

A Handbook on

Chemical Engineering

Contains well illustrated formulae
& theory key concepts

~~~~~ *For* ~~~~~

# GATE, PSUs

& OTHER COMPETITIVE EXAMS





## **MADE EASY Publications Pvt. Ltd.**

**Corporate Office:** 44-A/4, Kalu Sarai (Near Hauz Khas Metro Station), New Delhi-110016

**Contact:** 9021300500

**E-mail:** infomep@madeeasy.in

**Visit us at:** [www.madeeasypublications.org](http://www.madeeasypublications.org)

## **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,

(Mass in) + (Mass generated) = (Mass out) + (Mass consumed) + 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.
- This the required purge rate can be determined from the following relationship.

$$\begin{aligned} & (\text{Flow rate of feed stream}) \times (\text{Concentration of inert in feed stream}) \\ & = (\text{Flow rate of purge stream}) \times (\text{Desired concentration of inert in} \\ & \text{recycle stream}) \end{aligned}$$

#### By Pass

- Flow stream may be divided and some part diverted around some units. This procedure often used to control stream composition or temperature.
- Material balance calculations 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 (OH<sup>-</sup>) donated or the hydrogen ions (H<sup>+</sup>) accepted for each atomic weight or molecular weight.

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

## I System and Surroundings

- A thermodynamic system is defined as a quantity of matter area region in space upon which our attention is concentrated in the analysis of a problem. The mass or region outside the system is called the surroundings. The real or imaginary surface that separates the system from its surroundings is called a boundary.
- The boundary of a system can be fixed or movable. Boundary is the contact surface shared by both the system and surroundings. Mathematically the boundary has zero thickness and it can neither contain any mass nor occupy any volume in space.

### Types of Thermodynamic System

| Types of system              | Mass Transfer | Energy Transfer | Example                        |
|------------------------------|---------------|-----------------|--------------------------------|
| Closed system (control mass) | No            | Yes             | Piston cylinder without valves |
| Open system (control volume) | Yes           | Yes             | Pump, compressor               |
| Isolated system              | No            | No              | Universe                       |

**Property:** Any characteristic of a system is called a property.

**Intensive properties:** Intensive properties are those which are independent of the size of the system.

**Example:** Chemical - Potential, Temperature Rate of reaction, etc.

**Extensive Properties:** Extensive properties are those whose value depends on the size or extent of the system. The properties which are dependent on the mass of the system under consideration.

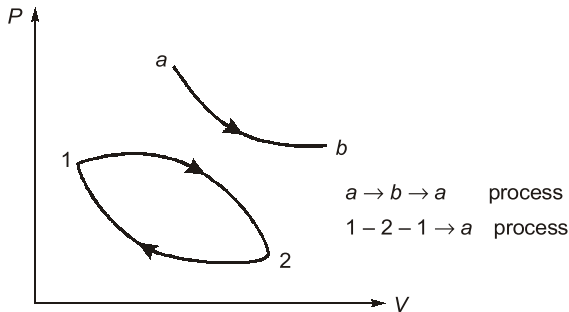
**Example:** Total volume, energy etc.

- Extensive properties per unit mass are called specific properties. All specific properties are intensive properties.

**Example:** Specific volume, specific heat, specific internal energy etc.

**Process:** The path of the succession of states through which the system passes is called the process.

- A change in state is called process:
- **Thermodynamic cycle:** A thermodynamic cycle is defined as a series of state changes such that the final state is identical with the initial state.



## II Reversible and Irreversible Process

- A process is said to be reversible if it can be reversed in direction following the same path as that of the forward process without leaving any change in the system as well as the surroundings otherwise the process is said to be irreversible.
- Reversible process yields the maximum amount of work.
- **Quasi-static /quasi-equilibrium process:** When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasi static process.
- All reversible process are quasistatic but all quasistatic process might not be reversible.

## Internally Reversible Process

- If only the reversibility of the system is considered not external surroundings then the process is called internal reversible i.e. the system is reversible but not the surroundings.

## III Thermodynamic Equilibrium

- Body is said to be in thermodynamic equilibrium if it is in.
- Thermal equilibrium-equality of temperature.

- Mechanical equilibrium-equality of forces.
- Chemical equilibrium-equality of chemical potentials.
- If there is no chemical reaction or transfer of matter from one part of the system to another such as diffusion the system is said to exist in state of chemical equilibrium.
- Properties are point function and are exact or perfect differentials. For a cycle change in property is zero.

## The State Postulate

The state of a simple compressible system is completely specified by two independent intensive properties.

## IV Path and Point Functions

- Path function are those functions which depend on the path while point function are independent of path and only depends on the initial and final states.
- Path dependent functions are represented by inexact differentials while point functions are represented by exact differentials.
- For a cyclic process the initial and final states of the system are the same and hence. The change in any property is zero.

## V Degree of Freedom

- It is the number of independent intensive variables that must be fixed to define the equilibrium state of the system.

$$F = C - P + 2$$

Here,  $P$  = Number of phases present in equilibrium

$C$  = Number of chemical components

$F$  = Degree of freedom

For azeotropes

$$F = (C - P + 2) - 1$$

- Temperature is a thermodynamic property that determines whether or not a system is in thermal equilibrium with other systems.

## VI Zeroth Law Thermodynamics

- When two bodies are in thermal equilibrium with a third one then they are in thermal equilibrium with each other. Zeroth law of thermodynamics is the basis of temperature measurement.

## VII Energy and Energy Interactions

- Energy is a fundamental concept. It has been as the capability to produce effect. Energy can be stored within a system and can be transferred from one system to another.
- The energy having the system as a whole with respect to an external reference frame constitute macroscopic forms of energy such as kinetic and potential energies.
- The energy having the system with respect to molecular structure and molecular level interactions constitute microscopic forms of energy. The sum of all microscopic forms of energy of a system is called internal energy. Energy interactions for a closed system with its surroundings can take place in two ways: (i) By work transfer (ii) By heat transfer

**Heat:** Heat is defined as the form of energy that's transferred between two systems by virtue of temperature difference. That is an energy interaction is heat only if it takes place because of temperature difference

### Sign Convention

- Heat given to the system is taken as positive and heat rejected by the system taken as negative.
- Heat is a work function so is inexact or imperfect differential.

### Specific Heat

- The specific heat of a substance is the amount of energy required to change the temperature of unit mass of the substance by unity.

$$Q = mc \Delta T$$

There,

$$Q = \text{Heat}$$

$$m = \text{Mass}$$

$$C = \text{Specific heat}$$

$$T = \text{Temperature difference}$$

- For gases specific heat depends on the process followed by the system. If the process is at constant pressure it's called  $C_p$  and if the process is at constant volume it's called  $C_v$ .

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v, \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

$$\gamma = \frac{C_p}{C_v}$$

where,

$\gamma$  = Specific heat ratio

$c_p$  = Specific heat at constant pressure

$c_v$  = Specific heat at constant volume

For air:

$$\gamma = 1.4$$

$$c_p = 1.005 \text{ KJ/kg-k}$$

$$c_v = 0.718 \text{ KJ/kg-k}$$

$$R = 0.287 \text{ KJ/kg-k}$$

- For ideal gases, the internal energy and enthalpy are the functions of temperature only and therefore in the heat capacity definitions the partial differentials are replaced by full differentials. For ideal gases the molar capacities are expressed in polynomial forms.

$$C_p^0 = \frac{dH}{dT}, \quad C_v^0 = \frac{dU}{dT}$$

$$C_p^0 - C_v^0 = R, \quad C_v^0 = \frac{R}{\gamma - 1}$$

$$C_p^0 = \frac{\gamma R}{\gamma - 1}$$

- $C_p^0$  and  $C_v^0$  are not constants but vary with temperature. The product of mass and specific heat is called the specific heat of the substance.

## Latent Heat

- Latent heat is the amount of heat transfer required to cause a phase change in unit mass of substance at constant  $P$  and  $T$ .
- The latent heat of fusion is the amount of heat transferred to melt a unit mass of solid into liquid at constant  $T$  and  $P$ .

$$Q_F = mL_F \text{ where } L_F = \text{Latent heat of fusion}$$

The latent heat of vaporization is the amount of heat transferred to vaporize a unit mass of liquid into vapor at constant  $P$  and  $T$ .

$$Q_v = mL_v$$

where,  $L_v =$  Latent heat of vaporization

### Energy Transfer by Work

- Work is an energy interaction between a system and its surroundings. If the energy crossing the boundary of a closed system is not heat it must be work.
- An energy interaction that is not caused by temperature difference between a system and its surroundings is work.

### Sign Convention

- Work done by the system is taken as positive and work done on the system is taken as negative.
- Work is a path function and an inexact differential.

#### Similarly between heat and work:

- Both are boundary phenomena.
- Both are associated with a process not a state.
- Both are path functions.

## VIII Displacement Work

Quasistatic process work done is calculated by  $= \int P dv$

Condition for applying above equation:

- System must be closed system.
- Process must be reversible process.
- Work should cross the boundary.

Work is done by a system to overcome some resistance, since vacuum doesn't offer any resistance there's no work transfer involves in free expansion. The closed system work is obtain by plotting it on volume axis and open system work is obtain by plotting it on pressure axis.

### Representation of various process on $P$ - $V$ diagram and work exchange for an ideal gas

We have general equation  $PV^k = \text{Constant}$