

# Thermodynamics

**System** The part of the universe selected for thermodynamic study.

**Surroundings** The remaining part of the universe around the system which is not under study.

**Isolated System** A system which can neither exchange energy nor matter with the surroundings is called an isolated system.

**Closed System** A System which can exchange energy but not matter with the surroundings is called a closed system.

**Open System** A system which can exchange matter as well as energy with the surroundings is called an open system.

**Macroscopic Properties** The properties of the system which depend on the bulk of the matter are called macroscopic properties. They are classified into two Intensive properties and extensive properties.

**Intensive Properties** Those properties of the system which are independent of the amount of substance present are called intensive properties. E.g. temperature, pressure, viscosity, surface tension, density, dielectric constant, specific heat capacity, refractive index, etc.

**Extensive properties** Are those properties that depend on the amount of substance present in the system. E.g. Volume, Mass, Internal energy, Enthalpy, Entropy, Gibbs Free Energy etc.

**State variables** The measurable properties required to describe the state of the system are called state variables.

**State function** It is a property of a system whose value depends only upon the state of the system and is independent of the path or manner by which the state is reached.

**Isothermal process** A process in which the temperature of the system remains constant.

**Adiabatic process** It is defined as a process in which no heat enters or leaves the system during any step of the process.

**Isobaric process** A process in which the pressure of the system remains constant.

**Isochoric process** A process in which the volume of the system remains constant.

**Reversible process** A process is said to be reversible if it is carried out infinitely slowly so that the driving force is only slightly greater than the opposing force.

**Irreversible process** A process is said to be irreversible if it is not carried out infinitely slowly so that the system does not get a chance to attain equilibrium.

An irreversible equilibrium cannot be reversed without the help of an external agency and without changing the properties of the surroundings.

**Cyclic process** A process in which the system undergoes a series of changes and ultimately returns to its original state.

## First Law of thermodynamics.

Energy can neither be created nor destroyed, it may be converted from one form to another.

Or

In a physical or chemical process, the energy of the system and surroundings taken together remains constant.

Or

Energy of the universe is always conserved.

## Internal Energy

It can be defined as the total intrinsic energy possessed by a system under a given set of conditions.

Change in internal energy at constant volume

$$E_2 = E_1 + q_v - w$$

$$E_2 - E_1 = q_v - w$$

$$\Delta E = E_2 - E_1$$

$$\Delta E = q_v - w$$

$q_v$  = heat change at constant volume and  $-w$  is the work done by the system.

## Enthalpy

It can be defined as the sum of internal energy (E) and the product of pressure and volume (PV).

It is change in internal energy at constant pressure.

$$\Delta E = q_p - w$$

At constant pressure the work done by the system is work due to expansion.

$$w = P(V_2 - V_1)$$

$$w = P\Delta V$$

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

$q_p$  = heat change at constant pressure or Enthalpy

$$q_p = \Delta H$$

$$\Delta H = \Delta E + P\Delta V$$

For an ideal gas  $P\Delta V = \Delta n RT$ ,

$$\Delta H = \Delta E + \Delta n_g RT$$

Where  $\Delta n_g$  is number of moles of the gaseous products minus number of moles of the gaseous reactants. R is the universal gas constant

When does enthalpy of a reaction becomes equal to the internal energy?

- 1) When the reactants and products are solids or liquids.
- 2) When the number of moles of the gaseous reactants is equal to the number of moles of the gaseous products.
- 3) When the reaction occurs at constant volume or  $P\Delta V = 0$ .

Problems.

**Enthalpy of Reaction  $\Delta H$**  The total amount of heat energy evolved or absorbed, when the number of moles of the reactants react completely to give the products as given in a balanced chemical equation.

$$\Delta H_r^\circ = \sum H_p^\circ - \sum H_r^\circ$$

**Enthalpy of Formation  $\Delta H_f$**  It is defined as the enthalpy change when one mole of a substance is formed from its elements.

**Standard Enthalpy of Formation  $\Delta H_f^\circ$**  It is defined as the enthalpy change when one mole of a substance is formed from its elements in the standard state i.e. one atmosphere pressure and 298K.

**Enthalpy of Neutralisation** It is defined as the enthalpy change when one gram equivalent of an acid is neutralised by a base or vice versa in dilute solution.

**Enthalpy of Combustion** The enthalpy change when one mole of a substance undergoes complete combustion.

**Calorific value of fuels** The amount of heat energy released by the complete combustion of one gram of the fuel.

**Enthalpy of Fusion** Defined as the change in enthalpy which takes place when one mole of a solid substance is converted into its liquid state at its melting point.

**Enthalpy of Vaporisation** Defined as the enthalpy change when one mole of a liquid is converted into its vapours at its boiling point.

**Enthalpy of Sublimation** The enthalpy change when one mole of a solid changes directly into its vapours at a temperature below its melting point.

**Application of First law**

1. Determination of enthalpies of reaction. It can be determined using **Hess's Law** of Constant heat summation which states that **The enthalpy change for a chemical reaction remains the same whether the reaction takes place in one step or in several steps.**
2. Determination of enthalpies of reaction from bond dissociation energies.

**Second Law of Thermodynamics.**

1. It is impossible to construct a machine, which is able to convey heat by a cyclic process, from one reservoir at a lower temperature to another at a higher temperature, unless work is done on the machine by the outside agency.
2. The entropy of the universe always increases in the course of every spontaneous (natural) change.
3. The energy of the universe is conserved whereas the entropy of the universe always increases in any natural process.

Need for the Second Law: The first law is incapable of predicting the feasibility of a reaction hence the need for the second law.

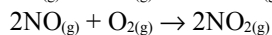
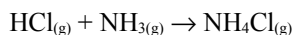
**Important features of the Second Law:**

- It helps in determining the direction in which energy can be transformed.
- It helps to predict whether a given process or chemical reaction can occur Spontaneously.
- It helps to know the equilibrium Condition.
- It helps in finding the maximum fraction of heat that can be converted into work.

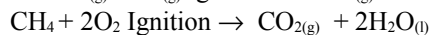
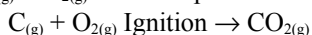
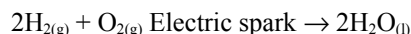
**Spontaneous Change** A process which can take place by itself without the assistance of an external agency under the given set of conditions is called a spontaneous process.

The term spontaneous also means feasible or probable process.

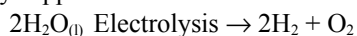
**Examples of Spontaneous processes**



Spontaneous processes which require some initiation.



**Non-Spontaneous process** is one which has no tendency to occur or that which is forbidden and is made to occur only if energy from outside is continuously supplied.



**Entropy**

It is the property of a system which measures the degree of disorder or randomness in the system.

$$\Delta S = \int C_p/T$$

$$\Delta S = S_{(\text{products})} - S_{(\text{reactants})}$$

For a reversible process at equilibrium the change in entropy can be expressed as.

$$\Delta S = q_{\text{rev}}/T$$

Units of entropy: Joules per Kelvin ( $\text{JK}^{-1}$ ) or calories per degree.

Characteristics of entropy

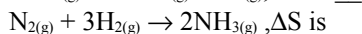
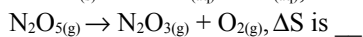
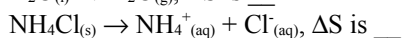
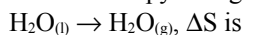
- It is an extensive property
- It is a state function  $\therefore$  depends on T,P,V& n change in entropy  $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- The total entropy change of an isolated system is equal to the entropy change of the system and surroundings  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ .
- For a reversible process  $\Delta S_{\text{universe}} = 0$  or  $\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$
- For an irreversible process  $\Delta S_{\text{universe}} > 0$  i.e. there is increase in entropy for every spontaneous change.

### When can there be entropy change?

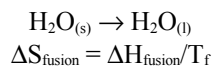
- When the number of moles of the reactants or products increase or decrease
- When there is change of state viz. Solid to liquid. Liquid to vapour. Solid to vapour or vice versa.
- When there is change in temperature.

When entropy increases  $\Delta S$  is +ve

Predict entropy changes for the following reactions.



**Entropy of fusion** Can be defined as the entropy change when one mole of the solid substance changes into liquid form at its melting point.



**Entropy of Vaporisation** Can be defined as the entropy change when one mole of the liquid changes into vapour at its boiling point.

$$\Delta S_{\text{vaporisation}} = \Delta H_{\text{vaporisation}}/T_b$$

**Gibbs Free Energy** The free energy of a system is defined as the maximum amount of energy available to a system that can be converted into useful work

Free energy can also be defined as the capacity of a system to do useful work.

$$G = H - TS$$

$$\Delta G_{T,P} = \Delta H - T\Delta S$$

The above equation is also known as Gibbs Helmholtz equation and  $\Delta G$  is referred to as the Change in free energy.

$$\Delta G_{T,P} = \Delta H - T\Delta S$$

$$- = (-) - (+)$$

Thus the condition for spontaneity is that  $\Delta G$  Should be -ve

Conclusion

$\Delta G = -ve$ , The reaction is Spontaneous

$\Delta G = +ve$ , The reaction is Non-Spontaneous

$\Delta G = 0$ , The reaction is in Equilibrium

Since non-expansion work serves some useful purpose the decrease in free energy of a system during a process is a measure of useful done during the change.

The free energy  $-\Delta G$  of a system is a measure of its capacity to do useful work.

Free energy and Equilibrium Constant