** Chapter 4: Material balances:

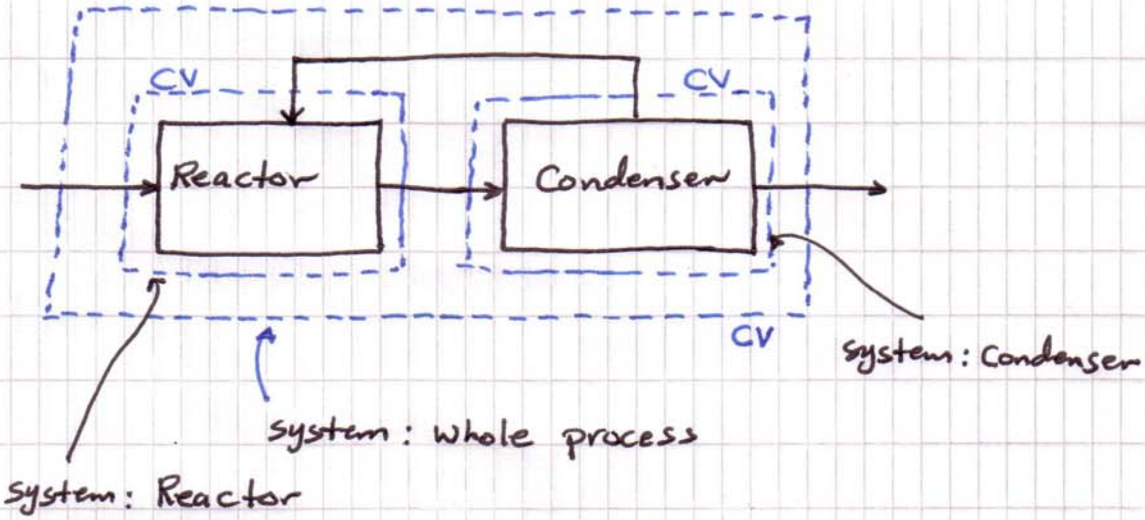
** Basic concepts:

- system: any arbitrary portion of the process or the whole process as specified by the engineer (you!) analyzing the problem.

- How to select system? what information is provided and what needs to be calculated.

- Control volume of the system (CV): the system boundary denoted by dashed lines.

Ex:



* system and process units are governed by the following Conservation principle:

Input + Generation − Output − Consumption = Accumulation

$$I + G - O - C = A$$

Input : what comes in across the system boundary

Generation : what is produced within the system boundary

Consumption: what is consumed within the system boundary

Output : what comes out across the system boundary.

Accumulation: changes in the amount, contained in the system, with time.

* Items give positive contribution to the system : I , G

* Items give negative contribution to the system : O , C

* Accumulation can give positive or negative contribution to the system.

→ General conservation principle ($I + G - O - C = A$) can be applied on mass, mole, energy, momentum, money, people... ,etc.

** Some simplifications :

* steady state process : process variables do NOT change with time ⇒ no accumulation : $A = 0$

⇒ For steady state processes, the conservation principle becomes :

$$I - O + G - C = 0$$

* Unsteady state (transient) process : process variables change with time : $A \neq 0$

Ex: startup operation; shutdown, external effects on the process, ... etc.

* Continuous process : process which has input and output

$$I \neq 0 \text{ and } O \neq 0$$

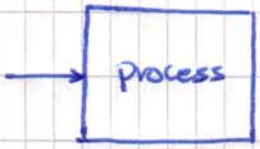
* Batch process : process which has NOT input and output

$$I = O = 0$$

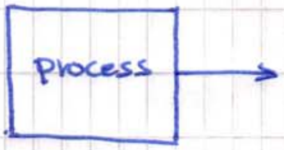
* Semibatch process : process which has either Input or output

$$I = 0 \text{ and } O \neq 0$$
$$\text{or } I \neq 0 \text{ and } O = 0$$

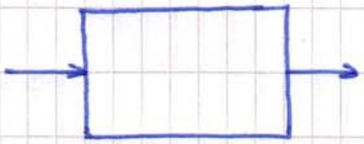
Ex:



semibatch



semibatch



Continuous

Batch

* Continuous process can be steady state or unsteady (transient) process

* Batch and semibatch processes are, by nature, unsteady state processes

* If no chemical reactions within the process : $G = C = 0$ and

$$In - Out = Acc.$$

Ex: what is the conservation principle for steady state continuous process without chemical reactions:

$$I - O + \underbrace{\cancelto{0}{G} - \cancelto{0}{C}}_{\text{no rxns}} = \cancel{A} \quad \text{st. st.}$$

$$\Rightarrow I - O = 0$$

$$\text{or} \quad \boxed{In = out}$$

** Conservation principle of mass:

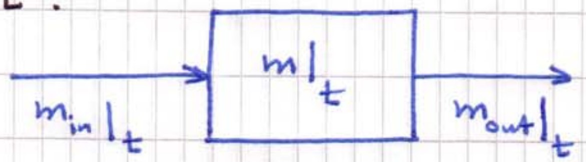
It is also known as : Mass balance (MB)
Material balance
Continuity equation

* Non-reactive Mass balance on a single unit process:

Gen. = Cons. = 0

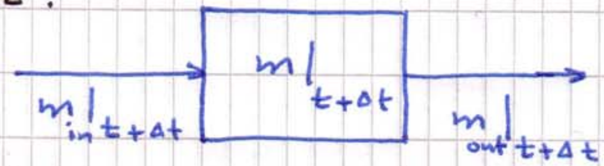
$$\Rightarrow In - Out = Acc$$

Apply MB at time t :



$$m_{in}|_t - m_{out}|_t = m|_t \quad \cdots \text{①}$$

Apply MB at time t + Δt :



$$m_{in}|_{t+\Delta t} - m_{out}|_{t+\Delta t} = m|_{t+\Delta t} \quad \cdots \text{②}$$

subtract eq. ① from eq. ②:

$$\left(m_{in}\big|_{t+\Delta t} - m_{in}\big|_{t}\right) - \left(m_{out}\big|_{t+\Delta t} - m_{out}\big|_{t}\right) = \left(m\big|_{t+\Delta t} - m\big|_{t}\right)$$

Divide eq. by Δt:

$$\frac{m_{in}|_{t+\Delta t} - m_{in}|_{t}}{\Delta t} - \frac{m_{out}|_{t+\Delta t} - m_{out}|_{t}}{\Delta t} = \frac{m|_{t+\Delta t} - m|_{t}}{\Delta t}$$

Take the limit of both sides of eq. when $\Delta t \rightarrow 0$:

$$\underset{\dot{m}_{in}}{\underset{\downarrow}{\boxed{\frac{dm_{in}}{dt}}}} - \underset{\dot{m}_{out}}{\underset{\downarrow}{\boxed{\frac{dm_{out}}{dt}}}} = \boxed{\frac{dm}{dt}}$$

$\dot{m}_{in}$: Total inlet mass flow rate ; Kg/s , slug/s , ... etc.

$\dot{m}_{out}$: Total outlet mass flow rate ; Kg/s, slug/s, ..., etc.

$\frac{dm}{dt}$: rate of change of mass (mass accumulation) within the system; kg/s, slug/s, ... etc.

→ Differential form of MB : $\dot{m}_{in} - \dot{m}_{out} = \frac{dm}{dt}$

→ Integral form of MB : multiply the diff. form of MB by dt and integrate from one time, t_1, to another, t_2:

$$\int_{t_1}^{t_2} (\cancel{dt}) \frac{dm_{in}}{\cancel{dt}} - \int_{t_1}^{t_2} \cancel{dt} \frac{dm_{out}}{\cancel{dt}} = \int_{t_1}^{t_2} \cancel{dt} \frac{dm}{\cancel{dt}}$$

$$\Rightarrow \Delta m_{in} - \Delta m_{out} = \Delta m$$

or $\displaystyle\int_{t_1}^{t_2} \dot{m}_{in}\, dt - \int_{t_1}^{t_2} \dot{m}_{out}\, dt = \int_{t_1}^{t_2} dm$ "Integral form"

→ usually;

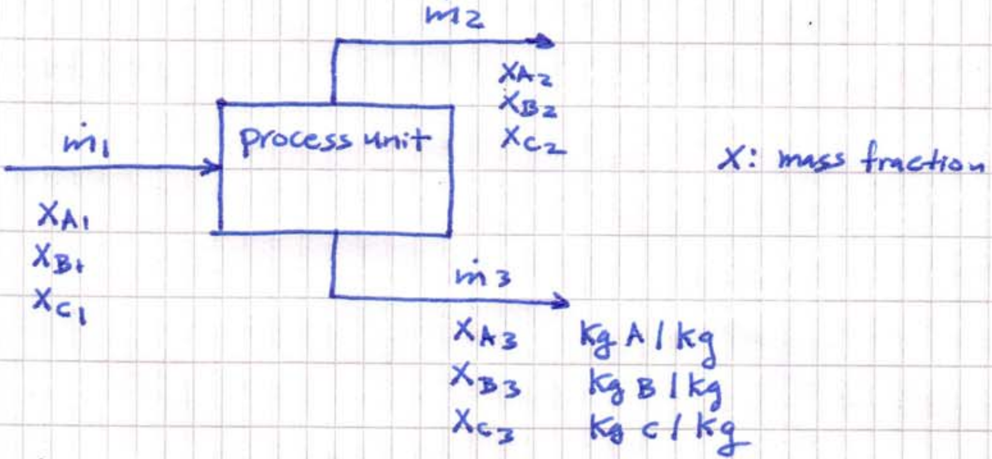
differential form is used for continuous processes
Integral form is used for batch/semibatch processes

* Material balance can refer to a balance on a system for:

1. Total Mass → Total mass balance
2. Total Moles → Total mole balance
3. Mass of component → Component mass balance
4. Moles of component → Component mole balance.
5. Moles of atomic species → Atomic mole balance
6. Mass of atomic species → Atomic mass balance
7. Volume balance → possible if the density of inlet outlet and within the system is the same.

Thus 7 forms of MB are possible

Ex: Three Components (A, B, C) are involved in the single unit process shown below. The process is st. st. without any Chemical reaction. How many independent MB equations can you write :



- Component A MB :

$$X_{A_1}\dot{m}_1 = X_{A_2}\dot{m}_2 + X_{A_3}\dot{m}_3 \quad \cdots ①$$

- Component B MB :

$$X_{B_1}\dot{m}_1 = X_{B_2}\dot{m}_2 + X_{B_3}\dot{m}_3 \quad \cdots\cdots ②$$

- Component C MB :

$$X_{C_1}\dot{m}_1 = X_{C_2}\dot{m}_2 + X_{C_3}\dot{m}_3 \quad \cdots\cdots ③$$

- Total MB :

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_3 \quad \cdots ④$$

But we have 3 indept. eqns. why ?

Eq. 1 + Eq. 2 + Eq 3 $\Rightarrow \dot{m}_1[X_{A_1} + X_{B_1} + X_{C_1}]$

$= \dot{m}_2[X_{A_2} + X_{B_2} + X_{C_2}] + \dot{m}_3[X_{A_3} + X_{B_3} + X_{C_3}]$

Remember from chapter 3 that the $\sum_{i=1}^{N} X_i = 1.0 \Rightarrow$

$\dot{m}_1 = \dot{m}_2 + \dot{m}_3$ the same as eq. 4

In general:

For a nonreactive process: # of indept. MB that can be written = # of indept. components involved in the process.

For a reactive process: # of indept. MB eqns. that can be written = # of indept. atomic species involved in the process.

* Useful summary of steady state processes (Acc. = 0) in which In − Out + Gen − Cons. = 0 :

Type of MB	St. st. process: In $\overset{?}{=}$ out without chem. rxns.	 with chem. rxns.
Total Mass Balance	yes	yes
Total Moles	yes	No
Component mass balance	yes	No
Component mole balance	yes	No
Mass of atomic species balance	yes	yes
Moles of atomic species balance	yes	yes

Yes: $G = C = \text{zero}$: No: $G \neq 0$, $C \neq 0$

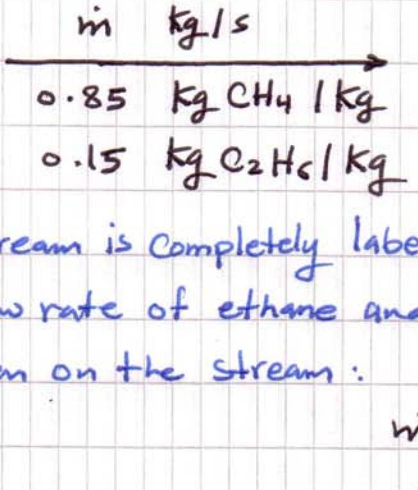
** Systematic approach for solving material balance problems:

Step 1 Draw and completely label the flowchart.

Rule. a stream on the flowchart is completely labeled when you can write an expression for the amount or flow rate of each species in the stream in terms of quantities and variables written on the flowchart.

Then a flowchart is completely labeled if every stream on it is completely labeled.

Ex: A continuous stream of natural gas containing 85 wt% methane and the balance ethane:



This stream is completely labeled. since we can express the mass flow rate of ethane and methane in terms of what is written on the stream:

$$\dot{m}_{CH_4} = 0.85\,\dot{m}$$
$$\dot{m}_{C_2H_6} = 0.15\,\dot{m}$$

* Rules for stream labeling:

- you may label either a total flow rate (or total amount) and component mass or mole fractions or individual component flow rates (amounts).

Ex: label a stream of an aqueous solution of NaCl and KCl:

$$\xrightarrow{m \text{ kg}}$$

x_1 kg NaCl/kg

x_2 kg KCl/kg

$1-x_1-x_2$ kg H_2O/kg

3 unknowns

or

$$\xrightarrow{\hspace{3cm}}$$

m_1 kg NaCl

m_2 kg KCl

m_3 kg H_2O

3 unknowns

Ex: Label a gas stream containing SO_2 and air (21 mol% O_2 and 79 mol% N_2) flows at rate of 125 mol/s:

$$\xrightarrow{125 \text{ mol/s}}$$

y mol SO_2/mol

$1-y$ mol air/mol

0.21 mol O_2/mol air

0.79 mol N_2/mol air

This is completely labeled stream:

$$\dot{n}_{SO_2} = 125y$$

$$\dot{n}_{O_2} = (125)(1-y)(0.21)$$

$$\dot{n}_{N_2} = (125)(1-y)(0.79)$$

- If process variables such as T, P, ρ, SG, $\dot{Q}$, V of streams ar either given or required; include labels both for them and for mass molar quantities.

Step 2 Choose basis of calculation. At least one stream quantity (flow rate) must be given or specified before any MB calculations are done. If the problem statement does NOT do it, you choose a convenient basis (flowrate of stream with known composition).

Step 3 Do a degree of freedom (DOF) analysis:

for non-reactive processes:

DOF = # of unknown variables on the flow chart
- # of indept. molecular species
- # of other equations relating unknowns

for a reactive processes:

DOF = # of unknown variables on the flowchart
- # of indept. molecular species
- # of other equations relating unknowns
+ # of independent chemical reactions.

If DOF = 0 ⇒ It is okay and go to step 4

If DOF > 0 ⇒ More unknowns than indept. eqns. problem is underspecified, specify some unknowns such that DOF = 0

If DOF < 0 ⇒ More indept. eqns. than unknowns problem is overspecified. some known quantities must be unknowns such that DOF = 0

Step 4 Write the independent equations

step 5 solve for the required quantities. adopt some solution strategy to simplify method of solution.

** Important point: scaling the flowchart.

If one stream flow rate or amount is changed, do NOT resolve problem from zero, what you can do is to calculate scale factor, SF:

$$SF = \frac{\text{The desired amount or flow rate of the stream}}{\text{The calculated amount or flow rate of the stream}}$$

$$= \frac{\dot{m}_{desired}}{\dot{m}_{calculated}}$$

$$\therefore \quad \dot{m}_{desired} = SF \; \dot{m}_{calculated}$$

But all streams amount or flowrated also will be changed, i.e they must be multiply by SF.

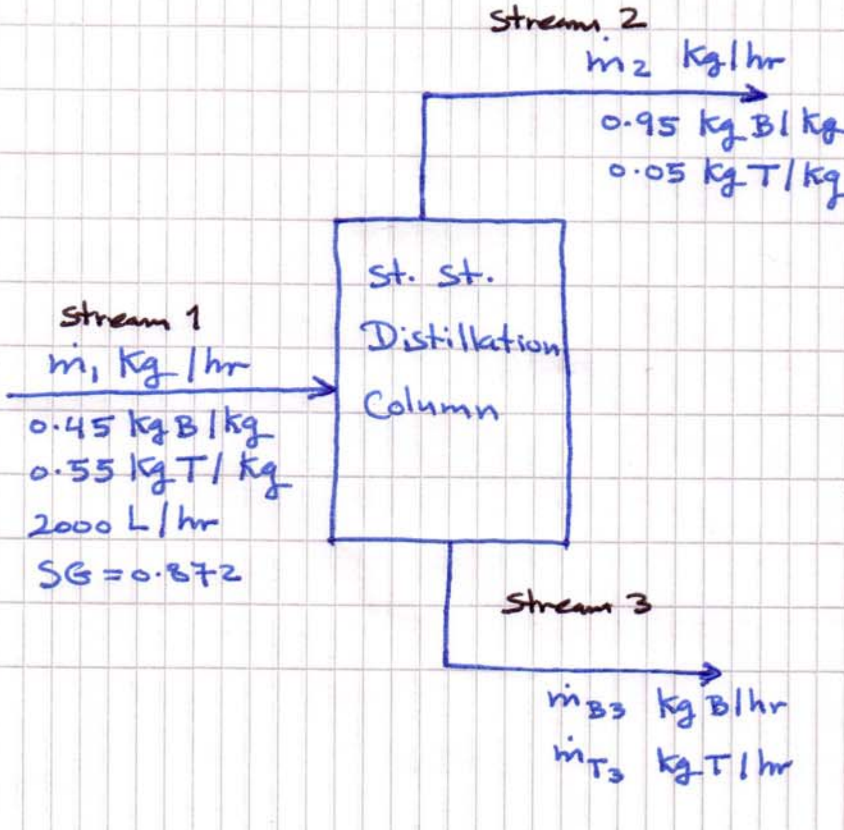
- Sometime scaling is used to simplify solution of problem. How? some known quantity is left as unknown and at the same time one unknown variable is given a value (becomes known) to keep DoF = 0. Then and after solving problem SF is used to return the original value of that quantity which was left as unknown.

Example. A liquid mixture containing 45 wt % benzene (B) and Toluene (T) is fed to a distillation column operating at steady state. product streams emerge from the top and bottom of the column. The top product stream contains 95 wt% B and the bottom product stream contains 8% of the benzene fed to the column. The volumetric flow rate of the feed stream is $2000 \frac{L}{hr}$ and the specific gravity of the feed mixture is 0.872.

(a) Determine the mass flow rate of the overhead product stream and the mass flow rate and composition of the bottom product stream.

(b) what is the volumetric feed flow rate in $\frac{L}{hr}$ needed to produce $2500 \frac{lbm}{day}$ of the overhead product?

Step 1 Draw and completely label the flowchart.



Step 2. At least one stream flow rate must be given or specified before any MB calculations. Then it will be chosen as basis of calculation

Here no any stream has mass flow rate to choose it as basis? is it possible to specify one? yes we have the volumetric flow rate of the feed stream and its SG

⇒

$$\dot{m}_1 = \rho Q = SG\,\rho_w\,Q$$

$$= \frac{0.872 \;\Big|\; 1000\,kg \;\Big|\; 2000\,L \;\Big|\; 1\,m^3}{\quad\;\Big|\; m^3 \;\Big|\; hr \;\Big|\; 1000\,L}$$

$$= 1744\ kg/hr$$

⇒ The basis of calculation now is specified and it is 1744 kg/hr of the feed stream.

Step 3 DOF analysis

This is non-reactive process ⇒

DOF = # of unknowns on the flowchart − # of indept. components − # of other eqns.

# of unknowns = 3 : $\dot{m}_2$, $\dot{m}_{B3}$, $\dot{m}_{T3}$

# of indept. components = 2 : Benzene, Toluene

# of other equation = 1 : The problem statement itself gives us information to produce another eq.:

$$\dot{m}_{B3} = (0.08)(0.45 * \dot{m}_1)$$

∴ DOF = 3 − 2 − 1 = 0 Go to step 4

Step: 4 + 5 Write the equations: Mass balance equations and other equations in the order that it is easier to solve

other eq. : $\dot{m}_{B3} = (0.08)(0.45)(\dot{m}_1)$

$= (0.08)(0.45)(1744) = 62.8 \ \frac{\text{kg B}}{\text{hr}}$

Benzene MB : $(0.45)(\dot{m}_1) = \dot{m}_{B3} + 0.95 \ \dot{m}_2$

$(0.45)(1744) = 62.8 + 0.95 \ \dot{m}_2$

$\Rightarrow \dot{m}_2 = 760 \text{ kg/hr}$

Toluene MB : $(0.55)(\dot{m}_1) = (0.05)\dot{m}_2 + \dot{m}_{T3}$

$(0.55)(1744) = (0.05)(760) + \dot{m}_{T3}$

$\Rightarrow \dot{m}_{T3} = 921.2 \text{ kg T/hr}$

Now calculate the required quantities of part (a)

mass flow rate of the bottom stream $= \dot{m}_{B3} + \dot{m}_{T3}$

$= 62.8 + 921.2$

$= 984 \text{ kg/hr}$

Composition of the bottom stream :

$$x_B = \frac{\dot{m}_{B3}}{\dot{m}_{B3} + \dot{m}_{T3}} = \frac{62.8}{984} = 0.0638 \text{ kg B/kg}$$

$$x_T = 1 - x_B = 1 - 0.0638 = 0.9362 \text{ kg T/kg}$$

(b) Calculate scale factor, SF

$$\dot{m}_{2,new} = \frac{2500\ \text{lbm}}{\text{day}}\left|\frac{1\ \text{Kg}}{2.20462\ \text{lbm}}\right|\frac{1\ \text{day}}{24\ \text{hr}} = 47.249\ \frac{\text{Kg}}{\text{hr}}$$

$\dot{m}_{2,old} = \dot{m}_{2,\text{calculated in part (a)}} = 760\ \text{Kg/hr}$

$$SF = \frac{\dot{m}_{2,new}}{\dot{m}_{2,old}} = \frac{47.249}{760} = 0.0622$$

$$\Rightarrow \dot{m}_{1,new} = SF\ \dot{m}_{1,old} = (0.0622)(1744)$$
$$= 108.48\ \text{Kg/hr}$$

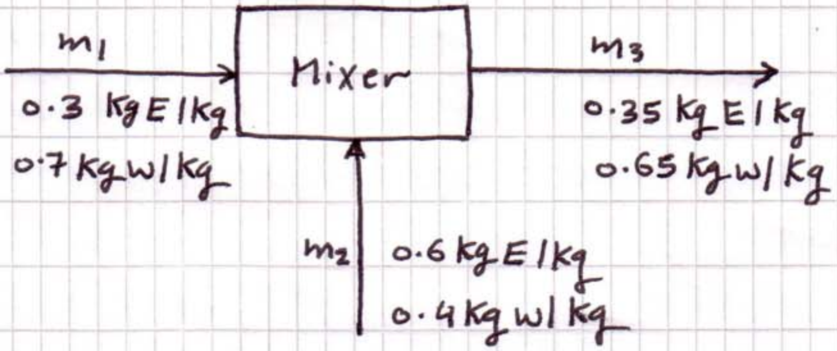
$$Q_{1,new} = \frac{\dot{m}_{1,new}}{\rho} = \frac{\dot{m}_{1,new}}{SG\ \rho_w} = \frac{108.45}{(1000)(0.872)}$$
$$= 0.1244\ \frac{m^3}{hr} = 124.37\ \frac{L}{hr}$$

and the bottom stream mass flow rate will be $(SF)(984)$
$= (0.0622)(984) = 61.2\ \text{Kg/hr}$.

Ex: A stream containing 30 wt% ethanol and water is blended with a stream containing 60 wt% ethanol and water. The product contains 35 wt% ethanol. what is the mass ratio of stream 1 to stream 2 ?

Ethanol : E   Water : W

Step 1.



Step 2: Basis of calculation the amounts of all streams are not given and there is no any information to calculate at least one of them to be the basis

Thus we will assume basis: 100 kg of stream 1

$$\Rightarrow \boxed{m_1 = 100 \text{ kg} : \text{Basis}}$$

Step 3 : DOF analysis

$$\text{DoF} = \underset{\substack{m_3\\ m_2}}{\underset{\downarrow}{2}} - \underset{\substack{E\\ W}}{\underset{\downarrow}{2}} = 0 \quad \text{ok go ahead}$$

Step 4+5 : Ethanol MB : $(0.3)(100) + (0.6)m_2 = 0.35\, m_3$

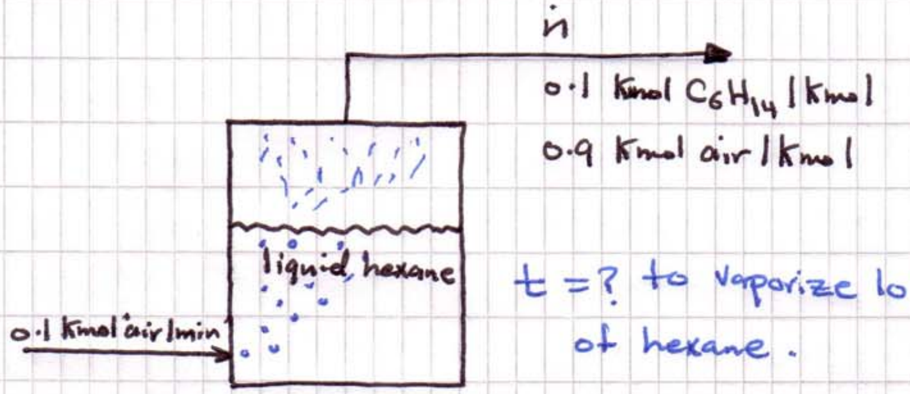
Total MB : $100 + m_2 = m_3$

solve to obtain: $m_2 = 20$ kg , $m_3 = 120$

∴ the ratio: $\frac{m_1}{m_2} = \frac{100}{20} = 5$

Ex: Air is bubbled through a drum of liquid hexane at a rate of 0.100 kmol/min. The gas stream that is leaving the drum contains 10 mol% hexane vapor. Air may be considered as insoluble in liquid hexane. Find the time required to vaporize 10 m³ of liquid hexane.

step 1



t = ? to vaporize 10 m³ of hexane.

Since air is insoluble in hexane ⇒ The process is steady state for air $I_{air} = O_{air}$ no accumulation of air inside the system

But for Hexane the process is semibatch:

$$I_{Hex} = 0 \qquad O_{Hex} \neq 0 \qquad \text{no rxn} \Rightarrow G = C = 0$$

$$\Rightarrow -\text{out}_{hex} = \text{Acc}_{Hex}$$

Step 2 Basis: $0.1 \frac{\text{kmol air}}{\text{min}}$

Step 3: DoF analysis:

\# of unknowns = 2 : $\dot{n}$, t

\# of MB equ. = 2 : air, hexane

DoF = 2 - 2 = 0 ok other eqns. = 0

step 4+5

Air molar balance : $0.1 = (0.9)\,\dot{n} \Rightarrow \dot{n} = 0.111$ Kmol/min

Hexane molar balance : In − out = Acc

$$0 - \dot{n}_{hex,out} = \frac{dn_{hex}}{dt}$$

$$0 - (0.1)(0.111) = \frac{dn}{dt}$$

$$\int_{t=0}^{t_f} -0.0111\,dt = \int_{n_i}^{n_f} dn$$

at $t = 0$ $\quad V_i = 10$ m³

$t = t_f$ $\quad V_f = 0$ m³ $\Rightarrow n_f = 0$

$m_i = \rho V_i = SG\,\rho_w V_i$

from table B.1 in the appendix of your textbook.

$SG_{Hex} = 0.659$

$\Rightarrow m_i = (0.659)(1000)(10) = 6590$ kg hexane

and $n_i = \dfrac{6590 \text{ kg}}{} \Big| \dfrac{1 \text{ Kmol hex}}{86.2 \text{ kg hex}} = 76.45$ Kmol hex

$\Rightarrow -0.0111(t_f - 0) = n_f - n_i = 0 - 76.45$

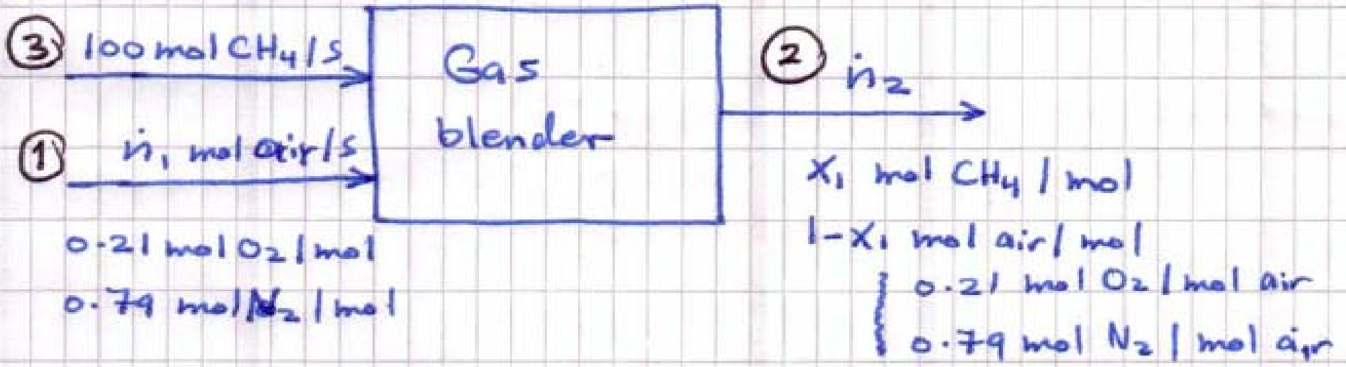
$$\Rightarrow t_f = \frac{76.45}{0.0111} = 6887.4 \text{ min}$$

* It is mentioned that : # of MB equations = # of indept. molecular species involved in the process

* When molecular species are not independent ?

Rule : if two molecular species are in the same ratio every-where in the process and the ratio is incorporated in the flowchart labeling , these two species are NOT independent.

Ex :



# of unknowns = 3

# of indept. rxns = 0

# of independent molecular species $\overset{?}{=}$ 3 (CH_4, O_2, N_2)

NO. apply the rule. in streams ② and ① O_2 and N_2 have the same ratio :

stream 1 : $\frac{\text{mol } O_2}{\text{mol } N_2} = \frac{0.21\,\dot{n}_1}{0.79\,\dot{n}_2} = \frac{0.21}{0.79}$

stream 2 : $\frac{\text{mol } O_2}{\text{mol } N_2} = \frac{(0.21)(1-x_1)(\dot{n}_2)}{(0.79)(1-x_1)(\dot{n}_2)} = \frac{0.21}{0.79}$

In other words if you write :

O$_2$ mole balance : $\cancel{0.21}\,\dot{n}_1 = (1-x_1)(\dot{n}_2)(\cancel{0.21})$

$$\dot{n}_1 = (1-x_1)\,\dot{n}_2$$

N$_2$ mole balance : $\cancel{(0.79)}\,\dot{n}_1 = (1-x_1)(\dot{n}_2)\cancel{(0.79)}$

$$\dot{n}_1 = (1-x_1)(\dot{n}_2)$$

The two eqns are identical :

⇒ N_2 and O_2 are not independant

# of indept. eqns. = # of indept. species

= 2 : CH_4 and N_2 or O_2

∴ DOF = 3 − 2 = 1

we need more eq. for the problem to be solved.

** Stoichiometry and reactive system balances:

* Stoichiometry: proportions in which chemical species combine in a chemical reaction as represented by a $\boxed{\text{balanced reaction equation.}}$

* Stoichiometric equation: statement of the relative number of molecules or moles of reactants and products (but not mass) that participate in the reaction.

* Stoichiometric Coefficients: numbers preceeding each species in the balanced reaction equation.

These coefficients define conversion factors from moles of one species consumed or formed in the reaction to moles of another species consumed or formed.

Remark: always check the reaction eq. to be balanced.

Ex: $N_2 + H_2 \longrightarrow 2\,NH_3$

The reaction eq. is not balanced. Balance it:

$N_2 + 3H_2 \longrightarrow 2\,NH_3$

Stoichiometric coefficients give the following conversion factors:

$$\frac{1 \text{ mol } N_2 \text{ Consumed}}{3 \text{ mol } H_2 \text{ Consumed}} \; ; \; \frac{2 \text{ mol } NH_3 \text{ generated}}{3 \text{ mol } H_2 \text{ consumed}} \; ; \; \ldots \text{ etc.}$$

For instant if 50 mol/s of NH_3 are produced, then the molar flow rate of N_2 consumed is :

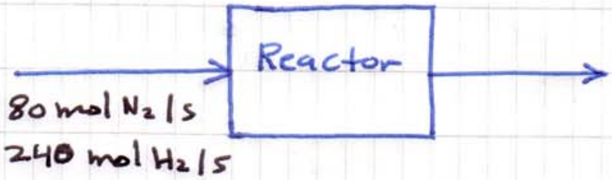
$$\left(\dot{n}_{N_2}\right)_{\text{consumed}} = \frac{50 \text{ mol } NH_3 \text{ formed}}{s} \left| \frac{1 \text{ mol } N_2 \text{ consumed}}{2 \text{ mol } NH_3 \text{ formed}} \right. = 25 \frac{\text{mol}}{s}$$

* Limiting and excess reactants:

Δ If feed reactants are in stoichiometric proportion :

⇒ all reactants will run out at the same time :

Ex : $N_2 + 3H_2 \longrightarrow 2NH_3$



what if the feed reactants are not in stoichiometric proportion ?

Here, limiting reactant is defined.

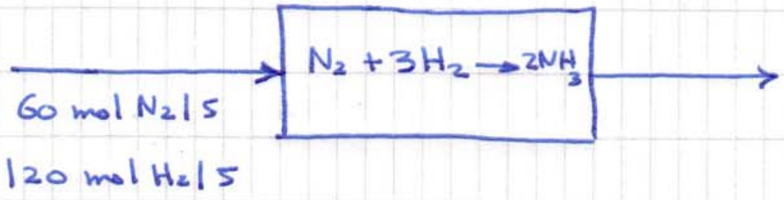
Δ Limiting reactant (LR) : reactant that runs out first.

How to identify the LR ?

$$\text{If } \left(\frac{n_x}{n_y}\right)_{\text{feed}} > \left(\frac{n_x}{n_y}\right)_{\text{stoichiometric}} \Rightarrow \text{reactant } x \text{ is NOT LR}$$

$$\text{or } \left(\frac{n_x}{n_y}\right)_{\text{feed}} < \left(\frac{n_x}{n_y}\right)_{\text{stoichiometric}} \Rightarrow \text{reactant } x \text{ is LR}$$

Ex:



Determine the limiting reactant (LR)?

$$\left(\frac{n_{N_2}}{n_{H_2}}\right)_{feed} = \frac{60}{120} = 0.5 \quad ; \quad \left(\frac{n_{N_2}}{n_{H_2}}\right)_{stoich} = \frac{1}{3}$$

$$\left(\frac{n_{N_2}}{n_{H_2}}\right)_{feed} > \left(\frac{n_{N_2}}{n_{H_2}}\right)_{stoich} \Rightarrow N_2 \text{ is not LR and } H_2 \text{ is the LR}$$

△ Excess reactants : all other reactants but limiting one.

In the previous example N_2 is excess reactant.

* Theoritical (stoichiometric) requirement of an excess reactant; $\dot{n}_{theor.}$: How much would be required to react completely with the LR when the reaction goes to completion.

In the previous example the theoritical molar flow rate of N_2 is $40 \frac{mol}{s}$

* Fractional excess; $\boxed{f_{xs,i} = \frac{\dot{n}_{feed,i} - \dot{n}_{theor,i}}{\dot{n}_{theor,i}}}$

In the previous example, the fractional excess of N_2 is:

$$f_{xs,N_2} = \frac{60 - 40}{40} = 0.5$$

* percent excess of reactant ; $\% XS_i = f_{xs,i} * 100$

$$\boxed{\% XS_i = \frac{\dot{n}_{feed,i} - \dot{n}_{theor,i}}{\dot{n}_{theor,i}} * 100}$$

This eq. can be also rearranged to have:

$$\boxed{\dot{n}_{feed,i} = \dot{n}_{theor,i}\left[1 + \frac{\% XS}{100}\right]}$$

* Remark: theoritical, excess and limiting quantities depend only on the feed molar amounts and the stoichiometric reaction, and not on what actually happens inside the reactor.

* Fractional conversion of a reactant ; f_i :

$$\boxed{f_i = \frac{\text{reacted moles of reactant } i}{\text{fed moles of reactant } i} = \frac{\dot{n}_{in,i} - \dot{n}_{out,i}}{\dot{n}_{in,i}}}$$

If reaction goes to completion $\Rightarrow f_{LR} = 1.0$

Ex: If you feed 10 g of N_2 gas and 10 g of H_2 gas in a reactor to produce NH_3 where the reaction goes to completion:

(a) what is the limiting reactant (LR) ?

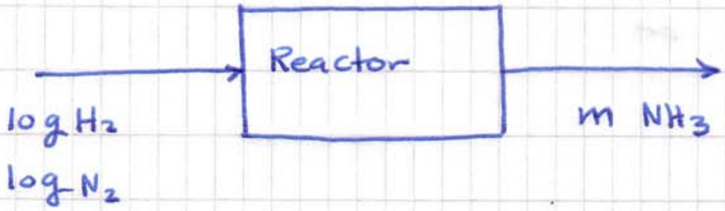
(b) what is the excess reactant ?

(c) Find the percent excess of excess reactant if the reaction goes to completion.

(d) what is the maximum number of grams of NH_3 that can be produced.

(a) LR = ?

Convert mass quantities to molar quantities:



$$\frac{10\,g\,H_2 \;\big|\; 1\,mol\,H_2}{\;\big|\; 2\,g\,H_2} = 5\ gmol\ H_2$$

$N_2 + 3H_2 \longrightarrow 2\,NH_3$

" Balanced eq. "

$$\frac{10\,g\,N_2 \;\big|\; 1\,mol\,N_2}{\;\big|\; 28\,g\,N_2} = 0.357\ gmol\ N_2$$

$$\left(\frac{n_{H_2}}{n_{N_2}}\right)_{stoich.} = 3 \quad ; \quad \left(\frac{n_{H_2}}{n_{N_2}}\right)_{feed} = \frac{5}{0.357} = 14.0$$

$$\left(\frac{n_{H_2}}{n_{N_2}}\right)_{feed} > \left(\frac{n_{H_2}}{n_{N_2}}\right)_{stoich} \Rightarrow H_2 \text{ is NOT limiting}$$

$\therefore$ N_2 is LR

(b) H_2 is in excess

(c) $$(n_{H_2})_{theor.} = \frac{0.357\,mol\,N_2 \;\big|\; 3\,mol\,H_2}{\;\big|\; 1\,mol\,N_2} = 1.1\ mol\ H_2$$

$$XS_{H_2}\,\% = \frac{n_{feed,\,H_2} - n_{theor,\,H_2}}{n_{theor,\,H_2}} * 100$$

$$= \frac{5. - 1.1}{1.1} * 100 = 354$$

(d) $$n_{out,\,NH_3} = \frac{0.357\,mol\,N_2 \;\big|\; 2\,mol\,NH_3}{\;\big|\; 1\,mol\,N_2} = 0.714\ mol\ NH_3$$

$$m_{out,\,NH_3} = \frac{0.714\,mol\,NH_3 \;\big|\; 17\,g\,NH_3}{\;\big|\; 1\,mol\,NH_3} = 12.14\ g\ NH_3$$

is produced when rxn goes to completion

Ex: In the previous example suppose that you are told that H_2 is fed in 60% excess (instead of quantity of 10 g). Find number of grams of H_2 in the feed.

$$n_{H_2,feed} = n_{theor,H_2}\left[1 + \frac{\% xs_{H_2}}{100}\right]$$

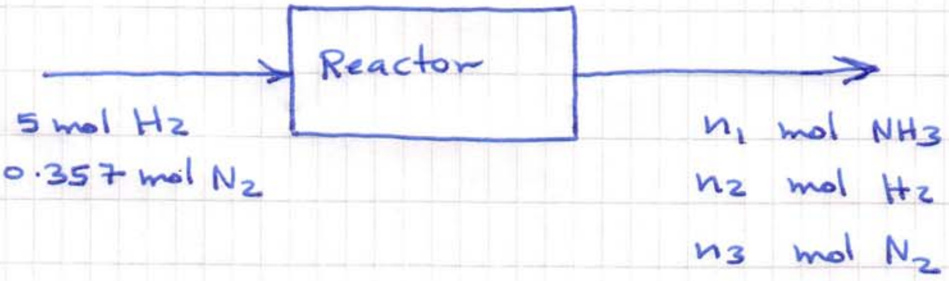
$$= 1.1\left[1 + \frac{60}{100}\right] = 1.1(1 + 0.6) = 1.76 \text{ gmol } H_2$$

$\Rightarrow$

$$m_{H_2,feed} = \frac{1.76 \text{ gmol } H_2 \,\big|\, 2 \text{ g } H_2}{\big|\, 1 \text{ gmol } H_2} = 3.52 \text{ g } H_2 \text{ in the feed.}$$

If the reaction of previous example does NOT go to Completion, is it possible to find the amount of NH_3 produced under the same information?

If rxn does not go to completion $\Rightarrow$ the outlet stream will have product (NH_3) and LR (N_2) and excess reactant (H_2):



It looks like we should have:

DOF = 3 − 3 − 0 = 0

But the actual DOF = 1 (you have reaction and in case of chemical reactions DOF must be redefined). No matter how hard you try, you can not find n_1, n_2, and n_3 unless you get more information.

** Balances on reactive processes:

Component mole balances can be written and solved in three methods:

Ⓐ Molecular species balances
Ⓑ Atomic species balances
Ⓒ Extent of reaction method

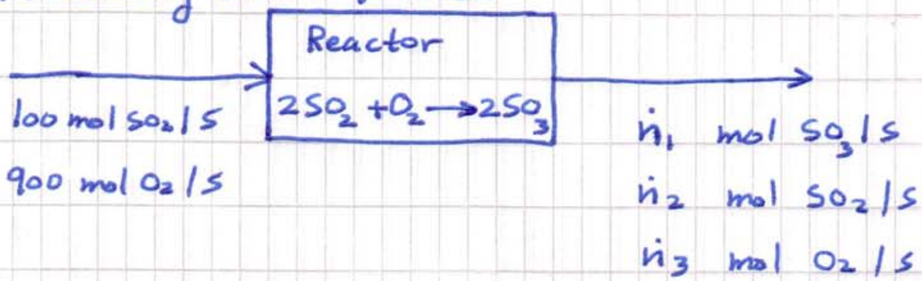
Ⓐ Molecular species balances:

using this method the degree of freedom (DOF) can be defined as follows:

DOF = # of unknowns − # of independent molecular balances − other eqns. + # of independent rxns

# of independent molecular balances = # of independent species

Ex: steady state process



# of unknowns = 3 : $\dot{n}_1, \dot{n}_2, \dot{n}_3$
# of indept. molecular species = 3 O_2, SO_2, SO_3
# of indept. rxns = 1 : one reaction
other equs = 0

DOF = 3 − 3 − 0 + 1 = 1 (underspecified problem)

we need one information more to solve the problem (to have DOF = 0):

Let us say that we told that the Conversion of SO_2 is 80%.

Now we have one other eqn.: Conversion eq.:

$$f_{SO_2} = \frac{\dot{n}_{reacted, SO_2}}{\dot{n}_{feed, SO_2}} = \frac{100 - \dot{n}_2}{100}$$

Now DOF = 3 − 3 + 1 − 1 = 0 (ok)

Let us start solving problem:

Conversion eq.: $f_{SO_2} = 0.8 = \frac{100 - \dot{n}_2}{100}$

$$\Rightarrow \boxed{\dot{n}_2 = 20 \text{ mol } SO_2 / s}$$

SO_2 mole balance: $I - O + \overset{=0}{\cancel{G}} - C = \overset{=0 \text{ St.st}}{\cancel{A}}$

$$C = I - O = 100 - 20 = 80 \ \frac{\text{mol } SO_2 \text{ Consumed}}{s}$$

SO_3 mole balance: $\overset{0}{\cancel{I}} - O + G - \overset{0}{\cancel{C}} = \overset{0}{\cancel{A}}$

$$-\dot{n}_1 + G = 0$$

$$G = \frac{80 \text{ mole } SO_2 \text{ Consumed}}{s} \left| \frac{2 \text{ mol } SO_3 \text{ generated}}{2 \text{ mol } SO_2 \text{ Consumed}} \right.$$

$$= 80 \ \frac{\text{mol } SO_3}{s}$$

$$\boxed{\dot{n}_1 = G = 80\ \frac{\text{mol } SO_3}{s}}$$

O₂ mole balance: $I - O + \cancel{G}^{\,0} - C = \cancel{A}^{\,0}$

$$90 - \dot{n}_3 - C = 0$$

$$\dot{n}_3 = 90 - C$$

$$C = \frac{80 \text{ mol } SO_2 \text{ Consumed}}{s} \bigg| \frac{1 \text{ mol } O_2 \text{ Consumed}}{2 \text{ mol } SO_2}$$

$$= \frac{80}{2}\ \frac{\text{mol } SO_2 \text{ Consumed}}{s}$$

$$\therefore\ \dot{n}_3 = 90 - \frac{80}{2} = 90 - 40 = 50\ \frac{\text{mol } O_2}{s}$$

* When chemical reactions are NOT independant ?

If we can NOT get one chemical reaction eq. in terms of others.

Ex: are the following three reactions independant? why?

$$A \longrightarrow 2B \qquad (1)$$

$$B \longrightarrow C \qquad (2)$$

$$A \longrightarrow 2C \qquad (3)$$

No they are Not since the reaction eq. (3) can be obtained by adding eq. (1) to the eq. (2) multiplied by 2:

$$\begin{array}{l} A \longrightarrow 2B \\ \underline{2B \longrightarrow 2C} \\ A + \cancel{2B} \longrightarrow \cancel{2B} + 2C \end{array} \Rightarrow A \rightarrow 2C \text{ which}$$

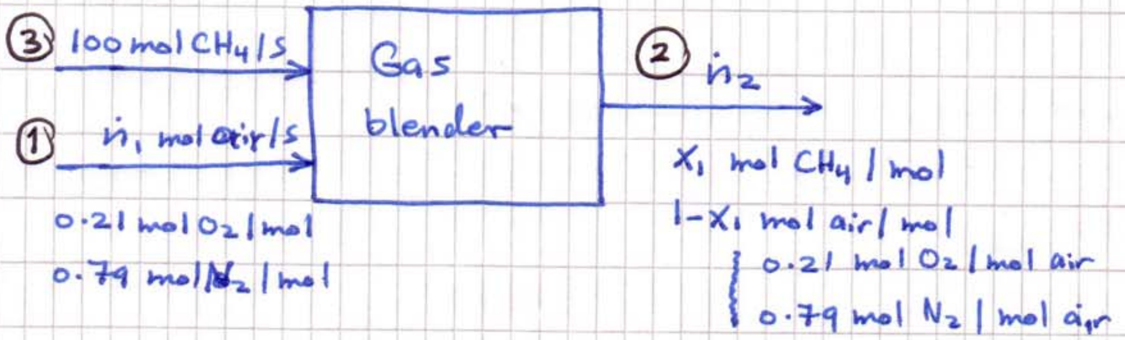
is reaction eq. (3)

The the # of independant chemical reactions = 2 (not 3)

* When molecular species are not independent?

Rule: if two molecular species are in the same ratio every-where in the process and the ratio is incorporated in the flowchart labeling, these two species are NOT independant.

Ex:



\# of unknowns = 3

\# of indept. rxns = 0

\# of independent molecular species $\overset{?}{=}$ 3 (CH_4, O_2, N_2)

NO. apply the rule. in streams ② and ① O_2 and N_2 have the same ratio:

$$\text{stream 1: } \frac{\text{mol } O_2}{\text{mol } N_2} = \frac{0.21\,\dot{n}_1}{0.79\,\dot{n}_2} = \frac{0.21}{0.79}$$

$$\text{stream 2: } \frac{\text{mol } O_2}{\text{mol } N_2} = \frac{(0.21)(1-x_1)(\dot{n}_2)}{(0.79)(1-x_1)(\dot{n}_2)} = \frac{0.21}{0.79}$$

In other words if you write :

O_2 mole balance : $\cancel{0.21}\,\dot{n}_1 = (1-x_1)(\dot{n}_2)(\cancel{0.21})$

$$\dot{n}_1 = (1-x_1)\,\dot{n}_2$$

N_2 mole balance : $\cancel{(0.79)}\,\dot{n}_1 = (1-x_1)(\dot{n}_2)\cancel{(0.79)}$

$$\dot{n}_1 = (1-x_1)(\dot{n}_2)$$

The two eqns. are identical :

$\Rightarrow$ N_2 and O_2 are not independent

\# of indept. eqns. = \# of indept. species

$= 2$: CH_4 and N_2 or O_2

$\therefore$ DOF $= 3 - 2 = 1$

we need more eq. for the problem to be solved.

Ⓑ Atomic species balances :

atomic species are neither generated no consumed.

$$G = C = 0$$

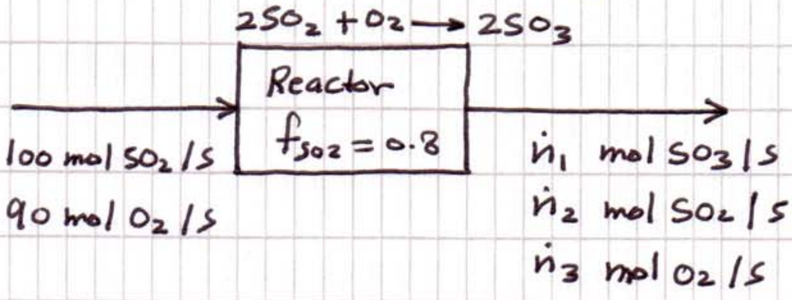
Exception : nuclear reactions that wo do NOT consider here.

Defintion of DOF :

DOF = # of unknowns − # of independent atomic atomic balances − # of other eqns.

# of indept. atomic balances = # of indept. atomic species

Ex :



# of unknowns = 3

# of atomic balances = 2 (S , O)

# of other eqns. = 1 (Conversion eq.)

$$DOF = 3 - 2 - 1 = 0$$ ✓ (Go ahead)

Conversion eq. : $f_{SO_2} = \dfrac{\dot{n}_{in,SO_2} - \dot{n}_{out,SO_2}}{\dot{n}_{in,SO_2}}$

$$0.8 = \frac{100 - \dot{n}_2}{100} \Rightarrow \boxed{\dot{n}_2 = 20 \ \frac{\text{mol } SO_2}{s}}$$

S atomic balance: $I = 0$

$$\frac{100\ \text{mol SO}_2}{\text{s}}\left|\frac{1\ \text{mol S}}{1\ \text{mol SO}_2}\right. = \dot{n}_1\ \frac{\text{mol SO}_3}{\text{s}}\left|\frac{1\ \text{mol S}}{1\ \text{mol SO}_3}\right. + \frac{20\ \text{mol SO}_2}{\text{s}}\left|\frac{1\ \text{mol S}}{1\ \text{mol SO}_2}\right.$$

$$\Rightarrow \dot{n}_1 = 100 - 20 = 80\ \frac{\text{mol SO}_3}{\text{s}}$$

$$\boxed{\dot{n}_1 = 80\ \frac{\text{mol SO}_3}{\text{s}}}$$

O atomic balance: $I = 0$

$$\frac{100\ \text{mol SO}_2}{\text{s}}\left|\frac{2\ \text{mol O}}{1\ \text{mol SO}_2}\right. + \frac{90\ \text{mol O}_2}{\text{s}}\left|\frac{2\ \text{mol O}}{1\ \text{mol O}_2}\right. =$$

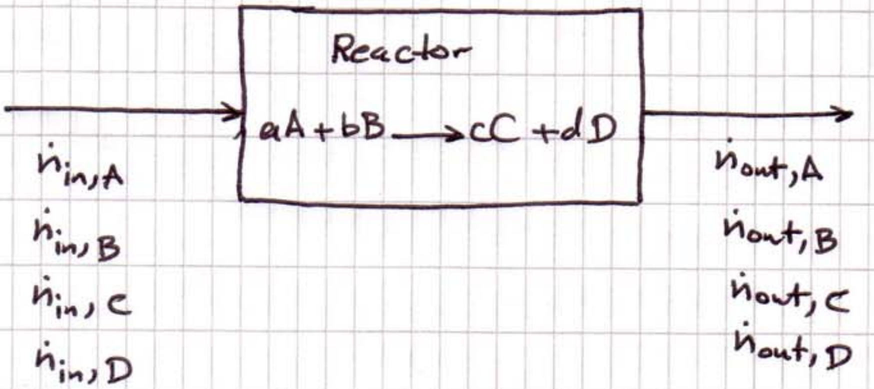
$$\frac{80\ \text{mol SO}_3}{\text{s}}\left|\frac{3\ \text{mol O}}{1\ \text{mol SO}_3}\right. + \frac{20\ \text{mol SO}_2}{\text{s}}\left|\frac{2\ \text{mol}}{1\ \text{mol SO}_2}\right. + \dot{n}_3\ \frac{\text{mol O}_2}{\text{s}}\left|\frac{2\ \text{mol O}}{1\ \text{mol O}_2}\right.$$

$$\Rightarrow 200 + 180 = 240 + 40 + 2\dot{n}_3$$

$$80\ \boxed{\dot{n}_3 = 50\ \frac{\text{mol O}_2}{\text{s}}}$$

© Extent of reaction method:

In this method the degree of freedom DOF is define as molecular species balances method:



Let the unknow # of moles of species A consumed $= a\xi$ $\quad\quad \xi$: pronounced kzi

Then moles B consumed $= \dfrac{\cancel{a}\xi \text{ mol A consumed}}{} \Bigg| \dfrac{b \text{ mol B consumed}}{\cancel{a} \text{ mol A consumed}}$

$= b\xi$

moles C generated $= \dfrac{a\xi}{} \Bigg| \dfrac{b}{c} = c\xi$

mole D generated $= \dfrac{a\xi}{} \Bigg| \dfrac{d}{a} = d\xi$

ξ: is called the extent of reaction. It must be the same for all species and it must be positive.

If there are more than one independent reaction; each independent rxn must have ξ.

Now let us write the molecular species balances using the defined extent of reaction (ξ) for steady state process:

A mole balance: $I - O + G - C = \cancel{A}^{0}$ st.st.

$$\dot{n}_{in,A} - \dot{n}_{out,A} + 0 - a\xi = 0 \Rightarrow \boxed{\dot{n}_{out,A} = \dot{n}_{in,A} - a\xi}$$

B mole balance: $I - O + G - C = A$

$$\dot{n}_{in,B} - \dot{n}_{out,B} + 0 - b\xi = 0$$

$$\Rightarrow \boxed{\dot{n}_{out,B} = \dot{n}_{in,B} - b\xi}$$

C mole balance: $I - O + G - C = A$

$$\dot{n}_{in,C} - \dot{n}_{out,C} + c\xi - 0 = 0$$

$$\Rightarrow \boxed{\dot{n}_{out,C} = \dot{n}_{in,C} + c\xi}$$

D mole balance: $I - O + G - C = A$

$$\dot{n}_{in,D} - \dot{n}_{out,D} + d\xi - 0 = 0$$

$$\Rightarrow \boxed{\dot{n}_{out,D} = \dot{n}_{in,D} + d\xi}$$

* Some remarks :

* for any single reaction:

$$\sum_{i=1}^{N} \dot{n}_{out,i} = \sum_{i=1}^{N} \dot{n}_{in,i} + \xi \sum \nu_i$$

$i = 1, 2, \cdots N$

where i is index for species involved in the process and N is the total number of all species.

ν_i is the stoichiometric coefficient of species i. it must be +ve for products and -ve for reactants.

* one extent of reaction equation must be written for every independent molecular species in the process. In general:

$$\underset{\text{Continuous process}}{\underset{\downarrow}{\boxed{\dot{n}_{out,i} = \dot{n}_{in,i} + \nu_i \xi}}} \quad \text{or} \quad \underset{\text{Batch process}}{\underset{\downarrow}{\boxed{n_{final,i} = n_{initial,i} + \nu_i \xi}}}$$

* Every independent reaction has its ξ .

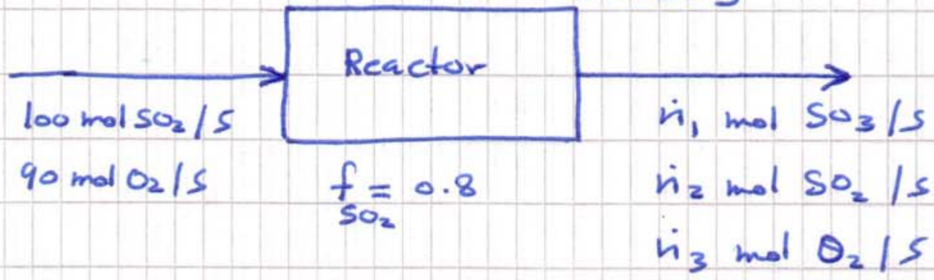
* Extent of reaction method for systems of multiple reactions:

$$\dot{n}_{out,i} = \dot{n}_{in,i} + \sum_{j=1} \nu_{ij} \xi_j$$

i : index for species
j : index for indept. reaction

Ex :

$$2SO_2 + O_2 \longrightarrow 2SO_3$$



$$DOF = 3 - 3 - 1 + 1 = 0$$

Conversion eq. : $0.8 = \frac{100 - \dot{n}_2}{100} \Rightarrow \boxed{\dot{n}_2 = 20 \frac{\text{mol } SO_2}{s}}$

Now write the extent of reaction equations:

SO_3 : $\dot{n}_1 = 0 + (2)\xi = 2\xi$

SO_2 : $\dot{n}_2 = 100 - 2\xi = 20 \Rightarrow \xi = \frac{100-20}{2} = 40 \frac{\text{mol}}{s}$

O_2 : $\dot{n}_3 = 90 - (1)(\xi) = 90 - 40 = 50 \frac{\text{mol } O_2}{s}$

and $\dot{n}_1 = 2\xi = (2)(40) = 80 \frac{\text{mol } SO_3}{s}$

** Multiple chemical reactions :

Example : production of Ethylene process:

Target reaction :

$C_2H_6 \longrightarrow C_2H_4 + H_2$: Ethylene (C_2H_4) is the desired product.

side reaction :

$C_2H_6 + H_2 \longrightarrow 2CH_4$: Methane (CH_4) is undesired by-product

another side reaction :

$C_2H_4 + C_2H_6 \longrightarrow C_3H_6 + CH_4$: propylene (C_3H_6) is also undesired by-product.

→ An undesired byproduct is the result of a Competing side reactions that result in a less of the undesired product.

→ Sometimes byproducts can be sold, but at other times they are worthless and possibly hazardous and have to be disposed (add another cost).

* For multiple reactions processes, other quantities are defined:

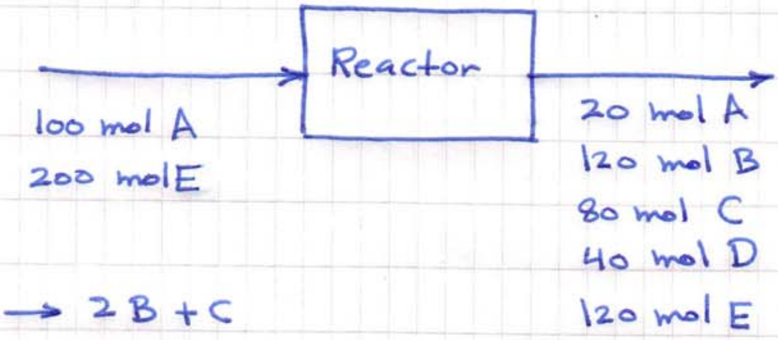
$$\Delta\ \text{yield};\ Y = \frac{(\text{moles of desired product})}{\left\{\begin{array}{l}(\text{moles of desired product that would be generated}\\ \text{if there are no side reactions and the target rxn}\\ \text{goes to completion})\end{array}\right.}$$

Max. possible desired product produced

$$\Delta\ \text{Selectivity};\ S_{AB} : \frac{\text{moles of desired product A}}{\text{moles of undesired product B}}$$

* If yield and selectivity are high $\Rightarrow$ we have successfully suppressed the undesired side reactions.

Ex:



$$E + A \rightarrow 2B + C$$

$$B \rightarrow D$$

B : Desired product

D : undesired product

(a) Find the yield of B, Y_B

(b) Find the selectivity S_{BD}

(a) The Limiting reactant is A

maximum possible B produced $\Rightarrow$ If no side reactions and target reaction goes to completion

$\Rightarrow$ Max possible B produced = $\dfrac{100 \text{ mol A}}{} \Big| \dfrac{2 \text{ mol B produced}}{1 \text{ mol A consumed}}$

= 200 mol B produced

$$Y_B = \frac{120}{200} = 0.6$$

(b) $S_{AB} = \dfrac{n_B}{n_D} = \dfrac{120}{40} = 3$

Remark: a process engineer might take two different approaches to this reaction system:

→ Maximize yield: Get most B you can even if it means producing more D.

→ Maximize selectivity: Hold down production of D even if it means producing less B.

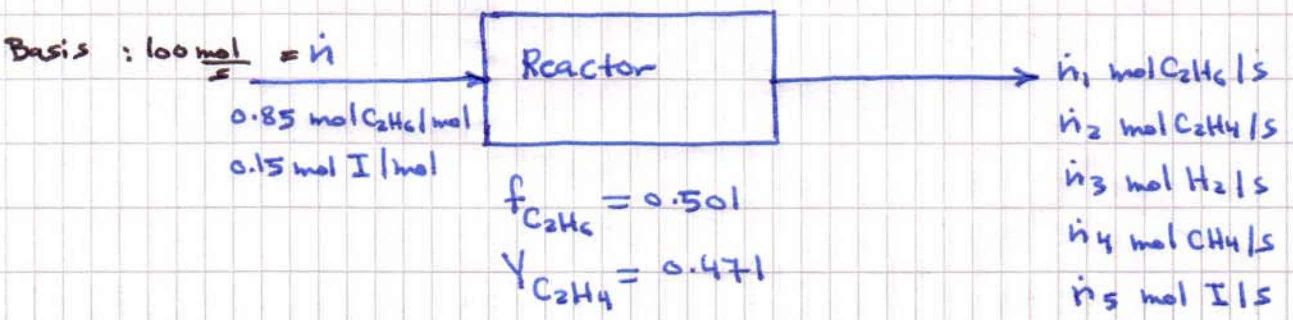
In other words, yield corresponds to quantity of desired product while selectivity corresponding to quality (Purity) of desired product.

Ex: The following two reactions take place in a continuous dehydrogenation reactor at steady state:

$C_2H_6 \longrightarrow C_2H_4 + H_2$

$C_2H_6 + H_2 \longrightarrow 2CH_4$

The feed contains 85 mol% ethane (C_2H_6) and the balance inerts (I). The fractional conversion of ethane is 0.501 and the fractional yield of ethylene (C_2H_4) is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.



Basis of Calculations : $\dot{n} = 100 \dfrac{\text{mol feed}}{\text{s}}$

DOF = # of unknowns − # of indept. molecular species − other eqns. + # of indept. rxns.

$= 5 - 5 - \underset{\hookrightarrow}{2} + 2 = 0$ → It can be solved.

↳ Conversion of C_2H_6
yield of C_2H_4

– Ethane Conversion eq. : $f_{C_2H_6} = \dfrac{\dot{n}_{in, C_2H_6} - \dot{n}_{out, C_2H_6}}{\dot{n}_{in, C_2H_6}}$

$$0.501 = \frac{(0.85)(100) - \dot{n}_1}{(0.85)(100)}$$

$$\Rightarrow \boxed{\dot{n}_1 = 42.4 \frac{\text{mol } C_2H_6}{\text{s}}}$$

– Ethylene yield eq. : $Y_{C_2H_4} = \dfrac{\text{moles produced of } C_2H_4 \text{ per sec.}}{\text{Max possible production of } C_2H_4}$

$$\text{Max possible production} = \frac{(100)(0.85) \text{ mol } C_2H_6}{\text{s}} \left| \frac{1 \text{ mol } C_2H_4}{1 \text{ mol } C_2H_6} \right.$$

$$= 85 \frac{\text{mol } C_2H_4}{\text{s}}$$

$$Y_{C_2H_4} = \frac{\dot{n}_2}{85} = 0.471 \Rightarrow \boxed{\dot{n}_2 = 40 \frac{\text{mol } C_2H_4}{\text{s}}}$$

Using Molecular species balances method:

C_2H_6 balance : $I - O + \cancelto{0}{G} - C = 0$

$$(0.85)(100) - \dot{n}_1 - C_{C_2H_6} = 0$$

$$\Rightarrow C_{C_2H_6} = 85 - \dot{n}_1 = 85 - 42.4 = 42.6 \ \frac{\text{mol } C_2H_6}{s}$$

C_2H_4 balance : $\cancelto{0}{I} - O + G - \cancelto{0}{C} = 0$

$$O = G \Rightarrow \dot{n}_2 = G_{C_2H_4}$$

$$\therefore G_{C_2H_4} = 40 \ \frac{\text{mol } C_2H_4}{s}$$

H_2 balance $\cancelto{0}{I} - O + G - C = 0$

$$0 - \dot{n}_3 + G_{H_2} - C_{H_2} = 0$$

$$\dot{n}_3 = G_{H_2} - C_{H_2}$$

$$G_{H_2} = \frac{40 \text{ mol } C_2H_4 \text{ gen}}{s} \left| \frac{1 \text{ mol } H_2}{1 \text{ mol } C_2H_4} \right. = 40 \ \frac{\text{mol } H_2 \text{ gen}}{s}$$

$$C_{H_2} = \dot{n}_4 \ \frac{\text{mol } CH_4 \text{ gen}}{s} \left| \frac{1 \text{ mol } H_2}{2 \text{ mol } CH_4} \right. = \frac{\dot{n}_4}{2}$$

$$\Rightarrow \dot{n}_3 = 40 - \frac{\dot{n}_4}{2}$$

CH_4 balance : $\cancelto{0}{I} - O + G - \cancelto{0}{C} = 0$

$$-\dot{n}_4 + G_{CH_4} = 0 \Rightarrow \dot{n}_4 = G_{CH_4}$$

$$\left(C_{C_2H_6}\right)_{rxn\,1} = \frac{40 \text{ mol } C_2H_4}{s}\left|\frac{1 \text{ mol } C_2H_6}{1 \text{ mol } C_2H_4}\right. = 40\ \frac{\text{mol } C_2H_6}{s}$$

$$\left(C_{C_2H_6}\right)_{rxn\,2} = 42.6 - 40 = 2.6\ \frac{\text{mol } C_2H_6}{s}$$

$$G_{CH_4} = \frac{2.6 \text{ mol } C_2H_6 \text{ consumed in rxn 2}}{s}\left|\frac{2 \text{ mol } CH_4}{1 \text{ mol } C_2H_6}\right.$$

$$= 5.2\ \frac{\text{mol } CH_4}{s}$$

$$\Rightarrow \boxed{\dot{n}_4 = G_{CH_4} = 5.2\ \frac{\text{mol } CH_4}{s}}$$

$$\dot{n}_3 = 40 - \frac{\dot{n}_4}{2} = 40 - \frac{5.2}{2} = 37.4\ \frac{\text{mol } CH_4}{s}$$

$$\boxed{\dot{n}_3 = 37.4\ \frac{\text{mol } CH_4}{s}}$$

Inert (I) balance: $I - O + \cancelto{0}{G} - \cancelto{0}{C} = 0$

$$I = O$$

$$(0.15)(100) = \dot{n}_5 \Rightarrow \boxed{\dot{n}_5 = \frac{15 \text{ mol I}}{s}}$$

Total molar flow rate of the outlet stream $= \dot{n}_1 + \dot{n}_2 + \dot{n}_3 + \dot{n}_4 + \dot{n}_5$

$= 42.4 + 40 + 37.4 + 5.2 + 15 = 140\ \frac{\text{mol}}{s} = \dot{n}_T$

Now, let us determine the molar composition:

$y_{C_2H_6} = \frac{\dot{n}_1}{\dot{n}_T} = 0.303$; $y_{C_2H_4} = \frac{\dot{n}_2}{\dot{n}_T} = 0.286$; $y_{H_2} = \frac{\dot{n}_3}{\dot{n}_T} = 0.267$

$y_{CH_4} = \frac{\dot{n}_4}{\dot{n}_T} = 0.037$; $y_I = \frac{\dot{n}_5}{\dot{n}_T} = 0.107$

Using atomic species method:

C balance : I = 0

$$\frac{(0.85)(100)\text{ mol } C_2H_6}{s}\bigg|\frac{\text{mol C}}{1\text{ mol } C_2H_6} = \frac{\dot{n}_1\text{ mol } C_2H_6}{s}\bigg|\frac{2\text{ mol C}}{1\text{ mol } C_2H_6} + \frac{\dot{n}_2\text{ mol } C_2H_4}{s}\bigg|\frac{2\text{ C}}{1\text{mol } C_2H_4}$$

$$+ \frac{\dot{n}_4\text{mol } CH_4}{s}\bigg|\frac{1\text{ mol C}}{1\text{ mol } CH_4}$$

$$\Rightarrow (2)(0.85)(100) = (2)\dot{n}_1 + 2\dot{n}_2 + \dot{n}_4$$

$$(85)(2) = (2)(42.4) + (2)(40) + \dot{n}_4$$

$$\Rightarrow \boxed{\dot{n}_4 = 5.2\ \frac{\text{mol } CH_4}{s}}$$

H balance : I = 0

$$\frac{(0.85)(100)\text{ mol} C_2H_6}{s}\bigg|\frac{6\text{ mol H}}{1\text{mol} C_2H_6} = \frac{\dot{n}_1\text{ mol } C_2H_6}{s}\bigg|\frac{6\text{ mol H}}{1\text{ mol } C_2H_6} + \frac{\dot{n}_2\text{ mol } C_2H_4}{s}\bigg|\frac{4\text{ mol H}}{1\text{mol} C_2H_4}$$

$$+ \frac{\dot{n}_3\text{ mol } H_2}{s}\bigg|\frac{2\text{ mol H}}{1\text{mol } H_2} + \frac{\dot{n}_4\text{mol } CH_4}{s}\bigg|\frac{4\text{ mol H}}{1\text{mol } CH_4}$$

$$(6)(0.85)(100) =$$

$$(6)(\dot{n}_1) + (4)(\dot{n}_2) + (2)(\dot{n}_3) + (4)(\dot{n}_4)$$

$$= (6)(42.4) + (4)(40) + 2\dot{n}_3 + (4)(5.2)$$

$$\Rightarrow \boxed{\dot{n}_3 = 37.4\ \frac{\text{mol } H_2}{s}}$$

Inert balance: $I = 0 \Rightarrow (0.15)(100) = \dot{n}_5 \Rightarrow \boxed{\dot{n}_5 = 15\ \frac{\text{mol I}}{s}}$

Then find the composition which will be same.

Using extent of reaction method:

Two reactions:

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad \xi_1$$
$$C_2H_6 + H_2 \longrightarrow 2CH_4 \qquad \xi_2$$

Now write the extent of reaction equations:

C_2H_6 : $\dot{n}_1 = (0.85)(100) - (1)(\xi_1) - (1)(\xi_2)$

$\dot{n}_1 = 85 - \xi_1 - \xi_2 = 42.4 \quad \text{---- (1)}$

C_2H_4 : $\dot{n}_2 = 0 + (1)(\xi_1) = 40 \Rightarrow \boxed{\xi_1 = 40 \frac{mol}{s}}$

from eq. (1) : $\xi_2 = 85 - \xi_1 - 42.4 = \boxed{2.6 \frac{mol}{s} = \xi_2}$

H_2 : $\dot{n}_3 = 0 + (1)(\xi_1) - (1)(\xi_2)$

$= 40 - 2.6 = \boxed{37.4 \frac{mol\ H_2}{s}}$

CH_4 : $\dot{n}_4 = 0 + (2)\xi_2 = (2)(2.6)$

$\Rightarrow \boxed{\dot{n}_4 = 5.2 \frac{mol\ CH_4}{s}}$

Inert : $\dot{n}_5 = (0.15)(100) + 0 \Rightarrow \boxed{\dot{n}_5 = 15 \frac{mol\ I}{s}}$

Note that the simplest method is the extent of reaction. Thus for multiple reaction processes use extent of rxn method.

$$S_{C_2H_4,CH_4} = \frac{\dot{n}_2}{\dot{n}_4} = \frac{40}{5.2} = 7.7$$

** Chemical Equilibrium Calculations:

→ what is the difference between steady state and equilibrium?

steady state: no change with time. : $\frac{d}{dt} = 0$

Equilibrium : no change in space and time :

$$\frac{\partial}{\partial t} = 0, \quad \frac{\partial}{\partial x} = 0, \quad \frac{\partial}{\partial y} = 0, \quad \frac{\partial}{\partial z} = 0$$

Equilibrium is special case of steady state.

* Irreversible reaction: the equilibrium composition for irreversible reactions is the composition at complete consumption of limiting reactant (reaction goes to completion)

$A \longrightarrow B$

* Reversible reactions: the equilibrium composition for reversible reactions is the composition at which the reaction rate of the forward and reverse reactions are equal.

$A \rightleftharpoons B$

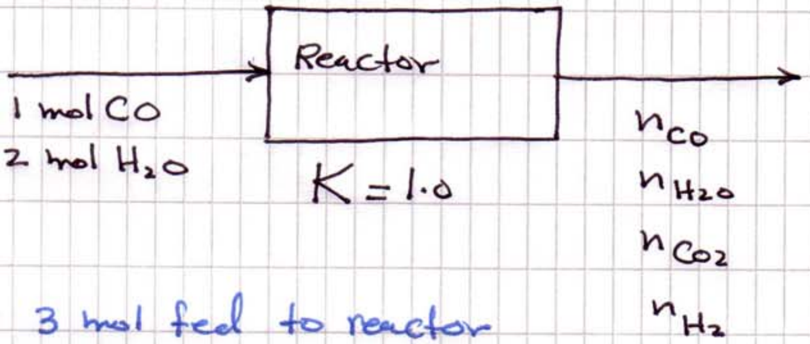
How to find the equilibrium composition of reversible reaction mixtures?

using extent of reaction method. Here ξ_e : the extent of reversible reaction at equilibrium is defined.

Ex: suppose that the following gas-phase reversible reaction occurs in a reactor:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

The feed to reactor contains 1 mol of CO, 2 mol of H_2O, and no CO_2 or H_2. The reaction comes to equilibrium at temperature, T = 1105 K with reaction equilibrium constant; K = 1. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.



Basis: 3 mol feed to reactor

$$DOF = 4 - 4 - \underbrace{1}_{\text{other eq.: equilibrium constant eq.}} + \overset{\text{one rxn}}{1}$$

$= 0$ ✓ ok

For gas-phase reactions: $K = \dfrac{(P_{CO_2})^1 (P_{H_2})^1}{(P_{CO})^1 (P_{H_2O})^1}$

P_i: partial pressure of species i:

$$y_i = \frac{P_i}{P}$$

P: total pressure.

$$P_i = y_i P$$

$$\Rightarrow K = 1.0 = \frac{(y_{CO_2} P)^1 (y_{H_2} P)^1}{(y_{CO} P)^1 (y_{H_2O} P)^1} = \frac{(y_{CO_2})(y_{H_2})}{(y_{CO})(y_{H_2O})}$$

write extent of reaction equations!

$$n_{CO} = 1 - (1)\,\xi_e$$
$$n_{H_2O} = 2 - (1)(\xi_e)$$
$$n_{CO_2} = 0 + (1)(\xi_e)$$
$$n_{H_2} = 0 + (1)(\xi_e$$

$$n_{total} = 3 \text{ mol}$$

Note the $n_{in,tot} = 3 = n_{out,total} = 3$ why?

because : $\sum \nu_i = (-1) + (-1) + (+1) + (+1) = 0$

Now the outlet composition will be:

$$y_{CO} = \frac{n_{CO}}{n_{total}} = \frac{1 - \xi_e}{3} \;;\; y_{H_2O} = \frac{2 - \xi_e}{3}$$

$$y_{CO_2} = \frac{\xi_e}{3} \;;\; y_{H_2} = \frac{\xi_e}{3}$$

$$\Rightarrow 1 = \frac{(\xi_e/3)(\xi_e/3)}{[(1-\xi_e)/3][(2-\xi_2)/3]} \Rightarrow \frac{\xi_e^2}{(1-\xi_e)(2-\xi_e)} = 1$$

$$\text{and } (1-\xi_e)(2-\xi_e) = \xi_e^2 \Rightarrow 2 - 3\xi_e + \cancel{\xi_e^2} = \cancel{\xi_e^2}$$

$$\Rightarrow \boxed{\xi_e = \frac{2}{3}}$$

$$y_{CO} = \frac{1-\xi_e}{3} = 0.111 \; ; \; y_{H_2O} = \frac{2-\xi_e}{3} = 0.444$$

$$y_{H_2} = \frac{\xi_e}{3} = 0.222 \; ; \; y_{CO_2} = \frac{\xi_e}{3} = 0.222$$

In this problem LR is CO :

$$f_{CO} = \frac{n_{in,CO} - n_{out,CO}}{n_{in,CO}} = \frac{1 - n_{out,CO}}{1}$$

$$n_{out,CO} = 1 - (1)\xi_e = 1 - \frac{2}{3} = \frac{1}{3}$$

$$\therefore \; f_{CO} = \frac{1-\frac{1}{3}}{1} = \frac{2}{3} = 0.667$$

** Combustion reactions :

→ Combustion: burning or oxidation of fuel to produce (release) energy)

→ Fuel typically Contains C, H, and S (eg. methane, propane, ...etc)

→ Two types of combustion reactions :

Ⓐ Complete Combustion : No production of CO
- all C's go to CO_2
- all H's go to H_2O
- all S's go to SO_2

Ⓑ Incomplete (Partial) Combustion : C's go to CO_2 and CO

Ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ (Complete combustion)

Ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ (Incomplete combustion)
$2C_3H_8 + 7O_2 \longrightarrow 6CO + 8H_2O$

→ product gas from combustion is called "stack gas" or "flue gas"

→ The composition of stack (flue) gas is denoted based on :
- Dry basis : Composition excludes $H_2O_{(v)}$
- Wet basis : Composition includes $H_2O_{(v)}$

How to Convert from :

(a) wet basis → Dry basis

Take a basis of 100 mol of wet gas.

(b) Dry basis → wet basis

Take a basis of 100 mol of dry gas.

Ex : A stack gas Contains 60 mol% N_2 , 15 mol% CO_2, 10 mol% O_2 and the balance H_2O. Calculate the molar Composition based on dry basis :

Basis: 100 mol of wet gas ⇒

$$\begin{array}{l} 60 \text{ mol } N_2 \\ 15 \text{ mol } CO_2 \\ \underline{10 \text{ mol } O_2} \\ 85 \text{ mol dry gas} \end{array}$$

$$\frac{60}{85} = 0.706 \frac{\text{mol } N_2}{\text{mol dry gas}} \quad ; \quad \frac{15}{85} = 0.176 \frac{\text{mol } CO_2}{\text{mol dry gas}}$$

$$\frac{10}{85} = 0.118 \frac{\text{mol } O_2}{\text{mol dry gas}} \quad ; \quad \text{Check } \sum y_i \overset{?}{=} 1$$

Ex: an Orsat analysis (technique for stack gas analysis) yields the following dry basis Composition : 65 mol% N_2 , 14 mol% CO_2, 11%. CO , 10 mol% O_2 . In addition, a humidity measurement shows the the mole fraction of water vapor in the stack gas is 0.07 . Calculate the stack gas Composition on a wet basis.

Basis: 100 moles of dry gas

$$y_{H_2O} = 0.07 \frac{\text{mol } H_2O}{\text{mol wet gas}} \Rightarrow 1 - 0.07 = 0.93 \frac{\text{mol dry gas}}{\text{mol wet gas}}$$

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

Thus 100 moles of dry gas contains:

$$\rightarrow \left(0.0753 \frac{\text{mol } H_2O}{\text{mol dry gas}}\right)\left(100 \text{ mol dry gas}\right) = 7.53 \text{ mol } H_2O$$

$\rightarrow (0.65)(100) = 65$ mol N_2

$(0.14)(100) = 14$ mol CO_2

$(0.11)(100) = 11$ mol CO

$(0.10)(100) = 10$ mol O_2

$$\sum = 107.5 \text{ mol wet gas}$$

Now

$$y_{H_2O} = \frac{7.53}{107.5} = 0.07$$

$$y_{N_2} = \frac{65}{107.5} = 0.605$$

$$\sum y_i \overset{?}{=} 1.0$$

$$y_{CO_2} = \frac{14}{107.5} = 0.130$$

$$y_{CO} = \frac{11}{107.5} = 0.102$$

$$y_{O_2} = \frac{10}{107.5} = 0.093$$

* The source of O_2 for Combustion is usually air (21 mol% O_2, 79 mol% N_2) :

$$\frac{3.76 \text{ mol } N_2}{1 \text{ mol } O_2} \; ; \; \frac{4.76 \text{ mol air}}{1 \text{ mol } O_2} \; ; \; \overline{Mwt}_{air} \cong 29 \frac{\text{g air}}{\text{gmol air}}$$

* The following definitions are helpful in Combustion reactions Calculations :

→ Theoritical O_2 : moles of O_2 required by stoichiometry for Complete combustion of all fuel feed to the reactor.

→ Theoritical air : quantity of air that contains theoritical O_2

→ Excess air : quantity by which air fed to the reactor exceeds theoritical air :

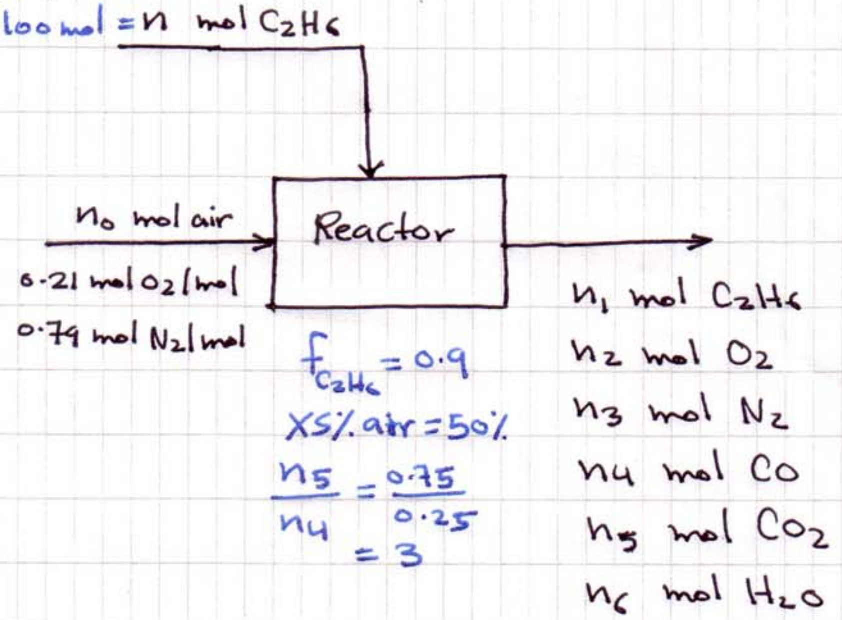
$$= (\text{mole air})_{fed} - (\text{moles air})_{theoritical}$$

→ percent excess air $= \dfrac{(\text{mole air})_{fed} - (\text{mole air})_{theoritical}}{(\text{mole air})_{theoritical}} * 100\%$

This can be rearranged to have also :

$$(\text{mole air})_{fed} = (\text{mole air})_{theoritical} \left[1 + \frac{\text{Percent excess air}}{100} \right]$$

Ex: Ethane is burned with 50% excess air. The percentage Conversion of ethane is 90%. 25% of the ethane burned reacts to form CO and the balance will react to form CO_2. Calculate the molar Composition of stack gas on a dry basis and molar ratio of water to dry stack gas?



$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_6 + \frac{5}{2}O_2 \longrightarrow 2CO + 3H_2O$$

Basis : 100 mol of C_2H_6 feed to reactor ⇒ n = 100 mol

$$DOF = 7 - 4 - \underbrace{3}$$

4 → N, C, O, H

3 → 3 other eqns.:

① $f_{C_2H_6}$

② XS% air.

③ $\frac{n_5}{n_4} = 3$

= 0 ✓ ok

→ 50% excess air: $n_0 = n_{theor,air}\left[1 + \frac{50}{100}\right]$

$$= 1.5\, n_{theor,air}$$

$$n_{theor,O_2} = \frac{100 \text{ mol } C_2H_6}{} \left| \frac{\frac{7}{2} \text{ mol } O_2}{1 \text{ mol } C_2H_6} \right. = 350 \text{ mol } O_2$$

$$n_{theor,air} = \frac{350 \text{ mol } O_2}{} \left| \frac{1 \text{ mol air}}{0.21 \text{ mol } O_2} \right. = 1666.67 \text{ mol air}$$

$$n_0 = (1.5)(1666.67) = \boxed{2500 \text{ mol air fed to reactor}}$$

→ $f_{C_2H_6} = 0.9 = \frac{100 - n_1}{100} \Rightarrow \boxed{n_1 = 10 \text{ mol } C_2H_6}$

→ <u>C MB</u>: In = out

$$\frac{100 \text{ mol } C_2H_6}{} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right. = \frac{n_1 \text{ mol } C_2H_6}{} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right. + \frac{n_4 \text{ mol CO}}{} \left| \frac{1 \text{ mol C}}{1 \text{ mol CO}} \right.$$

$$+ \frac{n_5 \text{ mol } CO_2}{} \left| \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \right.$$

$$\Rightarrow 200 = 2n_1 + n_4 + n_5$$

$$200 = (2)(10) + n_4 + n_5 \Rightarrow \boxed{n_4 + n_5 = 180}$$

→ other eq. from the problem statement: $\frac{n_5}{n_4} = 3$

$$\Rightarrow n_5 = 3n_4$$

$$\Rightarrow n_4 + 3n_4 = 180 \Rightarrow \boxed{n_4 = 45 \text{ mol CO}}$$

$$n_5 = 3n_4 = (3)(45) \Rightarrow \boxed{n_5 = 135\ \text{mol CO}_2}$$

H MB : In = out

$$\frac{100\ \text{mol C}_2\text{H}_6}{}\bigg|\frac{6\ \text{mol H}}{1\ \text{mol C}_2\text{H}_6} = \frac{10\ \text{mol C}_2\text{H}_6}{}\bigg|\frac{6\ \text{mol H}}{1\ \text{mol C}_2\text{H}_6} + \frac{n_6\ \text{mol H}_2\text{O}}{}\bigg|\frac{2\ \text{mol H}}{1\ \text{mol H}_2\text{O}}$$

$$600 = 60 + 2n_6 \Rightarrow \boxed{n_6 = 270\ \text{mol H}_2\text{O}}$$

O MB : In = out

$$\frac{2500\ \text{mol air}}{}\bigg|\frac{0.21\ \text{mol O}_2}{1\ \text{mol air}}\bigg|\frac{2\ \text{mol O}}{1\ \text{mol O}_2} = \frac{n_2\ \text{mol O}_2}{}\bigg|\frac{2\ \text{mol O}}{1\ \text{mol O}_2} + \frac{n_4\ \text{mol CO}}{}\bigg|\frac{1\ \text{mol}}{1\ \text{mol CO}}$$

$$+ \frac{n_5\ \text{mol CO}_2}{}\bigg|\frac{2\ \text{mol O}}{1\ \text{mol CO}_2} + \frac{n_6\ \text{mol H}_2\text{O}}{}\bigg|\frac{1\ \text{mol O}}{1\ \text{mol H}_2\text{O}}$$

$$1050 = 2n_2 + 45 + (2)(135) + 270$$

$$\Rightarrow \boxed{n_2 = 232.5\ \text{mol H}_2\text{O}}$$

$$\text{N}_2\ \text{MB} : (2500)(0.79) = n_3 \Rightarrow \boxed{n_3 = 1975\ \text{mol N}_2}$$

To calculate the molar composition of the stack dry gas:

$$n_{\text{total, dry gas}} = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 = 2397.5\ \text{mol dry gas}$$

$$y_1 = \frac{n_1}{n_{\text{total, dry gas}}} = 0.00417\ \text{mol C}_2\text{H}_6/\text{mol dry gas}$$

$$y_2 = \frac{n_2}{n_{\text{total, dry gas}}} = 0.0970\ \text{mol O}_2/\text{mol dry gas}$$

$$y_3 = \frac{n_3}{n_{total, dry\ gas}} = 0.8238 \text{ mol } N_2 / \text{mol dry gas}$$

$$y_4 = \frac{n_4}{n_{total, dry\ gas}} = 0.0188 \text{ mol CO / mol dry gas}$$

$$y_5 = \frac{n_5}{n_{total, dpy\ gas}} = 0.0563 \text{ mol } CO_2 / \text{mol dry gas}$$

ratio of moles of H_2O to moles of dry gas $= \frac{n_6}{n_{total, dry\ gas}}$

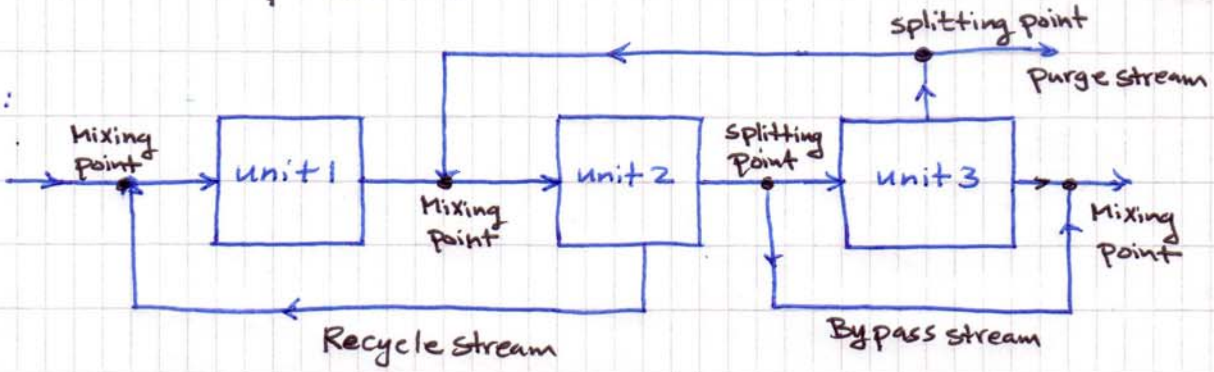
$$= \frac{270}{2397.5} = 0.113$$

* **Remark** : Since the source of O_2 is air which contains N_2 there is a possibility of formation of Nitrogen oxides like : NO_x , N_2O_4 .

This is neglected in the previous example.

** Multiple – unit processes :

Ex :



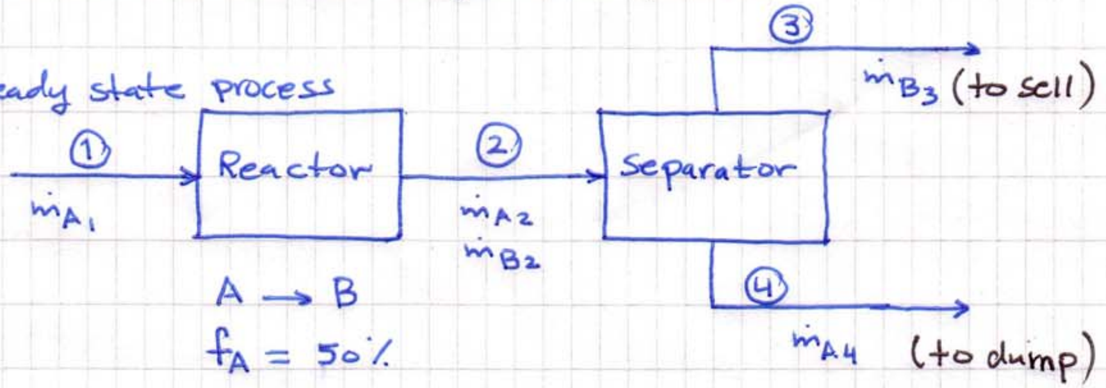
How do you analyze multiple – unit process ?

– overall system : large control volume around the whole process enclosing all units, recycles and bypass streams.

– subsystem : individual units or combination of adjacent units, stream mixing points, and stream splitting points.

→ Do degree-of-freedom analysis for the selected system as we did before with single-unit process.

Ex : steady state process



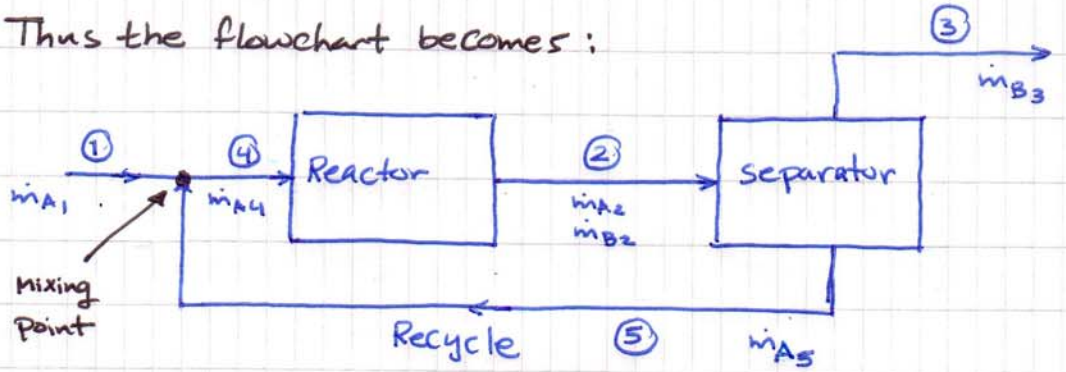
$A \rightarrow B$

$f_A = 50\%$

How would you redraw the flow chart above to be more cost efficient and environmentally conscious?

Recycle stream ④ to be mixed with stream ①

Thus the flowchart becomes :



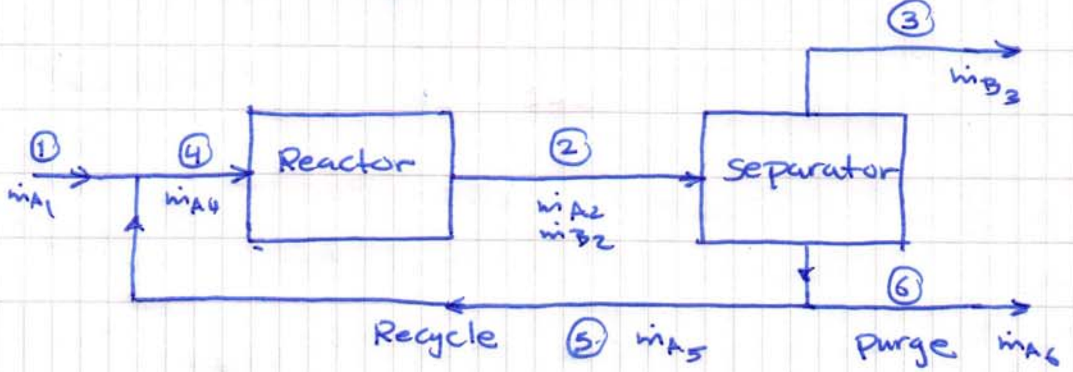
* Recycle : unused material being cycled back to the feed stream

* Recycling is not free (require pumping , pipes , ... etc).

→ The previous process becomes more economic and environmentally conscious using recycle . But what is wrong with the flowchart from physical point of view?

Since the process is at steady state situation and the Conversion of A is not 100% , there will be continuous accumulation of species A within the units and streams of the process, which may lead to dangerous situations (explosion , backflow ... etc .

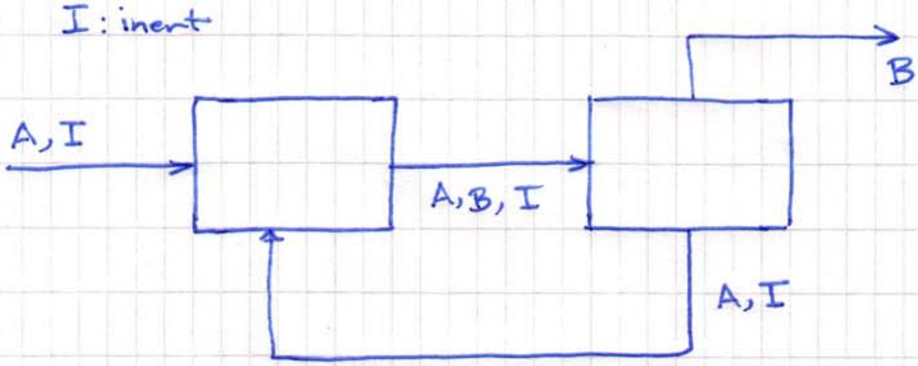
→ The solution for such situation is doing burging stream ; The optimum process situation (that take economic , environmental , and physical factors into account) is



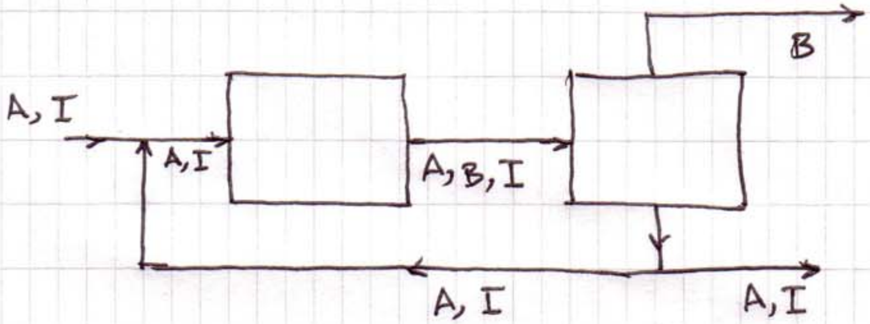
- purge : a stream bled off from the process to remove an accumulation of unwanted materials (such as inerts, or some of reactants) that might otherwise build up within the process units and streams.

Ex: what is wrong with the flowchart below?

I : inert



The wrong is build up of inert and species A within the system. purge is required to solve this problem

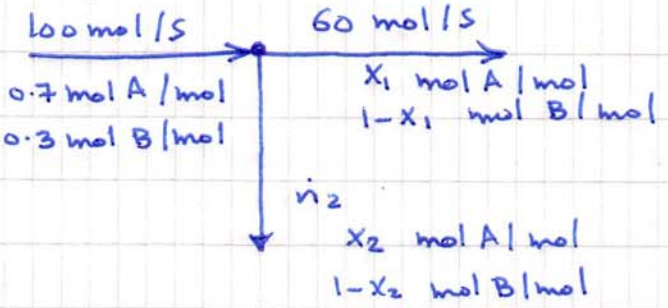


* The recycle will lead to generation of mixing point.

* The purge will lead to generation of splitting point.

* Splitting point : How many indept. MB equations can we write on the splitting point?

Ex



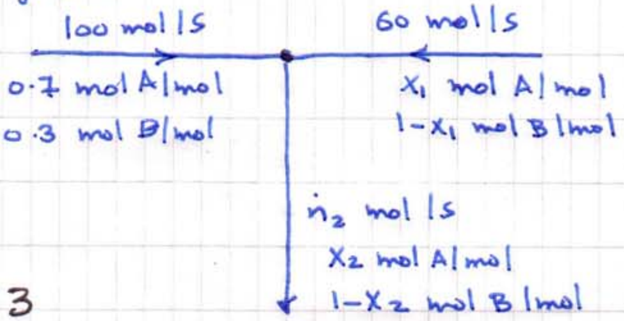
Just one indept. MB equation can be written on the splitting point : total (mass or mole) balance, since the composition of the outlet streams must be the same as the inlet stream

so $100 = 60 + \dot{n}_2 \Rightarrow \dot{n}_2 = 40$ mol/s

$x_1 = x_2 = 0.7$

* Mixing point : How many indept. MB equations can we write on mixing point.

Ex



\# of unknowns = 3

$x_1, x_2, \dot{n}_2$

of course, for mixing the outlet stream do not have the same composition as the inlet streams.

For mixing point: # of indept MB eqns. = # of indept. species

For this example : # of eqns. = 2 (A, B species)

DOF = 3 − 2 = 1 ⇒ one unknown must be specified for this problem to be solvable.

* When chemical reactions are involved in multiple-unit processes, another kind of conversion is defined:

- Overall Conversion: Conversion achived by the entire (overall) process

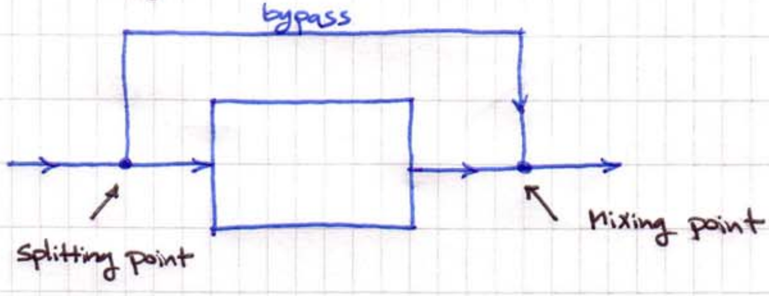
$$\equiv \frac{\text{moles reactant feed} - \text{moles reactant out from process}}{\text{moles reactant feed}}$$

- Single-Pass Conversion: Conversion achieved by one specific process unit (reactor):

$$\equiv \left[(\text{moles reactant fed to reactor}) - (\text{moles reactant out of reactant}) \right] / \text{moles reactant fed to reactor}$$

* Bypass: a stream that skips one or more process unit to go directly further downstream:

Ex:



→ Bypass goes from splitting to mixing point.

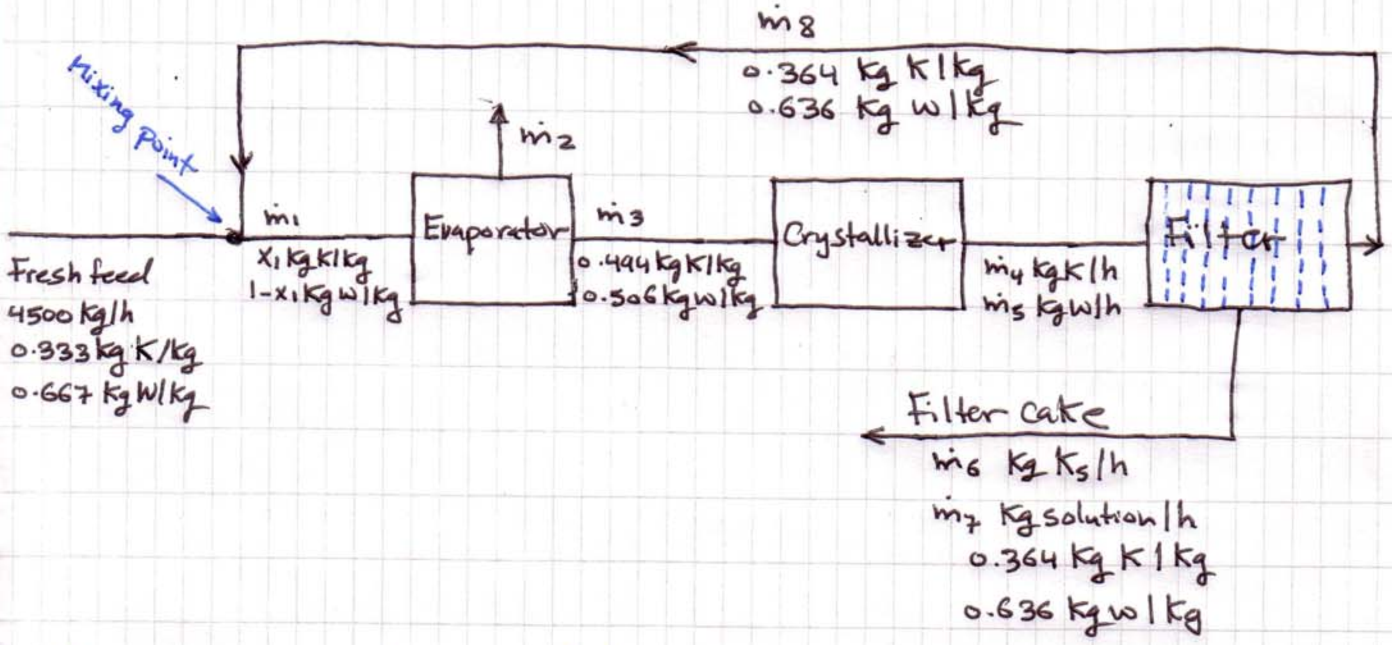
Ex : Crystalline potassium Chromate (K_2CrO_4) is recovered from an aqueous solution according to a steady state process. Forty-five hundred Kilograms per hour of a solution that is one-third K_2CrO_4 by mass is joined by a recycle filtrate stream containing 36.4% by mass K_2CrO_4 and the combined stream is fed to an evaporator. The concentrated stream leaving the evaporator contains 49.4% K_2CrO_4; this stream is fed into a crystallizer in which it is cooled (causing crystals of K_2CrO_4 to come out of solution) and then filtered. The filter cake consists of K_2CrO_4 crystals and a solution that contains 36.4% K_2CrO_4; the crystals account for 95% of the total mass of the filter cake.

(1) Draw and completely label the flowchart of this process

(2) Calculate the rate of water evaporation, the rate of production of crystalline K_2CrO_4, the feed rates to evaporator and crystallizer, and the recycle ratio. (mass of recycle / mass of fresh feed)

(3) suppose that the filtrate were discarded instead of being recycled Calculate the production rate of crystals. what are the benifits and costs of the recycling?

Water ≡ w ; K_2CrO_4 in solution ≡ K ; Crystals of K_2CrO_4 ≡ K_s



Basis : 4500 kg fresh feed / h

Global view of the process :

- → K and w are involved into the mixing point ⇒ 2 eqns.
- → K and w are involved into evaporator ⇒ 2 eqns.
- → K and w are involved into crystallizer ⇒ 2 eqns.
- → K and w are involved into filter ⇒ 2 eqns.

$\therefore$ 8 MB eqns.

→ other eqns. : yes one another eq. : $\dot{m}_6 = 0.95(\dot{m}_6 + \dot{m}_7)$

$\therefore$ # of indept. eqns. = 9

# of unknowns on the flowchart = 9

⇒ The problem can be solved. How to start solving it?

Can we start with evaporator?

Let us calculate DoF for evaporator:

$$\mathrm{DoF} = \underset{\substack{\downarrow\\ \dot{m}_1\\ \dot{m}_3\\ \dot{m}_2\\ x_1}}{4} - \underset{\substack{\downarrow\\ K\\ W}}{2} - \underset{\substack{\downarrow\\ \text{no other equs}}}{0} = 2$$

No we can not start with evaporator

Can we start with mixing point?

$$\mathrm{DoF} = 3 - 2 = 1$$

No

Can we start with Crystallizer?

$$\mathrm{DoF} = 3 - 2 = 1$$

No

Can we start with Filter?

$$\mathrm{DoF} = \underset{\substack{\downarrow\\ \dot{m}_4\\ \dot{m}_5\\ \dot{m}_6\\ \dot{m}_7\\ \dot{m}_8}}{5} - \underset{\substack{\downarrow\\ K\\ W}}{2} - 1 = 2$$

No

$$1 \rightarrow \dot{m}_6 = 0.95(\dot{m}_6 + \dot{m}_7)$$

Can we start with mixing point and evaporator (adjacent units)?

$$\mathrm{DoF} = \underset{\substack{\downarrow\\ \dot{m}_2\\ \dot{m}_3\\ \dot{m}_8}}{3} - \underset{\substack{\downarrow\\ K\\ W}}{2} = 1$$

No

Can we start with the overall system?

$$\mathrm{DoF} = \underset{\substack{\downarrow\\ \dot{m}_2\\ \dot{m}_6\\ \dot{m}_7}}{3} - \underset{\substack{\downarrow\\ K\\ W}}{2} - 1 = 0$$

Yes

$$1 \rightarrow \dot{m}_6 = 0.95(\dot{m}_6 + \dot{m}_7)$$

Thus let us start with the over all system:

K MB : In = out

$$(0.333)(4500) = \dot{m}_6 + (0.364)(\dot{m}_7) \quad --- \quad ①$$

other eq. : $\dot{m}_6 = 0.95(\dot{m}_6 + \dot{m}_7) \quad ----- \quad ②$

solve eqns. ① and ② to obtain:

$$\boxed{\dot{m}_6 = 1470 \text{ kg K}_s/\text{h}}$$

$$\boxed{\dot{m}_7 = 77.368 \text{ kg solution}/\text{h}}$$

Total MB : $4500 = \dot{m}_2 + \dot{m}_6 + \dot{m}_7$

$$\dot{m}_2 = 4500 - 1470 - 77.368$$

$$\boxed{\dot{m}_2 = 2952.6 \text{ kg w evaporated}/\text{h}}$$

→ Now Can we start with crystallizer and filter to find more unknowns ?

$$\text{DOF} = \underset{\substack{\downarrow \\ \dot{m}_3 \\ \dot{m}_8}}{2} - 2 = 0 \qquad \text{Yes}$$

Total MB $\dot{m}_3 = \dot{m}_6 + \dot{m}_7 + \dot{m}_8$

$$\dot{m}_3 = 1470 + 77.368 + \dot{m}_8$$

$$\dot{m}_3 - \dot{m}_8 = 1547.368 \quad ---- \quad ①$$

w MB : $0.506\,\dot{m}_3 = 0.636\,\dot{m}_7 + 0.636\,\dot{m}_8$

$$0.506\,\dot{m}_3 - 0.636\,\dot{m}_8 = (0.638)(77.368) \quad --- \quad ②$$

solve eqns. ① and ② to obtain:

$\boxed{\dot{m}_3 = 7106.2 \text{ kg solution}/\text{h}}$ $\boxed{\dot{m}_8 = 5558.8 \text{ kg solution recycled}/\text{h}}$

Now apply MB's on Mixing Point:

$$DoF = \underset{\substack{\downarrow \\ \dot{m}_1 \\ x_1}}{2} - 2 = 0 \quad \text{yes}$$

Total MB: $4500 + \dot{m}_8 = \dot{m}_1$

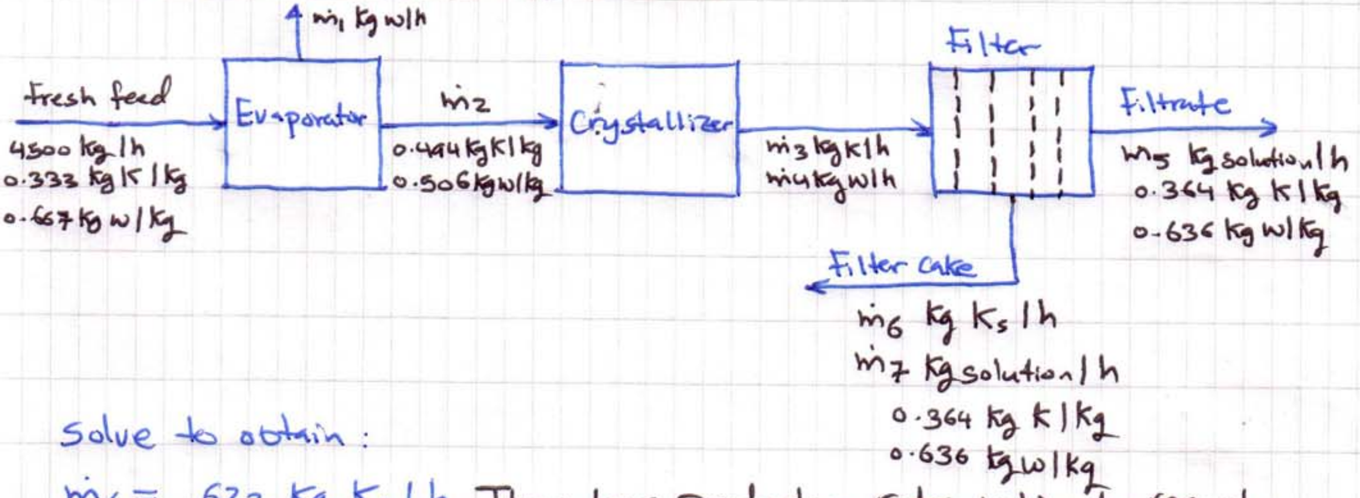
$4500 + 5558.8 = \dot{m}_1$

$\boxed{\dot{m}_1 = 10058.8 \text{ kg feed to evaporator / h}}$

you can apply K MB to find x_1 but we are not asked about its value $\Rightarrow$ Do Not waste time to find it.

The recycle to fresh feed ratio $= \dfrac{\dot{m}_8}{4500} = \dfrac{5558.8}{4500} = 1.24 \dfrac{\text{kg recycle}}{\text{kg fresh feed}}$

(3) Redraw the flowchart without recycle and completely label it then solve for unknowns as we did.



Solve to obtain:

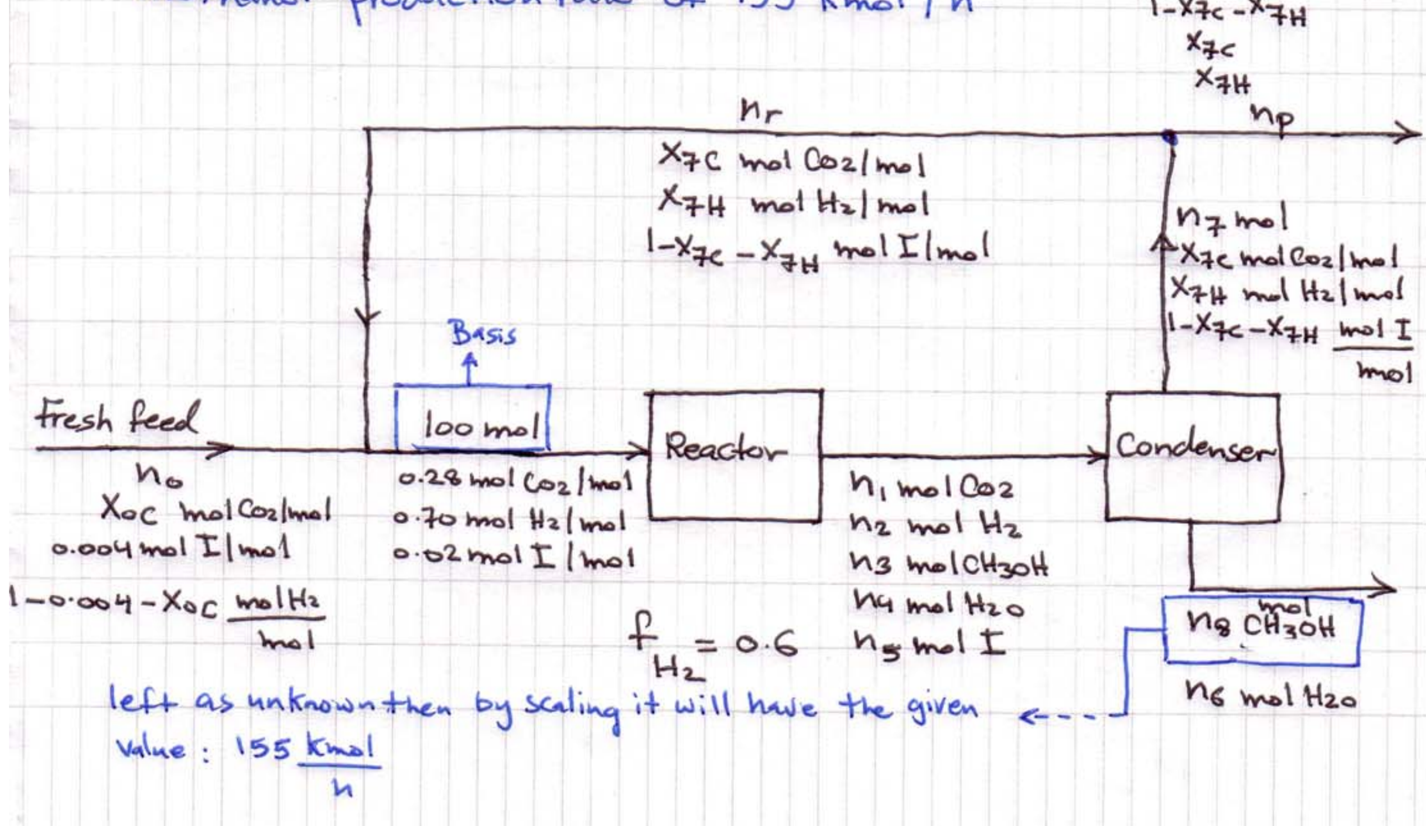
$\dot{m}_6 = 622$ kg K_s/h Thus less production rate without recycle and thus less profit. But remember that when there is recycle you have to pay for pumping, pipes, ...etc to have such recycle

Ex: Methanol (CH_3OH) is produced in the reaction of carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

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

The feed to the reactor (not the fresh feed to the process) contains 28.0 mol % CO_2, 70.0 mol % H_2, and 2.00 mol % inerts. The single-pass conversion of hydrogen is 60%. Calculate the molar flow rate and molar compositions of the fresh feed, the total feed to the reactor, the recycle stream, and the purge stream for methanol production rate of 155 Kmol / h



Basis : In general, the feed to reactor is a suitable and a convenient stream to use as a basis of calculation, even it is unknown. In such case take a basis of calculation and make some known molar flow rate as unknown to maintain DOF. Then and by scaling the calculated molar flow rate will be adjusted to have its orginal value.

In this example:

Basis : 100 mol fed to reactor

the production of methanol (155 kmol/h.) is made as unknown (n_8) then after calculating n_8 scaling will be performed to have production rate of 155 kmol methanol/h

Global view of the problem:

\# of unknowns on the flowchart = 14 : $n_0, x_{0C}, n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_p, n_r, x_{7C}, x_{7H}$.

\# of equations :

- Mixing Point : 3 : I, H_2, CO_2
- Reactor : 5 : I, H_2, CO_2, H_2O, CH_3OH
- Condenser : 5 : I, H_2, CO_2, H_2O, CH_3OH
- Splitting Point : 1 : total Mole balance
- other eqns. : $f_{H_2} = 0.6$

$$DOF = \underset{\downarrow \atop \text{unknowns}}{14} - \underset{\downarrow \atop \text{indept MB eqns}}{14} - \underset{\text{other eq.}}{1} + \underset{\text{\# of reactions}}{1} = 0$$ ✓ problem can be solved.

From where should we start to solve the problem?

Let us start with reactor:

$$DOF = \underset{\substack{\downarrow\\ n_1\\ n_2\\ n_3\\ n_4\\ n_5}}{5} - \underset{\substack{\downarrow\\ CO_2\\ H_2\\ CH_3OH\\ H_2O\\ I}}{5} - \underset{\substack{\downarrow\\ f_{H_2}=0.6}}{1} + \underset{\text{one rxn}}{1} = 0 \checkmark$$

Yes we can start with reactor.

Conversion eq.: $f_{H_2} = 0.6 = \frac{(0.7)(100) - n_2}{(0.7)(100)} \Rightarrow \boxed{n_2 = 28 \text{ mol } H_2}$

Extent of reaction eqns.:

H_2 : $n_2 = (0.7)(100) - (3)(\xi)$

$28 = 70 - 3\xi \Rightarrow \boxed{\xi = 14 \text{ mol}}$

CO_2 : $n_1 = (0.28)(100) - (1)(\xi) \Rightarrow \boxed{n_1 = 14 \text{ mol } CO_2}$

CH_3OH : $n_3 = 0 + (1)(\xi) \Rightarrow \boxed{n_3 = 14 \text{ mol } CH_3OH}$

H_2O : $n_4 = 0 + (1)(\xi) \Rightarrow \boxed{n_4 = 14 \text{ mol } H_2O}$

I : $n_5 = (0.02)(100) \Rightarrow \boxed{n_5 = 2 \text{ mol } I}$

Now can we apply MB eqns. on Condenser?

$$DOF = \underset{\substack{\downarrow\\ n_6, n_7, n_8\\ x_{7C}, x_{7H}}}{5} - 5 - 0 + 0 = 0 \quad \text{Yes} \checkmark$$

H_2O MB : $n_4 = n_6 \Rightarrow \boxed{n_6 = 14 \text{ mol } H_2O}$

CH_3OH MB : $n_3 = n_8 \Rightarrow \boxed{n_8 = 14 \text{ mol } CH_3OH}$

Total MB : $n_1 + n_2 + n_3 + n_4 + n_5 = n_6 + n_7 + n_8$

$\Rightarrow \boxed{n_7 = 44 \text{ mol}}$

CO_2 MB : $n_1 = X_{7C}\, n_7 \Rightarrow \boxed{X_{7C} = \frac{n_1}{n_7} = \frac{14}{44} = 0.3182 \frac{\text{mol}\,CO_2}{\text{mo}}}$

H_2 MB : $n_2 = X_{7H}\, n_7 \Rightarrow \boxed{X_{7H} = \frac{n_2}{n_7} = \frac{28}{44} = 0.6364 \frac{\text{mol}\,H_2}{\text{mol}}}$

Can we use Mixing point now?

$DoF = 3 - 3 - 0 + 0 = 0$ yes

$\downarrow$

n_o
n_r
X_{oc}

I MB : $(0.004)\, n_o + (1 - X_{7C} - X_{7H})\, n_r = (0.02)(100)$

$0.004 n_o + (1 - 0.3182 - 0.6364)\, n_r = 2$ --- ①

Total MB : $n_o + n_r = 100$ --- ②

Solve to obtain : $\boxed{n_o = 61.4 \text{ mol}}$

$\boxed{n_r = 38.4 \text{ mol}}$

CO_2 MB : $X_{oc}\, n_o + X_{7C}\, n_r = (0.28)(100)$

$(X_{oc})(61.4) + (0.3182)(38.4) = 28$

$\Rightarrow \boxed{X_{oc} = 0.256}$

The molar composition of H_2 in the fresh feed is:

$$X_{0H} = 1 - X_{0C} - 0.004 = 1 - 0.256 - 0.004 = 0.740$$

To find n_p, Now we can apply total mole balance on splitting point ($DOF = 1 - 1 = 0$):

$$n_7 = n_r + n_p$$

$$44 = 38.4 + n_p \Rightarrow \boxed{n_p = 5.4\ \text{mol}}$$

Now it is time for scaling to adjust n_8 to be $\frac{155\ \text{Kmol CH}_3\text{OH}}{h}$

given in the problem ←

$$\therefore \text{Scaling factor; } SF = \frac{155\ \text{Kmol CH}_3\text{OH/h}}{14\ \text{mol CH}_3\text{OH}} = 11.1\ \frac{\text{Kmol/h}}{\text{mol}}$$

obtained from our calculations ←

Then multiply all calculated mole amounts by this SF value

$$\dot{n}_0 = SF\ n_0 = (11.1)(61.4) = 681.54\ \frac{\text{Kmol fresh feed}}{h}$$

$\dot{n}_1 = (11.1)(n_1) =$

$\dot{n}_2 = (11.1)(n_2) =$

$\dot{n}_3 = (11.1)(n_3) =$

$\dot{n}_4 = (11.1)(n_4) =$

$\dot{n}_5 = (11.1)(n_5) =$

$\dot{n}_6 = (11.1)(n_6) =$

$\dot{n}_7 = (11.1)(n_7) =$

$\dot{n}_8 = (11.1)(n_8) = 155\ \text{Kmol/h}$

$\dot{n}_p = (11.1)(n_p) =$

$\dot{n}_r = (11.1)(n_r) =$

Remember that composition must not be scaled since it is intensive property that does not depend on quantity.