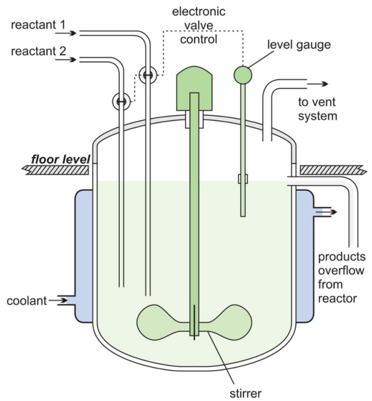
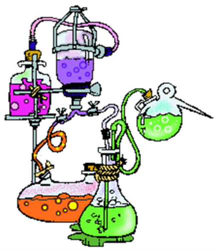
CHAPTER 4.1 - 4.3

Balances on Reactive Process





Topic Learning Outcomes

At the end of this course students will be able to

- Write and balance chemical reaction equations
- Define excess reactant, limiting reactants, fractional or percentage conversion, selectivity and yield in a reaction
- Perform material balance calculations for a reactive system using an extent of reaction method

Balance on Continuous Steady-State Reactive Process

- ✓ **General material balance**

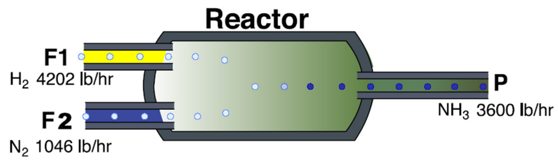
Input - Output + Generation - Consumption = Accumulation

- ✓ **For steady state, accumulation = 0**
- ✓ **Then,**

Input - Output = Consumption - Generation

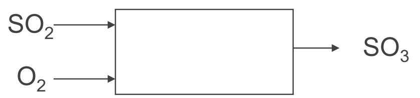
Balance on Continuous Steady-State Reactive Process

Input - Output = Generation - Consumption



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

- Stoichiometry
  - The theory of proportions in which chemical species combine with one another.
- Stoichiometric equation



input → output

- Write the stoichiometric reaction of gaseous methane with pure oxygen to produce carbon dioxide and water vapour

- Stoichiometric Ratio :
  - Ratio of stoichiometric coefficients can be used as a conversion factor.
  - It can be used to calculate the amount or reactant (or product) that was consumed (or produced) given another quantity of another reactant or product that participated in reaction.

Stoichiometry equation : $2SO_2 + O_2 \longrightarrow 2SO_3$
(A) (B) (C)

Stoichiometry ratio ;

$$\frac{\text{2 mol (}\textit{or kmol, lb-mole}\text{) } SO_3 \text{ produced}}{\text{1 mol (}\textit{or kmol, lb-mole}\text{) } O_2 \text{ reacted}}$$

$$\frac{\text{2 mol (}\textit{or kmol, lb-mole}\text{) } SO_2 \text{ reacted}}{\text{2 mol (}\textit{or kmol, lb-mole}\text{) } SO_3 \text{ produced}}$$

produced=generated ; reacted=consumed

Two reactants, A and B are in **Stoichiometry proportion** when:

$$\frac{\text{mole A present}}{\text{mole B present}}$$ = **Stoichiometry proportion** ratio obtained from the balanced equation

For the production of 1600 kg/hour of SO_3, calculate the mole and mass flowrate of oxygen needed :

Working Session IV – Q#1

Consider the reaction

$$C_4H_8 + O_2 \rightarrow CO_2 + H_2O$$

1) Write the stoichiometric equation of the above reaction?
2) What is the stoichiometric coefficient of CO_2?
3) What is the stoichiometric ratio of H_2O to O_2? *(Include units)*
4) How many lb-moles of O_2 react to form 400 lb-moles of CO_2? *(Use a dimensional equation)*
5) One hundred g-moles of C_4H_8 are fed into a reactor, and 50% reacts. At what rate is water formed?

Limiting and Excess Reactants

- Limiting reactants
  - Reactant that its present is less than its stoichiometric proportion relative to every other reactant
  - Reactant that would be first fully consumed / reacted
- Excess reactants
  - Reactant that if it is more than its stoichiometric proportion relative to every other reactant
  - Reactant that would have some unconsumed / unreacted after the reaction is complete

Limiting and Excess Reactants – Example

Limiting reactant will disappear first for a complete reaction

	$2SO_2$	+ O_2	→ $2\ SO_3$
n_i =	200 mol	100 mol	0 mol
n_f =	0 mol	0 mol	200 mol

Fractional Conversion

$$\text{Fractional Conversion, } f = \frac{\text{mol reacted}}{\text{moles feed}}$$

$$\text{Percentage Conversion} = \frac{\text{mol reacted}}{\text{moles feed}} \times 100\%$$

Example : Calculate the percentage conversion of SO_2 and O_2 for the following reaction.

	$2SO_2$	+ O_2	——> $2SO_3$
$n_{initial}$ =	200 mol	100 mol	
$n_{reacted}$ =	? mol	? mol	
n_{final} =	? mol	? mol	150 mol

Extent of Reaction

Suppose we start with 100 mol of H_2 , 50 mol of Br_2 and 30 mol of HBr.

a) Which reactant is limiting?
b) What is the percentage excess of other reactant?
c) If 30 mol of H_2 reacts with Br_2 to form HBr, calculate the molar compositions of the product?

H_2 + Br_2 → 2HBr

Extent of Reaction – Ex part (c)

If 30 mol of H_2 reacts with Br_2 to form HBr, calculate the molar compositions of the product?

	H_2 +	Br_2 →	2HBr
$n_{initial}$ =	100 mol	50 mol	30 mol
$n_{reacted}$ =	30 mol	30 mol	60 mol
n_{final} =	70 mol	20 mol	90 mol

60 mol: $\left\{\frac{2 \text{ mol HBr produced}}{1 \text{ mol } H_2 \text{ reacted}} \text{ x } 30 \text{ mol } H_2 \text{ reacted}\right\}$

20 mol: $\left\{50 \text{ mol } Br_2 \text{ fed} - \frac{1 \text{ mol } Br_2 \text{ reacted}}{1 \text{ mol } H_2 \text{ reacted}} \text{ x } 30 \text{ mol } H_2 \text{ reacted}\right\}$

90 mol: $\left\{30 \text{ mol HBr fed} + \frac{2 \text{ mol HBr produced}}{1 \text{ mol } H_2 \text{ reacted}} \text{ x } 30 \text{ mol } H_2 \text{ reacted}\right\}$

Extent of Reaction

$$(n_{H_2})_{final} = (n_{H_2})_{initial} - \xi$$
$$(n_{Br_2})_{final} = (n_{Br_2})_{initial} - \xi$$
$$(n_{HBr})_{final} = (n_{HBr})_{initial} + 2\xi$$

ξ is the extent of reaction (30 mol of H_2 reacted)

Recall stoichiometric coefficient (v_i) :-

v_i = negative for reactant
v_i = positive for products

Example

$1H_2$ + $1Br_2$ → $2HBr$
v_{H2} = -1, v_{Br2} = -1, v_{HBr} = +2

$$n_i = n_{i0} + \beta_i \xi$$

where

$$\beta_i = +\nu_i \quad \text{(products)}$$
$$\beta_i = -\nu_i \quad \text{(reactants)}$$
$$\beta_i = 0 \quad \text{(inert)}$$

ξ : extent of reaction

Extent of Reaction

Output = Input + Generation - Consumption

$$(n_{H_2})_{final} = (n_{H_2})_{initial} - \xi$$
$$(n_{Br_2})_{final} = (n_{Br_2})_{initial} - \xi$$
$$(n_{HBr})_{final} = (n_{HBr})_{initial} + 2\xi$$
$$\xi = 30 \text{ mol } H_2 \text{ reacted}$$

$$(n_{H_2})_{final} = 100 - 30 = 70 \text{ mol } H_2$$
$$(n_{Br_2})_{final} = 50 - 30 = 20 \text{ mol } Br_2$$
$$(n_{HBr})_{final} = 30 + 2(30) = 90 \text{ mol HBr}$$

Working Session IV – Q#2

The oxidation of ethylene to produce ethylene oxide proceeds according to the equation:

$$2C_2H_4 + O_2 \text{ -----> } 2C_2H_4O$$

ethylene, oxygen, ethylene oxide

The feed to the reactor contains 100 kmol C_2H_4 and 100 kmol O_2.

(1) Which reactant is limiting?
(2) What is the percentage excess of the excess reactant?
(3) If the reaction proceeds to completion, how much of the excess reactant will be left; how much C_2H_4O will be formed; and what is the extent of reaction?
(4) If the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50%, how much of each reactant and product is present at the end, and what is the extent of reaction?
(5) If the reaction proceeds to a point where 60 mol O_2 are left, what is the fractional conversion of C_2H_4? The fractional conversion of O_2? The extent of reaction?

The oxidation of ethylene to produce ethylene oxide proceeds according to the equation:

$$2C_2H_4 + O_2 \text{ -----> } 2C_2H_4O$$

ethylene, oxygen, ethylene oxide

The feed to the reactor contains 100 kmol C_2H_4 and 100 kmol O_2.

(1) Which reactant is limiting? **C_2H_4**
(2) What is the percentage excess of the excess reactant? **100%**
(3) If the reaction proceeds to completion, how much of the excess reactant will be left; how much C_2H_4O will be formed; and what is the extent of reaction? **50 mol O_2, 100 mol C_2H_4O, ξ = 50 mol**.
(4) If the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50%, how much of each reactant and product is present at the end, and what is the extent of reaction? **50 mol C_2H_4, 75 mol O_2, 50 mol C_2H_4O, ξ = 25 mol**
(5) If the reaction proceeds to a point where 60 mol O_2 are left, what is the fractional conversion of C_2H_4? The fractional conversion of O_2? The extent of reaction?
$f_{C2H4} = 0.8$, $f_{O2} = 0.4$, ξ = 40 mol

Working Session IV – Q#3

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%. Calculate the mole fractions of the product stream components using the extent of reaction.

i) **Draw a process flow chart**

ii) **Basis :**

$2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$

III. Total moles of air required with 35% excess O_2

$2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$

or

V. Extent of Reaction

$2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$

Working Session IV – Q#4

Ammonia is occasionally oxidized to produce nitric oxide which is can be subsequently used along with more ammonia in the production of ammonium nitrate (a fertilizer). When ammonia is oxidized at relatively low temperatures (about 400°C), the oxidation occurs by the following reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

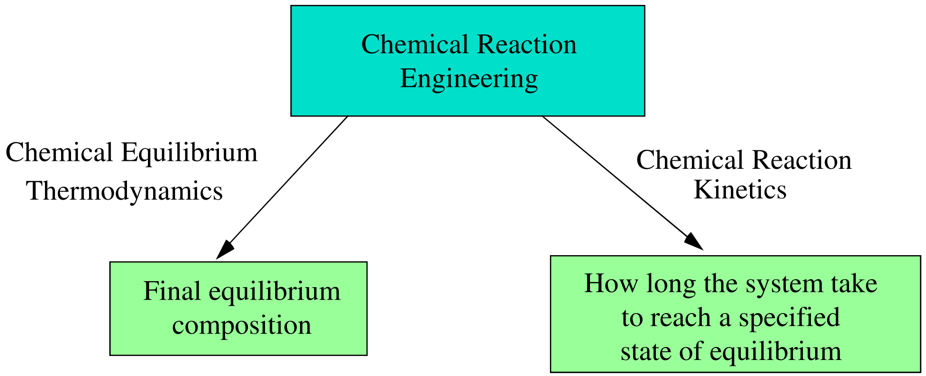
The feed stream contains 1000 kmol/h ammonia and 1750 kmol/h oxygen. 70% of the ammonia fed to the reactor is converted:

a. What is the limiting reactant? What is the excess reactant?

b. What percentage is the excess reactant in excess?

c. Calculate the flow rate (kmol/h) and mole fraction compositions of the product stream using the extent of reaction

Chemical Equilibrium



Chemical Equilibrium

Reversible reaction $CO(g) + H_2O(g) \Longleftrightarrow CO_2(g) + H_2(g)$

- ✓ The rates of forward and reverse reactions are identical when the equilibrium is reached.
- ✓ The compositions of product and reactant do no change when the reaction mixture is in chemical equilibrium.

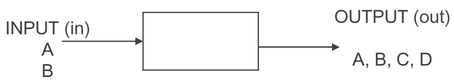
$$\frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = K(T)$$

Irreversible reaction: $2C_2H_4 + O_2 \Longrightarrow 2C_2H_4O$

- ✓ The reaction proceeds only in a single direction (reactants → products)
- ✓ The reaction ceases and hence equilibrium composition is attained when the limiting reactant is fully consumed.

Mass Balance involving Process in Chemical Equilibrium State

aA + bB <===> cC + dD



$$K(T) = \frac{y_C\, y_D}{y_A\, y_B}$$

$$y_c = \frac{n_{out,C}}{n_T},\ y_c = \frac{n_{out,D}}{n_T},\ y_c = \frac{n_{out,A}}{n_T},\ y_c = \frac{n_{out,B}}{n_T}$$

$$n_T = n_A + n_B + n_C + n_D$$

Mass Balance involving Process in Chemical Equilibrium State

aA + bB <===> cC + dD

Extent of Reaction, ξ ...... $n_{out,i} = n_{in,i} \pm v_i \xi$

$$K(T) = \frac{y_C y_D}{y_A y_B} = \frac{\left[\left(\frac{n_{out,C}}{n_T}\right)\left(\frac{n_{out,D}}{n_T}\right)\right]}{\left[\left(\frac{n_{out,A}}{n_T}\right)\left(\frac{n_{out,B}}{n_T}\right)\right]}$$

$$= \frac{\left[\left(\frac{(n_{in,C} + c\xi)}{n_T}\right)\left(\frac{(n_{in,D} + d\xi)}{n_T}\right)\right]}{\left[\left(\frac{(n_{in,A} - a\xi)}{n_T}\right)\left(\frac{(n_{in,B} - b\xi)}{n_T}\right)\right]} = \frac{(n_{in,C} + c\xi)(n_{in,D} + d\xi)}{(n_{in,A} - a\xi)(n_{in,B} - b\xi)}$$

Working Session IV – Q#5 Example 4.6-2

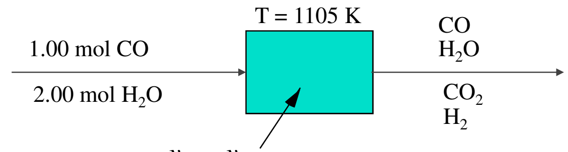
If the water-gas shift reaction

$$CO(g) + H_2O(g) <===> CO_2(g) + H_2(g)$$

Proceeds to equilibrium at a temperature T(K), the mole fractions of the four reactive species satisfy the relation

$$\frac{y_{co_2} y_{H_2}}{y_{co} y_{H_2O}} = K(T)$$

where *K* (T) is the reaction equilibrium constant. At *T* = 1105 K, *K* = 1.0. Suppose the feed to a reactor contains 1 mol of CO, 2 mol of H_2O and no CO_2 or H_2, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.



$$\frac{y_{co_2} y_{H_2}}{y_{co} y_{H_2O}} = K(T) = 1.0$$

Strategy:

1. Express all mole fraction in terms of a single variable x_e (extent of reaction)
2. Substitute x_e in the equilibrium relation and solve for x_e.
3. Use x_e to calculate mole fractions and any other desired quantity.

1. Express all moles and mole fractions in terms ξ_e

$$\begin{aligned} n_{CO} &= 1.00 - \xi_e \\ n_{H2O} &= 2.00 - \xi_e \\ n_{CO2} &= \xi_e \\ n_{H2} &= \xi_e \\ \hline n_{total} &= 3.00 \end{aligned} \quad ====> \quad \begin{aligned} y_{CO} &= (1.00 - \xi_e)/3.00 \\ y_{H2O} &= (2.00 - \xi_e)/3.00 \\ y_{CO2} &= \xi_e /3.00 \\ y_{H2} &= \xi_e /3.00 \end{aligned} \quad ===> (1)$$

2. Substitute mole fractions from (1) in the equilibrium reaction

$$\frac{\xi_e^{\ 2}}{(1.00 - \xi_e)(2.00 - \xi_e)} = 1.00; \qquad \xi_e = 0.667$$

3. $y_{CO} = 0.111$; $y_{H2O} = 0.444$; $y_{CO2} = 0.222$; $y_{H2} = 0.222$
   (a) limiting reactant → CO;
   (b) At equilibrium, $n_{CO} = 1.00 - 0.667 = 0.333$

Fractional conversion at equilibrium $= f_{co} = \dfrac{(1.00 - 0.333)\ \text{mol reacted}}{1.00\ \text{mol fed}} = \boxed{0.667}$

Multiple Reaction, Yield, Selectivity

- ✓ Multiple reaction : one or more reaction
  - Main Reaction
  - Side Reaction : undesired reaction
    - Example :- Production of ethylene (dehydrogenation of ethane)

      Main reaction

      $C_2H_6 \rightarrow C_2H_4 + H_2$

      Side Reactions

      $C_2H_6 + H_2 \rightarrow 2CH_4$

      $C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$

How do you control the reaction, i.e. minimize the side reaction?

- Design Objective
  - Maximize desired products (C_2H_4)
  - Minimize undesired products (CH_4, C_3H_6)

Learn more in chemical reaction engineering course

- Yield

$$\text{Yield} = \frac{\text{(moles of desired product formed at given fractional conversion of limiting reactant)}}{\text{(moles of desired product formed, assuming no side reactions and the limiting reactant is completely reacted)}}$$

- Selectivity

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

- Calculation of molar flow rates for multiple reactions

$$n_i = n_{i0} + \sum_j v_{ij}\xi_j$$

$+v_{ij}$ if i is a product in reaction j

$-v_{ij}$ if i is a reactant in reaction j

$v_{ij} = 0$ if i does not appear in reaction j

Working Session IV – Q#6

Consider the following pair of reactions

A → 2B (desired)
A → C (undesired)

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

a) The fractional conversion of A.
b) The percentage yield of B.
c) The selectivity of B relative to C.
d) The extents of the first and second reactions.

a) The fractional conversion of A.

b) The percentage yield of B

c) The selectivity of B relative to C.

d) The extents of the first and second reactions.

A → 2B (desired) …………rxn 1
A → C (undesired) …………rxn 2

Working Session IV – Q#7

Consider the following pair of reactions

4A + 5B → 4C + 6D (desired)
4A+ 6C → 5E + 6D (undesired)

Component A undergoes complete reaction, however, 70% takes in the desired reaction and the balance is the undesired reaction. Based on a feed stream containing 1000 kmol/h A and 1750 kmol/h B .

a. What is the limiting reactant? What is the excess reactant?
b. What percentage is the excess reactant in excess?
c. Write down the mass balance of each component using the extent of reaction
d. Calculate the molar flow rate of each component in the product stream
e. Calculate the percentage yield of C
f. Calculate the selectivity of C relative to E
g. What percentage of the C component produced by the desired reaction is consumed by the undesired reaction?

SOLVE AT YOUR OWN TIME

Consider the following pair of reactions

4A + 5B → 4C + 6D (desired) ………(1)
4A+ 6C → 5E + 6D (undesired) ………….(2)

What is the limiting reactant (LR) ?

HINT !! LR is determined using the main (i.e. desired) reaction

A feed stream contains 1000 mol/h A and 1750 mol/h B.

Write down the mass balance of each component using the extent of reaction.

$$n_{out,i} = n_{in,i} + \sum_{j=1,2} v_{ij}\xi_j$$

A bal. $n_1 = 1000 - 4\xi_1 - 4\xi_2$ .. (1)
B bal. $n_2 = 1750 - 5\xi_1$ .. (2)
C bal. $n_3 = 0 + 4\xi_1 - 6\xi_2$ .. (3)
D bal. $n_4 = 0 + 6\xi_1 + 6\xi_2$ .. (4)
E bal. $n_5 = 0 + 5\xi_2$ ..(5)

Calculate the extents of the first and second reactions (ξ_1 & ξ_2 ?)

Working Session IV – Q#8

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.

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