiting reactant and oxygen is the excess reactant.

(B)

Consider the reaction



Feed to reactor contains 1.1 moles of A, 3.2 moles of B and 2.4 moles of C

The extents of reaction based on complete reaction of A, B and C are

$$\xi_A^{\max} (\text{based on A}) = \frac{-1.1 \text{ mol A}}{-1} = 1.1$$

$$\xi_B^{\max} (\text{based on B}) = \frac{-3.2 \text{ mol B}}{-3} = 1.07$$

$$\xi_C^{\max} (\text{based on C}) = \frac{-2.4 \text{ mol C}}{-2} = 1.2$$

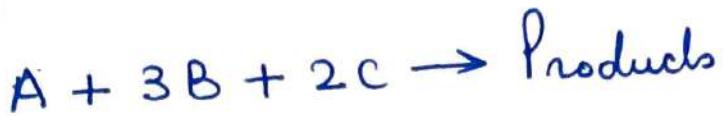
B is the limiting reactant while A & C are the excess reactants

Alternately, calculate the mole ratio ( $\lambda$ ) of the reactants and compare each ratio with the compounding ratio of the coefficients of the reactants in chemical equation

	Ratio in feed	Ratio in chemical eqn.
$\frac{\text{O}_2}{\text{C}_4\text{H}_{16}}$	$\frac{12}{1} = 12$	$> \frac{11}{1} = 11$

(c)

For more than two reactants, use one reactant as reference substance, calculate the ratios(mole) of the other reactants in the feed relative to the reference, make pairwise comparisons versus the analogous ratios in the chemical equation



1.1 moles of A, 3.2 moles of B, 2.4 moles of C are fed as reactants in the reactor;

Choose A as reference substance

	Ratio in feed	Ratio in chem. eqn.
$\frac{B}{A}$	$\frac{3.2}{1.1} = 2.91 < \frac{3}{1} = 3$	

$\frac{C}{A}$	$\frac{2.4}{1.1} = 2.18 > \frac{2}{1} = 2$
---------------	--

B is the limiting reactant relative to A, A is the limiting reactant relative to C, hence C is the limiting reactant among three reactants

$$B < A, C > A \text{ (i.e } A < C\text{)}$$

$$B < A < C$$

$$\text{Conversion} = \frac{\text{Moles Reacted}}{\text{Moles Fed}}$$

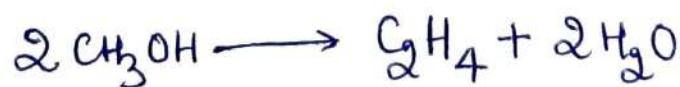
Conversion in terms of 'Extent of Reaction'

$$\text{Conversion} = \frac{\text{Extent of Reaction (Actual)}}{\text{Extent of Reaction that would occur if complete reaction take place}}$$

$$\text{Conversion} = \frac{\xi_p}{\xi_p^{\max}}$$

### Selectivity

Selectivity is the ratio of moles desired product formed to the moles of undesired product formed in a set of reactions.



Selectivity of  $\text{C}_2\text{H}_4$  relative to  $\text{C}_3\text{H}_6$

Ethylene  $C_2H_4$  can be produced by dehydrogenation of ethane



$$\text{Selectivity} = \frac{\text{Moles of Desired Product Formed}}{\text{Moles of Undesired Product Formed}}$$

$$\text{Yield} = \frac{\text{Moles of Desired Product Formed}}{\text{Moles that would have been formed if there were no side reactions and the limiting reactant had reacted completely}}$$

Yield is always a fraction; can be expressed as percentage by multiplying by 100.

A is the desired product, B is the undesired product - Selectivity of A relative to B.

High values of Yield and Selectivity signifies that the undesired side rxns have been suppressed relative to desired reaction.

$$\text{Yield (based on feed)} = \frac{\text{Amount (mass/moles) of desired product formed}}{\text{Amount of limiting reactant fed}}$$

$$\text{Yield (based on reactant consumed)} = \frac{\text{Amount (mass/moles) of desired product formed}}{\text{Amount of limiting reactant consumed}}$$

$$\text{Yield (based on theoretical consumption of limiting reactant)} = \frac{\text{Amount (mass/moles) of product obtained}}{\text{Theoretical (expected) amount of the product that would be formed based on the limiting reactant in the chem. rxn. if it were completely consumed}}$$

$$\left[ \text{Yield} = \frac{\text{Amount of limiting reactant consumed for the formation of desired product}}{\text{Amount of limiting reactant consumed}} \right]$$

The actual yield in a reaction is not equal to the theoretical yield predicted from chemical reaction equation due to

- Impurities among the reactants
- Leaks to the environment
- Side Reactions
- Reversible Reactions



Yield of B (First Definition)

$$= \frac{\text{(Moles) Mass of B produced}}{\text{Moles of A fed}}$$

Yield of B (Second Definition)

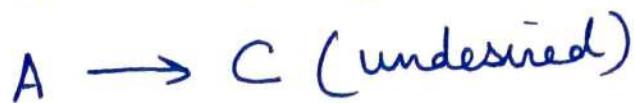
$$= \frac{\text{Moles (or Mass) of B produced}}{\text{Moles of A consumed}}$$

Yield (Third Definition)

$$= \frac{\text{Moles (Mass) of B produced}}{\text{Max. Amount of B that could be produced in the reaction / Segments}}$$

(G)

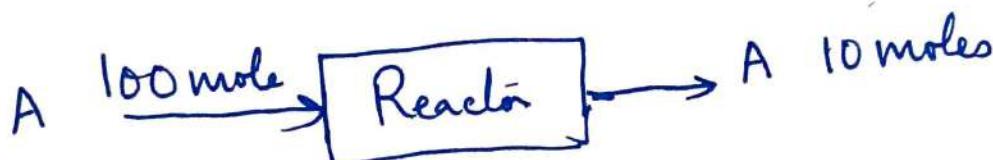
Ex. Consider the following pair of rxns



Suppose 100 mol of A is fed to a batch reactor and final product contains 10 mol of A, 160 mol of B and 10 mol of C.

C. Calculate

### 1. Fractional Conversion of A



$$\text{Moles fed} = 100$$

$$\text{Moles reacted} = 90$$

$$\text{Conversion} = \frac{90}{100} = 0.9$$

### 2. Percentage Yield of B

$$\text{Yield} = \frac{80 \text{ moles}}{100 \text{ moles}} = 80\%$$

$$\text{Yield} = \frac{80 \text{ moles}}{90 \text{ moles}} = 88.89\%$$

(H)

### 3. Selectivity of B relative to C

$$B \text{ formed} = 160 \text{ moles}$$

$$C \text{ formed} = 10 \text{ moles}$$

$$16 \text{ mol B/mol C}$$

Amount of limiting reactant used for the formation of desired product

Amount of limiting reactant used for the formation of undesired product

$$= \frac{80 \text{ mol}}{10 \text{ mol}} = 8 \cancel{\text{mol}}$$

### 4. The Extents of the first and second reactions

Extent of Reaction (First Reaction)

$$\bar{x}_1 = \frac{n_i - n_{i0}}{2V}$$

$$(\text{Based on B}) \bar{x}_1 = \frac{160 - 0}{2} = 80 \text{ mol}$$

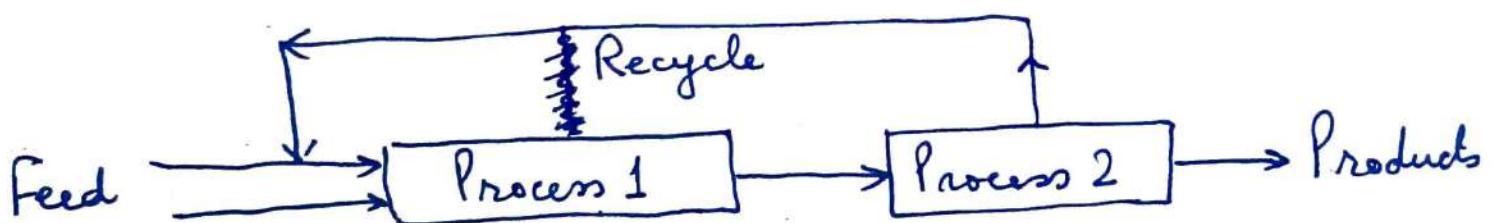
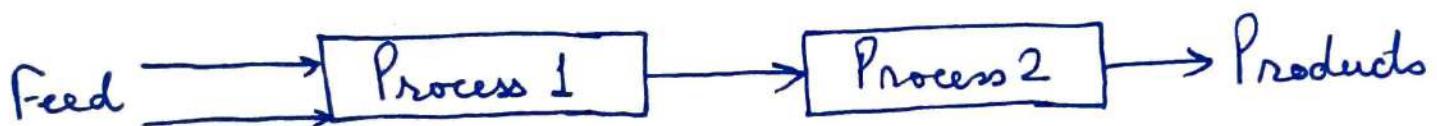
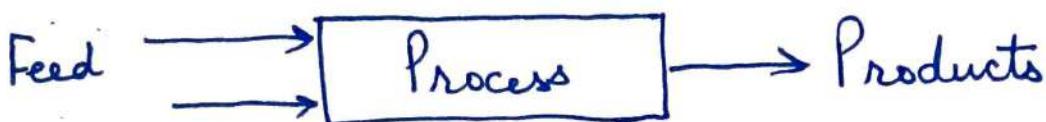
Extent of Reaction (Second Reactor)

$$\bar{x}_2 = \frac{n_e - n_{e0}}{2V}$$

$$(\text{Based on C}) \bar{x}_2 = \frac{10 - 0}{1} = 10 \text{ mol}$$

## Recycle Systems

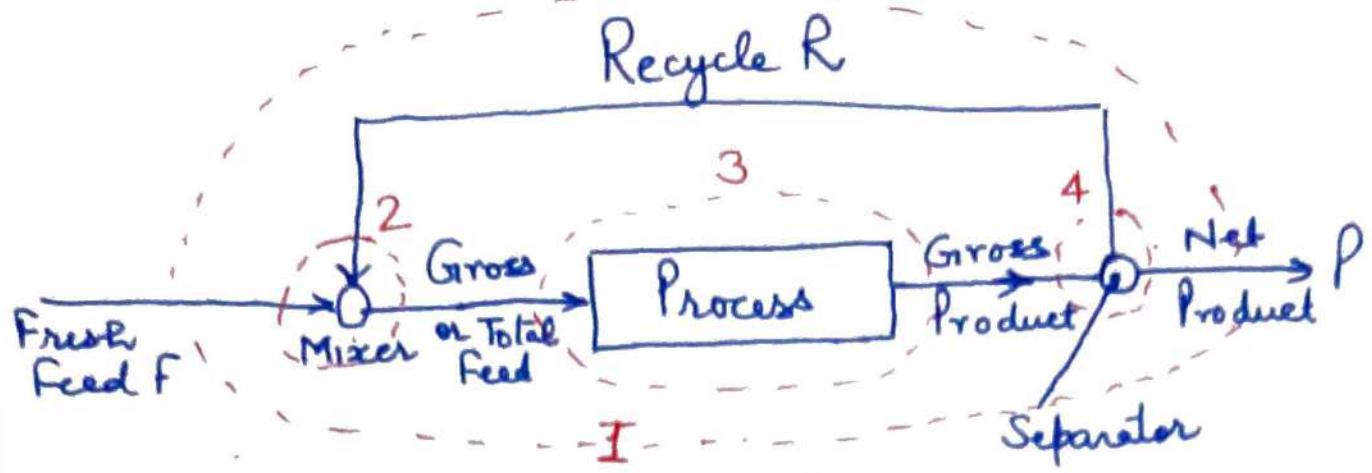
- Used newspaper — Ink Removal, Deforestation Strength of Paper
- Recycle of glass, plastics, copper, iron
- Water Recycle



Recycle Stream: Material is fed back from a downstream unit to an upstream unit.

Recycle of unused reactants to the reactor

Energy Recycle: Heat Recovery in a processing unit



### Material Balance

[Recycle without Chem. Rxn.]

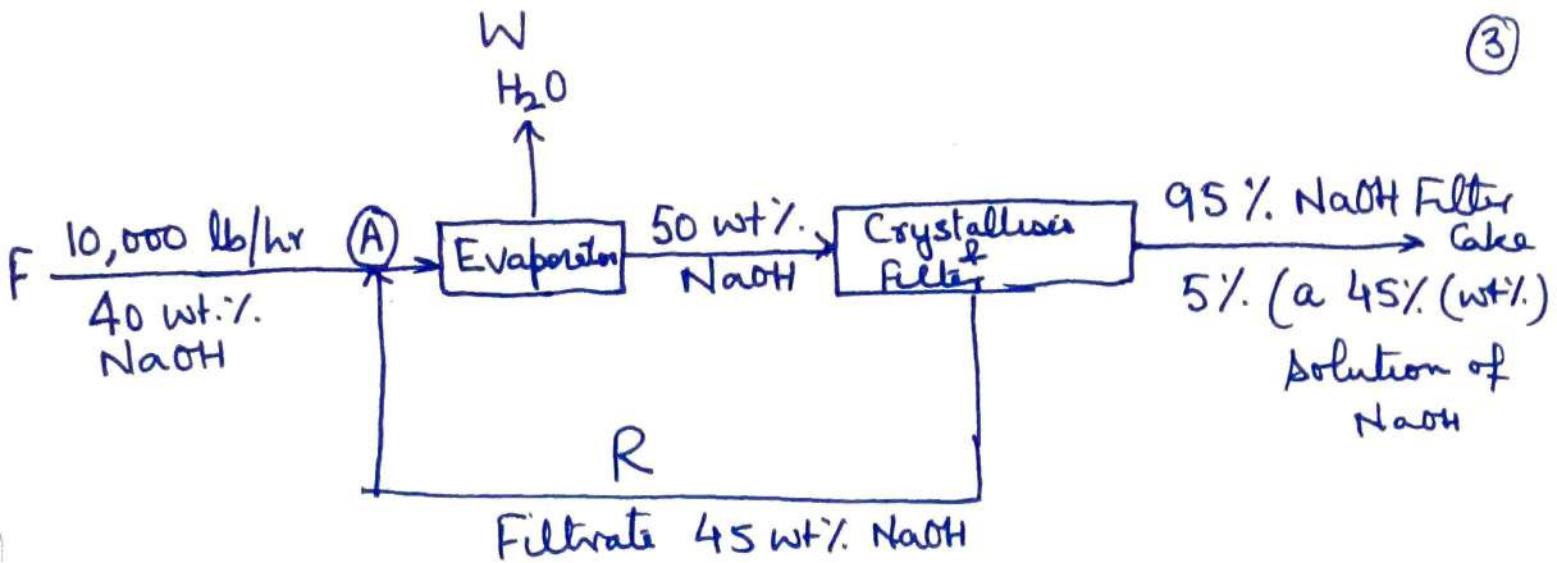
1. About the entire process, including the recycle stream (Denoted by dashed line 1). Contains no information about recycle stream. Fresh feed & net product.
2. At the mixer (Denoted by dashed line 2). Fresh feed combines with recycle stream to produce total or gross feed. Contains information about recycle stream.
3. At the basic process itself (dashed line 3). No information about recycle stream. Gross feed , Gross product
4. At the separator (dashed line 4) Contain information about recycle stream Gross product separated into Net Product and Recycle Stream.

Balance on combination of subsystems can be made.

Process plus Separator (3 + 4)

Mixer plus Process (2 + 3)

(3)



Fresh feed 10000 lb/h of 40% aqueous NaOH soln

Fresh feed combined with recycled filtrate & fed to evaporator to produce 50% NaOH soln.

Crystallizer produces a filter cake (95% NaOH crystals)

and 5% solution that itself consists of 45% NaOH.

Filtrate contains 45% NaOH

Determine:

- Flow rate of water removed by evaporator & the recycle rate
- Filtrate is not recycled  
Same production rate of NaOH flakes.  
What would be the total feed rate of 40% NaOH. Assume product solution from evaporator still contains 50% NaOH.

Open System  
Steady State Process

Base: 10,000 lb fresh feed.

Unknowns  $W, G, P \& R$

Overall NaOH balance

$$(0.4)(10,000) = [0.95 + (0.45)(0.05)]P$$

$$P = 4113 \text{ lb}$$

Overall  $H_2O$  balance

$$(0.6)(10,000) = W + [(0.55)(0.05)](4113)$$

$$W = 5887 \text{ lb.}$$

(or use total overall balance)  
 $10,000 = 4113 + W$

Amount of NaOH exiting with P

$$[(0.95) + (0.45)(0.05)](4113) = 4000 \text{ lb}$$

Amount of water in P = 113 lb; Check  $113 + 5887 = 6000 \text{ lb}$

$W \& P$  have been determined

Make balance on a subsystem that involves R (Mixer, Separator)

(5)

NaOH balance on crystalliser

$$0.5G_1 = 4000 + 0.45R$$

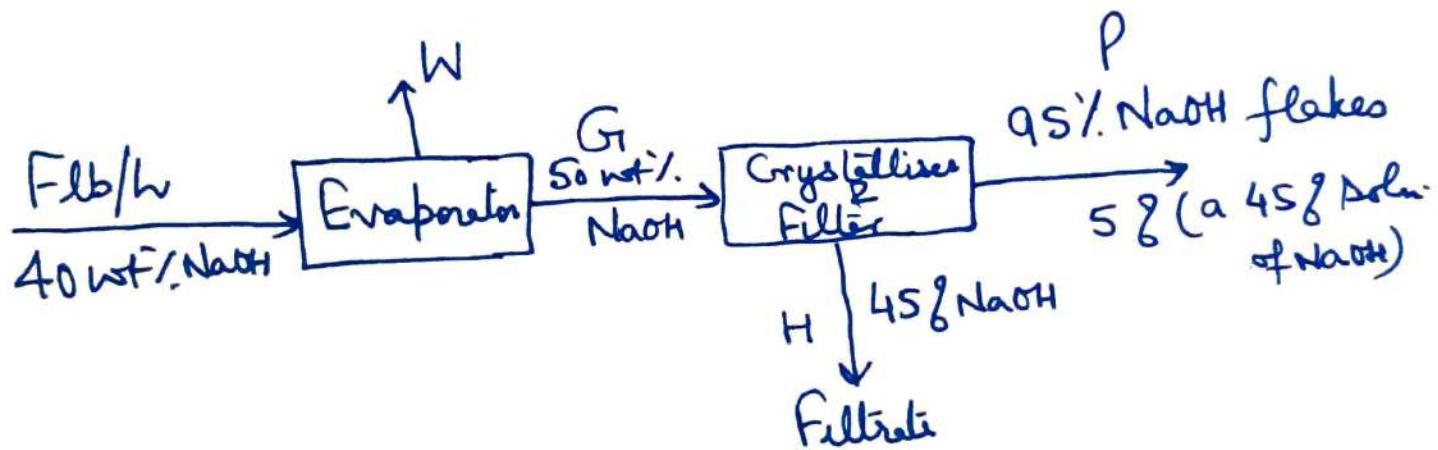
H<sub>2</sub>O balance on crystalliser

$$0.5G_1 = 113 + 0.55R$$

(or use total balance  $G_1 = R + 4113$ )

$$R = 38,870 \text{ lb.}$$

- b. Now, no recycle from crystalliser  
 Production & Composition of P  
 remains same.



Basis :  $P = 4113 \text{ lb.}$

Unknowns  $F, W, G_1, H$ .

NaOH balance on Crystalliser

$$0.5G_1 = [(0.95) + (0.05)(0.45)](4113) + 0.45H$$

(6)

$H_2O$  balance on crystalliser

$$0.5 G_1 = (0.05)(0.55) 4113 + 0.55 H$$

$$H = 38870 \text{ lb}$$

Overall NaOH balance

$$0.4 F = 0.45(38,870) + 4000$$

$$F = 53730 \text{ lb}$$

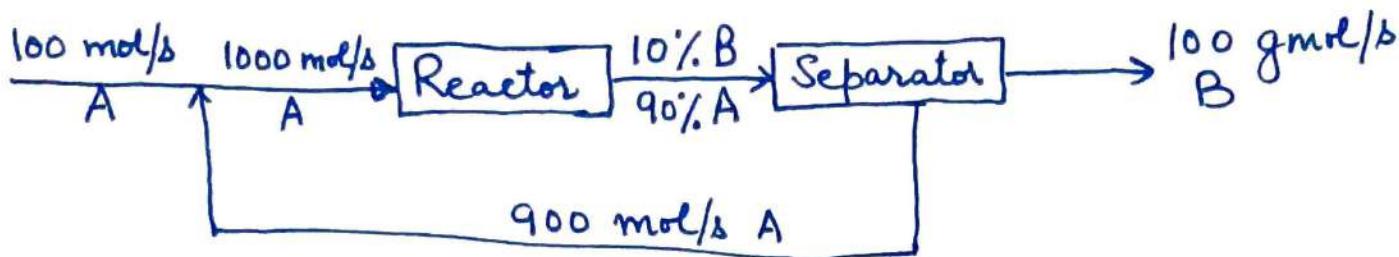
Without recycle 5.37 times larger

Disposal of Filtrate

(1)

## Recycle with Chemical Reaction

Recycle of Reactants to enhance the overall conversion in a reactor.



Steady State Material Balances for Mixer, Reactor & Separator are satisfied.

Overall Material Balance

Extent of Reaction 100 reacting mol/s

Extent of Reaction for the Overall Process  
(Based on B)

$$\sum_{\text{overall}} = \frac{100 - 0}{1} = 100 \text{ moles}$$

Material Balance to Determine the output P of the reactor (on basis of 1 s)

$$A = 900 \text{ mol}$$

$$B = 100 \text{ mol}$$

\* or a material balance for a reactor is used.

Extent of Reaction (based on B) for the reactor

$$\sum_{\text{reactor}} = \frac{100 - 0}{1} = 100 \text{ moles}$$

Extent of Reaction is the same regardless of whether an overall material balance is used \*

$$\text{Overall Fraction Conversion} = \frac{\frac{\text{Mass (Moles) of reactant in the reactor}}{\text{Mass (Moles) in the fresh feed}} - \frac{\text{Mass (Moles) of reactant in the output to overall process}}{\text{Mass (Moles) of reactant in the fresh feed}}}{\text{Mass (Moles) of reactant in the fresh feed}}$$

$$\text{Single-Pass (Once-Through) fraction conversion} = \frac{\frac{\text{Mass (Moles) of reactant fed into the reactor} - \cancel{\text{Mass (Moles) of Reactant exiting the reactor}}}{\text{Mass (Moles) of reactant fed into reactor}}}{\text{Mass (Moles) of reactant fed into reactor}}$$

Overall conversion: Depends on what enters and leaves the overall process

Single-Pass Conversion: Depends on what enters and leaves the reactor.

In the Example, overall conversion is 100%.

$$\frac{100 - 0}{100} \times 100 = 100\%$$

Single-Pass Conversion is 10%.

$$\frac{1000 - 900}{1000} \times 100 = 10\%$$

When the fresh feed consists of more than one reactant, the conversion can be expressed for single reactant, usually the limiting reactant

(3)

Overall Conversion of A,  $f_{OA} = \frac{-2\bar{v}_A \bar{\xi}_P}{n_A}$

$$\left\{ \bar{\xi}_P = \frac{n_i - n_{i0}}{2\bar{v}_i} \right\} \Rightarrow 2\bar{v}_i \bar{\xi}_P = \frac{n_i - n_{i0}}{\text{Moles Reacted}}$$

Single Pass Conversion,  $f_{SP} = \frac{-2\bar{v}_A \bar{\xi}_P}{n_A}$

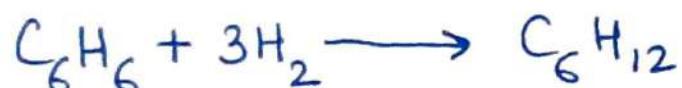
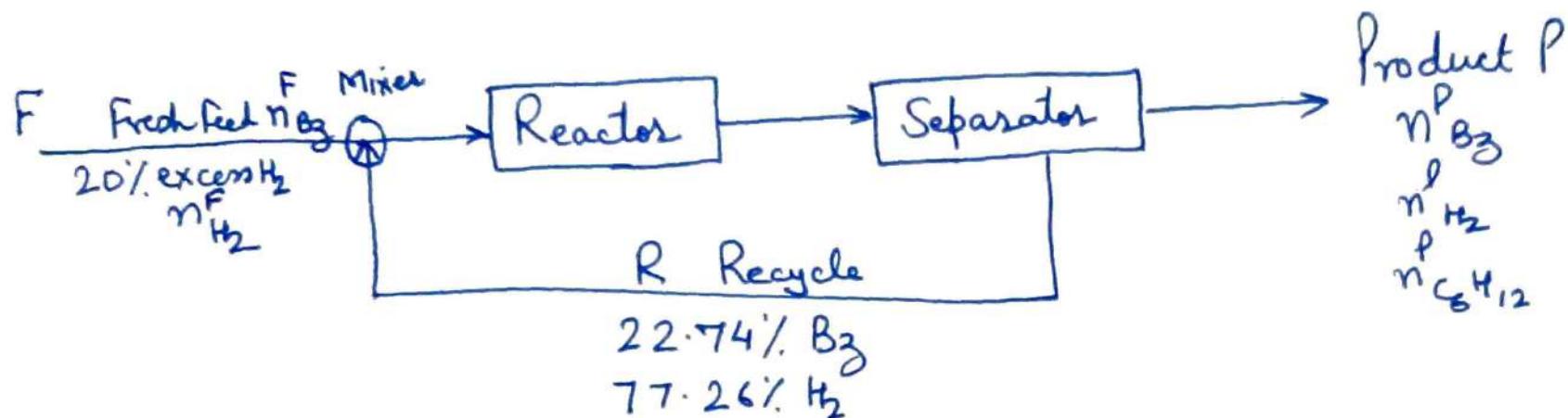
$$n_{LR}^{\text{Reactant Feed}} = n_{LR}^{\text{Fresh Feed}} + n_{LR}^{\text{Recycle}}$$

$$\frac{f_{SP}}{f_{OA}} = \frac{n_A^{\text{Fresh Feed}}}{n_A^{\text{Fresh Feed}} + n_A^{\text{Recycle}}}$$

$$= \frac{100}{100 + 90} = 0.1$$

(As derived earlier)

(4)



Overall Conversion of benzene is 95%.

Single Pass Conversion is 20%.

20% Excess  $H_2$  is used in fresh feed

Composition of Recycle Stream is 22.74 mol% benzene and  $\frac{77}{22.74} = 3.4$  mol% hydrogen.

Determine the ratio of recycle stream to fresh feed?

Open System  
Steady State Process

Basis: 100 mol fresh feed Benzene

$$n_{H_2}^F = 100(3)(1+0.2) = 360 \text{ mol}$$

(20% Excess; for complete reaction)

Total Fresh Feed = 460 mol

For Benzene ( $\nu_{B_2} = -1$ )

$$\left\{ f_{O_A} = \frac{-\nu_A \bar{\epsilon}_P}{n_A^{\text{fresh feed}}} \right\}$$

$$0.95 = \frac{(-1) \bar{\epsilon}_P}{100}$$

$\bar{\epsilon}_P = 95$  reacting moles

Unknowns  $R, n_{B_2}^P, n_{H_2}^P, n_{C_6H_{12}}^P$

Species Overall Balance

$$n_i^{\text{out}} = n_i^{\text{in}} + \nu_i \bar{\epsilon}_P^{\text{overall}}$$

$$B_2: n_{B_2}^P = 100 + (-1)95 = 5 \text{ mol}$$

$$H_2: n_{H_2}^P = 360 + (-3)95 = 75 \text{ mol}$$

$$C_6H_{12}: n_{C_6H_{12}}^P = 0 + (1)(95) = 95 \text{ mol}$$

$P = 175 \text{ mol}$

Single-Pass Conversion 20%.  
Reactor

Amount of Benzene feed to Reactor  $100 + 0.2274R$

$\xi_F = 95$  (Same as calculated for overall conversion)

$$0.2 = \frac{-(-1)95}{100 + 0.2274R}$$

$$R = 1649 \text{ mol}$$

Rates of Recycle to Fresh Feed

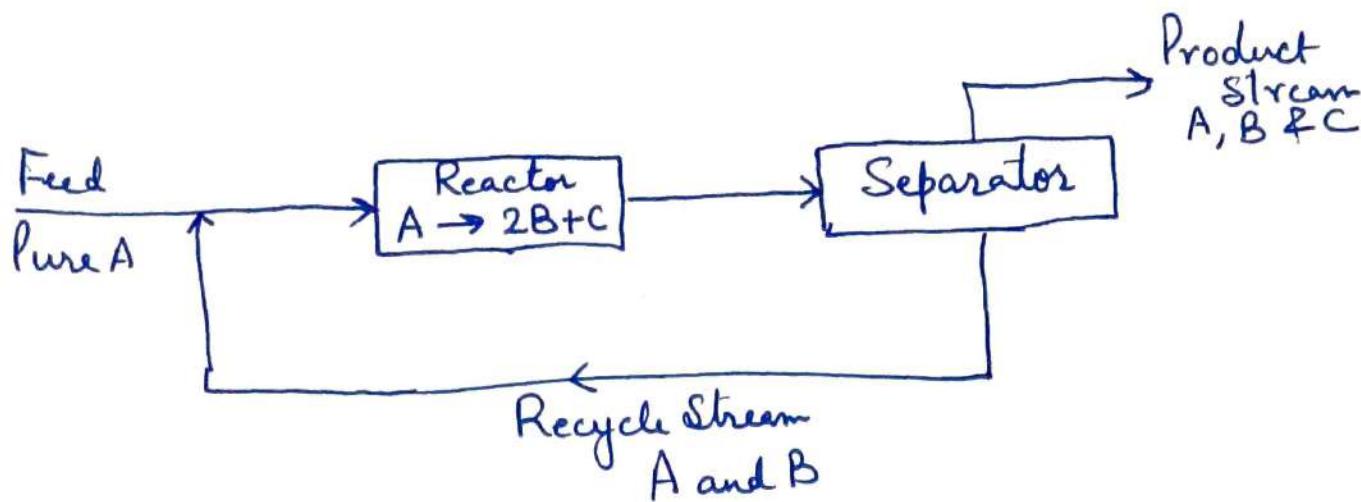
$$\frac{R}{F} = \frac{1649 \text{ mol}}{460 \text{ mol}} = 3.58$$

Ex. The reaction  $A \rightarrow 2B + C$  takes place in a catalytic reactor. The reactor effluent is sent to a separator. The overall conversion of A is 95%. The product stream from the separator consists of B, C and 0.5% of A entering the separator, while the recycle stream consists of remainder of unreacted A and 1% of B entering the separator.

Calculate

- Single-Pass Conversion of A in the reactor
- Molar Ratio of Recycle to Feed.

(7)



Basis : 100 mol feed A

Overall Conversion is 95%.

A in Product Stream 5 mol  
 B in Product Stream 190 mol  
 C in Product Stream 95 mol

Product stream from separator consists of B, C and 0.5% of A entering the separator

A in product stream 5 mol

Let A entering the separator be  $x$  mol

$$x \times \frac{0.5}{100} = 5$$

$$x = 1000 \text{ mol}$$

$\therefore$  1000 mol A is entering the separator

Recycle stream consists of remainder of unreacted A i.e 995 mol. and 1% of B entering separator

Let B entering separator be ~~Y<sub>100</sub>~~ mol

$$\frac{Y}{1000} \times 100$$

## Making Balance for B at Separator

Moles of B entering Separator Y

Moles of B in product stream 190

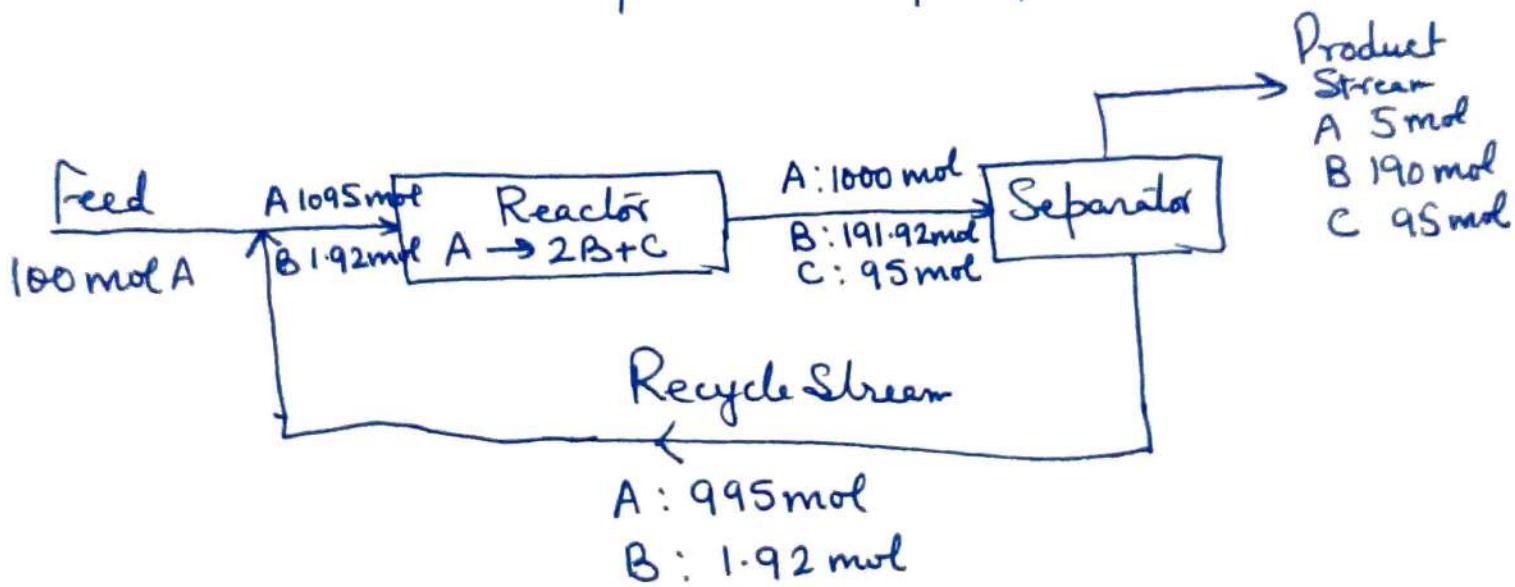
Moles of B in recycle stream  $Y \times \frac{1}{100}$

$$Y = 190 + 0.01Y$$

$$Y[1 - 0.01] = 190$$

$$Y = \frac{190}{0.99} = 191.92 \text{ mol}$$

Moles of B entering Separator 191.92



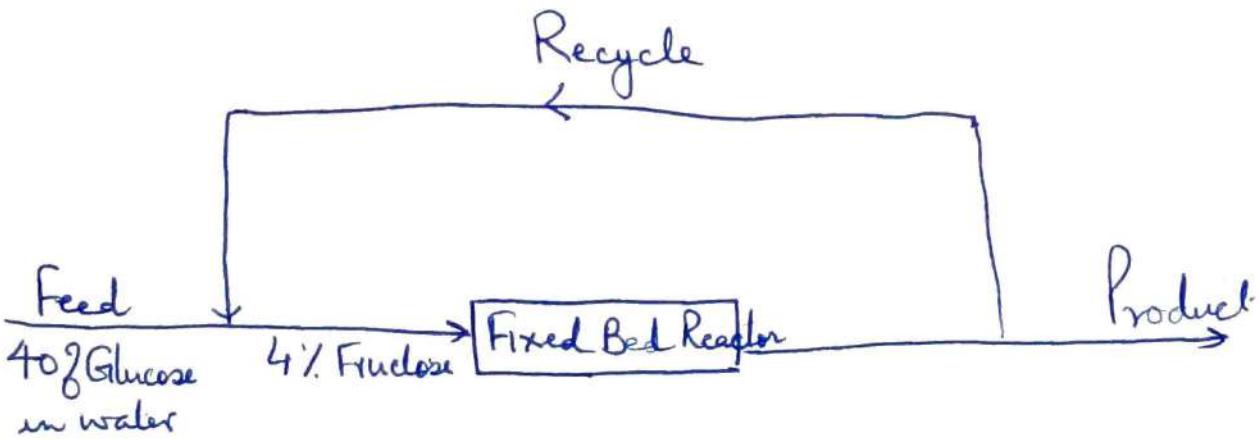
Single-Pass Conversion of A in reactor

$$= \frac{95 \text{ mol}}{1095 \text{ mol}} = 0.0867$$

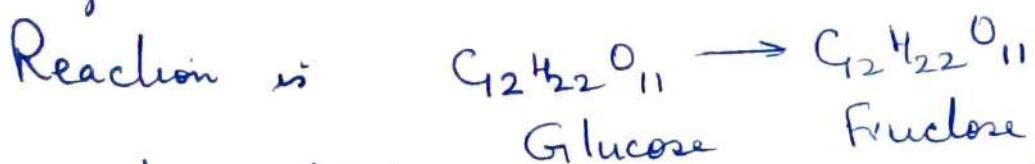
8.67%

Molar Ratio of Recycle to Feed

$$\frac{99.5 \text{ mol}}{100 \text{ mol}} = \underline{\underline{9.95}}$$

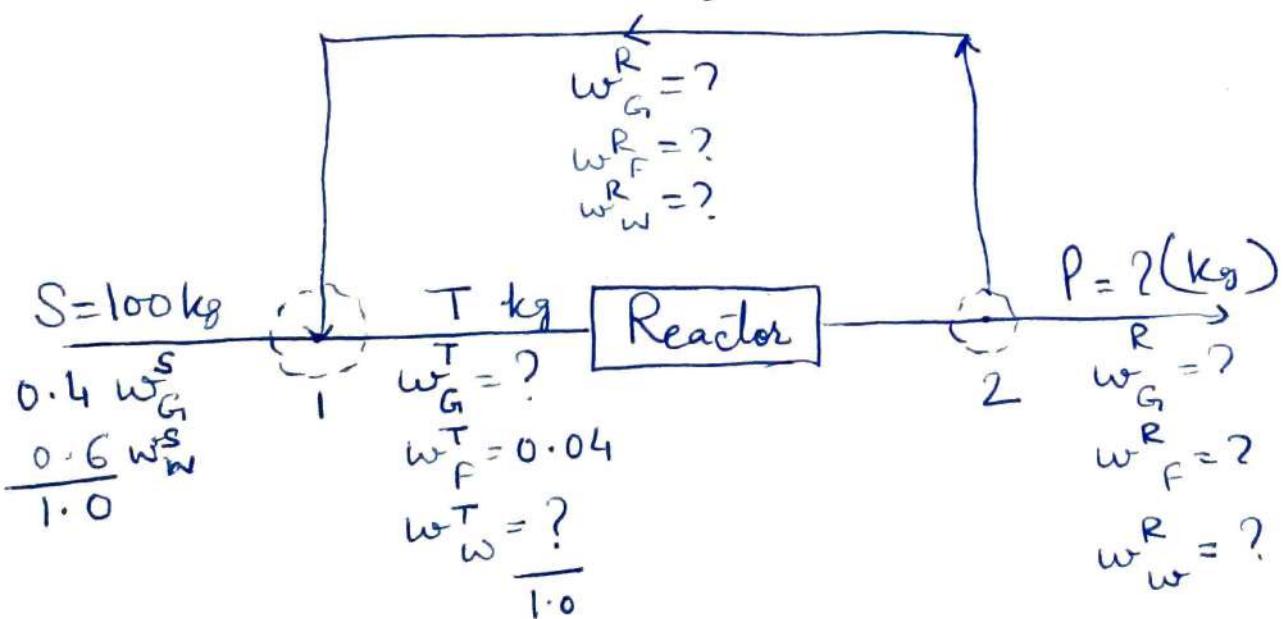


What percent conversion of glucose results on one pass through the reactor when the ratio of the exit stream to the recycle stream is equal to 8.33.



Open, steady state process with recycle & reaction occurring

$R$  (kg)



Basis:  $S = 100 \text{ kg}$

Overall Balance

Total

$$P = S = 100 \text{ kg}$$

$$R = \frac{100}{8.33} = 12 \text{ kg} \quad (R = P/8.33)$$

Overall no water is generated or consumed

$$\text{Water} \quad 100(0.6) = P w_w^R = 100 w_w^R$$

$$w_w^R = 0.6$$

Mixing Point 1

No reaction occurring

$$\text{Total} \quad 100 + 12 = T = 112$$

$$\text{Glucose} \quad 100(0.4) + 12 w_g^R = 112 w_g^T$$

$$\text{Fructose} \quad 0 + 12 w_f^R = 112(0.04)$$

$$w_f^R = 0.373$$

$$w_g^R + w_f^R + w_w^R = 1$$

$$w_g^R = 1 - 0.373 - 0.6 = 0.027$$

from Glucose Balance

$$w_g^T = 0.36$$

Reactor plus Separator 2

$$\text{Glucose} \quad w_g^T T - (R+P)(w_g^R) = (f) w_g^T T$$

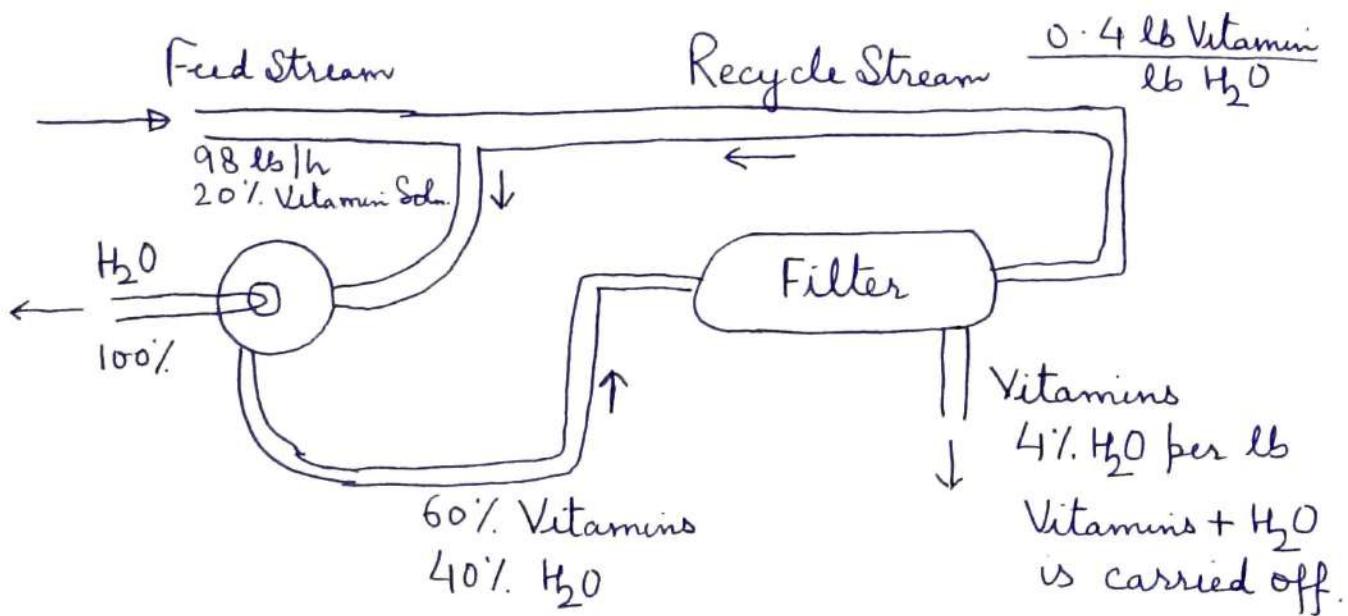
$$(0.36)(112) - (112)(0.027) = f(0.36)(112)$$

$$40.3 - 3.02 = f(40.32)$$

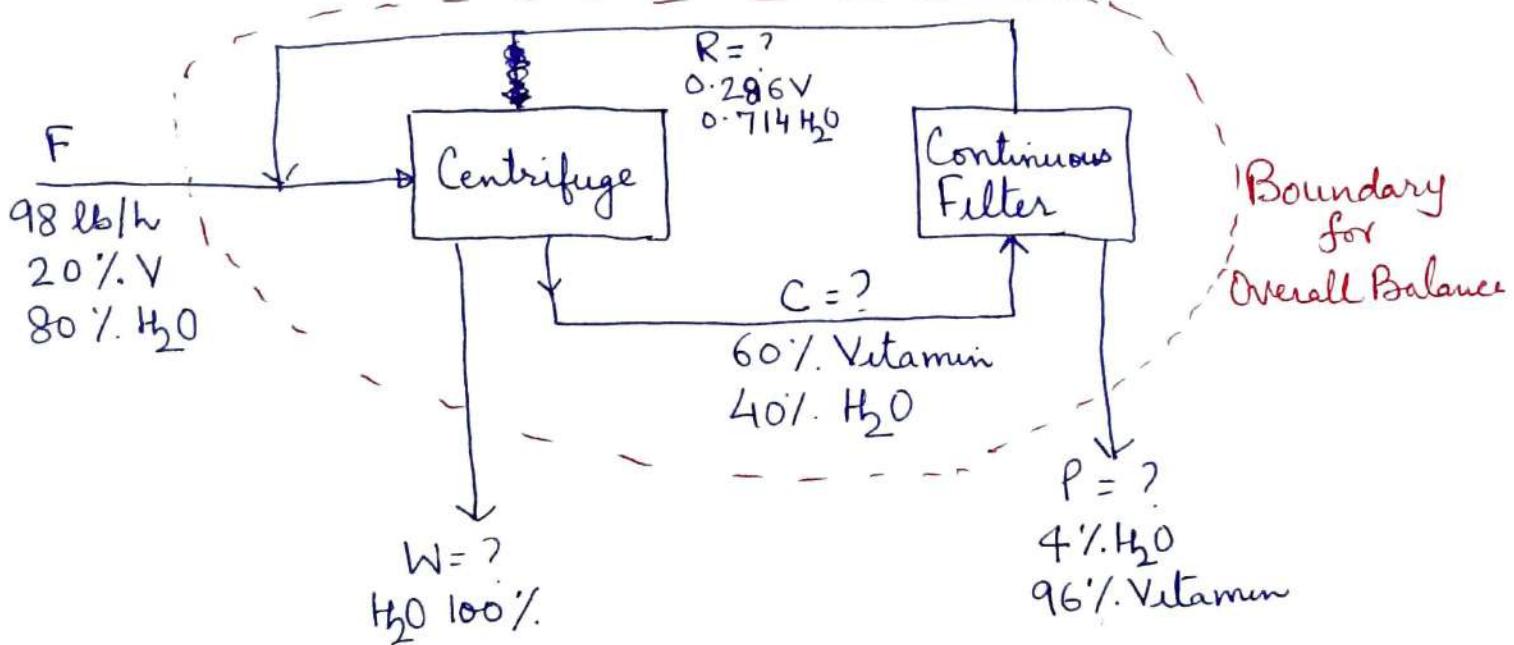
$$\underline{f = 0.93}$$

$$\text{Check: } z_4 = \frac{3.02 - 40}{-1} = 37 \quad f = \frac{-(-1)(37)}{40} = 0.93$$

(1)



Determine the lb/h of recycle stream R.



Steady-State; Without Chem. Rxn. & With Recycle

Recycle Stream Composition

$$\frac{0.4 \text{ lb V}}{1 \text{ lb } H_2O} \left| \frac{1 \text{ lb } H_2O}{1.4 \text{ lb solution}} \right. = 0.286 \frac{\text{lb V}}{\text{lb solution}}$$

Vitamins  $0.714/\text{lb soln.}$

Basis: 1 Hour

$$F = 98 \text{ lb}$$

(2)

Four Unknowns

W, C, P, R

Overall Material Balance

$$\text{Vitamin} : 0.2(98) = 0 + 0.96P$$

$$H_2O : 0.8(98) = (1.0)W + 0.04P$$

$$\text{Total} : 98 = W + P$$

$$P = 20.4 \text{ lbs}$$

$$W = 98 - 20.4 = 77.6 \text{ lbs.}$$

Total balance on Filter

$$C = R + P$$

$$C = R + 20.4$$

Component V balance on filter

$$Cw_C = R w_R + P w_P$$

$$0.6C = 0.286R + 0.96(20.4)$$

$$R = 23.4 \text{ lbs/h}$$

Check: Make balance around centrifuge



# भारतीय प्रौद्योगिकी संस्थान दिल्ली

## INDIAN INSTITUTE OF TECHNOLOGY DELHI

अनुक्रमांक  
Entry No.

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सभी पृष्ठों पर लिखें। Write on all pages.

अनुवर्ती पुस्तिका संख्या  
CONTINUATION BOOK No.

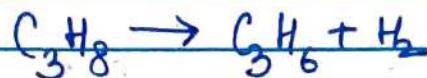
पाठ सं.  
Course No.

ग्रुप संख्या  
Group No.

दिनांक  
Date  -  -

### Dehydrogenation of Propane

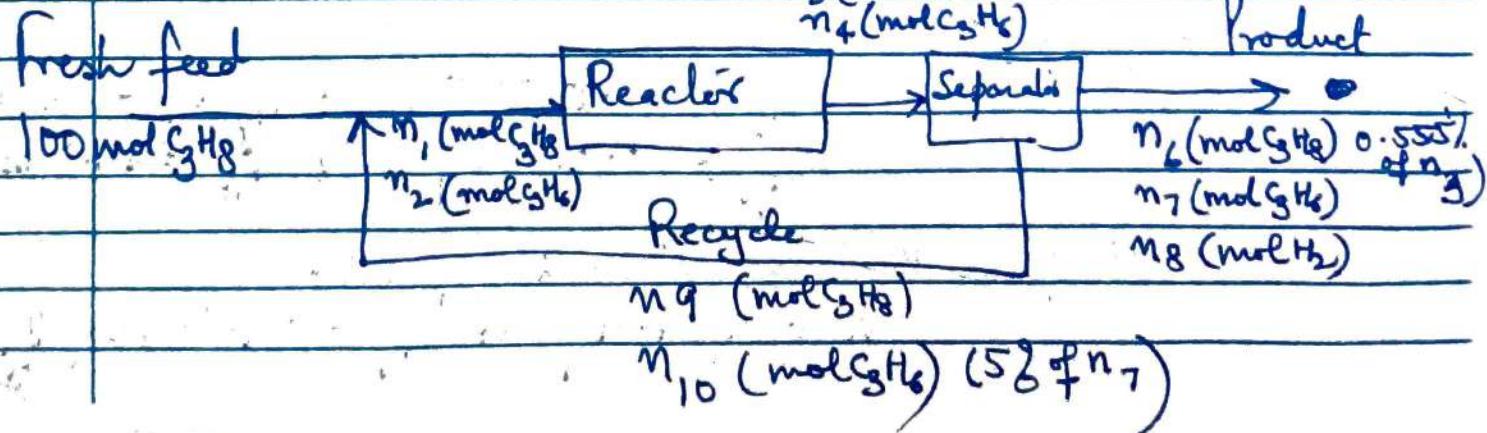
Propane is dehydrogenated to form propylene in a catalytic reactor



overall

The process is to be designed for a 95% conversion of propane. The reaction products are separated into two streams: the first, which contains  $\text{H}_2$ ,  $\text{C}_3\text{H}_6$  & 0.555% of propane that leaves the reactor, is taken off as product; the second stream, which contains the balance of unreacted propane and 5% of the propylene in the first stream, is recycled to the reactor.

Calculate the composition of product, the ratio (moles recycled / moles fresh feed) and the single-pass conversion.



Basis: 100 mol fresh feed

95 % overall propane conversion ( $\Rightarrow 5\% \text{ unconverted}$ )

$$n_6 = 0.05(100 \text{ mol}) = 5 \text{ mol } C_3H_8$$

Overall C Balance

$$(100 \text{ mol } C_3H_8)(3 \text{ mol C/mol } C_3H_8) = n_6 (\text{mol } C_3H_8)(3 \text{ mol C/mol } C_3H_8)$$

$$n_6 = 5 \text{ mol} + n_7 (\text{mol } C_3H_6)(3 \text{ mol C/mol } C_3H_6)$$

$$\rightarrow n_7 = 95 \text{ mol } C_3H_6$$

Overall H Balance

$$(100)(8) = n_6(8) + n_7(6) + n_8(2)$$

$$\Rightarrow n_8 = 95 \text{ mol } H_2$$

Product Contains

$$\begin{array}{ll} 5 \text{ mol } C_3H_8 & 2.6 \text{ mol } C_3H_8 \\ 95 \text{ mol } C_3H_6 & \Rightarrow 48.7 \dots \text{ mol } C_3H_6 \\ 95 \text{ mol } H_2 & 48.7 \dots \text{ mol } H_2 \end{array}$$

Separator

$$n_6 = 0.0555 n_3 \Rightarrow n_3 = 900 \text{ mol } C_3H_8$$

$$n_{10} = 0.05 n_7 \Rightarrow n_{10} = 4.75 \text{ mol } C_3H_6$$

Propane Balance around Separator

$$n_3 = n_6 + n_9 \Rightarrow n_9 = 895 \text{ mol } C_3H_8$$

Propane Balance around mixing point

$$100 \text{ mol} + n_9 = n_{10} \Rightarrow n_{10} = 99.5 \text{ mol}$$

$n_9$        $n_{10}$



$$\text{Recycle Ratio} = \frac{(n_9 + n_{10})}{100} = \frac{99.5}{100} = 9 \frac{\text{mol recycle}}{\text{mol fresh feed}}$$

$$\text{Single-pass loss} = \frac{n_1 - n_3}{n_1} \times 100\% \\ = 9.6\%$$

## Recycle Stream:

### Chemical Reaction Occurring

In the Example

Single Pass Conversion  $\sim 10\%$ .

Overall Conversion  $\sim 95\%$ .

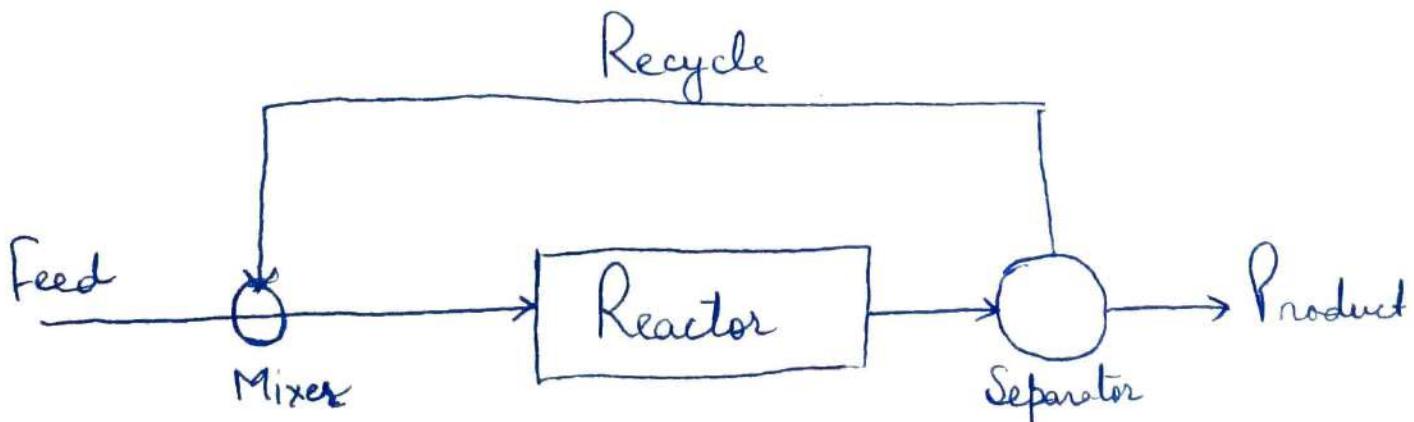
High Overall Conversion is desired

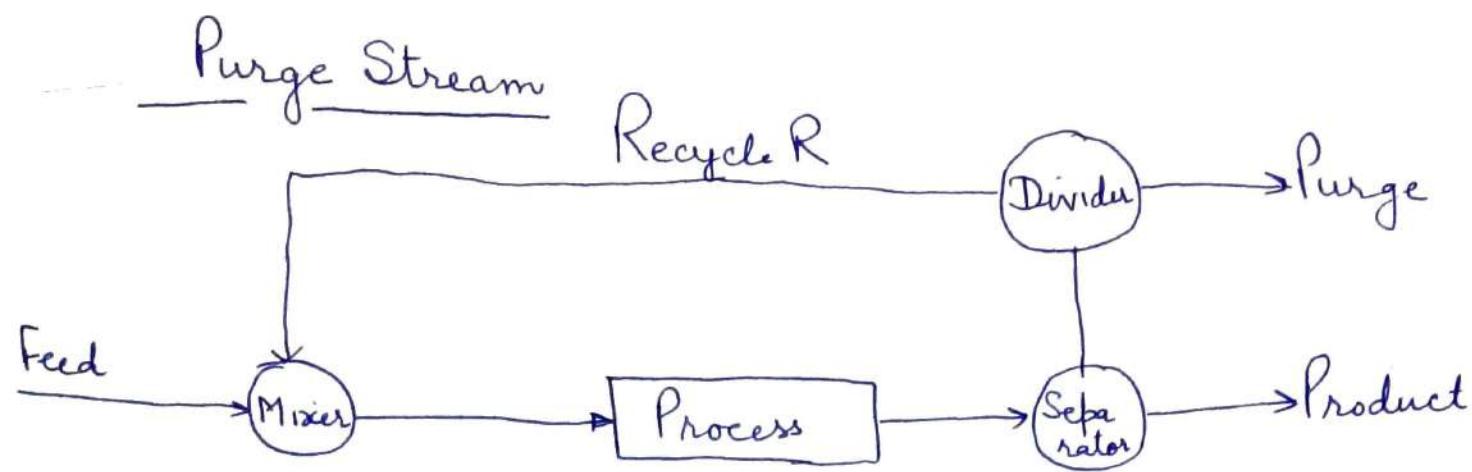
- High Single-Pass Conversion (Vol. of Reactor needed will be more.)
- Low Single-Pass Conversion with Recycle (Separator)

Cost of Reactor Increases for high conversion  
but additional cost of Recycling  
(Separator)

Reactor has to handle (process)  
higher throughputs

### Economic Analysis





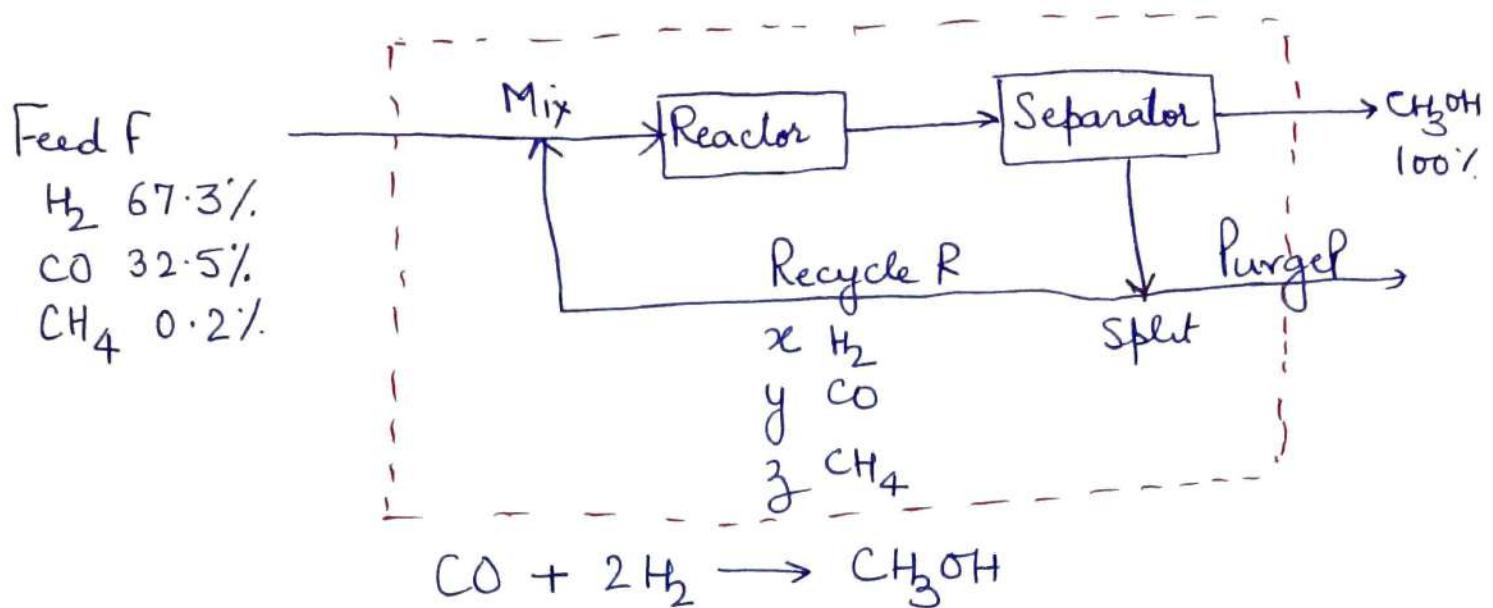
Purge Stream: A stream bled off from the process to remove an accumulation of inert or unwanted material that might otherwise buildup in the recycle stream.

A material that enters with the fresh feed or is produced in a reaction remains entirely in the recycle stream (rather than being carried out in process product); will steadily accumulate making attainment of steady state

To prevent this buildup, a portion of the recycle stream must be withdrawn as purge stream

Initial design of a process, trace components (impurities) not considered in the Material Balances; buildup in the recycle loops

(3)



A purge stream is used to maintain the  $CH_4$  concn. in the exit from the separator at no more than 3.2 mol%. and prevent hydrogen buildup as well. The once-through conversion of CO in the reactor is 18%.

Compute the moles of recycle,  $CH_3OH$  and purge per mole and also compute purge gas composition.

Steady-State with Chemical Reaction

Purge & Recycle stream have same composition  $x, y, z$  mole fraction of  $H_2, CO$  &  $CH_4$  respectively

Basis:  $F = 100$  mole

Unknown  $x, y, z, E, P, R$

Making an overall mass balance is not convenient as problem is presented in terms of moles.

### Element Balances for Overall Process H, C, O

Assume  $z = 0.032$

(Max. Allowed  $\text{CH}_4$  in purge stream)

$$x + y + z = 1$$

CO Balance

### Overall Element Balance (in moles)

$$2\text{H}: 67.3 + 0.2(2) = E(2) + P(x+2z)$$

$$\text{C: } 32.5 + 0.2 = E(1) + P(y+z)$$

$$\text{O: } 32.5 = E(1) + P(y)$$

### CO Balance for Reactor plus Separator

$$(32.5 + Ry) - y(R+P) = (0.18)(32.5 + Ry)$$

In	Out	Consumed
$E \text{ CH}_3\text{OH}$		31.25
$P \text{ Purge}$		6.25
$R \text{ Recycle}$		705
$x \text{ H}_2$		0.768
$y \text{ CO}$		0.2
$z \text{ CH}_4$		0.032

Ex. Methanol is produced in the reaction of carbon dioxide and hydrogen



The fresh feed to the process contains hydrogen, carbon dioxide and 0.4%. (mole) inert (I). The reactor effluent passes to a condenser that removes essentially all of the methanol and water formed and none of the reactants or inert. The latter substances are recycled to the reactor. To avoid buildup of inert in the system, a purge stream is withdrawn from the recycle.

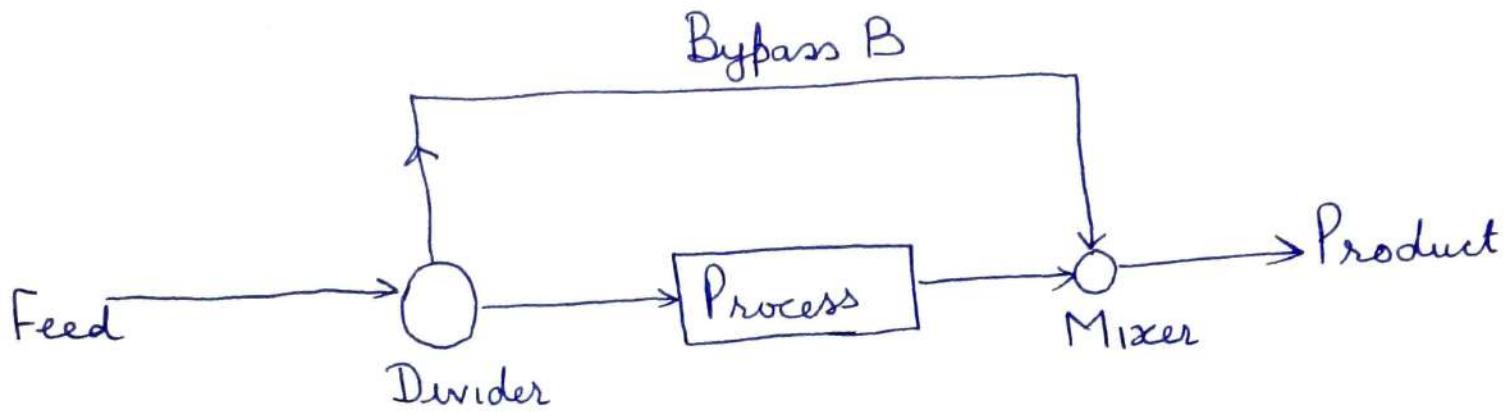
The feed to the reactor (not the fresh feed to the process) contains 28 mole%  $\text{CO}_2$ , 70 mole%  $\text{H}_2$  and 2 mole% inert. The single pass conversion of hydrogen is 60%.

Calculate the molar flow rates and molar compositions of the fresh feed, the total feed to the reactor, the recycle stream, and the purge stream for a methanol production rate of 155 kmol  $\text{CH}_3\text{OH}/\text{hour}$ .

Ex. An  $\text{NH}_3$  plant is operated with a 1:3  $\text{N}_2\text{-H}_2$  mixture as feed. The conversion to  $\text{NH}_3$  is 20%. The ammonia formed is separated completely and the unconverted gases are recycled to the reactor. The fresh  $\text{N}_2\text{-H}_2$  mixture contains 0.1 part of an impurity per 100 parts of  $\text{N}_2\text{-H}_2$  mixture by volume. The tolerance limit of the impurity entering the reactor is assumed to be 3 parts to 100 parts of  $\text{N}_2\text{-H}_2$  mixture by volume. To maintain this concentration, a small quantity of recycle stream is purged. Calculate the quantity of the purge stream and the ratio of the purge stream to the stream which is recycled finally.

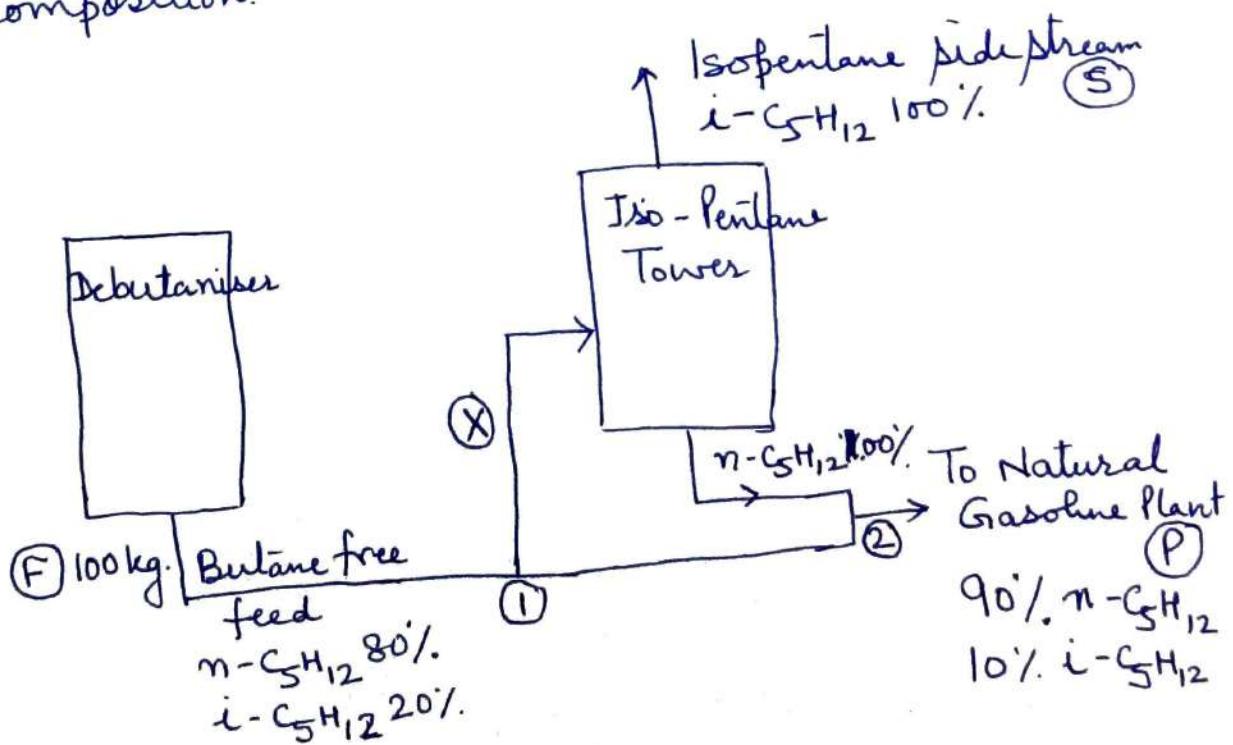
## Bypass Stream

A stream that skips one or more stages of the process and goes directly to another downstream stage.



A bypass stream can be used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.

Ex.



What fraction of butane-free gasoline is passed through the isopentane tower?

Steady State, No Reaction Occurring

Basis: 100 kg Feed

### Overall Balances

$$\text{Total Material Balance} \quad \text{In} \quad \text{Out} \\ 100 = S + P$$

Component Balance for  $n\text{-C}_5$

$$\text{In} \quad \text{Out} \\ 100(0.8) = S(0) + P(0.9)$$

$$P = 100 \frac{(0.8)}{(0.9)} = 88.9 \text{ kg}$$

$$S = 11.1 \text{ kg.}$$

### Balance Around Isopentane Tower

$x$ : kg of butane-free gas going to isopentane tower

$y$ : kg of  $n\text{-C}_5\text{H}_{12}$  stream leaving the isopentane tower

Total Material Balance

$$\text{In} \quad \text{Out} \\ x = 11.1 + y$$

Component Balance for  $n\text{-C}_5\text{H}_{12}$

$$x(0.8) = y$$

$$x = 55.5 \text{ kg or desired fraction is } 0.55.$$

Another Approach Balance Around Mixing Point<sup>2</sup>

$$\text{Total Material: } (100-x) + y = 88.9$$

$$\text{Component (n-C}_5\text{H}_{12}): (100-x)(0.2) + 0 = 88.9(0.1)$$

$$x = 55.5 \text{ kg}$$

# Gibbs Phase Rule

- Describe a two-phase system
- Extensive Variables
- Intensive Variables
- The number of intensive variables that can be specified independently for a system at equilibrium is called the Degrees of Freedom of the system.

# Gibbs Phase Rule (contd.)

- If no reactions occur among the system, the phase rule is  $F = C - P + 2$  ; F:Degrees of Freedom; C: No of chemical species; P :No of phases in a system at eqm.
- If  $r$  independent reactions occur among the system components and the reactions proceed to eqm, then the RHS of the equation must be reduced by  $r$ .

# Exercise

- Determine the degrees of freedom for each of the following systems at eqm.
- Pure liquid water
- A mixture of liquid, solid and vapor water
- A vapor-liquid mixture of acetone and methyl ethyl ketone

# Exercise

- NaCl crystals suspended in an aqueous NaCl solution
- Humid air in equilibrium with condensed water (dry air may be considered a single specie)
- A vapor-liquid mixture of four hydrocarbons
- A gaseous mixture of  $\text{H}_2$ ,  $\text{Br}_2$  and  $\text{HBr}$  given that the single rxn  $\text{H}_2 + \text{Br}_2 = 2 \text{ HBr}$  has proceeded to equilibrium.

# Gas – Liquid Systems: one condensable component

- Separation Processes – evaporation, drying, humidification- involve transfer of liquid into the gas phase
- Condensation, dehumidification- transfer of the condensable species from the gas to liquid phase
- Gas phase saturated with water- it contains all the water it can hold at the system T & P
- Water in the gas phase – Saturated Vapor

# Raoult's Law

- Applying Phase rule  $F = 2 - 2 + 2 = 2$
- $T, P, y_{H_2O}$  Intensive Variables
- If a gas at temp  $T$  & pressure  $P$  contains a saturated vapor whose mole fraction is  $y_i$  (mol vapor/ mol total gas), & if this vapor is the only species that would condense if the temp were slightly lowered, then the partial pr of the vapor in the gas equals the pure-component vapor pr  $p^*_i(T)$  at the system  $T$

# Raoult's Law (contd.)

- Raoult's Law, Single Condensable Species
- $p_i = y_i P = p^*_{\text{vap}}(T)$

# Exercise

- Air and liquid water are contained at eqm in a closed chamber at 75 C and 760 mm Hg, calculate the molar composition of the gas phase
- $y_{\text{water}} = p^*_{\text{water}}(75 \text{ C}) / P$
- $= 289 \text{ mm Hg} / 760 \text{ mm Hg} = 0.38$

# Discussion

- A gas in eqm with a liquid must be saturated with the volatile components of that liquid.
- The partial pr of a vapor at eqm in a gas mixture containing a single condensable component can't exceed the vapor pr of the pure component at system T. If  $p_i = p^*_i$ , the vapor is saturated; any attempt to increase  $p_i$  – either by adding more vapor to gas phase or by increasing the total pr at constant T- must instead lead to condensation

# Discussion (contd.)

- A vapor present in a gas in less than its saturation amount is referred to as a superheated vapor;  $p_i = y_i P < p^*_i(T)$ . Since only a saturated vapor can condense; to achieve condensation in a system containing superheated vapor- increase the pr at constant T (the LHS increases) or decreasing the T at constant P (RHS decreases)

# Discussion (contd.)

- If a gas containing a single superheated vapor is cooled at constant P, the temperature at which the vapor becomes saturated is referred to as the dew point of the gas.
- The difference between the temperature and dew point of the gas is called the degree of superheat of the gas.

# Exercise

- If water vapor is in eqm with liquid water, must the vapor be saturated. Can a vapor be saturated if there is no liquid present in the system.

# Exercise

- The vap pr of acetone is 200 mm Hg at 22.7 C.
- Liquid acetone is kept in a sealed flask at 22.7 C, and the gas above the liquid contains air & acetone vapor at a pr of 960 mm Hg. What is
  - a. partial pr of acetone in the gas
  - b. the partial pr of nitrogen
  - c. the mole fraction of acetone in the gas

# Multicomponent Gas-Liquid System

- Apply Gibbs phase rule to a multicomponent gas-liquid system; composition of two phases at a given T & P are not independent.
- A is a substance contained in a G-L system at T & P
- Raoult's Law:  $p_A = y_A P = x_A p^*_A(T)$
- Raoult's Law is an approximation that is generally valid when  $x_A$  is close to 1 (pure A)

# Henry's Law

- Henry's Law:  $p_A = y_A P = x_A H_A(T)$  where  $H(T)$  is the Henry's Law constant for A in a specific solvent.
- Generally valid for solutions in which  $x_A$  is close to zero (dilute solutions of A) provided that A does not dissociate, ionise or react in the liquid phase

# Relative Saturation (Humidity)

- Relative Saturation

$$RS = p_{Vap} / p_{sat} (p^*)$$

- $p_{Vap}$  partial pressure of vapor in gas mixture.
- $p_{sat}$  partial pressure of vapor in gas mixture if the gas were saturated at given temp of mixture ( i.e. vapor pressure of pure component)

- $RS = p_1/p^*_1 = (p_1 / p_{\text{tot}}) / (p^*_1 / p_{\text{tot}})$
- $= (V_1/V_{\text{tot}}) / (V_{1\text{sat}}/V_{\text{tot}}) = \text{mass}_1/\text{mass}_{1\text{sat}}$
- Fractional approach to saturation.
- Molal saturation = ratio of moles of vapor to moles of vapor-free gas

- Molal Saturation= 
$$\frac{n_{\text{vap}}}{n_{\text{vap.free gas}}}$$

# Exercise

- The weather report on the radio this morning was that the temperature this afternoon would reach 94F, the RH would be 43%, the barometer was 29.67 in. Hg. How many pounds of water vapor would be in 1 mile<sup>3</sup> of afternoon air. The vapor pr of water at 94 F is 1.61 in. Hg.

# Dehydration of Moist Air

- To avoid deterioration of drugs in a container, you proceed to remove all (0.93 kg) of the water from the moist air in the container that is at  $15^{\circ}\text{C}$  and 98.6 kPa by adsorption in silica gel. The residual dry air measures  $1000 \text{ m}^3$  at  $20^{\circ}\text{C}$  and 108 kPa. What was the relative humidity of the moist air originally in the container.

# Humidification of Air

- To condition the air in an office building in the winter,  $1000 \text{ m}^3$  of moist air per hour at 101 kPa and  $22^\circ\text{C}$  with a dew point of  $11^\circ\text{C}$  enter the system. The air leaves the system at 98 kPa with a dew point of  $58^\circ\text{C}$ . How many kilograms of water vapor are added to each kilogram of wet air entering the process.

# Condensation of Water from Air

- It is a summer day. The temperature is  $100^{\circ}\text{F}$ , the relative humidity is 90 %, & the barometer is 29.76 in. Hg. The corner gasoline station is compressing air for its “free air” supply, & compresses the atmospheric air to a pressure of 50 psig, but the work of compression increases the temperature of compressed air to  $120^{\circ}\text{F}$ . Does water condense out of the air during compression? If so, how many lb of water per ton of dry air that enters?

- Ratio of the moles of vapor to the moles of vapor-free gas
- $p_1 + p_2 = p_{\text{tot}}$
- $n_1 + n_2 = n_{\text{Tot}}$

$$\frac{n_1}{n_2} = \frac{p_1}{p} = \frac{v_1}{v_2} = \frac{n_1}{n_{\text{Tot}} - n_2} = \frac{p_1}{p_{\text{Tot}} - p_1} = \frac{v_1}{v_{\text{Tot}} - v_2}$$

1 – vapor

2 – dry gas

Absolute saturation (Humidity)

Ratio of moles vapor per mole of vapor-free gas to the moles of vapor that would be present per mole of vapor-free gas if the mixture were completely saturated at the existing temp and pressure.

$$AS = \frac{\frac{moles\ vapor}{moles\ vapor - free\ gas}_{actual}}{\frac{moles\ vapor}{moles\ vapor - free\ gas}_{satd}}$$

$$\%AS = \frac{\frac{n_1}{n_2}_{actual}}{\frac{n_1}{n_2}_{satd}} * 100 = \frac{\frac{p_1}{p_2}_{actual}}{\frac{p_1}{p_2}_{satd}} * 100$$

- 1 – vapor
- 2 – vapor-free gas
- $P_1$  saturated =  $p^*_1$
- $P_{tot} = P_1 + p_2$

$$\% AS = 100 \frac{\frac{p_1}{p_{tot} - p_1}}{\frac{p^*_1}{p_{tot} - p^*_1}} = \frac{p_1}{p^*_1} \left[ \frac{p_{tot} - p^*_1}{p_{tot} - p_1} \right] 100$$

- $p_1 / p^*_1 = RS$

$$\% AS = RS \left[ \frac{p_{tot} - p^*_1}{p_{tot} - p_1} \right] 100$$

- % AS is always less than RS

- **Dew Point**
- is the temp to which a mixture of air and vapor must be cooled in order to become saturated.
- As a partially satd gas cools either at constant volume or at const pressure, the non condensable gas eventually becomes satd with vapor and the vapor starts to condense.
- If the process takes place at const total pressure the mole fraction and partial pressure of vapor remain const until condensation starts.

- The vapor pressure of styrene is 100mm Hg at  $82^{\circ}\text{C}$  and 200 mm Hg at  $100^{\circ}\text{C}$ . A gas that consists of 10 mol% styrene and 90 mol% non condensable is contained in a tank at  $100^{\circ}\text{C}$  and 1000 mm Hg. Calculate
  - a) The dew point of gas
  - b) Relative saturation
  - c) Molal saturation, percentage (absolute) saturation

- **Humidity H** is the mass (lb or kg) of water vapor per mass (lb or kg) of bone-dry air.

$$H = \frac{18pH_2O}{29(p_T - pH_2O)} = \frac{18nH_2O}{29(n_T - nH_2O)}$$

- **Humid heat** is the heat capacity of an air-water vapor mixture expressed on the basis of 1 lb or kg of bone-dry air
- Number of BTU (cals) necessary to raise the temp of 1 lb (1gm) of dry air plus whatever moisture it may carry  $1^{\circ}\text{F}$  ( $1^{\circ}\text{C}$ )

- **Humid heat**  $C_s = C_{\text{pair}} + (C_p_{\text{H}_2\text{Ovapor}})(H)$   
where the heat capacities are all per mass and not per mol
- Assuming heat capacities of air and water vapor to be const for the narrow range of conditions experienced for air-conditioning & humidification
- $C_s = 0.24 + 0.45(H) \text{ Btu}/({}^{\circ}\text{F})$  (lb dry air)
- SI units  $C_s = 1.00 + 1.88 (H) \text{ kJ / (K)}$  (kg dry air)
- **Humid Volume** is the volume of 1 lb or 1 kg of dry air plus the water vapor in air.

$$\bullet \quad V^{\wedge} = \frac{359 \text{ ft}^3}{\frac{1 \text{ lb mol air}}{1 \text{ lb mol}} \frac{T^0 \text{ F} + 460}{29 \text{ lb air}}} + \frac{32+460}{32+460}$$

$$\frac{359 \text{ ft}^3}{\frac{1 \text{ lb mol H}_2\text{O}}{1 \text{ lb mol}} \frac{T^0 \text{ F} + 460}{18 \text{ lb H}_2\text{O}}} + \frac{\text{H lb H}_2\text{O}}{32+460 \text{ lb air}}$$

$V^{\wedge}$  is in  $\text{ft}^3 / \text{lb dry air}$

$$V^{\wedge} = \frac{22.4 \text{ m}^3}{\frac{1 \text{ kg mol air}}{1 \text{ kg mol}} \frac{T_K}{29 \text{ kg air}}} + \frac{273}{273}$$

$$\frac{22.4 \text{ m}^3}{\frac{1 \text{ kg mol H}_2\text{O}}{1 \text{ kg mol}} \frac{T_K}{18 \text{ kg H}_2\text{O}}} + \frac{\text{H kg H}_2\text{O}}{273 \text{ kg air}}$$

- $V^{\wedge} = 2.83 * 10^{-3} T(K) + 4.56 * 10^{-3} T(K) H$   
where  $V^{\wedge}$  is in  $m^3 / kg$  dry air

To determine the volume of a given mass of wet air using psychometric chart, determine the corresponding mass of dry air from absolute humidity, multiply this mass by  $V^{\wedge}_H$

Ex. Determine volume occupied by 150kg of humid air at  $T = 30^0C$  and  $h_r = 30\%$

From chart  $ha = 0.008 \text{ kg H}_2\text{O (v)/kg DA}$   
 $V^{\wedge}_H = 0.87 \text{ m}^3 / \text{kg DA}$

- Volume can be calculated as
  - $V = \frac{150\text{kg humid air}}{1\text{kg DA}} \times \frac{0.87\text{m}^3}{1.008\text{ kg humid air} \times \text{kg DA}}$
- $$V = 129 \text{ m}^3$$

- **Dry- bulb temp**
  - Is the air temp as measured by a thermometer, thermocouple or other conventional measuring instrument.
- **Dew point** the temp at which humid air becomes satd if it is cooled at constant pressure.
  - For ex. Locate the point corresponding to air at  $29^{\circ}\text{C}$  and 20% RH

- Cooling this air at const pressure (1 atm) corresponds to moving horizontally (at const abs humidity) to the saturation curve.  $T_{\Delta p}$  is the temp at the intersection or  $4^{\circ}\text{C}$ .
- **Wet-bulb temp**
- Porous material like cloth or cotton is soaked water and wrapped around bulb of thermometer to form a wick, thermometer placed in a stream of flowing air. Evaporation of water from the wick into the flowing air is accompanied by a transfer of heat from bulb which in turn causes a drop in bulb temp & hence thermometer reading.

- Provided that the wick remains moist, the bulb temp falls to a certain value & remains there.
- The final temp reading is the wet-bulb temp of air flowing past the wick wet-bulb temp of humid air depends on both the dry-bulb temp and moisture content of air.
- If air is satd (100% RH), no water evaporates from wick and wet-bulb and dry-bulb temps are same.
- The lower the humidity the greater the difference between two temps.
- constant wet-bulb temperature line

- Determine wet-bulb temp of air at  $30^{\circ}\text{C}$ (dry bulb) with a RH of 30%
- Locate the point at the intersection of vertical line corresponding to  $T = 30^{\circ}\text{C}$  & curve corresponding to  $hr = 30\%$  . The diagonal line through the point is the constant wet-bulb temp line for air at given condition .
- Follow that line upward to the left until you reach saturation curve.
- The temp value you need on the curve ( or vertically down from it on abscissa) is wet-bulb temp of air ( $18^{\circ}\text{C}$ )

- It means if you wrap a wet wick around a thermometer bulb and blow air with  $T = 30^{\circ}\text{C}$  &  $h_r = 30\%$  the bulb , the thermometer reading will drop and eventually stabiles at  $18^{\circ}\text{C}$
- Use psychometric chart to estimate
- I. Absolute humidity, wet-bulb temp, humid volume, dew point at  $41^{\circ}\text{C}$  and 10% RH.
  - II. The amount of water in  $150\text{m}^3$  of air at these conditions

- $H_a = 0.0048 \text{ kg H}_2\text{O / Kg DA}$
- $T_{wb} = 19^{\circ}\text{C}$
- $V^* (\text{m}^3 / \text{Kg DA}) = 0.895$
- $T_{dp} = 3^{\circ}\text{C}$
- Moles of humid air
- $150 \text{ m}^3 \mid 1\text{kg DA} \mid 0.0048\text{kg H}_2\text{O}$

$$\begin{array}{c|c}
 & 0.895\text{m}^3 \ 1\text{kg DA} \\
 \hline
 & \\
 \end{array}$$

$= 0.803 \text{ Kg H}_2\text{O}$

# Ideal Gases

- Making material balances, need physical properties of the process materials (density, vapor pressure, solubility etc.)
- Literature
- Estimation
- Measurement
- Solids and liquids – incompressible; looking up a density at one T & P and using it at another T & P; solids or liquid but gas

# Equation of State

- Equation of State relates the molar quantity and volume of a gas to temperature and pressure.
- Ideal Gas Equation of State ( $PV = nRT$ )
- Derived from kinetic theory of gases by assuming that gas molecules have a negligible volume, exert no forces on one another and collide elastically with the walls of the container.

# Ideal Gas

- A gas whose behaviour is well represented by  $PV = nRT$  is said to behave as an ideal gas
- 1 mol of an ideal gas at 0 C and 1 atm occupies 22.415liters ; any single species or mixture of gases
- Ideal gas equation of state is an approximation Temperatures above about 0 C and pressure below about 1 atm
- Rule of thumb for assumption

# Ideal Gas Eqn of State

- One hundred grams of nitrogen is stored in a container at 23 C and 3 psig.
- Assuming ideal gas behavior, calculate container volume in liters
- Verify that the ideal gas equation of state is a good approximation for the given conditions.

# Exercise

- Ten cubic feet of air at 70 F & 1 atm is heated to 610 F and compressed to 2.5 atm. What volume does the gas occupy in the final state.
- The flow rate of a methane stream at 285F and 1.3 atm is measured with an orifice meter. The calibration chart for the meter indicates that the flow rate is  $3.95 \times 10^5$  SCFH. Calculate the molar flow rate and true volumetric flow rate of the stream.

# Ideal Gas Mixture

- Partial pressure
- $p_A = y_A P$
- Dalton Law : partial pressures of the components in an ideal gas mixture add up to the total pressure.
- Pure component volume
- Amagat's Law
- Vol. fraction of a substance in an ideal gas mixture equals mole fraction of this substance

# Exercise

- Liquid acetone is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of  $419 \text{ m}^3 \text{ STP/min}$ . The combined gases are then compressed to a total pressure  $P = 6.3 \text{ atm gauge}$  at a temperature of  $325 \text{ C}$ . The partial pressure of acetone in this stream is  $501 \text{ mm Hg}$ . Atm pr  $763 \text{ mm Hg}$

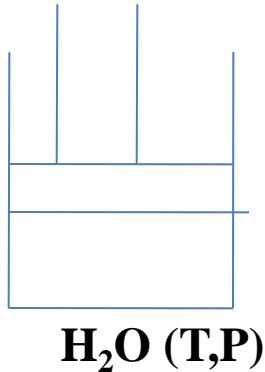
## Exercise (contd.)

- What is the molar composition of the stream leaving the compressor
- What is the volumetric flow rate of nitrogen entering the evaporator if the temperature and pressure of this stream are 27 C and 475 mm Hg.
- The density of liquid acetone is 0.791 g /cm<sup>3</sup>.

## Non ideal gases

- Ideal gas
- Basis of the simplest & most convenient eqn of state.
- Calculation independent of the species of gas
- Same for single species and mixtures
- Seriously inaccurate
- Low temp or high pressures
- For one species at given temp & pressure predicted value could be too high; for other species at same T & P could be too low; for third species could be quite close to true value.

# Critical temp and pressure



- Suppose a quantity of water is kept in a closed piston-fitted, cylinder.
- The cylinder temp is first set to a specified value with cylinder pressure low enough for all water to be vapor; water is compressed at const temp by lowering the piston until a drop of liquid water appears(i.e. until condensation occurs) .

The pressure at which condensation begins ( $P_{\text{cond}}$ ), density of liquid ( $\rho_L$ ) & density of vapor ( $\rho_V$ ) noted, expts at high temp

Run	$T^0$ (C)	$P_{\text{cond}}$ (atm)	$\rho_V$ (kg/m <sup>3</sup> )	$\rho_L$ (kg/m <sup>3</sup> )
1	25	0.0329	0.0234	997.0
2	100	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	> 374.15	No Condensation occurs		

- At  $25^{\circ}\text{C}$  water condenses at very low pressure;  
 $\rho_L > \rho_V$
- At higher temp condensation pressure increases;  $\rho_L \sim \rho_V$
- At  $374.15$   $\rho_L = \rho_V$  Above  $374.15$  no phase separation; no matter how high the pressure is raised.
- The highest temp at which a species can coexist in two phases ( liquid & vapor) is the critical temp of that species  $T_C$  & corresponding pressure is critical pressure  $P_C$ .

- A substance at  $T_c$  &  $P_c$  is said to be at its critical state.
- For water  $T_c = 374.15\text{ C}$ ;  $P_c = 218.3\text{ atm}$
- A vapor is gaseous species below its critical temp
- A gas is a species above its critical temp at a pressure low enough for the species to be more like a vapor than liquid.
- Vapor can be condensed by compressing isothermally

- Gas becomes denser & denser by compressing isothermally; separation in to two phases can't be achieved
- Substance above  $T_c$  &  $P_c$  super critical fluids.

## Virial equations of state.

- Virial equation of state express  $\frac{pV^{\wedge}}{RT}$  as a power series in the inverse of specific volume

$$\frac{pV^{\wedge}}{RT} = 1 + \frac{B}{V^{\wedge}} + \frac{C}{V^{\wedge}} + \frac{D}{V^{\wedge}} + \dots$$

# Exercise

- The critical temp and pressure of isopropanol are  $T_C = 508.8 \text{ K}$  and  $P_C = 53 \text{ atm}$ .
1. Isopropanol is in a gaseous state at  $T = 400 \text{ K}$  and  $P = 1 \text{ atm}$ . Would it be classified as a vapor or gas

# Exercise (contd.)

- Isopropanol is compressed isothermally at 400 K until at pressure  $P_A$  a liquid phase forms. The vapor and liquid densities at that point are respectively  $d_{VA}$  and  $d_{LA}$ . In a second experiment, isopropanol is compressed at 450 K until condensation occurs  $P_B$ ,  $d_{VB}$ ,  $d_{LB}$

# Exercise (contd.)

- If isopropanol at 550 K and 1 atm is compressed isothermally to 100 atm, will a condensate form. What term might you use to refer to the fluid at its initial condition? And at final condition?

- Ideal gas eqn of state if  $B = C = D = \dots = 0$
- $B, C, D$  second , third & fourth virial coefficients function of temp.
- Caution: For polar compounds ( asymmetrical compounds will a non -zero dipole moment, water)
- Follow these steps to estimate  $V^\wedge$  or  $P$  for a given  $T$  for non- polar species ( dipole moment close to zero & all other molecularly symmetrical compounds)

- Get the value of critical temp & pressure  $T_c, P_c$   
Get the Pitzer acentric factor,  $w$ , that reflects the geometry & polarity of a molecule.
- Calculate reduced temp  $T_r = T / T_c$
- Estimate  $B$  using following eqn.

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

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

$$B = \frac{RT_c}{p_c} (B_0 + wB_1)$$

➤ Soln. for  $p$  is straightforward. If  $v^\wedge$  is to be determined – quadratic; in doubtful case, estimate  $V^\wedge$  from ideal gas eqn and accept the value closest to  $V_{\text{ideal}}^\wedge$

Ex. 2 g moles of  $N_2$  are placed in a 3 liter tank at  $-150.8^{\circ}\text{C}$ . Estimate the tank pressure using the ideal gas eqn. of state & then the virial eqn. of state truncated after second term. Taking the second estimate to be correct, calculate the % error that results from the use of ideal gas eqn.

# Cubic Equations of State

Analytical PVT relations referred C.E.S because when expanded, they yield third order eqns for specific volume.

Van der Waals eqn. of state (useful for discussing deviation from ideal behavior)

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$a = \frac{27 R^2 T_c^2}{64 p_c}$$

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

- $\frac{a}{V^2}$  accounts for attractive forces between molecules and  $b$  is a correction accounting for volume occupied by molecules themselves.

## Soave – Redlich- Kwong (SRK)

$$p = \frac{RT}{V^2 - b} - \frac{\alpha a}{V^2(V^2 + b)} \quad a = 0.42747 \frac{(RT_c)^2}{p_c}$$

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2 \quad m = 0.48508 + 1.55171w - 0.1561w^2$$

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

- Ex. A gas cylinder with a volume of 2.5 m<sup>3</sup> contains 1 kmol of CO<sub>2</sub> at T = 300K. Use the SRK eqn of state to estimate gas pressure in atm. T<sub>c</sub> = 304.2K, P<sub>c</sub> = 72.9 atm , w = 0.225

The compressibility factor equation of state

Compressibility factor of a gaseous species

$$Z = \frac{pV^{\wedge}}{RT} \text{ ideal gas } Z = 1$$

The extent to which Z differs from 1 is a measure of the extent to which gas is behaving non ideally

$$pV^{\wedge} = ZRT$$

- Ex. Fifty cubic meters per hour of methane flows through pipeline at 40 bar and 300K. Estimate mass flow rate in Kg/ hr.

$$Z = 0.934 \text{ at 40 bar and 300K}$$

$$n = pV / ZRT$$

$(40 \text{ bar})(50\text{m}^3/\text{h})$	kmol K	$101.325 \text{ K pa}$
$(0.934)(300\text{K})$	$8.314 \text{ m}^3 \cdot \text{K pa}$	$1.01325 \text{ bar}$
$= 85.9 \text{ kmol}$	$16.04 \text{ Kg}$	$= 1370 \text{ kg / hr}$
$\text{h}$	kmol	

## The law of corresponding states

- Convenient if compressibility factor at single T & p were same for all gases

$Z(T, P)$  for  $N_2$  at  $0^\circ C$  & 100 atm is 0.9848

$Z(T, P)$  for  $CO_2$  at  $0^\circ C$  & 100 atm is 0.2020

- One has to measure compressibility as functions of T & P separately for every chemical species.

- van der Walls & SRK were developed to avoid having to compile massive volumes of Z data

## **Alternate approach**

- Z can be estimated for a species at a given T & p with this procedure
  - a) Get the value of  $T_c$  &  $P_c$  of the species
  - b) Calculate reduced temp  $T_r = T/T_c$
  - c) Calculate reduced pressure  $P_r = P/P_c$
  - d) Look up the value of Z on a generalized compressibility chart which plots Z versus  $P_r$  for specified value of  $T_r$

**Law of corresponding states** : The values of certain physical properties of a gas-such as Z-depend to great extent on the proximity of the gas to its critical state.  $T_r$  &  $P_r$  provide a measure of this proximity; the closer  $T_r$  &  $P_r$  to 1, the closer the gas to its critical state. A plot of Z vs  $T_r$  &  $P_r$  should be approx same for all substances ( in critical state all species should be alike)

# Procedure for using generalized compressibility chart

- i. Get the values of  $T_c$  &  $P_c$
- ii. If gas is  $H_2$  or He, determine adjusted critical constants from empirical formulae

$$T_{c'}^a = T_c + 8K$$

$$P_{c'}^a = P_c + 8 \text{ atm}$$

- iii. Calculate reduced values of two known variables

$$T_r = T/T_c \quad P_r = P/P_c$$

All the temp & pres used in these calculations must be absolute.

iv. Use compressibility chart to determine Z.

Ex. 100 g moles of N<sub>2</sub> is contained in a 5 liter vessel at – 20.6°C . Estimate the pressure in cylinder.

## Non ideal gas Mixture

Pseudo critical temp  $T'_c = y_A T_{cA} + y_B T_{cB} + y_c T_{cA}$

Pseudo critical press  $P'_c = y_A p_{cA} + y_B p_{cB} + y_c P_{cC}$

When  $y_A$ ,  $y_B$ ... are mole fraction of species A & B in the mixture

Assuming that system T & P are known

Pseudo reduced Temp  $T'_r = T/T_c$

Pseudo reduced press  $P'_r = P/P_c$

$$V^{\wedge} = Z_m RT / p$$

$Z_m$  compressibility factor for mixture

Ex. A mixture of 75%  $H_2$  and 25 %  $N_2$  ( molar basis) is contained in a tank at 800 atm and  $-70^{\circ}C$ . Estimate the specific volume of the mixture in L / mol using Kay's rule.

# Multiphase Systems

- Separation and Purification- Phase-change operations
- Brewing a cup of coffee- Leaching
- Removal of sulfur dioxide from a gas stream- absorption
- Recovery of methanol from an aqueous solution- Distillation
- Separation of paraffinic and aromatic hydrocarbons- Liquid Extraction

# Multiphase Systems (contd.)

- Transfer rate of a specie from one phase to another generally decreases with time till the second phase is saturated with the specie (holding as much as it can hold at the prevailing conditions)
- When the concentrations of all species in each phase no longer changes with time:phase eqm
- Effectiveness of separation processes

## Phase diagram

- Pure water is gas at  $130^{\circ}\text{C}$  & 100 mm Hg solid at  $-40^{\circ}\text{C}$  and 10 atm; at  $100^{\circ}\text{C}$  and 1 atm both; at  $0.0098^{\circ}\text{C}$  & 4.58 mm. Hg may be solid liquid, gas or any combination of three.
- A phase diagram of a pure substance is a plot of one system variable against another that shows the condition at which the substance exists as solid, liquid and a gas
- Pressure (vertical axis) vs temp (Horizontal axis). The boundaries between single-phase regions represent the pressure and temp at which two phases may co exist.

- Pure water placed in a cylinder fitted with a moveable piston
  - a. Initially  $20^{\circ}\text{C}$  & 3mm Hg Vapor
  - b.  $20^{\circ}\text{C}$  & 17.54 mm Hg Liquid
  - c.  $20^{\circ}\text{C}$  & 760 mm Hg Liquid
  - d.  $100^{\circ}\text{C}$  & 760 mm Hg Vapor
  - e.  $130^{\circ}\text{C}$  & 760 mm Hg Vapor
- Phase transitions – condensation at point B & evaporation at point D- take place at boundaries on the phase diagram; the system cannot move off these boundaries until transitions are complete.

- i. If  $T$  and  $P$  correspond to a point on the vapor-liquid equilibrium curve for a substance,  $P$  is the vapor pressure of the substance at temperature  $T$ , and  $T$  is the boiling point of the substance at pressure  $P$ .
- ii. The boiling point of a substance at  $P = 1 \text{ atm}$  is the normal boiling point of substance
- iii. If  $(T,P)$  falls on solid-liquid eqm curve, then  $T$  is the melting point or freezing point at pressure  $P$ .

- iv. If  $(T, P)$  falls on solid- vapor eqn curve then  $P$  is the vapor pressure of the solid at temp  $T$  &  $T$  is sublimation point at pressure  $P$ .
- v. The point  $(T,P)$  at which solid, liquid & vapor phases can all co exist is called triple point of the substance.

## **Estimation of vapor pressure**

If the vapor and liquid of a pure component are in equilibrium, then the equilibrium pressure is called the vapor pressure

- The vapor pressure of a species is a measure of its volatility : the higher the vapor pressure at a given temp; the greater the volatility of the species at that temp.
- The volatility of a species is the degree to which the species tends to transfer from the liquid ( or solid) state to vapor state.
- There is a need to know the vapor pressures of process species as function of temp.
- Measure  $p^*$  at the desired temp. or estimate the vapor pressure at desired temp.

$$\frac{dp^*}{dT} = \frac{\Delta H_v^\wedge}{T(V_G^\wedge - V_L^\wedge)}$$

- T: absolute temp
- $V_G^\wedge, V_L^\wedge$  specific volumes ( volume / mole of gas (vapor) & liquid
- $\Delta H_v^\wedge$  latent heat of vaporization or energy required to vaporize one mole of liquid
- Low pressures  $V_G^\wedge - V_L^\wedge \approx V_G^\wedge$

- Assuming the application of ideal gas eqn of state to vapor ( $V^{\wedge}_G$  is replaced with  $RT/ p^*$ )

$$\frac{d(\ln p^*)}{d(\frac{1}{T})} = -\frac{\Delta H_v^{\wedge}}{R}$$

- If vap pressure of a substance is measured at several temp,  $\ln p^*$  vs  $1/T$ , the slope of the curve at a given temp equals  $-\Delta H_v^{\wedge} / R$ .
- Most commonly used to determine heats of vap. Experimentally
- Assuming heat of vaporization of substance independent of temp. in the temp range over which vapor pressure are available,
-

# Clausius Clapeyron Equation

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

- B is a const that varies from one substance to another.
- Plot of  $\ln p^*$  vs  $1/T$  give a straight line with slope  $-\Delta H_v^\wedge / R$  and intercept B.
- If you know  $\Delta H_v^\wedge$  and  $p^*$  at a single temp  $T_0$ , solve eqn for B and use this eqn to estimate  $p^*$  at any temp close to  $T_0$

# Exercise

- The vapor pressure of benzene is measured at two temperatures:  $T_1 = 7.6\text{ C}$   $P_1 = 40\text{ mm Hg}$   
 $T_2 = 15.4\text{ C}$   $P_2 = 60\text{ mm Hg}$

Calculate the latent heat of vaporisation and parameter B in the Clausius-Clapyeron eqn and then estimate 42.2 C using this equation

- Antoine equation

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

- A,B,C constants for each substance, T- Temp, K.
- Tables of  $p^*$  at different temps. exists for many species but it is difficult to interpolate between tabulated values since  $p^*$  varies sharply with T.
- Logarithm of  $p^*$  varies with T in roughly the same way for large number of species.

- Equal – temp- reference – substance plot- A log plot of vapor pressure of a species at a given temp vs the vapor pressure of a reference species at same temp. consequently tends to be linear.
- If you have values of  $p^*$  for a species at two or more temp, you can find vapor pressure of a reference substance ( usually water) at same temp and plot  $p^*(T)$  Vs  $p^*_{ref}(T)$  on log axis .
- Draw a straight line through the points; use the plot to estimate  $p^*$  for any temp from the unknown value of  $p^*_{ref}$  at the same temp.

➤ Use of the plot is to determine  $p^*$  for a given  $T$ ;  $p^*_{\text{ref}}$  is an intermediate quantity used to relate these variables. Necessity of looking  $p^*_{\text{ref}}$  for each temp. can be avoided if values of  $T(p^*_{\text{ref}})$  are shown on a second abscissa scale. Now to found  $p^*(T)$  you need only find  $T$  on abscissa scale; the value of  $p^*_{\text{ref}}(T)$  will be located at same abscissa value & use  $p^*$  Vs  $p^*_{\text{ref}}$  to determine  $p^*(T)$ . Cox chart log  $p^*$  on ordinate and temp scale on abscissa.

- **Cox chart**
- Mark on the horizontal scale values of  $\log p^*$  so as to cover the desired range of  $p^*$
- Draw a straight line on the plot at a suitable angle, say  $45^0$ , that covers the range of  $p^*$ .
- Calibrate the vertical axis using a reference substance ( water) . For temp  $T_1$  find  $P^*_1$  from steam table. Locate  $p^*_1$  on x-axis , proceed vertical until the straight line, then proceed horizontal until vertical axis.
- Choose next temp.  $T_2$

- Calibrate the vertical axis
  - Vapor pressure of other substances plotted on this plot will yield straight lines over extensive temp. ranges facilitating extrapolation & interpolation of vapor pressure data. Only two sets of vapor-pressure data are needed to provide complete information about vapor-pressure of a substance over a considerable temp. range.
- Ex. The vapor pressure of benzene is measured at two temperatures with the following results

$$T_1 = 7.6^{\circ}\text{C},$$

$$p^*1 = 40 \text{ mm Hg}$$

$$T_2 = 15.4^{\circ}\text{C}$$

$$p^*2 = 60 \text{ mm Hg}$$

Calculate the latent heat of vaporization and estimate  $p^*$  at  $42.2^{\circ}\text{C}$  using clausius – clapeyron equation.

$P^*(\text{mm Hg})$	$T^0(\text{C})$	$T(\text{K})$
40	7.6	280.8
60	15.4	288.6

The slope of line through the two data points on a plot of  $\ln p^*$  Vs  $1/T$  is

$$\begin{aligned}
 -\frac{\Delta H_V^{\wedge}}{R} &= \frac{\ln(\frac{p_2}{p_1})^*}{[\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)]} = \frac{T_1 T_2 \ln(\frac{p_2}{p_1})^*}{T_1 - T_2} \\
 &= \frac{(280.8K)(288.6K)\ln(\frac{60mmHg}{40mmHg})}{(280.8 - 288.6)K} = -4123K
 \end{aligned}$$

- Intercept B

$$B = \ln p_1^* + \frac{\Delta H_V^{\wedge}}{RT_1}$$

$$= \ln 40 + (4213/280.8) = 18.69$$

$$\ln p^* = -4123/T(K) + 18.69; P^* \text{ in mm Hg}$$

$$\text{Check: } T = 15.4^\circ\text{C} = 288.6\text{K}$$

$$\ln p^* = -4123/288.6 + 18.69 = 4.093$$

$$p^* = \exp(4.093) = 60 \text{ mm Hg}$$

$$\text{finally at } T = 42.2^\circ\text{C} = 315.4\text{K}$$

$$\ln p^* = -4213/315.4 + 18.69 = 3.34$$

$$p^* = \exp(5.334) = 207 \text{ mm Hg} \quad (200 \text{ mm Hg Perry})$$

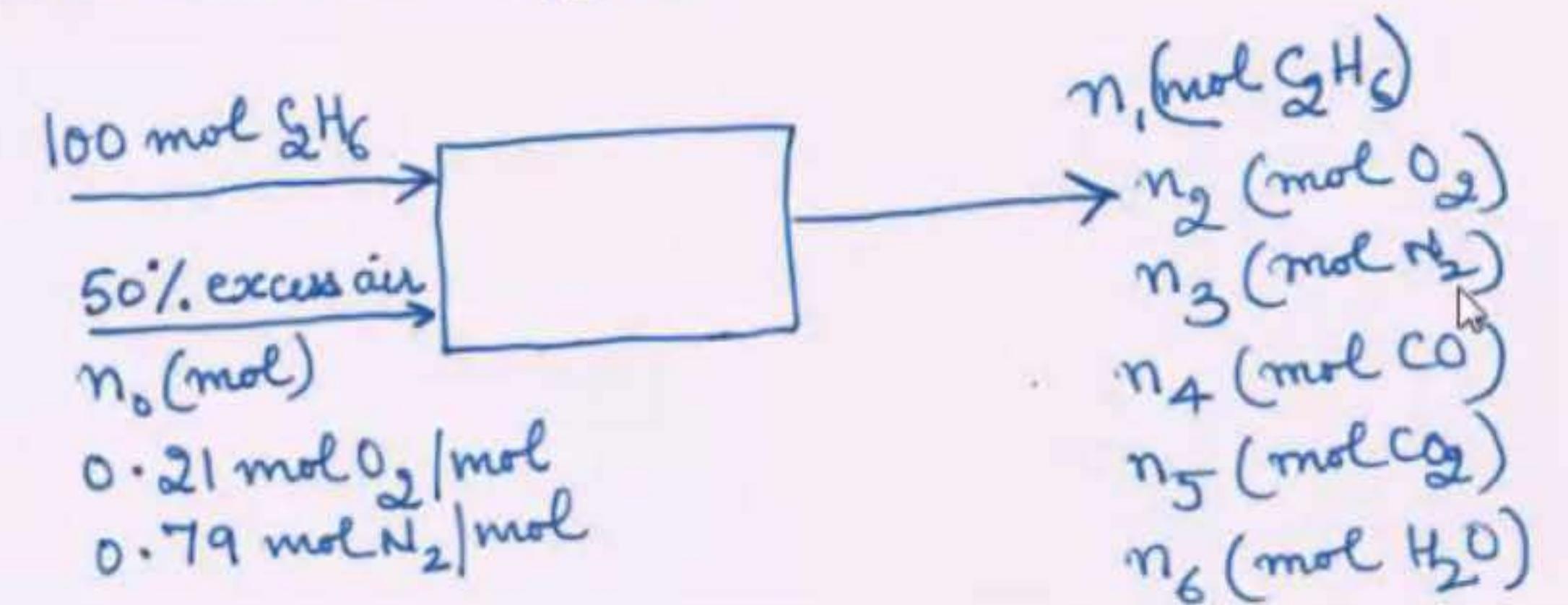
$$\begin{aligned}\Delta H_v^\wedge &= (\Delta H_v^\wedge / R)(R) \\ &= 4213 \mid 8.314 \text{ J/mol K} = 35,030 \text{ J/mol} \\ &\quad = 31,000 \text{ J/mol}\end{aligned}$$

## Material And Energy Balances

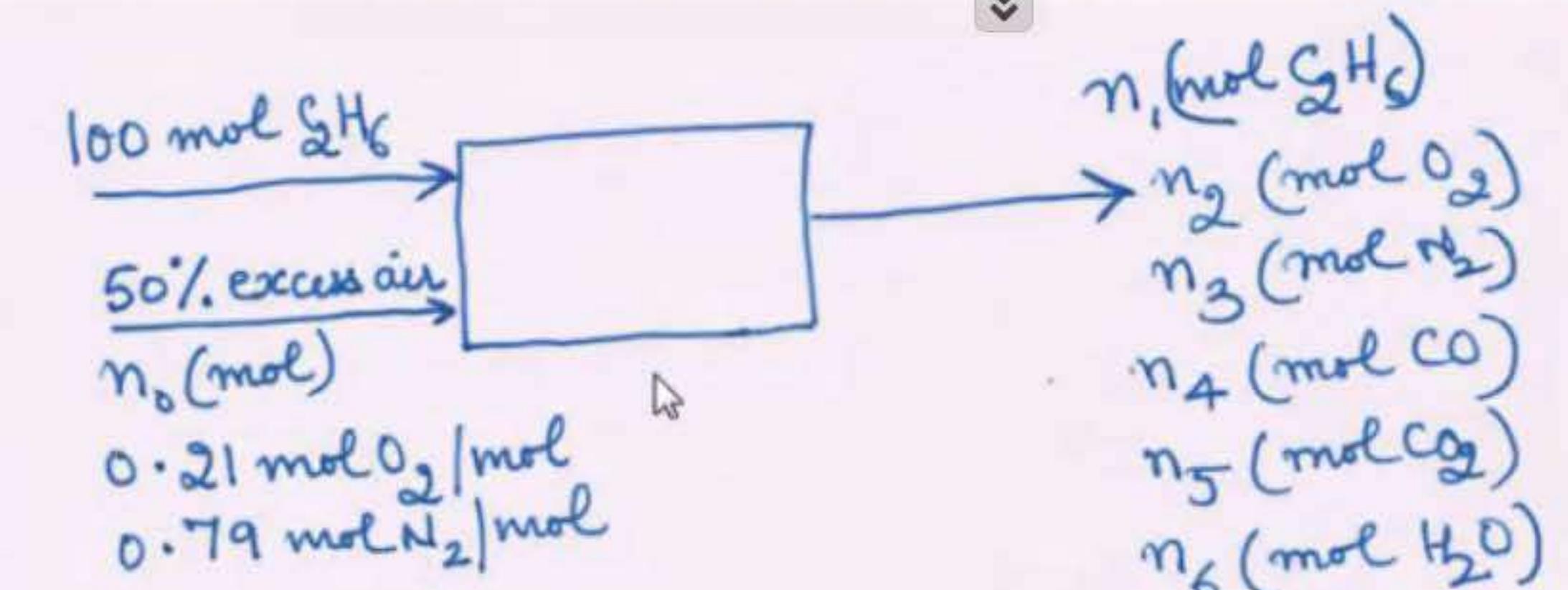
(3)

Ex. Ethane is burned with 50% excess air. The percentage conversion of ethane is 90%; of the ethane burned, 25% reacts to form CO and the balance to form  $\text{CO}_2$ . Calculate the molar composition of the stack gas on a dry basis and the molar ratio of water to dry stack gas.

Basis: 100 mol  $\text{C}_2\text{H}_6$



## Material And Energy Balances



- 7 unknown variables  $n_0, n_1, \dots, n_6$
- 3 atomic balances (C, H, O)
- 1  $\text{N}_2$  balance
- 1 excess air specification (relates  $n_0$  to the quantity of fuel)
- 1 ethane conversion specification
- 1 CO/CO<sub>2</sub> ratio specification

## Material And Energy Balances

50% Excess Air

(4)

$$(n_{O_2})_{\text{theoretical}} = \frac{100 \text{ mol } C_2H_6}{1 \text{ mole } C_2H_6} \left| \frac{3.5 \text{ mole } O_2}{1 \text{ mole } C_2H_6} \right.$$

$$= 350 \text{ mol } O_2$$

$$0.21 n_0 = 1.5 (350 \text{ mol } O_2) \Rightarrow n_0 = 2500 \text{ mol air fed}$$

90% Ethane Conversion  $\Rightarrow$  10% Unreacted

$$n_1 = 0.1 (100 \text{ mol } C_2H_6 \text{ fed}) = 10 \text{ mol } C_2H_6$$

25% Conversion to CO

$$n_4 = (0.25 \times 90) \text{ mol react to form CO} \left| \begin{array}{l} 2 \text{ mol CO formed} \\ 1 \text{ mol } C_2H_6 \text{ reacted} \end{array} \right.$$

$$= 45 \text{ mol CO}$$

## Material And Energy Balances

Nitrogen Balance : Input = Output  
 $n_1 = 0.79(2500 \text{ mol}) = 1975 \text{ mol N}_2$

Atomic Carbon Balance : Input = Output

$$100 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 2 \text{ mol C} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = n_1 (\text{mol C}_2\text{H}_6) \left| \begin{array}{l} 2 \text{ mol C} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right.$$

$$+ n_4 (\text{mol CO}) \left| \begin{array}{l} 1 \text{ mol C} \\ \hline 1 \text{ mol CO} \end{array} \right.$$

$$+ n_5 (\text{mol CO}_2) \left| \begin{array}{l} 1 \text{ mol C} \\ \hline 1 \text{ mol CO}_2 \end{array} \right.$$

Since  $n_1 = 10 \text{ mol}$ ;  $n_4 = 45 \text{ mol}$

$$n_5 = 135 \text{ mol CO}_2$$

Atomic Hydrogen Balance : Input = Output

$$100 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 6 \text{ mol H} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = 10 \text{ mol C}_2\text{H}_6 \left| \begin{array}{l} 6 \text{ mol H} \\ \hline 1 \text{ mol C}_2\text{H}_6 \end{array} \right.$$

$$+ n_6 (\text{mol H}_2\text{O}) \left| \begin{array}{l} 2 \text{ mol H} \\ \hline 1 \text{ mol H}_2\text{O} \end{array} \right.$$

$$\rightarrow n_6 = 270 \text{ mol H}_2\text{O}$$

## Material And Energy Balances

Atomic Oxygen Balance: Input = Output

(5)

$$525 \text{ mol O}_2 \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right. = n_2 (\text{mol O}_2) \left| \frac{2 \text{ mol O}}{1 \text{ mol O}_2} \right.$$

$$+ 45 \text{ mol CO} \left| \frac{1 \text{ mol O}}{1 \text{ mol CO}} \right.$$

$$+ 135 \text{ mol CO}_2 \left| \frac{2 \text{ mol O}}{1 \text{ mol CO}_2} \right.$$

$$+ 270 \text{ mol H}_2\text{O} \left| \frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}} \right.$$

$$n_2 = 232 \text{ mol O}_2$$

Composition

$$n_1 = 10 \text{ mol C}_2\text{H}_6 \quad 10/2396 = 0.00417 \frac{\text{mol C}_2\text{H}_6}{\text{mol}}$$

$$n_2 = 232 \text{ mol O}_2 \quad 232/2396 = 0.097 \frac{\text{mol O}_2}{\text{mol}}$$

$$n_3 = 1974 \text{ mol N}_2 \quad = 0.824 \frac{\text{mol N}_2}{\text{mol}}$$

$$n_4 = 45 \text{ mol CO} \quad = 0.019 \frac{\text{mol CO}}{\text{mol}}$$

$$n_5 = 135 \text{ mol CO}_2 \quad = 0.0563 \frac{\text{mol CO}_2}{\text{mol}}$$

$$\underline{2396 \text{ mol dry gas}}$$

$$n_6 = 270 \text{ mol H}_2\text{O}$$

Mole ratio of water to dry stack gas is

$$\frac{270 \text{ mol H}_2\text{O}}{2396 \text{ mol dry stack gas}} = 0.113 \frac{\text{mol H}_2\text{O}}{\text{mol dry stack gas}}$$

## Material And Energy Balances

Ex. A stack gas contains 60 mole% N<sub>2</sub>, 15% CO<sub>2</sub>, 10% O<sub>2</sub> and the balance H<sub>2</sub>O. Calculate the molar composition of the gas on dry basis ①

Basis: 100 mole Wet gas

$$\begin{array}{r} 60 \text{ mole } N_2 \\ 15 \text{ mole } CO_2 \\ 10 \text{ mole } O_2 \\ \hline 85 \text{ mole dry gas} \end{array}$$

$$\frac{60}{85} = 0.706 \frac{\text{mol } N_2}{\text{mol dry gas}}$$

$$\frac{15}{85} = 0.176 \frac{\text{mol } CO_2}{\text{mol dry gas}}$$

$$\frac{10}{85} = 0.118 \frac{\text{mol } O_2}{\text{mol dry gas}}$$

## Material And Energy Balances

Ex. An Orsat analysis yields the following dry basis composition:

$N_2$  65%

$CO_2$  14%

$CO$  11%

$O_2$  10%

A humidity measurement shows that the mole fraction of  $H_2O$  in the stack gas is 0.07. Calculate the stack gas composition on wet basis.

## Material And Energy Balances

Basis: 100 moles dry gas

Mole fraction of  $H_2O$  in stack gas is 0.07.

$$\Rightarrow 0.07 \frac{\text{mole } H_2O}{\text{mole wet gas}} \text{ or } 0.93 \frac{\text{mol dry gas}}{\text{mol wet gas}}$$

$$\frac{0.07 \text{ mol } H_2O / \text{mol wet gas}}{0.93 \text{ mol dry gas} / \text{mol wet gas}} = 0.0753 \frac{\text{mol } H_2O}{\text{mol dry gas}}$$

$$100 \text{ mole dry gas} \times 0.0753 \frac{\text{mol } H_2O}{\text{mol dry gas}} = 7.53 \text{ mole } H_2O$$

## Material And Energy Balances

$$\begin{aligned}100 \text{ mole dry gas} & \left| \frac{0.65 \text{ mole H}_2\text{O}}{\text{mole dry gas}} \right. = 65 \text{ mole N}_2 \\& = 14 \text{ mole CO}_2 \\& \quad \downarrow \\& = 11 \text{ mole CO} \\& = 10 \text{ mole O}_2 \\& \hline 107.53 \text{ mole wet gas}\end{aligned}$$

Mole fraction of each species can be calculated.

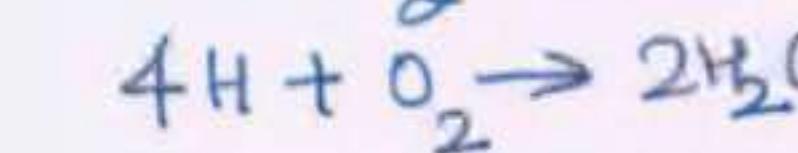
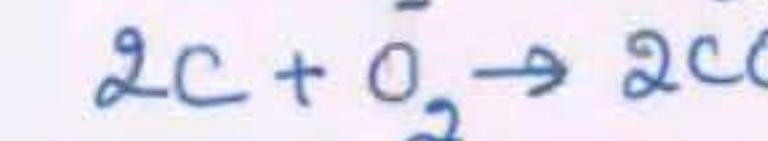
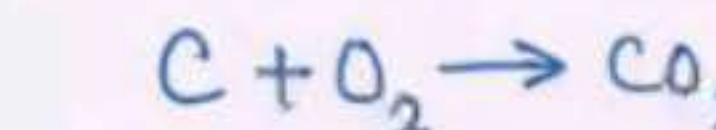
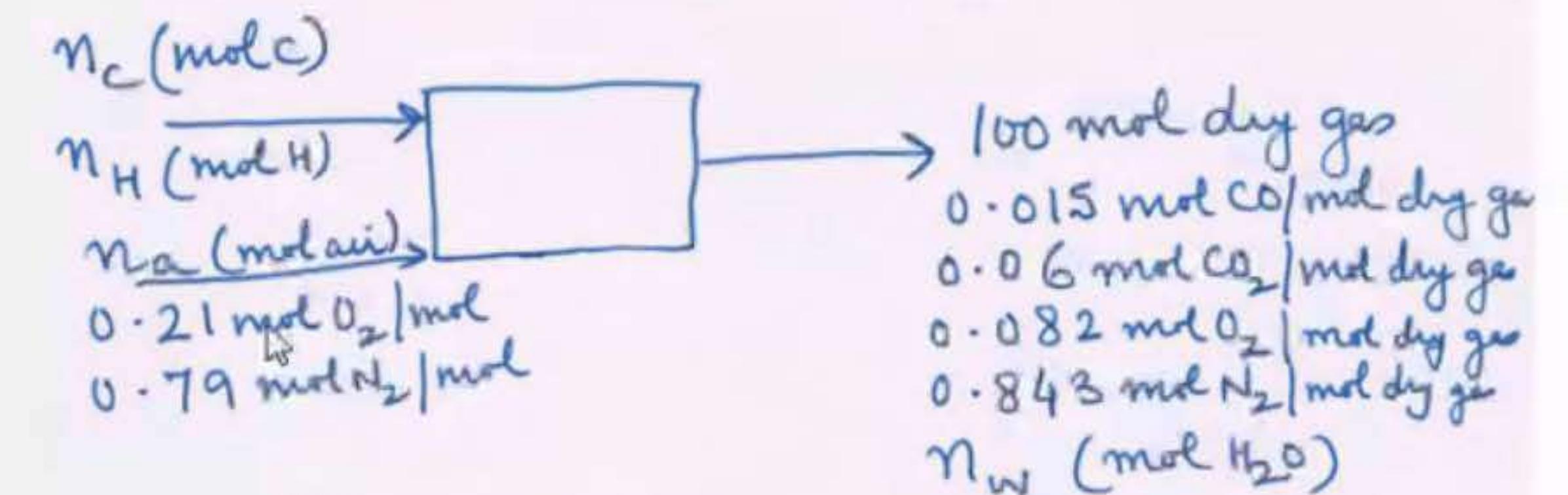
$$\text{Mole fraction H}_2\text{O} = \frac{7.53 \text{ mole H}_2\text{O}}{107.53 \text{ mole wet gas}} = 0.07 \frac{\text{mole H}_2\text{O}}{\text{mole wet gas}}$$

## Material And Energy Balances

Ex. A hydrocarbon gas is burned with air. The dry basis product gas composition is 1.5 mole% CO, 6% CO<sub>2</sub>, 8.2% O<sub>2</sub> and 84.3% N<sub>2</sub>. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate what the fuel might be. Then calculate the percent excess air fed to reactor.

## Material And Energy Balances

Basis: 100 mol Product gas



4 Variables ( $n_c, n_H, n_a, n_w$ )

3 Independent Atomic Balances (C, H, O)

1  $N_2$  Balance

$$N_2 \text{ Balance: } 0.79 n_a = 100 (0.843) \text{ mol H}_2O \Rightarrow n_a = 106.7 \text{ mol air}$$

$$\text{Atomic C Balance: } n_c = \frac{100 \text{ mol}}{\frac{0.015 \text{ mol CO}}{\text{mol}}} \frac{1 \text{ mol C}}{1 \text{ mol CO}} + (100)(0.06)(1) \text{ mol C}$$

$$\Rightarrow n_c = 7.5 \text{ mol C}$$

CO

## Material And Energy Balances

$$\text{Atomic O Balance: } 0.21 n_a(2) = n_w(1) + 100 [0.015](1) \\ + (0.06)(2) + (0.082)(2)$$

$\text{CO}_2 \quad \text{H}_2\text{O}$

Since  $n_a = 106.7 \text{ mol}$

$$\Rightarrow n_w = 14.9 \text{ mol H}_2\text{O}$$

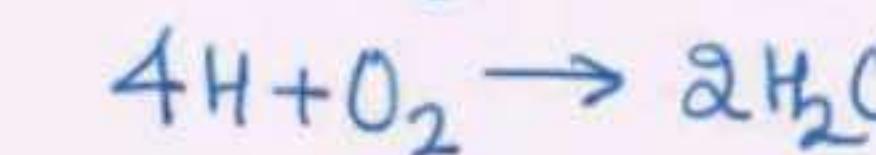
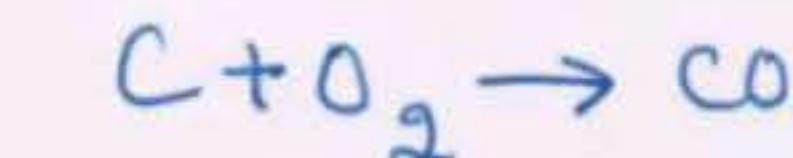
$$\text{Atomic H Balance, } n_H = n_w(2) \xrightarrow{\text{H}_2\text{O}} n_H = 29.8 \text{ mol H}$$

$$\text{C/H ratio in the fuel} = \frac{n_H}{n_c} = \frac{29.8 \text{ mol H}}{7.5 \text{ mol C}} = 3.97 \frac{\text{mol H}}{\text{mol C}}$$

$(\text{CH}_{3.97})_n$

## Material And Energy Balances

## Percent Excess Air



$$(n_{O_2})_{\text{theoretical}} = \frac{7.5 \text{ mol C}}{1 \text{ mol } O_2} + \frac{29.8 \text{ mol H}}{4 \text{ mol } H}$$

$$= 14.95 \text{ mol } O_2$$

$$(n_{O_2})_{\text{fed}} = 0.21 (106.7 \text{ mol air}) = 22.4 \text{ mol } O_2$$

$$\% \text{ Excess Air} = \frac{(n_{O_2})_{\text{fed}} - (n_{O_2})_{\text{theoretical}}}{(n_{O_2})_{\text{theoretical}}} \times 100$$

$$= \frac{(22.4 - 14.95) \text{ mol } O_2}{14.95 \text{ mol } O_2} \times 100\%$$

$$= 49.8\%$$

When it is reasonable to assume ideal gas behaviour

$$\epsilon = \frac{x_{\text{ideal}} - x_{\text{true}}}{x_{\text{true}}} \times 100\%.$$

$\epsilon$  : Error in estimated value

$x_{\text{ideal}}$ : Quantity calculated using the ideal gas equation of state.

$$x = P(\text{absolute}), T(\text{absolute}), V$$

An error of no more than about 1% may be expected if the quantity  $RT/P$  (the ideal specific molar volume) satisfies the following criterion

$$|\epsilon| < 1\% \text{ if } \hat{V}_{\text{ideal}} = \frac{RT}{P} > 5 \frac{\text{L}}{\text{mol}} \left( 80 \frac{\text{ft}^3}{\text{lb mol}} \right)$$

(diatomic gases)

$$> 20 \frac{\text{L}}{\text{mol}} \left( 320 \frac{\text{ft}^3}{\text{lb mol}} \right)$$

(other gases)

$$n = \frac{100 \text{ g}}{28 \text{ g/mol}} = 3.57 \text{ mol}$$

$$T = 296 \text{ K}$$

$$V(\text{liters}) = \frac{nRT}{P}$$

$$= \frac{(3.57 \text{ mol})(296 \text{ K})}{17.7 \text{ psi}} \cdot R \frac{(\text{lit. psi})}{\text{mol} \cdot \text{K}}$$

$$V = \frac{(3.57 \text{ mol})(296 \text{ K})}{17.7 \text{ psi}} \left| \frac{0.08206 \frac{\text{lit. atm}}{\text{mol} \cdot \text{K}}}{\frac{14.7 \text{ psi}}{\text{atm}}} \right| = 72 \text{ lit.}$$

$N_2$  diatomic gas

$$\hat{V}_{\text{ideal}} = \frac{V}{n} = \frac{72 \text{ lit}}{3.57 \text{ mol}} = 20.2 \frac{\text{lit}}{\text{mol}} > 5 \frac{\text{lit}}{\text{mol}}$$

Since the calculated value of  $\hat{V}_{\text{ideal}}$  exceeds the criterion value of 5 L/mol, the ideal gas equation of state should yield an error of less than 1%.

## Standard Conditions for Gases

System	$T_s$	$P_s$	$V_s$	$n_s$
SI	273 K	1 atm.	$0.022415 \text{ m}^3$	1 mol
CGS	237 K	1 atm	$22.415 \text{ L}$	1 mol
American Engg.	492 R	1 atm	$359.05 \text{ ft}^3$	1 lb mol

Standard Cubic Meters (or SCM) denotes  $\text{m}^3(\text{STP})$

Standard Cubic Feet (SCF) denotes  $\text{ft}^3(\text{STP})$

A volumetric flow rate of 10 SCMH means  $10 \text{ m}^3/\text{h}$  at  $0^\circ\text{C}$  and 1 atm.

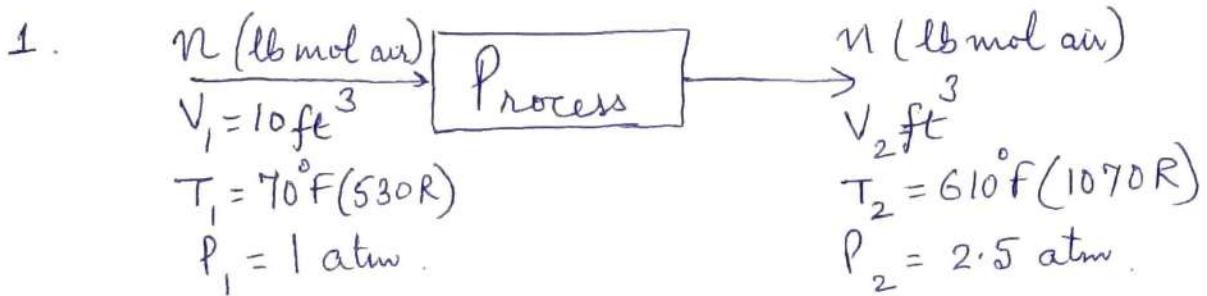
Flow rate of a gas stream is, say,  $X$  SCMH (or  $\text{m}^3(\text{STP})/\text{h}$ ) at  $150^\circ\text{C}$  & 2.5 atm

Looks contradictory

The gas is not at standard temperature and pressure. A flow rate specified in the given manner ( $X$  SCMH) is not the true volumetric flow rate of the stream at its actual temperature and pressure ( $150^\circ\text{C}$  & 2.5 atm) but the flow rate that would be obtained if the streams were brought from standard conditions to actual conditions to standard temp & pressure.

1. Calculate molar flow rate ( $\text{kmol}/\text{h}$ ) by dividing  $X \text{ m}^3/\text{h}$  by  $22.4 \text{ m}^3(\text{STP})/\text{kmol}$ .

2. Calculate true volumetric flow rate ( $\text{m}^3/\text{h}$ ) by multiplying  $X$  by  $(4234/273\text{K})(1\text{atm}/2.5\text{atm})$



1 : Initial State

2 : Final State

Number of moles of the gas does not change  $n_1 = n_2$

$$V_2 = V_1 \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right) = 10 \text{ ft}^3 \left| \frac{1 \text{ atm}}{2.5 \text{ atm}} \right| \left| \frac{1070 \text{ R}}{530 \text{ R}} \right| = 8.08 \text{ ft}^3$$

2. SCFH mean  $\text{ft}^3 (\text{STP})/\text{h}$

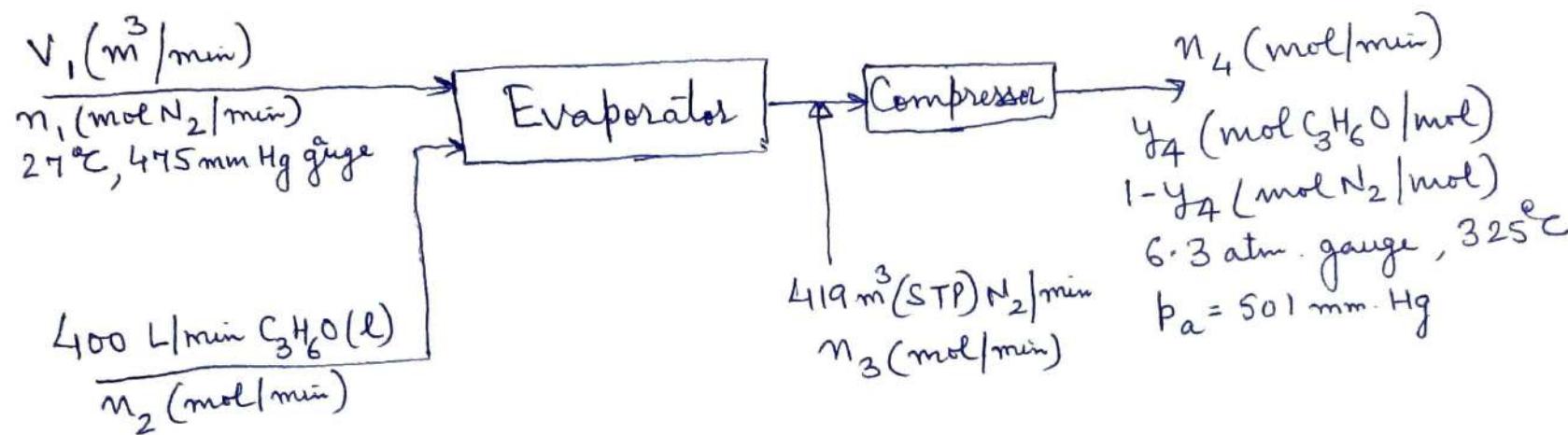
$$n = \frac{3.95 \times 10^5 \text{ ft}^3 (\text{STP})}{\text{h}} \left| \frac{1 \text{ lb mol}}{359 \text{ ft}^3 (\text{STP})} \right| = 1.1 \times 10^3 \frac{\text{lb mol}}{\text{h}}$$

You do not need to know the actual gas temp & pressure to calculate the molar flow rate from standard volumetric flow rate.

~~$$V_2 = V_1 \left( \frac{T_2}{T_1} \right) \left( \frac{P_1}{P_2} \right)$$~~

$$V_2 = V_1 \left( \frac{T_2}{T_1} \right) \left( \frac{P_1}{P_2} \right) = (3.95 \times 10^5 \text{ ft}^3/\text{h}) \left( \frac{745 \text{ R}}{492 \text{ R}} \right) \left( \frac{1 \text{ atm}}{1.3 \text{ atm}} \right)$$

$$= 4.6 \times 10^5 \text{ ft}^3/\text{h}$$



Molar Flow Rate of Acetone  
density of acetone 791 g/L

$$n_2 = \frac{400 \text{ L}}{\text{min}} \left| \frac{791 \text{ g}}{\text{L}} \right| \left| \frac{1 \text{ mol}}{58 \text{ g}} \right| = 54.50 \frac{\text{mol C}_3\text{H}_6\text{O}}{\text{min}}$$

In the stream leaving the compressor

$$\frac{p_a}{P} = y_4 \left( \frac{\text{mol C}_3\text{H}_6\text{O}}{\text{mol}} \right)$$

$$P = P_{\text{gauge}} + P_{\text{atm}} = 6.3 \text{ atm} \left| \frac{760 \text{ mm Hg}}{1 \text{ atm}} + 763 \text{ mm Hg} \right| = 5550 \text{ mm Hg}$$

$$y_4 = \frac{501 \text{ mm Hg}}{5550 \text{ mm Hg}} = 0.0903 \frac{\text{mol C}_3\text{H}_6\text{O}}{\text{mol}}$$

$$1-y_4 = 0.9097 \frac{\text{mol N}_2}{\text{mol}}$$

Calculate  $n_3$  from PVT information

$$n_3 = \frac{419 \text{ m}^3 (\text{STP})}{\text{min}} \left| \frac{1 \text{ mol}}{0.0224 \text{ m}^3 (\text{STP})} \right. = 18700 \frac{\text{mol}}{\text{min}}$$

Overall Mole Balance on Acetone  $n_2 = n_4 \gamma_4$

$$n_4 = 60400 \frac{\text{mol}}{\text{min}}$$

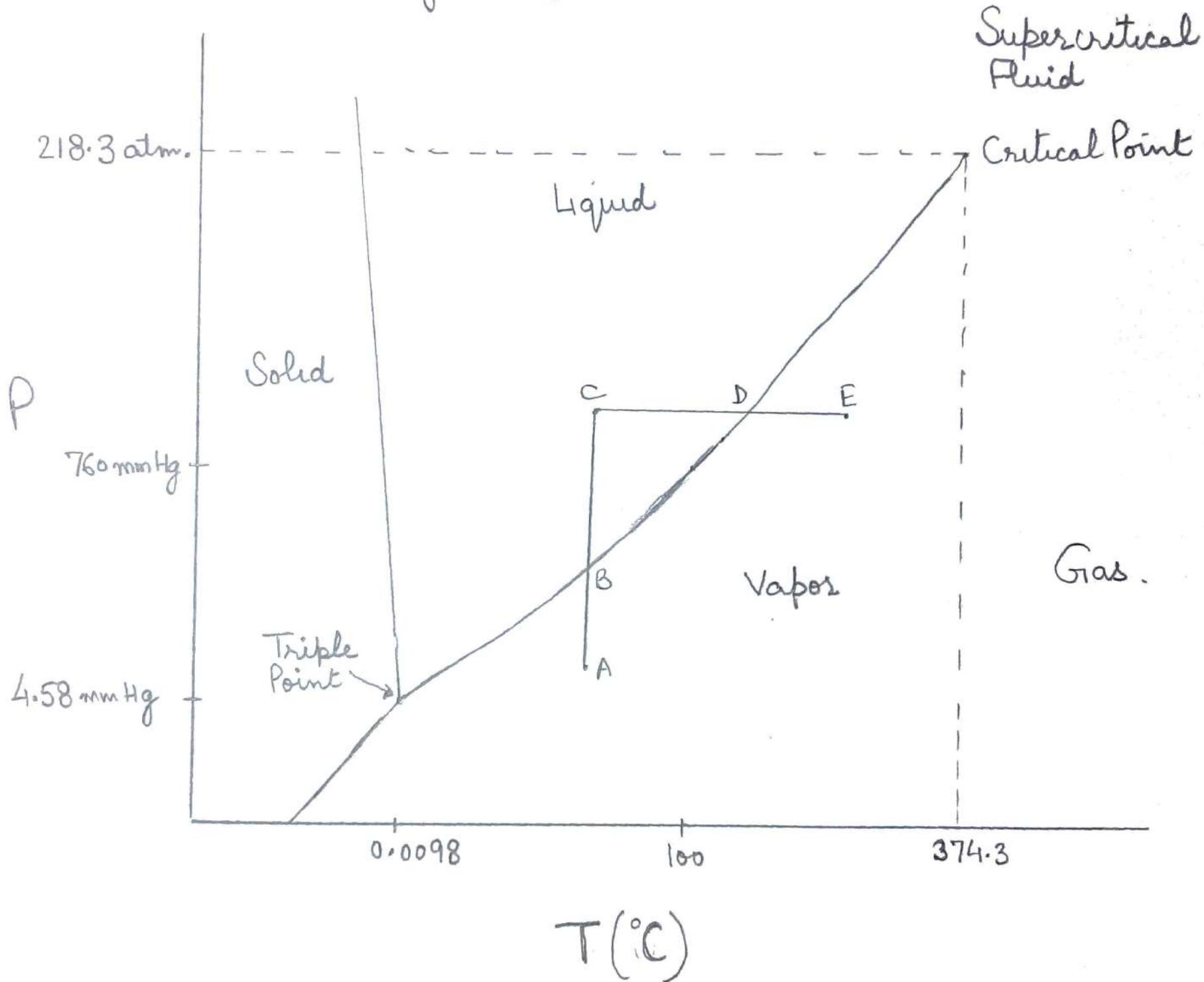
Overall Mole Balance  $n_1 + n_2 + n_3 = n_4$

$$n_1 = 36200 \frac{\text{mol}}{\text{min}}$$

Ideal Gas Equation of State  
 $T_1 = 27^\circ\text{C} (300 \text{ K})$ ;  $P_1 = 475 \text{ mm Hg}$  gauge ( $1238 \text{ mm Hg}$ )

$$\begin{aligned} V_1 &= n_1 \frac{V_s}{n_s} \frac{T_1}{T_s} \frac{P_s}{P_1} \\ &= 36200 \frac{\text{mol}}{\text{min}} \left| \frac{0.0224 \text{ m}^3}{1 \text{ mol}} \right| \left| \frac{300 \text{ K}}{273 \text{ K}} \right| \left| \frac{760 \text{ mm Hg}}{1238 \text{ mm Hg}} \right| \\ &= 550 \text{ m}^3 \text{ N}_2 / \text{min} \end{aligned}$$

# Phase Diagram of Water



## Humidification

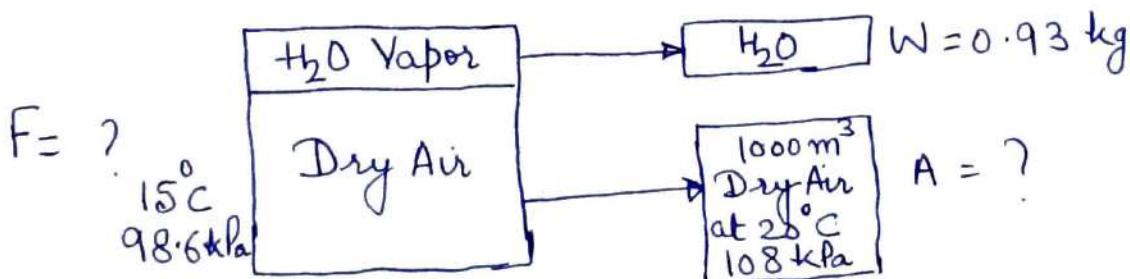
Ex. The vapor pressure of water at  $94^{\circ}\text{F}$  is 1.61 in. Hg.  
Calculate the partial pressure of water vapor in air from Relative Humidity.

$$P_{\text{H}_2\text{O}} = (1.61 \text{ in. Hg})(0.43) = 0.692 \text{ in. Hg.}$$

Basis: 1 mile  $^3$  water vapor at  $94^{\circ}\text{F}$  and 0.692 in. Hg.

$$1 \text{ mile}^3 \left| \left( \frac{5280 \text{ ft}}{1 \text{ mile}} \right)^3 \right| \frac{492^{\circ}\text{R}}{555^{\circ}\text{R}} \left| \frac{0.692 \text{ in. Hg}}{29.92 \text{ in. Hg}} \right| \frac{1 \text{ lb mol}}{359 \text{ ft}^3} \left| \frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mol}} \right. \\ = 1.51 \times 10^8 \text{ lb. H}_2\text{O}$$

Ex. Dehydration of Moist Air



Basis:  $1000 \text{ m}^3$  bone-dry air (BDA) at  $20^{\circ}\text{C}$  and 108 kPa

Calculate the amounts (in kg mol) of water vapor and dry air in the original air

$$W = 0.93 \text{ kg}$$

$$0.93 \text{ kg H}_2\text{O} \left| \frac{1 \text{ kg mol H}_2\text{O}}{18 \text{ kg H}_2\text{O}} \right. = 0.0517 \text{ kg mol H}_2\text{O}$$

## Bone Dry Air (BDA)

$$1000 \text{ m}^3 \text{ BDA} \left| \begin{array}{c} 273 \text{ K} \\ 293 \text{ K} \end{array} \right| \frac{108 \text{ kPa}}{101.3 \text{ kPa}} \left| \begin{array}{c} 1 \text{ kg} \\ 22.4 \text{ m}^3 \end{array} \right.$$

$$= 44.35 \text{ kg mol BDA}$$

To get relative humidity (RH) of moist air, calculate partial pressure of water vapor in moist air.

$$\frac{p_{H_2O}}{p_{\text{Tot}}} = \frac{n_{H_2O}}{n_{\text{Tot}}} = \frac{0.0517}{0.0517 + 44.35} = 1.164 \times 10^{-3}$$

$$p_{H_2O} = (1.164 \times 10^{-3})(98.6 \text{ kPa}) \\ = 0.1148 \text{ kPa}$$

Look up the vapor pressure at 15°C for water, namely 1.7 kPa.

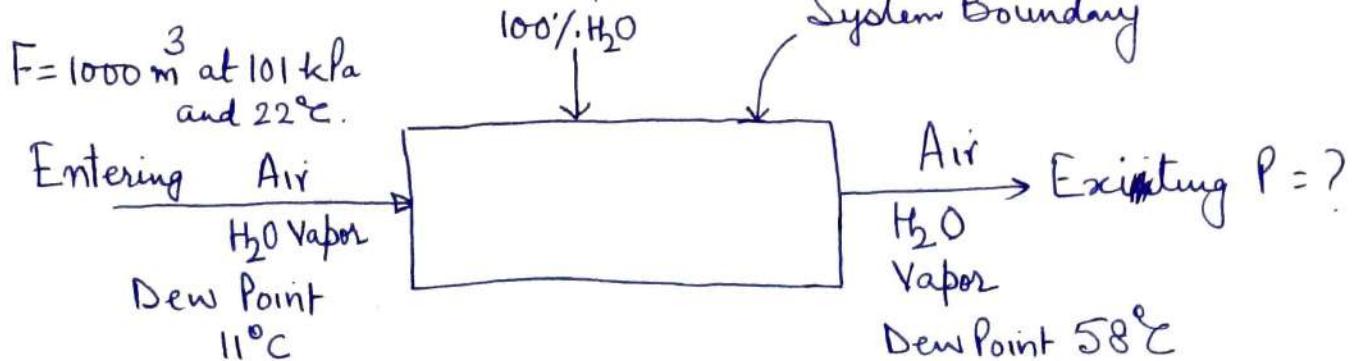
$$\text{Fractional RH of original air} \quad \frac{0.1148}{1.7} = 0.0676$$

## Ex. Humidification of Air

Vapor Pressure Data	Dew Point Temp (°C)	$p_{H_2O}^*(\text{mm.Hg})$	$p_{H_2O}^*(\text{kPa})$
	11	9.84	1.31
	58	136.1	18.14

- (+) These values gives the partial pressure of the water vapor in the initial and final gas mixtures.

(3)



Let the subscript W stand for the water vapor and BDA stand for dry air

$$\text{IN: } p_{\text{BDA}} = p_{\text{Tot}} - p_w = 101 - 1.31 = 99.69 \text{ kPa}$$

$$\text{OUT: } p_{\text{BDA}} = 98 - 18.14 = 79.86 \text{ kPa}$$

Basis:  $1000 \text{ m}^3$  moist air at 101 kPa and  $22^\circ\text{C}$ .

$$\begin{array}{c} 1000 \text{ m}^3 \\ \times 101 \text{ kPa} \\ \hline 101.3 \text{ kPa} \end{array} \quad \begin{array}{c} 273 \text{ K} \\ \times 293 \text{ K} \\ \hline 295 \text{ K} \end{array}$$

$$1000 \text{ m}^3 \left| \begin{array}{c} 101 \text{ kPa} \\ \hline 101.3 \text{ kPa} \end{array} \right| \left| \begin{array}{c} 273 \text{ K} \\ \hline 295 \text{ K} \end{array} \right| \left| \begin{array}{c} 1 \text{ kgmol} \\ \hline 22.4 \text{ m}^3 \end{array} \right| = 41.19 \text{ kgmol}$$

wet air

$$\text{BDA balance: } 41.19 \left( \frac{99.69}{101} \right) = P \left( \frac{79.86}{98} \right)$$

$$P = 49.89 \text{ kgmol}$$

$$\text{Total Balance: } F + W = P$$

$$W = 49.89 - 41.19 = 8.7 \text{ kgmol H}_2\text{O}$$

Check using the Water Balance

$$\text{Water Balance : } 41.19 \left( \frac{1.31}{101} \right) + W = 49.89 \left( \frac{18.1}{98} \right)$$

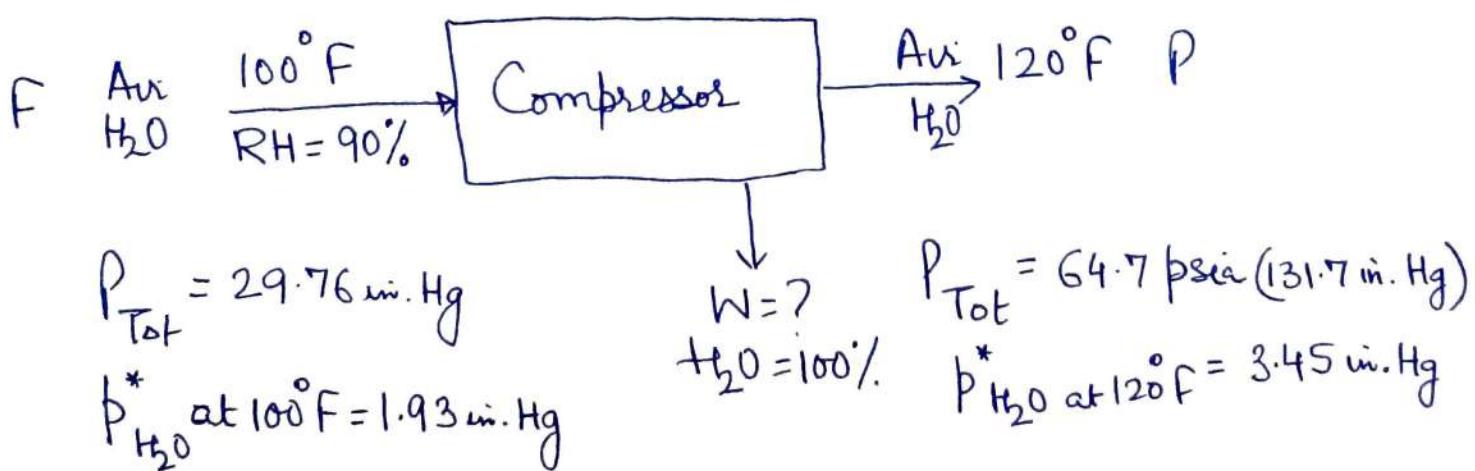
$$W = 8.68 \text{ kgmol (OK)}$$

To calculate the kg of wet air entering

Component	kgmol	Mol. wt.	kg
Dry Air	$41.19 \left( \frac{99.69}{101} \right)$	29	1179
+ $H_2O$	$41.19 \left( \frac{1.31}{101} \right)$	18	9.6
Total	41.19		1188.6

$$\text{Water Added} = \frac{(8.7)(18)}{1188.6} = 0.132 \frac{\text{kg water}}{\text{kg wet air in}}$$

Ex. Condensation of Water from Air



Determine the compositions of the inlet & outlet streams by calculating partial pressures of air & water vapor.

### Inlet Stream F

$$\frac{p_{H_2O}}{p_{H_2O}^*} = RH \text{ so that } p_{H_2O} = 1.93(0.9) = 1.74 \text{ in. Hg}$$

$$P_{\text{air}} = P_{\text{Tot}} - p_{H_2O} = 29.76 - 1.74 = 28.02 \text{ in. Hg}$$

You can initially assume that condensation takes place, and calculate the partial pressures of the air and water, respectively. You can subsequently check to see if this assumption is false by determining if  $W$  is positive or negative. The outlet gas  $P$  is saturated when condensation occurs.

### Outlet Stream P

$$p_{H_2O} = p_{H_2O}^*(1.00) = 3.45 \text{ in. Hg}$$

$$P_{\text{air}} = P_{\text{Tot}} - p_{H_2O} = 131.7 - 3.45 = 128.3 \text{ in. Hg}$$

Basis:  $F = 29.76 \text{ lbmol}$

$$H_2O \text{ Balance: } \frac{1.74}{29.76} (29.76) = W + P \left( \frac{3.45}{131.7} \right)$$

$$\text{Air Balance: } \frac{28.02}{29.76} (29.76) = 0 + P \left( \frac{128.3}{131.7} \right)$$

(6)

$$P = 28.76 \text{ lbmol}$$

$$W = 0.99 \text{ lbmol}$$

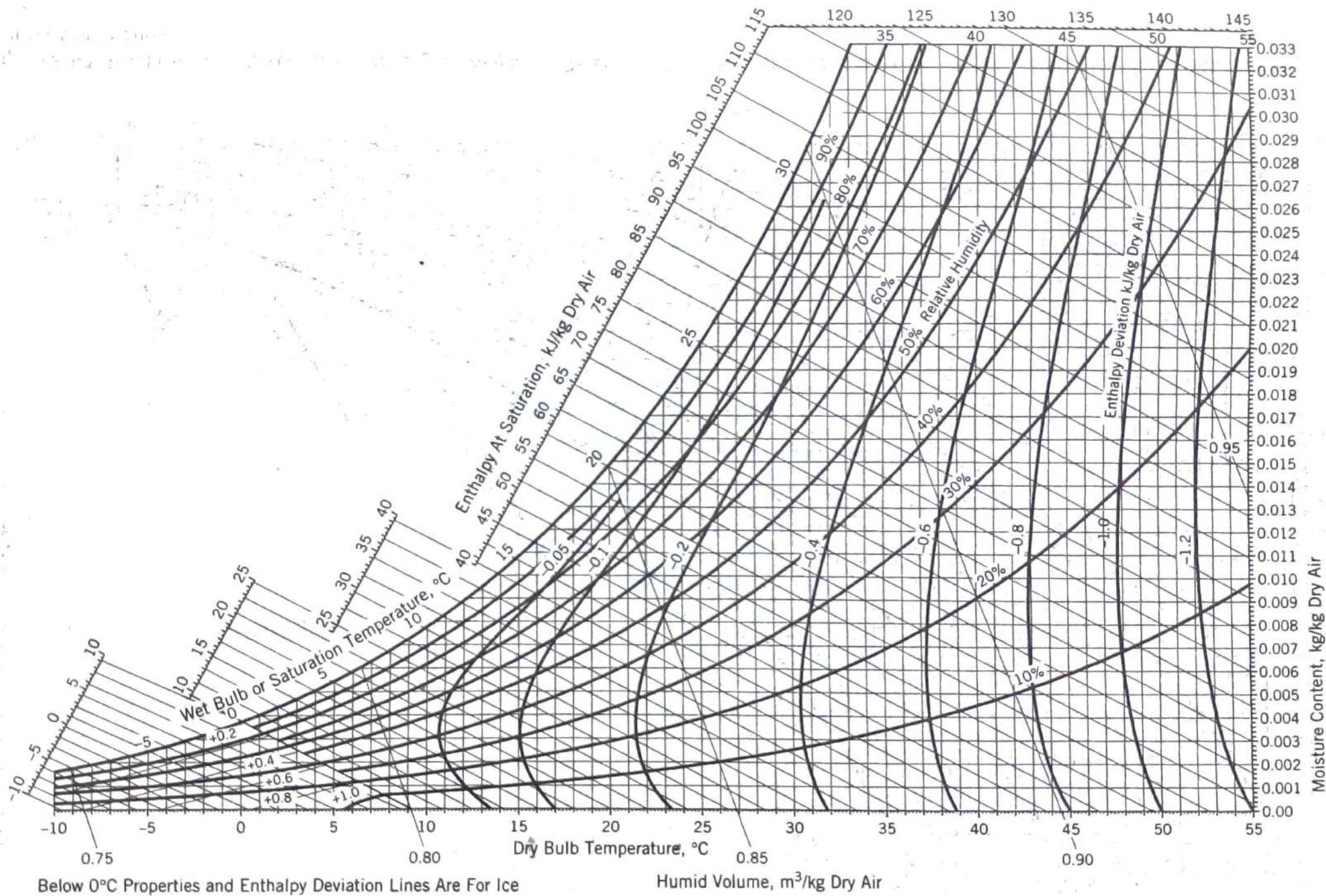
Since  $W$  is positive, water condenses during the compression process.

On the basis of 1 ton of dry air

$$\frac{0.99 \text{ lbmol H}_2\text{O out}}{28.02 \text{ lbmol dry air}} \left| \begin{array}{c} 18 \text{ lb water/lb mol water} \\ 29 \text{ lb air/lb mol air} \end{array} \right| \begin{array}{c} 2000 \text{ lb} \\ 1 \text{ ton} \end{array}$$

$$= 43.9 \text{ lbmol condensed per ton of dry air}$$

$$\text{Thus } (43.9)(18) = 790 \text{ lb water.}$$



**Figure 8.4-1** Psychrometric chart—SI units. Reference states: H<sub>2</sub>O (L, 0°C, 1 atm), dry air (0°C, 1 atm). (Reprinted with permission of Carrier Corporation.)

If a fluid enters a system with a mass flow rate  $\dot{m}$  (kg/s) and uniform velocity  $u$  (m/s), then

$$\dot{E}_K = \frac{1}{2} \dot{m} u^2$$

Ex. Water flows into a process unit through a 2 cm ID pipe at a rate of 2 m<sup>3</sup>/h. Calculate  $E_K$  for this stream in Joule/Second.

First calculate the linear velocity (volumetric flow rate divided by x-sectional area of pipe and mass flow rate of the fluid).

$$u = \frac{2 \text{ m}^3}{\text{h}} \left| \frac{100^2 \text{ cm}^2}{1^2 \text{ m}^2} \right| \left| \frac{1 \text{ h}}{\pi (1)^2 \text{ cm}^2} \right| \left| \frac{1}{3600 \text{ s}} \right| = 1.77 \text{ m/s}$$

$$\dot{m} = \frac{2 \text{ m}^3}{\text{h}} \left| \frac{1000 \text{ kg}}{\text{m}^3} \right| \left| \frac{1 \text{ h}}{3600 \text{ s}} \right| = 0.556 \text{ kg/s}$$

$$\dot{E}_K = \frac{0.556 \text{ kg/s}}{2} \left| \frac{(1.77)^2 \text{ m}^2}{\text{s}^2} \right| \left| \frac{1 \text{ N}}{1 \text{ kg} \cdot \frac{\text{m}}{\text{s}^2}} \right| = 0.87 \text{ N} \cdot \frac{\text{m}}{\text{s}}$$

$$= 0.87 \frac{\text{J}}{\text{s}}$$

Ex. Crude oil is pumped at a rate of 15 kg/s from a point 220m below the earth's surface to a point 20 meters above ground level. Calculate the rate of increase of Potential Energy.

1, 2 denote first and second points respectively

$$\Delta \dot{E}_p = \dot{E}_{p_2} - \dot{E}_{p_1} = \dot{m} g (z_2 - z_1)$$

A pump would have to deliver this much power to raise the oil at a given rate

$$= 15 \frac{\text{kg}}{\text{s}} \left| 9.81 \frac{\text{m}}{\text{s}^2} \right| \left| \frac{1 \text{ N}}{1 \text{ kg} \cdot \frac{\text{m}}{\text{s}^2}} \right| \left[ (20 - (-220)) \text{ m} \right]$$

$$= 35300 \text{ N} \cdot \frac{\text{m}}{\text{s}} = 35300 \text{ J/s} = 35.3 \text{ kW}$$

1. The mass flow rates are the same.

$$P_{\text{outlet}} < P_{\text{inlet}}$$

$$V_{\text{outlet}} > V_{\text{inlet}}$$

2.  $\Delta E_k > 0$ ,  $\Delta E_p > 0$

Ex. If 250 J is added to a system as heat, what is the value of Q in the energy balance equation. If 250 J of work is done to the system, what is the value of W?

$$Q = 250 \text{ J}$$

$$W = -250 \text{ J}$$

Ex. If a closed system has an internal energy of 100 kcal at the beginning of a process and 50 kcal at the end, what is  $\Delta U$ ?

$$\Delta U = -50 \text{ kcal}$$

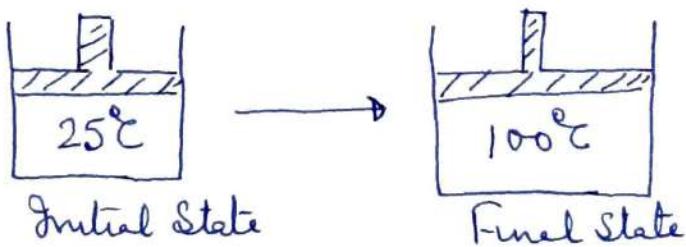
# ①

## Energy Balance on a Closed System

Ex. A gas is contained in a cylinder fitted with a moveable piston. The initial gas temp is  $25^{\circ}\text{C}$ . The cylinder is placed in boiling water with the piston held in a fixed position. Heat in the amount of 2 kcal is transferred to the gas, which equilibrates at  $100^{\circ}\text{C}$  (and a higher pressure). The piston is then released, and the gas does 100 J of work in moving the piston to its new eqm. position. The final gas temp is  $100^{\circ}\text{C}$ . Consider the gas in the cylinder to be the system, neglect the changes in the potential energy of the gas as the piston moves vertically and assume the gas behaves ideally.

Write the energy balance equation for each of the two stages of this process, and in each case solve for the unknown energy term in the equation. Express all energies in Joules.

Soln.



$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

$\Delta E_K = 0$  (System is stationary)

$\Delta E_P = 0$  (No vertical displacement)

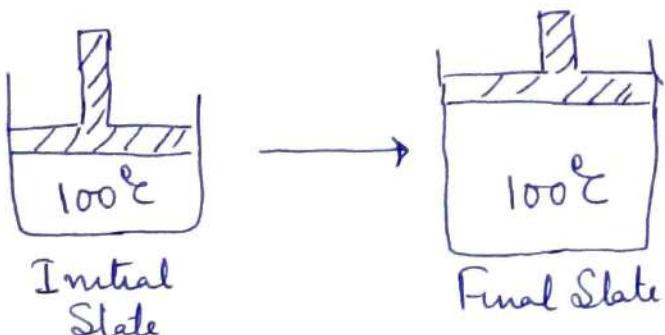
$W = 0$  (No moving boundaries)

$$\Delta U = Q$$

$$Q = -2 \text{ kcal}$$

$$\Delta U = 2 \text{ kcal} \left| \frac{10^3 \text{ cal}}{1 \text{ kcal}} \right| \left| \frac{1 \text{ J}}{0.23901 \text{ cal}} \right| = 8370 \text{ J}$$

The gas gains 8370 J of internal energy in moving from  $25$  to  $100^{\circ}\text{C}$



$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

$\Delta E_K = 0$  (the system is stationary at the initial and final states)

$\Delta E_P = 0$  (Assumed negligible by hypothesis)

$\Delta U = 0$  ( $U$  depends only on  $T$  for an ideal gas &  $T$  does not change)

$$0 = Q - W$$

$$W = +100 \text{ J}$$

$$Q = 100 \text{ J}$$

Thus an additional 100 J of heat is transferred as it expands and reequilibrates at 100°C.

## Flow Work



Fluid at a pressure  $P_{in} (\text{N/m}^2)$  enters a pipe at a volumetric flow rate  $V_{in} (\text{m}^3/\text{s})$  and exits at a pressure  $P_{out} (\text{N/m}^2)$  and volumetric flow rate  $V_{out} (\text{m}^3/\text{s})$ . The fluid that enters the system has work done on it by the fluid just behind

$$it at a rate W_{in} \left( \frac{\text{J}}{\text{s}} \right) = P_{in} (\text{N/m}^2) \cdot V_{in} (\text{m}^3/\text{s})$$

(3)

While the fluid leaving the system performs work on the surrounding at a rate

$$W_{out} = P_{out} \cdot V_{out}$$

The net rate at which work is done by the system at the inlet and outlet is therefore

$$W_{flow} = P_{out} V_{out} - P_{in} V_{in}$$

If several input and output streams enter and leave the system, the PV products for each stream must be summed to determine  $W_{flow}$ .

Soln.  $\dot{H} = \dot{P}\dot{V} + \dot{U} = 3800 \frac{\text{J}}{\text{mol}} + (1 \text{ atm.})(24.63 \frac{\text{L}}{\text{mol}})$

$$0.08206 \text{ L.atm}/(\text{mol.K}) = 8.314 \frac{\text{J}}{\text{mol.K}}$$

$$\frac{8.314 \text{ J/mol.K}}{0.08206 \text{ L.atm.}/(\text{mol.K})} = 101.3 \text{ J/(L.atm.)}$$

Therefore,

$$\dot{H} = 3800 \text{ J/mol} + 24.63 \frac{\text{L.atm}}{\text{mol}} \left| \frac{101.3 \text{ J}}{\text{L.atm}} \right.$$

$$= 6295 \text{ J/mol}$$

If  $n = 250 \text{ kmol/h}$

$$\dot{H} = n\dot{H} = 250 \frac{\text{kmol}}{\text{h}} \left| \frac{10 \text{ mol}}{\text{kmol}} \right| \left| \frac{6295 \text{ J}}{\text{mol}} \right|$$

$$= 1.57 \times 10^9 \text{ J/h.}$$

## Closed System

$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

$$Q = \Delta U + W$$

$$Q = \Delta U + \Delta PV$$

$$Q = \Delta U + P\Delta V$$

$$Q = \Delta H$$

## The Steady-State Open System Energy Balance

The first law of thermodynamics for an open system at steady state has the form

$$\text{Input} = \text{Output}$$

[Accumulation, generation, consumption terms of the general balance equation vanish.]

**Input:** Total rate of transport of kinetic energy, potential energy and internal energy by all process input streams plus the rate at which energy is transferred as heat

**Output:** Total rate of energy transport by the output streams plus the rate at which energy is transferred out as work.

$\dot{E}_j$  : Total rate of energy transport by the  $j^{\text{th}}$  input or output stream of a process

$Q$  : Rate of flow of heat into the process

$W$  : Rate of flow of work out of the process

$$Q + \sum_{\substack{\text{Input} \\ \text{Streams}}} \dot{E}_j = \sum_{\substack{\text{Output} \\ \text{Streams}}} \dot{E}_j + W$$

$$\sum_{\substack{\text{Output} \\ \text{Streams}}} \dot{E}_j - \sum_{\substack{\text{Input} \\ \text{Streams}}} \dot{E}_j = Q - W \quad \text{--- (A)}$$

(5)

If  $m_j$ ,  $\dot{E}_{kj}$ ,  $\dot{E}_p$  &  $\dot{U}_j$  are the flow rates of mass, kinetic energy, potential energy and internal energy for the  $j^{\text{th}}$  stream, then the total rate at which energy is transported into or out of the system by this stream is

$$\dot{E}_j = \dot{U}_j + \dot{E}_{kj} + \dot{E}_p$$

$$\downarrow \dot{U}_j = \dot{m}_j \hat{U}_j$$

$$\downarrow \dot{E}_{kj} = \dot{m}_j \frac{u_j^2}{2}$$

$$\dot{E}_p = \dot{m}_j g z_j$$

$$\dot{E}_j = \dot{m}_j \left( \hat{U}_j + \frac{u_j^2}{2} + gz_j \right) \quad \text{--- (B)}$$

where  $u_j$  is the velocity of the  $j^{\text{th}}$  stream and  $z_j$  is the height of this stream relative to a reference plane at which  $E_p = 0$

The total work  $w$  done by the system on its surroundings equals the shaft work  $w_s$  plus the flow work  $w_{\text{flow}}$ .

If  $v_j$  is the volumetric flow rate of the  $j^{\text{th}}$  stream and  $p_j$  is the pressure of this stream as it crosses the system boundary, then

$$w_{\text{flow}} = \sum_{\text{Output Streams}} p_j v_j - \sum_{\text{Input Streams}} p_j \hat{v}_j$$

$$\downarrow \hat{v}_j = \dot{m}_j \hat{V}_j$$

$$w = w_s + \sum_{\text{Output Streams}} \dot{m}_j p_j \hat{V}_j - \sum_{\text{Input Streams}} \dot{m}_j p_j \hat{V}_j$$

— (C)

Substituting  $\dot{E}_f$  (B) and  $\dot{W}(C)$  into (A) and bringing the  $PV$  terms to the left side yields

$$\sum_{\text{Output Streams}} m_j \left[ \hat{U}_j + \hat{P}_j \hat{V}_j + \frac{\hat{u}_j^2}{2} + g z_j \right] - \sum_{\text{Input Streams}} m_j \left[ \hat{U}_j + \hat{P}_j \hat{V}_j + \frac{\hat{u}_j^2}{2} + g z_j \right] = Q - W_s \quad \text{--- (D)}$$

$$\sum_{\text{Output Streams}} m_j \left( \hat{H}_j + \frac{\hat{u}_j^2}{2} + g z_j \right) - \sum_{\text{Input Streams}} m_j \left( \hat{H}_j + \frac{\hat{u}_j^2}{2} + g z_j \right) = Q - W_s \quad \text{--- (E)}$$

$$\left[ \begin{array}{l} \Delta H = \sum_{\text{Output Streams}} m_j \hat{H}_j - \sum_{\text{Input Streams}} m_j \hat{H}_j \\ \Delta \dot{E}_k = \sum_{\text{Output Streams}} m_j \frac{\hat{u}_j^2}{2} - \sum_{\text{Input Streams}} m_j \frac{\hat{u}_j^2}{2} \\ \Delta \dot{E}_p = \sum_{\text{Output Streams}} m_j g z_j - \sum_{\text{Input Streams}} m_j g z_j \end{array} \right]$$

In terms of these quantities, Eq (E) becomes

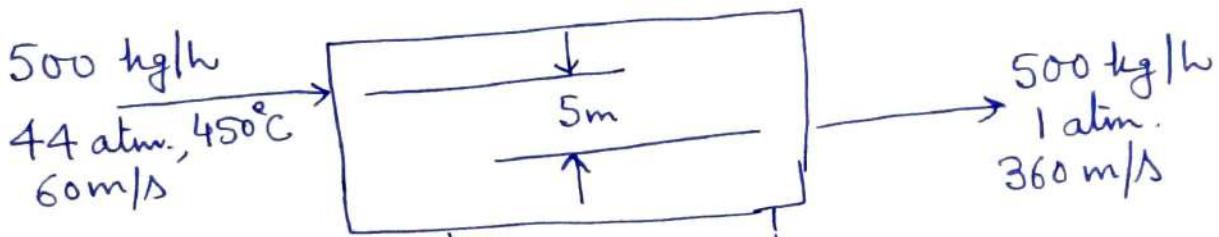
$$\boxed{\Delta H + \Delta \dot{E}_k + \Delta \dot{E}_p = Q - W_s}$$

The net rate at which energy is transferred to a system as heat and/or shaft work ( $Q - W_s$ ) equals the difference between the rates at which the quantity (Enthalpy + KE + PE) is transported into & out of the system ( $\Delta H + \Delta \dot{E}_k + \Delta \dot{E}_p$ ).

Ex. Energy Balance on a Turbine

(7)

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm &  $450^{\circ}\text{C}$  at a linear velocity of  $60 \text{ m/s}$  and leaves at a point  $5 \text{ m}$  below the turbine inlet at atmospheric pressure and a velocity of  $360 \text{ m/s}$ . The turbine delivers shaft work at a rate of  $70 \text{ kW}$  and the heat loss from the turbine is estimated to be  $10^4 \text{ kcal/h}$ . Calculate the specific enthalpy change associated with the process.



$$\dot{Q} = -10^4 \text{ kcal/h} \quad \dot{W}_s = 70 \text{ kW}$$

$$\Delta H = \dot{Q} - \dot{W}_s - \Delta E_K - \Delta E_P$$

$$\dot{m} = (500 \text{ kg/h}) / (3600 \text{ s/1h}) = 0.139 \text{ kg/s}$$

$$\Delta E_K = \frac{\dot{m}}{2} (u_2^2 - u_1^2) = \frac{0.139 \text{ kg/s}}{2} \left| \frac{1 \text{ N}}{1 \text{ kg} \cdot \text{m/s}^2} \right| \frac{(360^2 - 60^2) \text{ m}^2}{\text{s}^2}$$

$$\left| \frac{1 \text{ W}}{1 \text{ N} \cdot \text{m/s}} \right| \left| \frac{1 \text{ kW}}{10^3 \text{ W}} \right|$$

$$= 8.75 \text{ kW}$$

(8)

$$\dot{\Delta E_p} = mg(z_2 - z_1) = 0.139 \text{ kg/s} \left| \frac{9.81 \text{ N}}{\text{kg}} \right| (-5) \text{ m} \left| \frac{1 \text{ kW}}{10^3 \text{ N} \cdot \text{m/s}} \right|$$

$$= -6.81 \times 10^{-3} \text{ kW}$$

$$\dot{Q} = -10^4 \frac{\text{kcal}}{\text{h}} \left| \frac{1 \text{ J}}{0.239 \times 10^3 \text{ kcal}} \right| \left| \frac{1 \text{ h}}{3600 \text{ s}} \right| \left| \frac{1 \text{ kW}}{10^3 \text{ J/s}} \right| = -11.6 \text{ kW}$$

$$W_s = 70 \text{ kW}$$

$$\dot{\Delta H} = \dot{Q} - W_s - \dot{\Delta E_k} - \dot{\Delta E_p} = -90.3 \text{ kW}$$

$$\dot{\Delta H} = m (\hat{H}_2 - \hat{H}_1)$$

$$\hat{H}_2 - \hat{H}_1 = \dot{\Delta H} / \dot{m}$$

$$= -\frac{90.3 \text{ kJ/s}}{0.139 \text{ kg/s}} = \boxed{-650 \text{ kJ/kg}}$$