THE UNIVERSITY OF JORDAN

The University of Jordan
Faculty of Engineering & Technology
Chemical Engineering Department

# Chemical Engineering Principles (0905211)

## Material Balance
## Part 3: Balance on reacting system

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## Content

Stoichiometry

Limiting reactant, conversion and extent of the reaction.

Independent equations, independent species, and independent reactions

Balance on reactive processes:

- Extent of reaction and conversion
- Atomic balance
- Molecular balance.

Chemical Equilibrium

# Stoichiometry

1 mole=6.023x1023 particles (i.e., atoms or molecules).

Units : mol (g-mol), kmol (kg-mol), (lb-mol).

Moles=Mass/Molecular weight.

We use moles instead of number of molecules (quantities) because it is fixed number & easy to deal with.

How many moles (or molecules) of atomic hydrogen & oxygen would be released in 1 mol (or molecules) of $H_2O$ if the latter was broken up into its constituent parts?

As shown in the equation:

$2H_2O \longrightarrow 2H_2 + O_2$

Hydrogen:2 mol (or 2 molecules)

Oxygen:1 mol (or 1 molecules)



- How many Kg of $H_2$ can be obtained by electrolysis of 1 Kg of water?
- The relevant equation is
- $H_2O \longrightarrow H_2 + 1/2O_2$
- 1 mol of $H_2O$ yields 1 mol of $H_2$
- $n_{H2O}$=1Kg/18(Kg/Kmol)=1/18Kmol
- 1/18 Kmol of $H_2O$ yields 1/18 Kmol of $H_2$
- Mass$H_2$= 1/18 Kmol x 2 (Kg/Kmol)=1/9 Kg

Balance the equation of glucose oxidation to determine α, β & γ.

$$C_6H_{12}O_6 + \alpha O_2 \longrightarrow \beta CO_2 + \gamma H_2O$$

- C balance: $6 = \beta$   $\beta = 6$
- H balance: $12 = 2\gamma$   $\gamma = 6$
- O balance : $6 + 2\alpha = 2\beta + \gamma$   $\alpha = 6$

Solution:

$\alpha = 6$

$\beta = 6$

$\gamma = 6$

In general, stoichiometric equations can be represented as

$$aA + bB \rightarrow cC + dD$$



In the equation

*a,b,c,d* are the **Stoichiometric Coefficients**, representing the molar balance of the equation.

*a moles* of A react with *b moles* of B to form *c moles* of C and *d moles* of D.

The stoichiometric coefficients can refer to g-moles, lb-moles, kmols, etc., but NOT g, $lb_m$, kg or any units of mass.

The equation must be balanced to be valid, i.e. the number of atoms of each species are the same on both sides (atoms cannot be created or destroyed

$$\nu_1 C_1 + \nu_2 C_2 = \nu_3 C_3 + \nu_4 C_4$$

$$\sum \nu_i C_i = 0$$

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

$$1C, 4H, 4O \rightarrow 1C, 4H, 4O$$

Thus,

Stoichiometric coefficient are the values preceding each molecular species in a balanced stoichiometric equation.

Values defined to be positive for products & negative for reactants.

$$v_{CH4}=-1,\ v_{o2}=-2,\ v_{CO2}=2\ ,\ v_{H2O}=2$$

Stoichiometric ratios is the ratio of stoichiometric coefficients in a balanced stoichiometric equation.

$$\frac{2 \text{ moles } O_2 \text{ consumed}}{1 \text{ mole } CO_2 \text{ produced}} = 2{:}1$$

$$10 \text{ kgmoles } CO_2 \left(\frac{2 \text{ moles } O_2}{\text{mole } CO_2}\right) = 20 \text{ kgmoles } O_2$$

$$20 \text{ kgmoles } O_2 \left(\frac{32 \text{ kg}}{\text{kgmoles}}\right) = 640 \text{ kg } O_2$$



Example

For the reaction $2SO_2 + O_2 \rightarrow 2SO_3$

write the stoichiometric ratios

If 1600 kg/h of $SO_3$ is to be produced, calculate the amount of oxygen required

## Limiting & excess reactants

- Two reactant A and B are said to be in stoichiometric propostions if mole A/mole B is equal to the stoichiometric ratios.

Limiting reactant is reactant that is completely consumed when a reaction is run to completion.

Where as the other reactants are termed as excess reactant.

Suppose $x$ moles of A and $y$ moles of B are mixed. A and B react according to:

$$aA + bB \rightarrow cC + dD$$

$$\frac{n_{A_{stioc}}}{n_{B_{stioc}}} = \frac{a}{b} \quad \Rightarrow \quad \text{If } \frac{x}{y} < \frac{a}{b}$$

$$\frac{n_{A_0}}{n_{B_0}} = \frac{x}{y} \qquad \text{If } \frac{x}{y} > \frac{a}{b}$$



Fractional excess is the ratio of the amount by which the feed exceeds stoichiometric requirements in moles divided by the stoichiometric requirement in moles.

$$fractional\ excess = \frac{n(feed) - n(stoichiometric)}{n(stoichiometric)}$$

Example

For the reaction $2SO_2 + O_2 \rightarrow 2SO_3$

stoichiometric proportion,

200 mol of $SO_2$ and 100 mol of $O_2$ are initially present

if you start with 100 mol of $O_2$ and less than 200 mol of $SO_2$

if more than 200 mol of $SO_2$ is initially present

## Tasks

Determine which reactant is limiting & which is excess as well the percent excess for that component when:

1) Two moles of ($N_2$) reacting with 4 mole of ($H_2$) to form ammonia ($NH_3$) via the reaction.

$(MW_{N2}=28, MW_{H2}=2, MW_{NH3}=17)$

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

2) 100Kg of ethanol ($C_2H_5OH$) reacts with 100 Kg of acetic acid ($CH_3COOH$) to form ethyl acetate:

$$C_2H_50H + CH_3COOH \longrightarrow CH_3COOHC_2H_5 + H_2O$$

3) 64 g methanol ($CH_3OH$) reacts with 0.5 mol of Oxygen ($O_2$) to form formaldehyde.



## Independency

Algebraic equations are independent if you cannot obtain anyone of them by adding and subtracting multiples of any of the others.

For the equations,

$$[1] \quad x + 2y = 4$$
$$[2] \quad 3x + 6y = 12$$

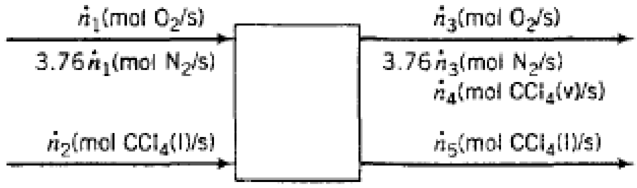
Note that

$$[2] = 3 \times [1].$$

→ They are not independent

If two molecular species are in the same ratio to each other wherever they appear in a process and this ratio is incorporated in the flowchart labeling, balances on chose species will not be independent equations.

If two atomic species occur in the same ratio wherever they appear in a process, balances on those species will not be independent equations.




Nitrogen and oxygen have the same ratio in the input and output (3.76 mol $N_2$/mol $O_2$),

➡ They cannot be counted as two independent species

⬇

Two independent molecular species balances in a degree-of-freedom analysis: one for either $O_2$ or $N_2$ and one for $CCl_4$ .



Upon using molecular species balances or extents of reaction to analyze a reactive system, *the degree-of-freedom analysis must account for the number of independent chemical reactions among the species entering and leaving the system.*

Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding and subtracting multiples of the stoichiometric equations of the others.

For the reactions,

$$[1] \quad A \longrightarrow 2B$$
$$[2] \quad B \longrightarrow C$$
$$[3] \quad A \longrightarrow 2C$$

Note that

$$[3] = [1] + 2 \times [2].$$

➡ These reactions are not all independent

# Methods of solving material balance involving chemical reaction

1. ## Conversion and extent of the reaction.

Chemical reactions proceed quite slowly.

Therefore, it is not practical to design a reactor for complete conversion of the limiting reactant.

Instead, the reactant is separated from the reactor outlet stream & recycled back to the reactor inlet.

### Conversion Approach

The fractional conversion of a reactant is the ratio of the amount reacted to the amount fed:

$$f = \text{fractional conversion} = \frac{\text{moles reacted}}{\text{moles fed}}$$



For reactant A, $f_A = \dfrac{n_{A_o} - n_A}{n_{A_o}}$ ➡ $n_A = n_{A_o}(1 - f_A)$

Where $n_{Ao}$, is the mole of A fed to the reactor, $n_A$, is the mole of A at the reactor outlet (unreacted)

Generally, for the reaction $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$

If A is selected as a base for calculations, then arrange the reaction expression in the form

$$\text{A} + \frac{b}{a}\text{B} \longrightarrow \frac{c}{a}\text{C} + \frac{d}{a}\text{D}$$

then

$$n_A = n_{A_o}(1 - f_A) \qquad n_B = n_{B_o} - \frac{b}{a} n_{A_o} f_A$$

$$n_C = n_{C_o} + \frac{c}{a} n_{A_o} f_A \qquad n_D = n_{D_o} + \frac{d}{a} n_{A_o} f_A$$

In summary

| Species | Initially (mol) | Change (mol) | Remaining (mol) |
|---|---|---|---|
| A | $N_{A0}$ | $-(N_{A0}X)$ | $N_A = N_{A0} - N_{A0}X$ |
| B | $N_{B0}$ | $-\frac{b}{a}(N_{A0}X)$ | $N_B = N_{B0} - \frac{b}{a}N_{A0}X$ |
| C | $N_{C0}$ | $\frac{c}{a}(N_{A0}X)$ | $N_C = N_{C0} + \frac{c}{a}N_{A0}X$ |
| D | $N_{D0}$ | $\frac{d}{a}(N_{A0}X)$ | $N_D = N_{D0} + \frac{d}{a}N_{A0}X$ |
| I (inerts) | $N_{I0}$ | — | $N_I = N_{I0}$ |
| Totals | $N_{T0}$ | | $N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$ |

**The basis of the conversion must be clearly stated.**
**The conversion of one component may not be the same as the conversion of another.**



## Example

For the reaction, $C_2H_2 + 2H_2 \rightarrow C_2H_6$

Suppose 20.0 kmol of acetylene, 50.0 kmol of hydrogen, and 50.0 kmol of ethane are charged into a batch reactor. Furthermore, suppose that after some time 30.0 kmol of hydrogen has reacted.

How much of each species will be present in the reactor at the moment?

## Extent of reaction Approach

The extent of reaction($\xi$) is the amount in moles that converted in a given reaction.

- For a continuous process at steady-state & for a batch process:

Where: $n_i = \nu_i \xi + n_{i0}$ $\dot{n}_i = \dot{n}_{i0} + \nu_i \dot{\xi}$

$n_i$ :molar flow rate of component *i* out of the system

$n_{i0}$ :molar flow rate of component *i* entering the system

$\nu_i$ :stoich. Coef. + for product and – for reactant

Generally for the reaction $aA + bB \rightarrow cC + dD$

The Molar Extent of Reaction

$$\xi = -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}$$

In the reaction of the previous example $C_2H_2 + 2H_2 \rightarrow C_2H_6$

$\nu_{C_2H_2}$ $\nu_{H_2}$ $\nu_{C_2H_6}$

## *Degree of Freedom Analysis*

No. unknown labeled variables
\+ No. independent reactions
\- No. independent reactive species (one equation for each species)
\- No. independent nonreactive species (one balance equation for each)
\- No. other equations relating unknown variables

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= No. degrees of freedom



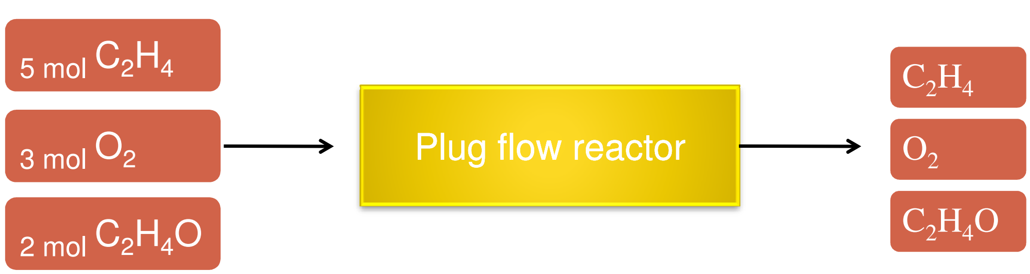
## Example

Ethylene oxide is produced by reacting ethylene with oxygen. The feed to the reactor contains 5 moles of ethylene,3 moles of oxygen and 2 moles of ethylene oxide.

a. Draw & label the process flow sheet.
b. Write the material balance equation as a function of the extent of reaction.

$2C_2H_4 + O_2 \longrightarrow 2C_2H_4O$

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



## Example

For the ammonia formation reaction $N_2 + 3H_2 = 2NH_3$

Suppose the feed to a continuous reactor consists of 100 mol/s $N_2$, 300 mol/s $H_2$, and mol/s Ar (an inert gas). What is the reactor outlet flow rates as a function of the extent of reaction.



## Example

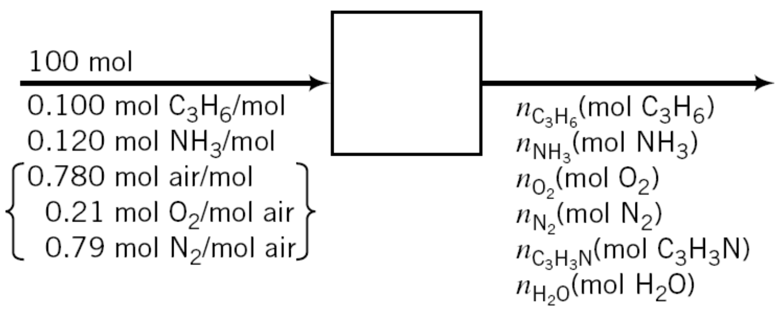
1 mole of methane and 3 mole of $O_2$ are mixed. 0.5 moles of methane burn. What is the limiting reactant, excess reactant, percent excess of the excess reactant, conversion of methane , oxygen, and of the total feed?

## Example

Acrylonitrile is produced in the reaction of propylene, ammonia, and oxygen:

$$C_3H_6 + NH_3 + (3/2)O_2 \longrightarrow C_3H_3N + 3\,H_2O$$

The feed contains 10.0 mole% propylene, 12.0% ammonia, and 78.0% air. A fractional conversion of 30.0% of the limiting reactant is achieved. Taking 100 mol of feed as a basis, determine which reactant is limiting, the percentage by which each of the other reactants is in excess, and the molar amounts of all product gas constituents for a 30% conversion of the limiting reactant.



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# Methods of solving material balance involving chemical reaction

2. Element or atomic balance

All balances on atomic species (C, H, O, etc.), for continuous ,steady-state processes, take the form

input = output

i.e. element balance have no generation or consumption terms

The element balance is based on the number of moles of that element regardless of the compound that it is in.

The number of moles of each compound must be multiplied by the stoichiometric number for the element.



*Degree of Freedom Analysis*

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

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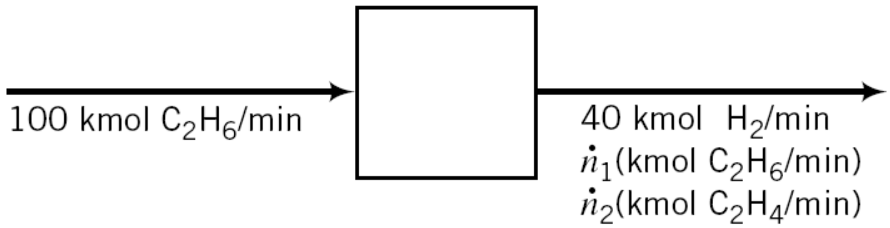
= No. degrees of freedom

## Example

For the dehydrogenation of ethane in a steady-state continuous Reactor,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

100 kmol/min of ethane is fed to the reactor. The molar flow rate of $H_2$ in the product stream is 40 kmol/min. Calculate the unknown stream composition.



# Methods of solving material balance involving chemical reaction

## 3. Molecular or Component balance

The balances on reactive species must contain generation and/or consumption terms.

for continuous ,steady-state processes, take the form

**input + generation= output + consumption**

*Degree of Freedom Analysis*

No. unknown labeled variables
+ No. independent chemical reactions
- No. independent molecular species balances
- No. other equations relating unknown variables

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= No. degrees of freedom

## Example

Re-solve the previous example using the molecular balance approach



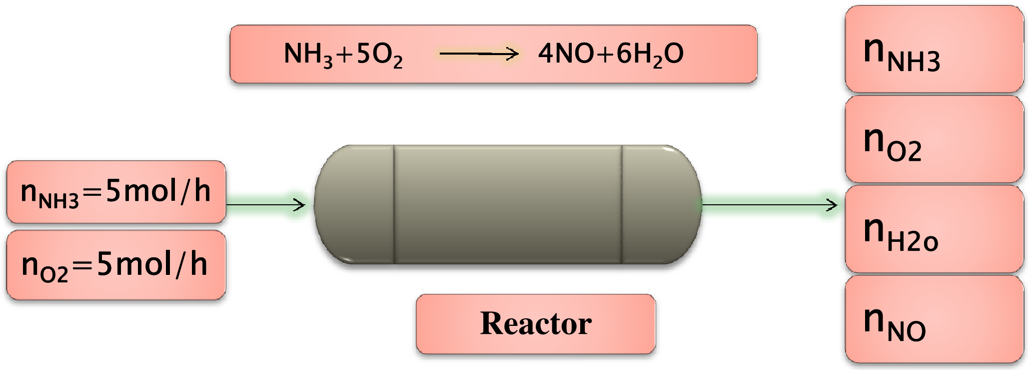
## Task

Re-solve the example using the extent and conversion approach

## Example

Ammonia is burned to form nitric oxide. The fractional conversion is 0.5. The inlet molar flow rates of $NH_3$ and $O_2$ are 5 mol/h. calculate the exit component molar flow rates using:

- A. extent of reaction method.
- B. atomic balance approach.
- C. Compound balance approach.



## Chemical Equilibrium

The final (equilibrium) composition of the reaction mixture is determined by Chemical Thermodynamics.

The time needed for a system to reach a specified state short of equilibrium is determined by Chemical kinetic

*Irreversible reactions* are reactions that proceed only in a single direction (from reactants to products) and the concentration of the limiting reactant eventually approaches zero.

The equilibrium composition for such a reaction is therefore the composition corresponding to complete consumption of the limiting reactant.

*Reversible reactions* are reactions in which reactants form products and products undergo the reverse reactions to reform the reactants.

The reaction conditions determine how far, and which direction, the reaction proceeds



In reversible reactions, the degree of conversion and the final composition is dictated by the value of the equilibrium coefficient

For the reaction $aA + bB \rightarrow cC + dD$

And if A, B, C, and D were all gases, then, the equilibrium constant

$$K = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

*Where $P_i$ is* the *partial pressure for gasses*

For ideal gas $P_A = y_A P$

$$K = \frac{y_C^c\, y_D^d}{y_A^a\, y_B^b}$$

## Example

If the water-gas shift reaction,

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

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 = 1.00.

Suppose the feed to a reactor contains 1.00 mol of CO, 2.00 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.