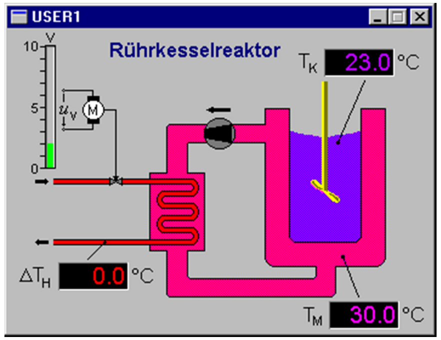
CHAPTER 4.4



Balances on Reactive Process

Topic Learning Outcomes

- ✓ Perform material balance calculations for a reactive system using extent of reaction, atomic and molecular methods
- ✓ Perform material balance calculations for a reactive system involving recycle and purging streams

Balances on Atomic and Molecular Species

- Methods for solving mass balances with reactions
  - Using the extent of reaction
  - Using balances on molecular species (e.g. N_2, CH_4, NO etc.)
  - Using balances of atomic species (e.g. N, C, H, N, O etc)
- Molecular balance (steady state)

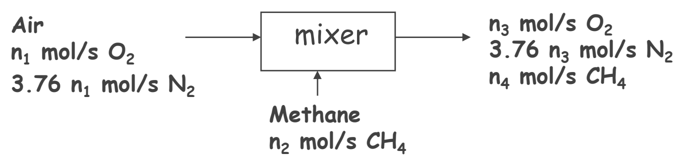
  Input + generation = Output + Consumption
- Atomic balance (steady state)

  Input = Output (WHY??)

Independent Equations, Independent Species and Independent Reactions

- If two molecular or atomic species are in the same ratio to each other where they appear in a process , balances on those species will not be independent (i.e. only one independent molecular or atomic species can be written.)
- Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding or subtracting multiples of the stoichiometric equations of the others

Example 1



Molecular (also atomic) nitrogen and oxygen are always in the same ratio (3.76 mol N_2/mol O_2 or 3.76 atom N/atom O) to each other in the process.

The same case applies to methane (1 atom C/4 atom H).

Thus,

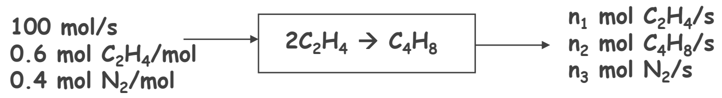
only two independent molecular species (CH_4 and O_2 or N_2) can be written.

Similarly,

only two independent atomic species (C or H and O or N) can be written

Example 1

A mixture of ethylene and nitrogen is fed to a reactor in which the ethylene is dimerized to butene



a) How many independent molecular species are involved in the process?. Show your analysis and list down all molecular species balances .

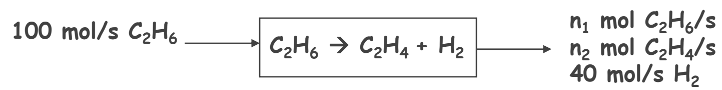
b) How many independent atomic species are involved in the process? Show your analysis and list down all atomic species balances .

Guidelines to Solving Mass Balances of Reactive Processes

- ***Atomic species balances*** generally lead to the most straight forward solution procedure, especially when more than one reaction is involved.
- ***Extents of reaction*** are convenient for chemical equilibrium problems and when equations solving software is to be used.
- ***Molecular species balances*** require more complex calculations than either of the other two approaches and should be used only for systems involving one reaction.

Working session V – Q1

Dehydrogenation of ethane



Mass balance analysis

1. Extent of reaction
   $n_{i,out} = n_{i,in} \pm v_i \xi$
2. Atomic species balances
   INPUT = OUTPUT ..... Conservation of mass
3. Molecular species balances
   INPUT + GENERATION = OUTPUT + CONSUMPTION

Strategies to Solving Mass Balances of Reactive Processes

1. Identify the appropriate mass balance method
   a. Extent of reaction
   b. Atomic species balances
   c. Molecular species balances
2. Perform the degree of freedom analysis
3. Solve unknowns that have relationships with given information (e.g. process specification such as fractional conversion, excess air/oxygen etc)

Working session V – Q2

In the Deacon process for the manufacture of chlorine (Cl_2), hydrochloride acid (HCl) and oxygen (O_2) react to form Cl_2 and water (H_2O). Sufficient air (21 mole % O_2, 79% N_2) is fed to provide 35% excess oxygen and the fractional conversion of HCl is 85%. Based on the HCl molar flow rate of 100 mol/min, perform the degree of freedom analysis and then calculate the mole fractions of the product stream components using

a. the extent of reaction
b. molecular species balances.
c. atomic species balances.

Solution – The main steps

Stoichiometric chemical reaction:

Process flow chart

Basis :

Solution
(a) using atomic species balance

General balance :- Input = output

Degree of freedom analysis

No. unknown labeled variables
No. independent atomic species balances
No. molecular species balances on independent non-reactive species
No. other equations relating unknown variables

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degree of freedom

Solution
(a) using atomic species balance

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Total air requirement **(n_{air}=?)** based on the stoichiometric chemical reaction with 35% excess O_2

85% HCl conversion (15% remains unreacted …… **(n_3=?)**)

Solution
(a) using atomic species balance

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N_2 bal. ; (input = output) …… n_5 = ?

Cl bal. ; (Input = Output) …… n_1 = ? $(2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O)$

Solution
(a) using atomic species balance

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H bal. ; (Input = Output) …… n_2 = ? $(2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O)$

O bal. ; (Input = Output) …… n_4 = ? $(2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O)$

Solution
(a) using atomic species balance

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Mole fraction of the product

Total air requirement based on the stoichiometric chemical reaction with 35% excess O_2

85% HCl conversion & HCl bal. ; (input = output + consumption)

Cl_2 bal. ; (generation = output) ($2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$)

H_2O bal. ; (generation = output) ($2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$)

O_2 bal. ; (input = output + consumption) ($2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$)

N_2 bal. ; (input = output)

Mole fraction of the product

Total air requirement based on the stoichiometric chemical reaction with 35% excess O_2

85% HCl conversion. (15% remains unreacted)

Extent of Reaction

Mole fraction of the product

Working session V – Q3

Methane (CH_4) and oxygen (O_2) react in the presence of a catalyst to form formaldehyde (HCHO). In a parallel reaction methane is oxidized to carbon dioxide (CO_2) and water (H_2O) :

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Suppose 50 mol/s of methane and 300 mol/s of air (21 mole % O_2, 79% N_2) are fed to a continuous reactor. The fractional conversion of methane is 0.9 and the fractional yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of formaldehyde production relative to carbon dioxide production using atomic species balances.

Basis : 50 mol/s of methane

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Working session V – Q4

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Methane (CH_4) and oxygen (O_2) react in the presence of a catalyst to form formaldehyde (HCHO). In a parallel reaction methane is oxidized to carbon dioxide (CO_2) and water (H_2O) :

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Suppose 100 mol/s of equimolar amount of methane and oxygen is fed to a continuous reactor. The fractional conversion of methane is 0.9 and the fractional yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of formaldehyde production relative to carbon dioxide production using atomic species balances.

SOLVE AT YOUR OWN TIME

Working session V – Q5

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Formaldehyde (HCHO) is produced industrially by the catalytic oxidation of methanol (CH_3OH) in a continuous reactor according to the following reaction;

$$CH_3OH + \tfrac{1}{2} O_2 \rightarrow HCHO + H_2O$$

Unfortunately, under the conditions used to produce formaldehyde at a profitable rate, a significant portion of the formaldehyde reacts with oxygen to produce carbon monoxide (CO) and water (H_2O), i.e.

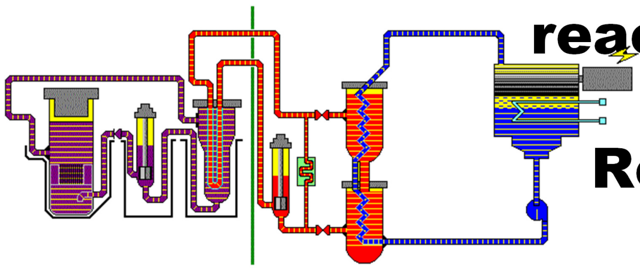
$$HCHO + \tfrac{1}{2} O_2 \rightarrow CO + H_2O$$

A chromatographic study of the product gas had the following analysis in mole percent; 1.6% methanol, 7.6% oxygen, 59.8% nitrogen, 11.9% formaldehyde, 16.7% water and 2.4% carbon monoxide. Assume that oxygen is obtained from the air and methanol is the limiting reactant. Determine the percentage excess of the air, the percentage conversion of the methanol and the percentage yield of the formaldehyde.

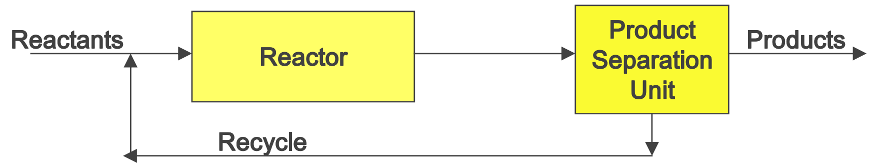
SOLVE AT YOUR OWN TIME

CHAPTER 4.5-4.6

Balances on reactive System involving Recycle and Purging



- Normally, reactions are not complete, thus requiring product separation and subsequently recycle of unconverted reactants to further improve the percentage yield and conversion

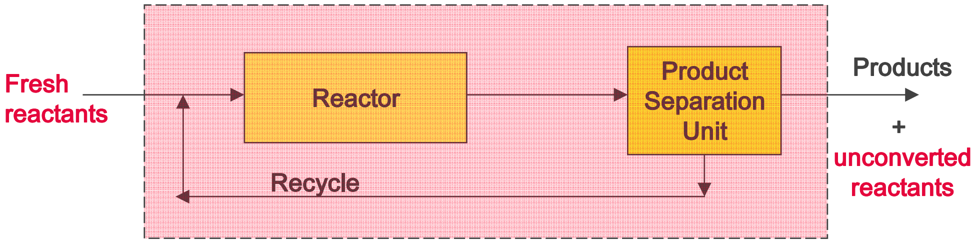


- Reactant conversion
  - Overall conversion
  - Single-pass conversion

Examples of product separation unit : condenser, absorber, distillation column, flash vessel

Compositions of product and recycle streams are not identical

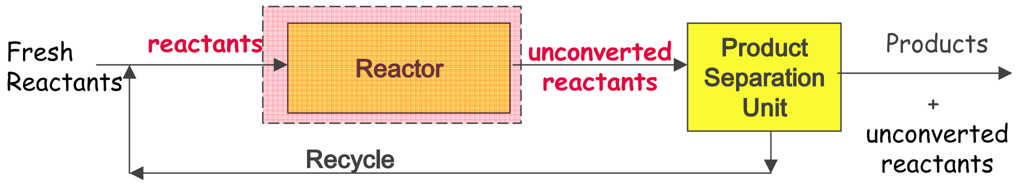
Boundary system



Overall conversion

$$\frac{(\text{reactant input to process}) - (\text{reactant output from process})}{(\text{reactant input to process})}$$

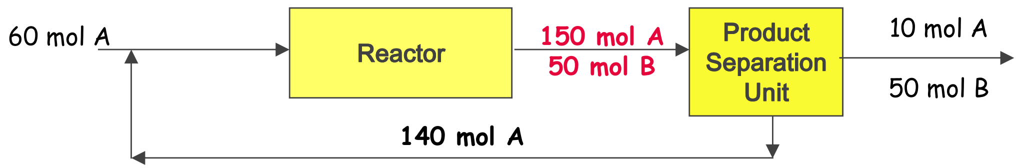
Boundary system



Single-pass conversion

$$\frac{(\text{reactant input to reactor}) - (\text{reactant output from reactor})}{(\text{reactant input to reactor})}$$

Product separation and recycle



Stoichiometric Reaction : A → B

1. What is the percentage overall conversion of A?
2. What is the percentage single pass conversion of A?

Working session V – Q6

Methanol (CH_3OH) is produced by reacting carbon monoxide (CO) and hydrogen (H_2). A fresh feed stream containing CO and H_2 joins a recycle stream and the combined stream is fed to a reactor. The reactor outlet stream flows at a rate of 350 mol/min and contains 63.2 mole% H_2, 27.3 mole% CO and 9.5 mole% CH_3OH . This stream enters a cooler in which most of the methanol is condensed. The liquid methanol condensate is withdrawn as a product and the gas stream leaving the condenser which contains CO, H_2 and 0.4 mole% uncondensed CH_3OH vapor is then recycled and combines with the fresh feed. Calculate

a) The production of liquid CH_3OH.
b) The molar flow rates of CO and H_2 in the fresh feed.
c) The molar flow rates of CO, H_2 and CH_3OH to the reactor
d) The percentage single pass and overall conversion of H_2 and CO.

Q6 Solution
The main steps

Stoichiometric chemical reaction:

Process flowchart

Basis:

Q6 Solution
using molecular species balance

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General balance :- Input + generation = output + consumption

Strategy : Start solving the unknown of any stream with the most available information and possibly without any reaction and perform the degree of freedom analysis

CO bal. (input = output)

H_2 bal. (input = output)

- Mass balance on the process system

- CO, H_2 and CH_3OH Bal. at the mixing point between the fresh feed and the recycled streams. (input = output)

Overall conversion

Single pass conversion

Working session V – Q7

A catalytic reactor is used to produce formaldehyde from methanol in the reaction

$CH_3OH \rightarrow HCHO + H_2$

A single pass conversion of 70% is achieved in the reactor. The methanol in the reactor product is separated from the formaldehyde and hydrogen in a multiple-unit process. The production rate of formaldehyde is 900 kg/h.

a. Calculate the required feed rate (kmol/h) of methanol if there is no recycle.
b. Suppose the recovered methanol is recycled to mix with the fresh methanol prior feeding to the reactor. Determine the required fresh feed rate of methanol (kmol/h) and the rates (kmol/h) at which methanol enters and leaves the reactor.

SOLVE AT YOUR OWN TIME

Working session V – Q8

Pure propane (C_3H_8) from the gas processing plant (GPP), Kerteh is dehydrogenated catalytically in a continuous reactor to obtain propylene (C_3H_6). All the hydrogen formed is separated from the reactor effluent gas with no loss of hydrocarbon. The hydrocarbon mixture is then fractionated in a continuous distillation column to give an overhead product stream containing 88 mole% propylene and 12 mole% propane. The bottom stream containing 70 mole% propane and 30 mole% propylene is then recycled. The one-pass conversion of propane in the reactor is 25% and 1000 kg of fresh propane is fed per hour. Find

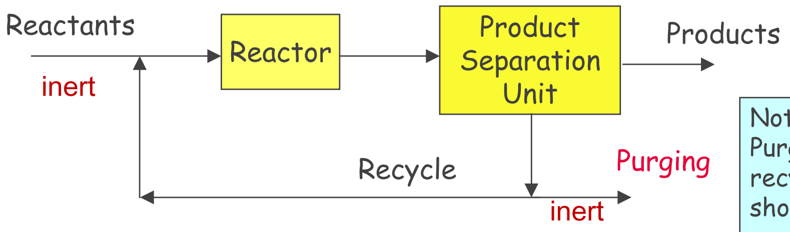
a. the mass flow rate of the product stream per hour
b. the mass flow rate of recycle stream per hour (kg/h) of feed to the reactor .
c. the percent overall conversion of propane

Draw a process flowchart and specify the method used to solve the problem.

SOLVE AT YOUR OWN TIME

PURGING

The presence of inert components in the reactor outlet stream may cause accumulation in the process and hence unwanted operating conditions such as pressure build-up and unsteady state process. It is important to remove some of these undesired materials in a recycle stream prior to feeding back to the reactor. This process is known as purging.



Note :
Purge stream and recycle stream should have the same composition

Working session V – Q9

Ethylene oxide (C_2H_4O) is produced by the oxidation of ethylene (C_2H_4) and oxygen (O_2) in the air (21 mole% O_2, 79% N_2) over a catalyst. The conversion per pass is 50%. The ethylene oxide formed is completely condensed out. The uncondensed gases containing 7.8 mole % C_2H_4, 3.9 mole % O_2 and 88.3 mole% N_2 leaving the condenser are then recycled and combined with a fresh ethylene-air mixture prior to feeding into the reactor. For safety considerations, a fraction of gases leaving the condenser has to be purged from the recycle stream to avoid build up of N_2 in the system. For a plant producing 440 kg/hr ethylene oxide, calculate

a) the molar flow rates of ethylene and air in the fresh feed to the process.
b) the molar flow rate of the purge stream.
c) the percentage overall conversion of C_2H_4 and O_2.
d) the ratio of recycle stream to feed stream to the reactor.

SOLVE AT YOUR OWN TIME

Q9 SOLUTION

Process flowchart:

Basis :