

*A Handbook on*

# Chemical Engineering

Contains well illustrated formulae  
& theory key concepts

~~~~~ *for* ~~~~~

# GATE, PSUs

& OTHER COMPETITIVE EXAMS



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## **A Handbook on Chemical Engineering**

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## A Handbook on Chemical Engineering

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# Process Calculations

## I Conservation of Mass

According to the law of conservation of mass, the total mass of various compounds remains unchanged during an unit operation or a chemical reaction. The general mass conservation equation for any process system can be written as,

$$(\text{Mass in}) + (\text{Mass generated}) = (\text{Mass out}) + (\text{Mass consumed}) + \text{Accumulation}$$

- For a steady state process the accumulation term will be zero. If there's no chemical reaction, the steady state material balance reduces to

$$\text{Mass in} = \text{Mass out}$$

A balance equation can be written for each species present and for the total material.

## II Measures of Composition

The most common measures of composition are mass fraction, mole fraction and molar concentration.

- Mass fraction is defined as the ratio of the mass of a particular chemical species in a mixture or solution to the total mass of the mixture or solution.
- Mole fraction is defined as the number of the moles of a particular chemical species in a mixture or solution to the total number of moles of mixture or the mole fraction of species  $i$ , is given as

$$x_i = \frac{n_i}{n}$$

where,  $n_i$  = The number of moles of chemical species  $i$  in the mixture  
 $n$  = The total number of moles of mixture

- Molar concentration of chemical species  $i$ ,  $C_i$  is defined as the ratio of number of mole of species  $i$  in a mixture to its molar volume ( $V$ )

$$C_i = \frac{n_i}{V}$$

- The molar mass of a mixture or solution is the mole fraction weighted sum of the molar masses of all species present.

$$M = \sum_i x_i M_i$$

- Number of independent components = (Number of chemical species) – (Number of independent chemical equations)

## Tie Component

- A tie component is that component whose quantity doesn't change during a particular operation.

## Limiting Reactant and Excess Reactant

In most chemical reactions, two or more components reacting together are in stoichiometric proportions due to technical, economical or safety considerations in such cases, a limiting reactant is defined as the one which decides the conversion in the reaction.

- An excess reactant is the one which is in excess amount over the stoichiometric requirement of the reactant as determined by the desired chemical reaction.

**Explanation:** In the manufacture of urea by the reaction of carbon dioxide and ammonia,  $\text{CO}_2$  is the limiting reactant and  $\text{NH}_3$  is the excess reactant.

## Conversion and Yield

- It's important to distinguish between conversion and yield. Conversion is to do with reactant and yield with products.
- Conversion is a measure of the fraction of the reactant that reacts. It is defined as.

$$\begin{aligned} \text{Conversion} &= \frac{\text{Amount of reactant consumed}}{\text{Amount of reactant supplied}} \\ &= \frac{\left( \text{Amount of reactant in feed stream} \right) - \left( \text{Amount of reactant in product stream} \right)}{\text{Amount of reactant in feed stream}} \end{aligned}$$

- The conversion of particular reactant is often less than 100%.
- Yield is a measure of the performance of reactor. For a reactor the yield is defined as

$$\text{yield} = \frac{\text{Moles of product of formed} \times \text{Stoichiometric factor}}{\text{Moles of reactant converted}}$$

- Stoichiometric factor = Stoichiometric moles of reactant required per mole of product formed.
- It's necessary to distinguish between reaction yield which includes only chemical losses to side products and the overall "Reactor yield" which will include physical loss.

### III Recycle Processes

- In which a flow stream is returned (recycled) to an earlier stage in the process sequence are commonly used. If the conversion of a valuable reactant in a reaction process is appreciable less than 100%, the un-reacted material is usually separated and recycled.
- The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

#### Purge

- It's usually necessary to bleed off a portion of a recycle stream to prevent the build up of unwanted material.
- A continuous purge would normally be used.

#### Under Steady-State Conditions

- Loss of inert in the purge = Rate of feed of inerts into the system
- The concentration of any component in the purge stream will be the same as that in recycle stream at the point where the purge is taken off.
- Thus the required purge rate can be determined from the following relationship.  
$$(\text{Flow rate of feed stream}) \times (\text{Concentration of inert in feed stream}) = (\text{Flow rate of purge stream}) \times (\text{Desired concentration of inert in recycle stream})$$

#### By Pass

- Flow stream may be divided and some part diverted around some units. This procedure is often used to control stream composition or temperature.
- Material balance calculations for process with by-pass streams are similar to those involving recycle, except that the stream is fed forward instead of backward.

- During unsteady state operation, the process variables vary with time and the accumulation term in the balance equation will not be equal to zero. The behaviour of a process during start-up and shut-down and the response to process upsets are examples of unsteady state operations.

## **IV Basic Chemical Calculations**

1. **Atomic weight:** The atomic weight of an element is the mass of the atom of this element based on the scale that assigns carbon a mass of exactly twelve.
2. **Molecular weight:** The molecular weight of a compound is the sum of the atomic weights of atoms that constitute a molecule of the compound.

The molecular weight of a monatomic element (e.g. sodium) is its atomic weight and the molecular weight of a diatomic element (e.g. oxygen, chlorine) is twice that of its atomic weight.

3. **Gram atom:** It is used to specify the amount of chemical elements. It is defined as the mass in grams of an element which is numerically equal to its atomic weight.

$$\text{Gram atoms of an element} = \frac{\text{Weight in grams}}{\text{Atomic weight}}$$

4. **Gram mole:** It is used to specify the amounts of chemical compounds. It is defined as the mass in grams of a substance that is equal numerically to its molecular weight.

$$\therefore \text{Gram moles of compound } B = \frac{\text{Weight in grams of } B}{\text{Molecular weight of } B}$$

A gram mole of a substance is the mass in grams of the substance that is numerically equal to its molecular weight.

5. **Equivalent weight of an element or a compound** is defined as the ratio of the atomic weight or molecular weight to its valence. The valence of an element or a compound depends on the number of hydroxyl ions ( $\text{OH}^-$ ) donated or the hydrogen ions ( $\text{H}^+$ ) accepted for each atomic weight or molecular weight.

$$\therefore \text{Equivalent weight} = \frac{\text{Molecular Weight}}{\text{Valence}}$$

$$\text{Normality } (N) = \frac{\text{Gram equivalents of solute}}{\text{Volume of solution in litre}}$$

- 6. Molarity:** It is defined as the number of gram moles of solute dissolved in one litre of solution. It is designated by the symbol  $M$ .

$$\text{Molarity } (M) = \frac{\text{Gram moles of solute}}{\text{Volume of solution in litre}}$$

- 7. Molality:** It is defined as the number of gram-moles (mol) of solute dissolved in one kilogram of solvent.

$$\text{Molality} = \frac{\text{Gram moles of solute}}{\text{Mass of solvent in kg}}$$

$$\text{Weight of } A = \frac{\text{Weight of } A}{\text{Total weight of system}} \times 100 = \frac{W_A}{W} \times 100$$

$$W_A = \text{Weight of the component } A$$

$W = W_A + W_B$  = Weight of the system... for a binary system of  $A$  and  $B$ .

$$\begin{aligned} \therefore \text{Volume \% of } A &= \frac{\text{Volume of pure component } A}{\text{Total volume of system}} \times 100 \\ &= \frac{V_A}{V} \times 100 \end{aligned}$$

$$V_A = \text{Pure component volume of } A$$

$V$  = Total volume of the system  $V_A + V_B$  ... for a binary system of  $A$  and  $B$ .

$$\text{Mole \% of } A = \frac{\text{Moles of } A}{\text{Total moles of system}} \times 100 = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \times 100$$

where,  $M_A$  and  $M_B$  are the molecular weights of the components  $A$  and  $B$  respectively.

## Boyle's Law

Boyle's law state that the product of the pressure and volume for a gas is a constant for a fixed amount of gas at a fixed temperature. Written in mathematical terms, this law is,

$$P \propto \frac{1}{V}; P = \frac{C}{V}; PV = C$$

where,

$P$  = Absolute pressure

$C$  = Constant,  $V$  = Volume occupied by gas

## Charles' Law

Charles' law states that if a given quantity of gas is held at a constant pressure, its volume is directly proportional to the absolute temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

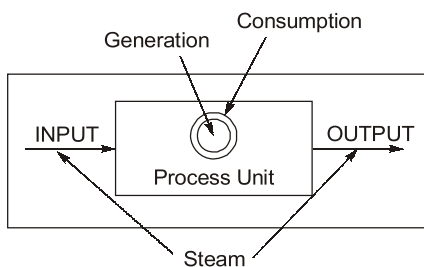
## V General Material Balance Equation

$$\left( \begin{array}{c} \text{Accumulation} \\ \text{within the} \\ \text{defined} \\ \text{system} \end{array} \right) = \left( \begin{array}{c} \text{Input} \\ \text{through} \\ \text{system} \\ \text{boundary} \end{array} \right) - \left( \begin{array}{c} \text{Output} \\ \text{through} \\ \text{system} \\ \text{boundary} \end{array} \right) + \left( \begin{array}{c} \text{Generation} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right) + \left( \begin{array}{c} \text{Consumption} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right)$$

Accumulation = (Input) – (Output) + (Generation) – (Consumption)

**Positive contributions to the system:** Input and Generation

**Negative contributions to the system:** Output and Consumption



## Material Balance Calculations

- **Without chemical reaction:**
  - Under steady state conditions,  
Input = output
  - Under unsteady state conditions  
Input = output + accumulation
- **Atom balances:** Input (of some species of atom) = output (of the some species of atom).
- The chemical reactions that take place in a process which are very complicated can be solved by atom balances without knowing the chemical reactions taking place in that.
- **Inert substance:** In most oxidation process air is used as the source of oxygen, and air is 79 mol percent nitrogen, an inert substance at the temperatures at which most substances are oxidized.

- **Tie substances:** Tie material is defined as a material, of necessarily inert or unreactive, which passes through a system from a single input stream to a single output stream and of course remains completely unchanged during this process.
- **Limiting reactant/component:** It is defined as the reactant that would disappear first if a reaction goes to completion.
- **Excess reactant:** It is defined as the reactant which is in excess of the theoretical or stoichiometric requirement at determined by the desired reaction.
- **Percent excess:** The excess reactant involved in the reaction is generally specified in terms of percent excess. It is the amount in excess of the stoichiometric (theoretical) requirement expressed as a percentage of the stoichiometric/theoretical requirement.

**Consider the Reaction:**



wherein  $B$  is the excess reactant. Then,

$\therefore$  Percent excess of  $B$ .

$$= \left[ \frac{\text{moles of } B \text{ supplied or fed} - \text{moles of } B \text{ theoretically required}}{\text{moles of } B \text{ theoretically required}} \right] \times 100$$

- **Conversion:** The conversion is always based on the limiting and it gives idea regarding to the degree of completion of a reaction.
- Selectivity is the ratio of the moles of a desired product to the moles of undesired or by product.
- Yield is defined on three basis:

$$(a) \text{ Yield (based on feed) } = \frac{\text{Amount of desired product}}{\text{Amount of key reactant consumed}}$$

(b) Yield (based on 100% conversion)

$$= \frac{\text{Amount of product obtained}}{\text{Amount of key reactant consumed}}$$

Key reactant is generally limiting reactant.

- If  $A$  is the limiting reactant, then
- Overall fractional conversion of  $A$

$$= \frac{A \text{ in fresh feed} - A \text{ in output of the overall process}}{A \text{ in fresh feed}}$$

% overall conversion of A = Overall fractional conversion of A  $\times$  100

Per pass fractional conversion of A

$$= \frac{A \text{ in exit stream from the reactor}}{A \text{ in feed to the reactor}}$$

• **Recycle:**

- Recycle is the operation or a process step whereby a part or fraction of the products from the reactor is returned and mixed with the incoming fresh feed to the reactor.
- Because of recycle, the overall conversion, which is based on the fresh feed, will be higher than the conversional per pass, which is based on the mixed feed to the reactor.
- The feed to the process itself is made up of two streams, the fresh feed and the recycled material. The gross product leaving the process is separated into two streams, the net product and the material to be recycled.

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

- **Purge stream:** A stream to be led off to remove an accumulation of inerts or unwanted material that might otherwise be in the recycle stream.

## VI General Energy Balance

$$\left( \begin{array}{c} \text{Accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right) = \left( \begin{array}{c} \text{Energy} \\ \text{flow} \\ \text{into the} \\ \text{system} \end{array} \right) - \left( \begin{array}{c} \text{Energy} \\ \text{flow} \\ \text{out of the} \\ \text{system} \end{array} \right) + \left( \begin{array}{c} \text{Energy} \\ \text{generated} \\ \text{in the} \\ \text{system} \end{array} \right) + \left( \begin{array}{c} \text{Energy} \\ \text{consumed} \\ \text{in the} \\ \text{system} \end{array} \right)$$

In simplified terms it can be written as

$$\Delta E_{\text{inside (accumulation)}} = D(U + K.E. + P.E)_{\text{inside}} = \underset{\text{Heat transfer}}{Q} + \underset{\text{Work}}{W}$$

**Heat capacity:** Heat capacity of any substance is defined as the heat required to raise the temperature of 1 kg of the substance 1°C. It is defined on a unit mole basis which is called molal (or molar) heat capacity.

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v$$

For a constant pressure process,

$$C_p = \left( \frac{\partial Q}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

## Standard Heat of Reaction

For the chemical reaction:  $aA + bB \longrightarrow cC + dD$

the standard heat of reaction is defined as the enthalpy change when  $a$  moles of  $A$  and  $b$  moles of  $B$  in their standard states at temperature  $T$  react to form  $c$  moles of  $C$  and  $d$  moles of  $D$  in their standard states at the same temperature  $T$ .

The standard heat of reaction  $\Delta H_R^0$  is defined as  $\Delta H_R^0 = \text{Enthalpy of products} - \text{enthalpy of reactants}$

$$= c\Delta H_{fC}^0 + d\Delta H_{fD}^0 - a\Delta H_{fA}^0 - b\Delta H_{fB}^0$$

where  $\Delta H_{fi}^0$  is the standard heat of formation of the  $i$ th component.

## Mean Molal Heat Capacities of Gases

To calculate the heat change during heating or cooling a gas between two temperatures, it is convenient to use mean molal heat capacity data. Assume any arbitrary base temperature  $T_0$  (in K) and if  $T$  and  $T_0$  are the two temperatures between which a heat change is desired then

$C_{pm}^0$  (mean molal heat capacity) is given as

$$C_{pm}^0 = \frac{\int_{T_0}^T C_p^0 dT}{(T - T_0)}$$

## VII Combustion

Combustion is an unit process in which oxidation reactions (Union of carbon, hydrogen and sulphur with oxygen) take place. If the products of combustion of carbon, hydrogen and sulphur are carbon dioxide, water and sulphur dioxide, the combustion is termed as complete. If carbon monoxide appears in the product gases, the combustion is called incomplete combustion because CO can further combine with oxygen to produce  $\text{CO}_2$ .

### Heat of Formation

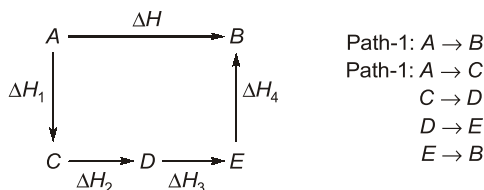
- When 1 mole of a substance is formed from its constituent elements, then heat is either evolved or released. The enthalpy change occurring in this process is called heat of formation.

- If formation of substance takes place at standard state, then heat of formation is called standard heat of formation.
- The enthalpy of formation of the element is taken as zero.

### Hess's Law of Constant Heat Summation

- It states that the enthalpy change (i.e., heat evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one or in several steps (i.e., in a series of steps).

For example,



According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

The temperature attained when a fuel is burned in air or oxygen under adiabatic conditions (i.e., without loss or gain of heat from the outside source) is called the adiabatic flame temperature or the theoretical flame temperature.

1. **Latent heat of vaporization:** It is the heat required to vaporize a unit amount of liquid at constant temperature and pressure or it is the heat removed to condense a unit amount of vapour into liquid at constant temperature and pressure. The condensation is a reverse of vaporization and hence, latent heat of condensation must be the negative of the latent heat of vaporization.
2. **Latent heat of fusion:** It is the heat required to melt a unit amount of solid to liquid or removed to convert a unit amount of liquid into solid at constant temperature and pressure.
3. **Latent heat of sublimation:** It is the heat required to vaporize a unit amount of solid at constant temperature and pressure.

### Calorific Values of Fuels

- When a unit mass of fuel is completely burnt with pure oxygen then total heat produced is called calorific or heating value.
- So when fuel calorific value is determined by considering that the water in vapour form is present then it is called net calorific value (NCV).