Lecture -2

Process Design & Development

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MATERIAL BALANCE

Conservation of mass

- Mass is neither created nor destroyed

{Input} - {Output} -{Accumulation-{Consumption}+ {Gen} = 0

Types of Systems

- **Systems**: Any arbitrary portion of or a whole process that is considered for analysis.

  Example:Reactor, the cell, mitochondria, human body, section of a pipe

- **Closed System**
  - ✓ Material neither enters nor leaves the system
  - ✓ Changes can take place inside the system
  - ✓ **Energy can enter and leave the system**

- **Open System**
  - ✓ Material and energy both can enter and leave through the boundaries

Steady-State/ Unsteady-State

❑ Steady-State

- ✓ Nothing is changing with time
- ✓ @ steady-state accumulation = 0

$$\textbf{100 kg/min } H_2O \longrightarrow \boxed{\textbf{500 kg } H_2O} \longrightarrow \textbf{100 kg/min } H_2O$$

Rate of addition = Rate of removal

❑ Unsteady-State (transient system)

- ✓ {Input} ≠ {Output}

Processes

- **Batch Process**
  - ✓ Feed is fed at the beginning of the process
- **Continuous Process**
  - ✓ The input and outputs flow continuously throughout the duration of proces
- **Semibatch Process**
  - ✓ Any process neither batch nor continuous

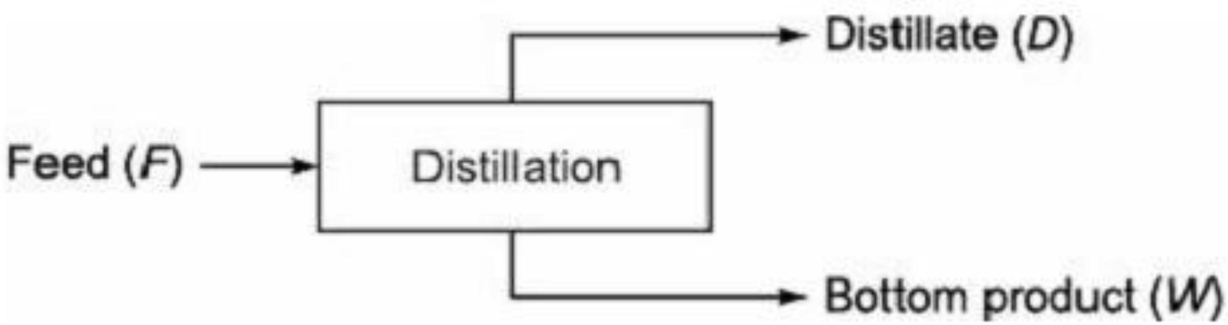
Material Balance without Chemical Reaction

The material balance problems without chemical reaction can be classified as follows:

1. Material balance at steady state operation.

2. Material balance at unsteady state operation.

Distillation



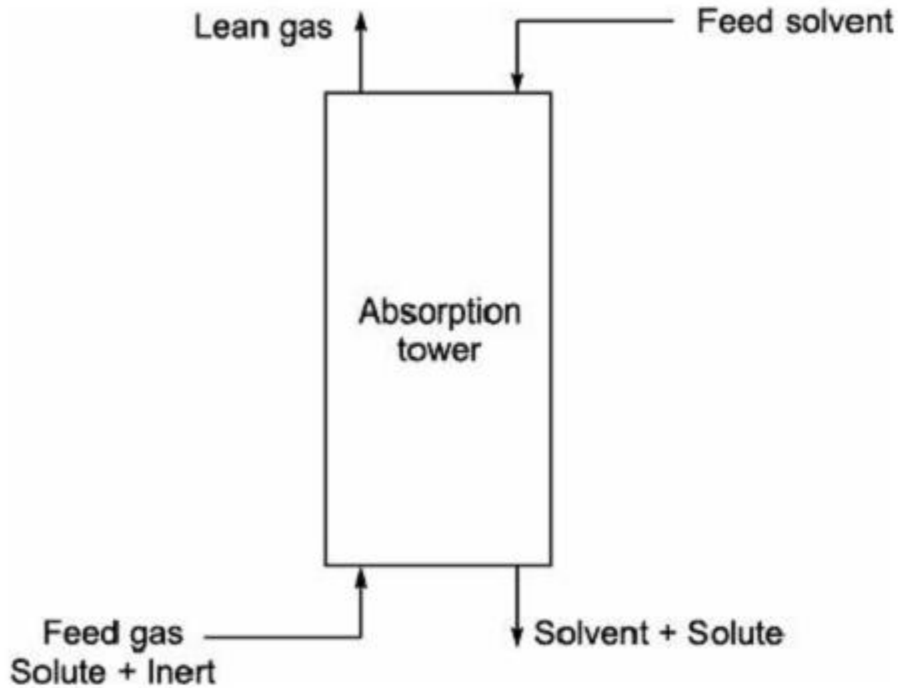
The overall material balance : $F = D + W$

Component balance in distillation column can be written as

Component A: $F\,x_F = D\,x_D + WX_W$

Component B: $F(1-x_{F)} = D\,(1-x_D) + W(1-X_W)$

Absorption column



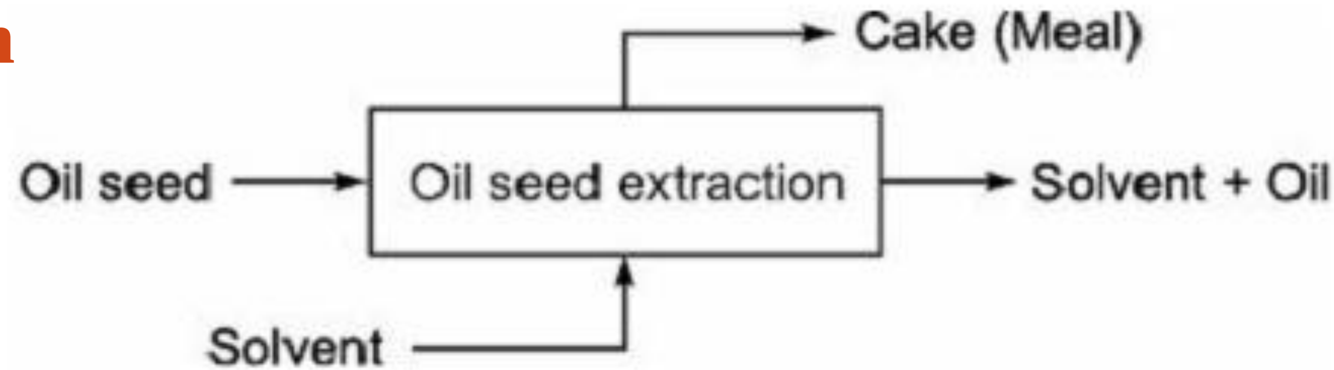
Material balance of Inert gas:

Inert gas in inlet = Inert gas in lean gas

Material balance of Solute:

Solute in inlet gas = Solute in out let gas + Solute absorbed in solvent

Extraction



Overall material balance:

Feed solution + Solvent = Extract phase + Raffinate phase

If 'A' is the solute to be extracted, then material balance of A for fresh solvent :

A in feed solution = A in extract phase + A in Raffinate phase

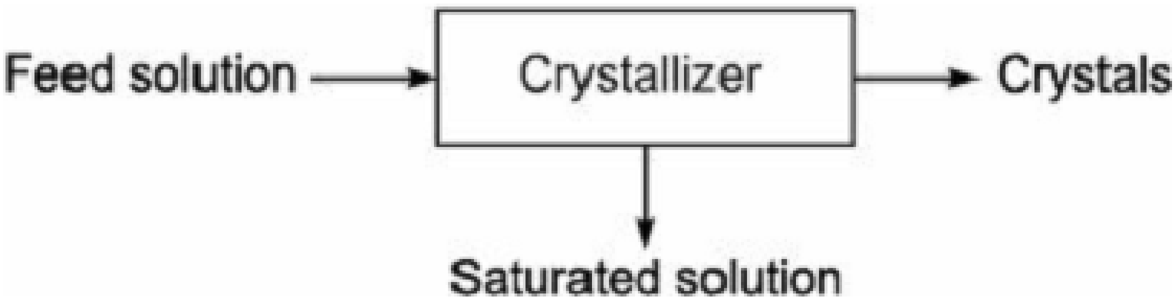
Material balance for Solids:

Solids in seeds = Solids in meal (if no solids in solvent)

Material balance for Oil :

Oil in seeds = Oil in meal + Oill in solvent

Crystallizer



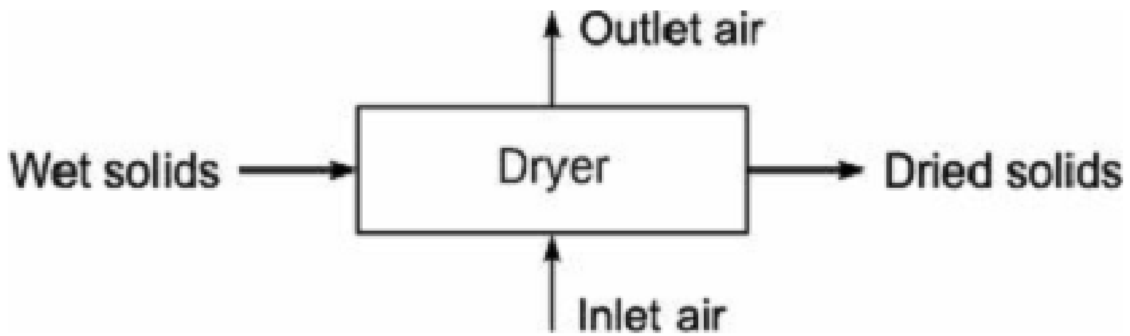
Overall material balance:

Feed solution = Saturated solution + Crystals

Material balance for crystals (Solute):

Crystals in feed solution = Crystals obtained + Crystals in saturated solution

Dryer



Material balance for moisture:

Moisture removed from solids = Moisture added in air

Moisture in (Wet solid– Dry solids) = Moisture in (outlet air– inlet air)

Material balance for Solids:

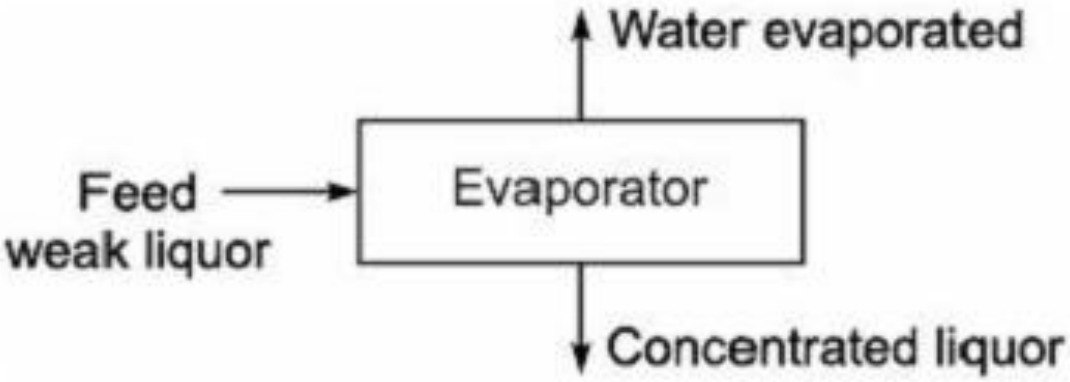
Solids in wet solids (Feed) = Solids in dried product

Mixer

Overall material balance:

Feed stream 1 + Feed stream 2 + Feed stream 3 = Desired product

Evaporator



Overall material balance:

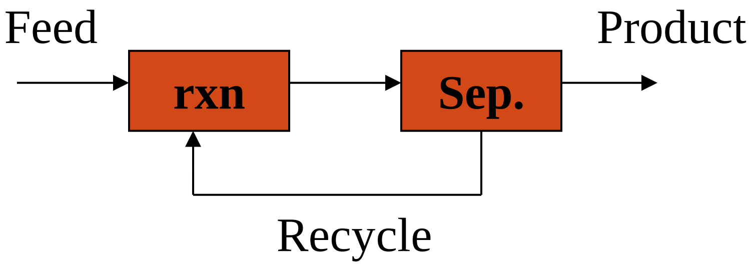
$$F = V + L$$

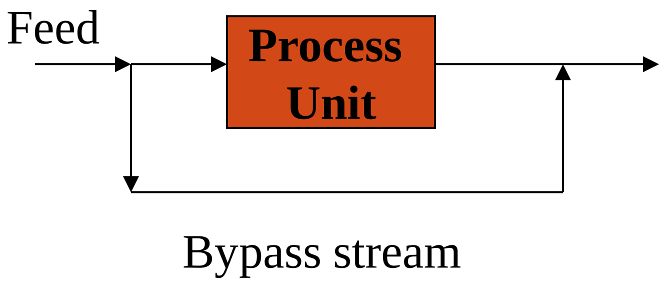
Material balance for solids:

$$Fx_F = Vx_v + L\,x_L$$

RECYCLE & BYPASS STREAM

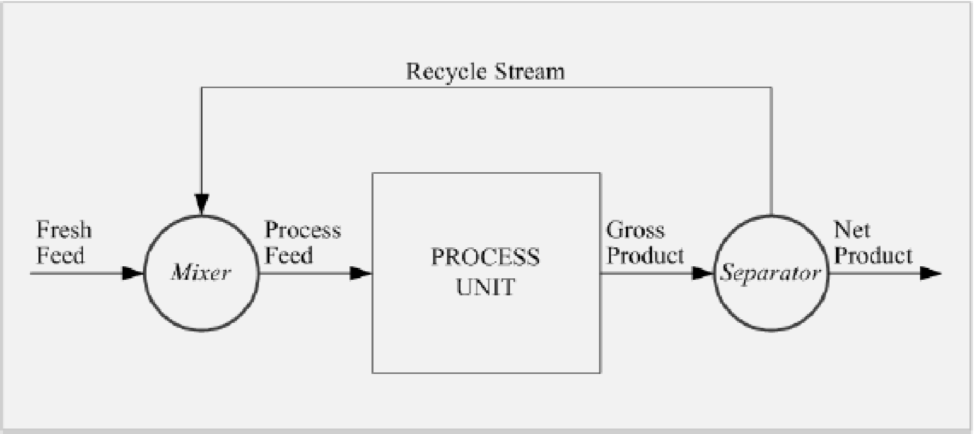
- It is rare that a chemical reaction A → B proceeds to completion in a reactor. Its efficiency is never 100. Some A in the product !
- To find a way to send the "A" back to feed, you need a seperation and recycle equipment, this would decrease the cost of purchasing more A.
- If a fraction of the feed to a process unit is diverted around the unit and combined with the output stream, this process is called bypass.





Recycle Stream

Recycle stream is a term denoting a process stream that returns material from downstream of a process unit back to the process unit.

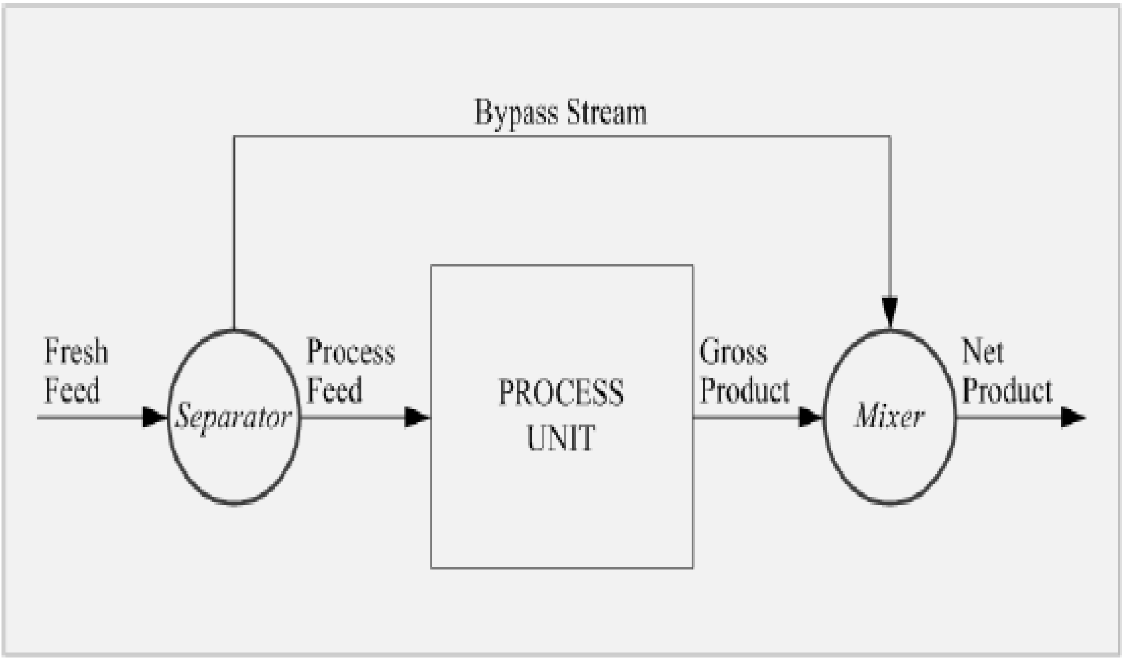


There are several reasons one might employ a recycle stream:

- increase conversion of a reactant to product
- recovery of catalyst
- dilution of a process stream (either to improve flow of the stream or control the rate of a reaction)
- re-use of a "working fluid" (like a lubricant or refrigerant)

Bypass Stream

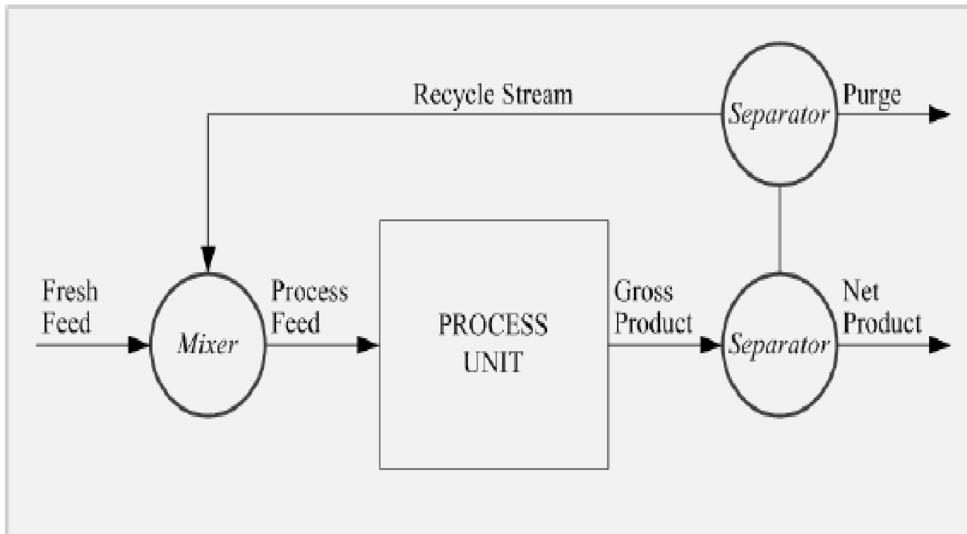
- Bypass stream is a stream that skips one or more stages of the process and goes directly to another downstream stage.



- This practice is far less common than recycle, but may be used if your ultimate goal is a material with properties "in-between" the untreated reactant and the process outlet product.

Purge Stream

- Purge stream is a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream.



- This is common with multi-phase systems where only 1 phase is either removed or recycled (i.e., if one recycles catalyst pellets, but adds "make-up" fresh catalyst a purge will be needed to discard some "spent" catalyst).

Solving Recycle and Bypass Problems

- The methods for solving recycle and bypass problems are basically the same.
- In the steady state, there is no buildup or depletion of material within the system or recycle stream of a properly designed and operated process.

When solving, you can write balances (total material or component) around:

- the entire process structure
- the mixing point
- the splitter
- the processing unit (inside the recycle/bypass)

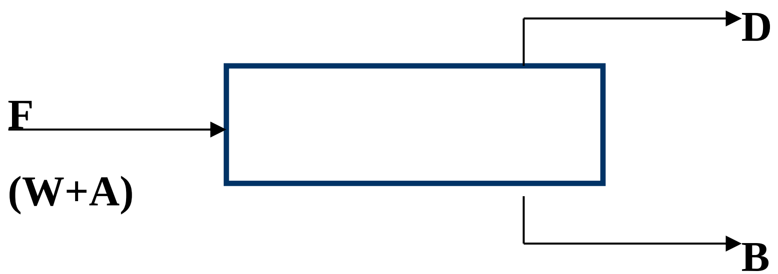
Solving Recycle and Bypass Problems

- Only three of these will be independent (the fourth is a linear combination).
- If you pick the right balances, you may be able to organize the problem for sequential solution.
- In particular, when you write the balance around the entire process system, terms describing the recycle/bypass stream do not appear; only the fresh feed and the product are required.

BALANCES ON BATCH PROCESSES

- Initial Input + Generation = Final Output + Consumption
  - ✓ Objective: generate as many independent equations as the number of unknowns in the problem

Example:



$$F = B + D$$

$$F.xF = D.xD + B.xB$$

$$F.yF = D.yD + B.yB$$

x: mole fraction of W

y: mole fraction of A

Balances on Continuous Steady-state Processes

- Input + Generation = Output + Consumption
  - ✓ If the balance is on a nonreactive species, the generation and consumption will be 0.
  - ✓ Thus, Input = Output
- Example

Input of 1000 kg/h of benzene+toluene containing 50% B by mass is separated by distillation column into two fractions.
B: the mass flow rate of top stream=450 kg/h
T: the mass flow rate of bottom stream=475 kg/h

1000 kg /h

Benzene + Toluene

%50 Benzene by mass

Distillation

m_1 kg Toluene/h

450 kg Benzene/h

475 kg Toluene/h

M_2 kg Benzene/h

Balances on Continuous Steady-state Processes

- Solution of the example

  Input = Output

- Benzene balance

  $(1000\ kg/h) \cdot 0.5 = 450\ kg/h + m_2$

  $m_2 = 50\ kg/h$ Benzene

- Toluene balance

  $(1000\ kg/h) \cdot 0.5 = 475\ kg/h + m_1$

  $m_1 = 25\ kg/h$ Toluene

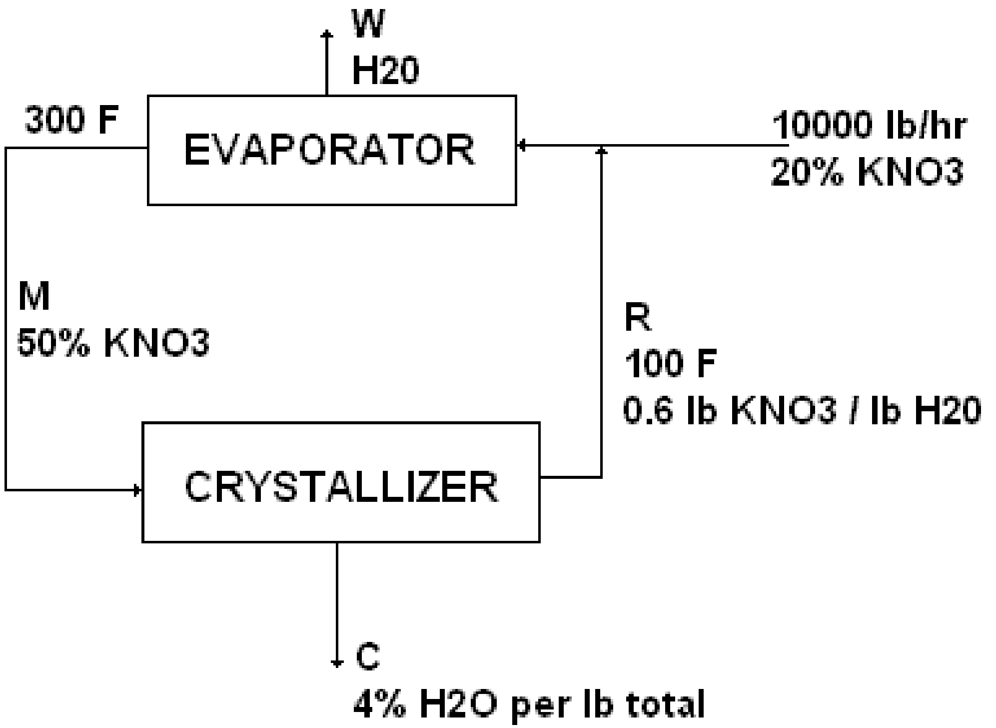
Example 1: Given the process shown, find the recycle flow in pounds/hour, the production rate of potassium nitrate, and the recycle ratio.

You are asked to find three things:

(i) the recycle flow (labeled R on the drawing),

(ii) the production rate (labeled C on the drawing), and

(iii) the recycle ratio, which will be calculated as R/10000 if we don't change the basis.



Basis: : 1 lb H_2O in stream R

We can write:

- On the entire system -- a total material, a nitrate, and/or a water balance
- On the evaporator -- a total material, a nitrate, and/or a water balance
- On the crystallizer-- a total material, a nitrate, and/or a water balance
- On the mixing point-- a total material, a nitrate, and/or a water balance

The system balances will only involve two unknowns (W and C), one of which is a desired answer.

System KNO_3 Balance

$$\text{Accumulation} = \text{In} - \text{Out} \pm \text{Generation}$$

$$\text{Steady state} \therefore \ \text{Accumulation} = 0$$

$$\text{No reaction} \therefore \ \text{Generation} = 0$$

$$0 = \text{In} - \text{Out}$$

$$0 = Fx_F - (Wx_0 + Cx_C)$$

$$0 = 10000(0.2) - W(0) - C(0.96)$$

$$C = \frac{10000(0.2)}{0.96} = 2083 \text{ lb crystals/hour}$$

Unknowns in the evaporator balance are R, M, and (R+F);
in the crystallizer R and M, and in the mixing point balance R and (R+F).
Note that having found C, I've reduced the number of unknowns in the crystallizer balance relative to the others, so we'll start there. There are still two unknowns, but this can be resolved by solving both the total and nitrate balances.

Crystallizer Material Balance

$$0 = In - Out$$
$$0 = M - (C + R)$$
$$0 = M - 2083 - R$$

Crystallizer Nitrate Balance

$$0 = In - Out$$
$$0 = Mx_M - (Cx_C + Rx_R)$$
$$0 = M(0.5) - (2083)(0.96) - R(0.375)$$

$$1.0 \text{ lb } H_2O + 0.6 \text{ lb } KNO_3 = 1.6 \text{ lb total}$$
$$x_R = \frac{0.6 \text{ lb } KNO_3}{1.6 \text{ lb total}} = 0.375 \frac{\text{lb } KNO_3}{\text{lb total}}$$

2 equations, 2 unknowns

R = 7667 lb/hour

$$\boxed{RR = \frac{R}{F} = \frac{7666}{10000} = 0.77}$$

Material balance with Chemıcal Reactıons

- If there is a chemical reaction in a process
  - ➔ More complications
- The stoichiometric ratios of the chemical reactions
  - ➔ Constraints
- The stoichiometric equation $2SO_2 + O_2 \rightarrow 2SO_3$

  2 molecules of SO2 reacts with 1 molecule of O2 and yields 2 molecules of SO_3
- 2, 1 and 2 are stoichiometric coefficients of a reaction

REACTION STOICHIOMETRY

2A + 3B → L +2M

The generalised representation of a chemical reaction is given by

$$0 = \sum_i \nu_i A_i$$

$$\frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_L}{\nu_L} = \frac{\Delta n_M}{\nu_M}$$

For differential amounts of the species, the above result can be written as

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_L}{\nu_L} = \frac{dn_M}{\nu_M}$$

Extent of Reaction (ϵ)

The reaction coordinate **(ϵ)** measures the progress of a reaction and is defined as the degree to which a reaction has advanced.

- It has the advantage that the change in the extent of reaction **($d\epsilon$)** is the same for each component , whereas the changes in the number of moles are different for different species taking part in the reaction .

$$\frac{dn_i}{\nu_i} = d\varepsilon$$

$$dn_i = \nu_i \, d\varepsilon$$

$$\Delta n_i = \nu_i \int_0^{\varepsilon} d\varepsilon = \nu_i \varepsilon$$

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

$$y_i = \frac{n_i}{\Sigma n_i} = \frac{n_{i0} + \nu_i \varepsilon}{\Sigma n_{i0} + \varepsilon \Sigma \nu_i} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu}$$

Conversion in terms of extent of reaction

$$z = \frac{\varepsilon}{n_{i0} / |\nu_i|}$$

LIMITING & EXCESS REACTANTS

$$A + B \rightarrow P$$

- If the reactants are not in stoichiometric proportion
  - ➔ one of them will be excess, the other will be limiting

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

$$\text{Fractional conversion of } A = \frac{\text{moles reacted}}{\text{moles fed}}$$

$$\text{Extent of reaction } (\zeta) = \frac{n_i - n_{i0}}{v_i}$$

Extent of Reaction (ϵ)

Multiple reactions

$$dn_i = \sum_i \nu_{i,j}\, d\varepsilon_j$$

$$n_i = n_{i0} + \sum_j \nu_{i,j}\, \varepsilon_j$$

$$n = \sum_i n_{i0} + \sum_i \sum_j \nu_{i,j}\varepsilon_j = n_0 + \sum_j \left(\sum_i \nu_{i,j} \right) \varepsilon_j$$

$$n = n_0 + \sum_j \nu_j \varepsilon_j$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j}$$

Example 1

Calculate the number of moles of CO_2 formed in the combustion of ethane C_2H_6 in a process when 35.0 mol of O_2 is consumed.

Hint...

The reaction is

$$2\ C_2H_6 + 7\ O_2 = 4\ CO_2 + 6\ H_2O$$

$$7 \text{ mol } O_2 \rightarrow 4 \text{ mol } CO_2$$

$$35.0 \text{ mol } O_2 \text{ ---------- } = 20.0 \text{ mol } CO_2$$

Discussion...

A balanced equation for the reaction is a basic requirement for identify the limiting reagent even if amounts of reactants are unknown.

Example 2

Two moles of Mg and five moles of O_2 are placed in a reaction vessel, and then the Mg is ignited according to the reaction

$$2Mg + O_2 = 2MgO.$$

Balance this equation and identify the limiting reagent in this experiment.

Hint...

The balanced reaction is, $2\ Mg + O_2 = 2\ MgO$

Thus, two moles of Mg require only ONE mole of O_2.

Four moles of oxygen will remain unreacted. Oxygen is the excess reagent, and Mg is the limiting reagent.

Discussion...

Answer these questions:

How many moles of MgO is formed?

What is the weight of MgO formed?

EX3: Suppose 316.0 g aluminum sulfide reacts with 493.0 g of water. What mass of the excess reactant remains?

The unbalanced equation is:

$Al_2S_3 + H_2O \text{ ---> } Al(OH)_3 + H_2S$

Solution:

1) Balance the equation:

$Al_2S_3 + 6H_2O \text{ ---> } 2Al(OH)_3 + 3H_2S$

2) Determine moles, then limiting reagent:

$Al_2S_3 \Rightarrow$ 316.0 g / 150.159 g/mol = 2.104436 mol

$H_2O \Rightarrow$ 493.0 g / 18.015 g/mol = 27.366 mol

1 mole of Al_2S_3 reacts with $\Rightarrow$ 6 moles of H_2O

2.104 moles of Al_2S_3 reacts with $\Rightarrow$ 12.624 moles of H_2O .

Unreacted water = 27.366-12.624 = 14.742 moles of H_2O

Al_2S_3 is the limiting reagent.

Excess reactant remains = 14.742 *18 = 265.356 g of H_2O

Ex-4 : **A gas mixture containing 2 moles nitrogen , 7 moles hydrogen and 1 mole ammonia initially, is undergoing the following reaction :**

$N_2 + 3H_2 \quad 2NH_3$

(a) Derive expression s for the mole fractions of various components in the reaction mixture in terms of the extent of reaction .

(b) Explain how the conversion of limiting reactant is related to the extent of reaction .

$$n_0 = \Sigma\, n_{i0} = 2 + 7 + 1 = 10$$

$$\nu = \Sigma\, \nu_i = 2 - 1 - 3 = -2$$

$$y_{N_2} = \frac{n_{N_2,0} + \nu_{N_2}\varepsilon}{n_0 + \varepsilon\nu} = \frac{2 - \varepsilon}{10 - 2\varepsilon}$$

$$y_{H_2} = \frac{n_{H_2,0} + \nu_{H_2}\varepsilon}{n_0 + \varepsilon\nu} = \frac{7 - 3\varepsilon}{10 - 2\varepsilon}$$

$$y_{NH_3} = \frac{n_{NH_3,0} + \nu_{NH_3}\varepsilon}{n_0 + \varepsilon\nu} = \frac{1 + 2\varepsilon}{10 - 2\varepsilon}$$

Ex-5: **A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions: Develop expression s for the mole fraction of the species in term s of the extent of reaction**

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$

The total moles initially present $n_0 = 3 + 5 + 1 = 9$

Stoichiometric constant for rx1 ϑ_1 = -1-3+1+1 = -2

rx2 ϑ_2 = -1-1+1+1 =0

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j}$$

$$y_{CO_2} = \frac{3 + (-1) \times \varepsilon_1 + (-1) \times \varepsilon_2}{9 + (-2) \times \varepsilon_1 + (0) \times \varepsilon_2} = \frac{3 - \varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}$$

$$y_{H_2} = \frac{5 - 3\varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CH_3OH} = \frac{\varepsilon_1}{9 - 2\varepsilon_1}$$

$$y_{H_2O} = \frac{1 + \varepsilon_1 + \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CO} = \frac{\varepsilon_2}{9 - 2\varepsilon_1}$$

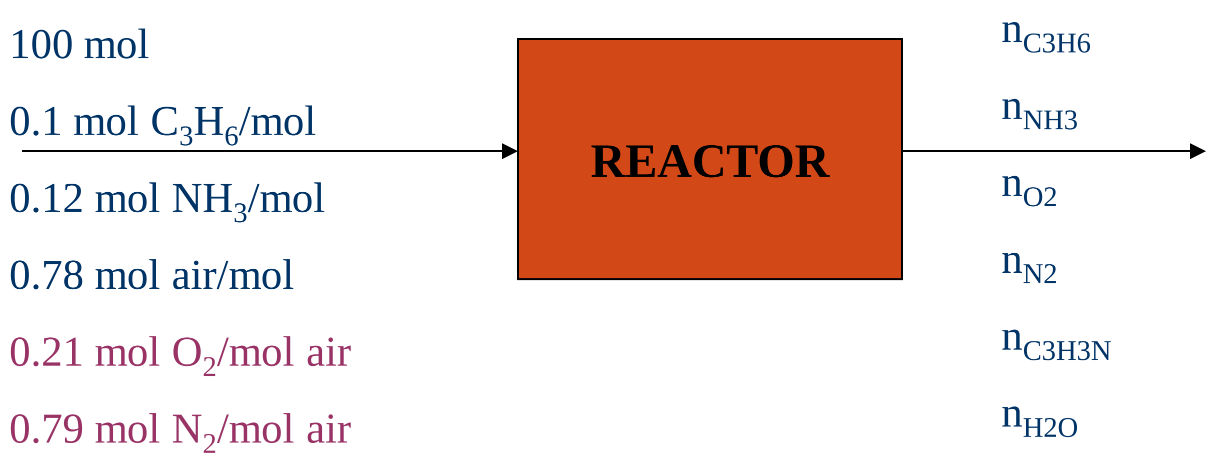
EXAMPLE 6

- $C_3H_6 + NH_3 + 3/2\ O_2 \rightarrow C_3H_3N + 3\ H_2O$

  Feed: 10 mol % of C_3H_6, 12 mole % NH_3 and 78 mole % air

  A fractional converison of limiting reactant = 30%

  Taking 100 mol of feed as a basis, determine which reactant is limiting, and molar amounts of all product gas constituents for a 30% conversion of the limiting reactant.



EXAMPLE 6 – continue

$$C_3H_6 + NH_3 + 3/2\ O_2 \rightarrow C_3H_3N + 3\ H_2O$$

Feed: $nC_3H_6 = 10$ mole $nNH_3 = 12$ mole $nO_2 = 78.(0.21) = 16.4$ mole

$nNH_3 / nC_3H_6 = 12/10 = 1.2$ $\rightarrow$ NH_3 is excess (stoich. 1)

$n\ O_2 / nC_3H_6 = 16.4/10 = 1.64$ $\rightarrow$ O_2 is excess (stoich. 1.5)

(nNH_3)stoich.= 10 mole (nO_2)stoich.= 15 mole

$$\frac{\text{Moles reacted}}{\text{Moles fed}}$$

(% excess) NH_3= (12-10) /10 x 100 = 20% excess NH_3

(% excess) O_2 = (16.4-15) /15 x 100 = 9.3% excess O_2

(nC_3H_6)out=0.7 x (nC_3H_6)0= 7 mole nC_3H_6 (since the fractional conversion of nC_3H_6 is 30%)

Extent of reaction = ζ = 3 mole   (since ni = ni0 + ni ξ => 7= 10 - 1. ξ)

$nNH_3 = 12 - \zeta = 9$ mole $nO_2 = 16.4 - 1.5.(\zeta) = 11.9$

$nC_3H_3N = \zeta = 3$ mole $nH_2O = 3.(\zeta) = 9$ mole

$nN_2 = (nN_2)_0 = 61.6$ mole

CHEMICAL EQUILIBRIUM

- If you are given a set of reactive species and reaction conditions;
  - a) **What will be the final (equilibrium) composition of the reaction mixture?**
  - b) **How long will the system take to reach a specified state short of equilibrium?**
- Chemical equilibrium thermodynamics & Chemical Kinetics
- A reaction can be
  - ✓ **Reversible**
  - ✓ **Irreversible**

EXAMPLE

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Given @ T=1105 K, equilibrium constant, K=1

nCO= 1 mol, nH_2O= 2mol, initially no CO_2 and H_2
Calculate the equilibrium composition and the fractional converison of the limiting reactant.

Equilibrium constant;

$$K(T) = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}}$$

EXAMPLE – continue

$nCO = 1\text{-}\varepsilon$, $nH_2O = 2\text{-}\ \varepsilon$, $nCO_2 = \varepsilon$, $nH_2 = \varepsilon$

$yCO = (1\text{-}\ \varepsilon)/3$; $yH_2O = (2\text{-}\ \varepsilon)/3$;

$CO_2 = \varepsilon\ /3$; $yH_2 = \varepsilon\ /3$

$K(T) = (\varepsilon)^2\ /\ (1\text{-}\ \varepsilon)\ (2\text{-}\ \varepsilon) = 1$

$\varepsilon = 0.667$ mole

$yCO = 0.111$ $yH_2O = 0.444$

$yCO_2 = 0.222$ $yH_2 = 0.222$

Limiting reactant is CO. $nCO = 1\text{-}0.667 = 0.333$

Fractional conversion $= (1\text{-}0.333)\ /\ 1$ mol feed $= 0.667$

Thank you