

- **System:** Specific part of universe in which observations are made.
- **Surroundings:** Everything which surrounds the system.
- **Types of the System:**
  - Open System:** Exchange both matter and energy with the surroundings.  
For example – Reactant in an open test tube.
  - Closed System:** Exchange energy but not matter with the surroundings.  
For example – Reactants in a closed vessel.
  - Isolated System:** Neither exchange energy nor matter with the surroundings.  
For example – Reactants in a thermos flask.
- **Thermodynamic Processes:**
  - (i) Isothermal Process:  $\Delta T = 0$
  - (ii) Adiabatic process:  $\Delta q = 0$
  - (iii) Isobaric process:  $\Delta P = 0$
  - (iv) Isochoric process:  $\Delta V = 0$
  - (v) Cyclic process:  $\Delta U = 0$
  - (vi) Reversible process: Process which proceeds infinitely slowly by a series of equilibrium steps.
  - (vii) Irreversible process: Process which proceeds rapidly and the system does not have chance to achieve equilibrium.
- **Extensive Properties:** Properties which depend upon the quantity or size of matter present in the system. For example – mass, volume, internal energy, enthalpy, heat capacity, work etc.

- **Intensive Properties:** Properties which do not depend upon the quantity or size of matter present in the system. For example – temperature, density, pressure, surface tension, viscosity, refractive index, boiling point, melting point etc.

## Thermodynamics Class 12 Key Points

- **State Functions:** The variables of functions whose value depend only on the state of a system or they are path independent.  
For example – pressure (P), volume (V), temperature (T), enthalpy (H), free energy (G), internal energy (U), entropy (S), amount (n) etc.
- **Internal Energy:** It is the sum of all kind of energies possessed by the system.
- First Law of Thermodynamics: “The energy of an isolated system is constant.”

Mathematical Form:  $\Delta U = q + w$

- **Sign Conventions for Heat (q) and Work (w):**

- (i)  $W = +$  ve , if work is done on system
- (ii)  $W = -$  ve , if work is done by system
- (iii)  $q = +$  ve , if heat is absorbed by the system
- (iv)  $q = -$  ve , if heat is evolved by the system

- **Work of Expansion/ compression:**  $\omega = -P_{ext} (V_f - V_i)$

- **Work done in Isothermal Reversible Expansion of an Ideal Gas:**

$$\omega_{rev} = -2.303 nRT \log V_f / V_i$$

$$\text{or } \omega_{rev} = -2.303 nRT \log P_i / P_f$$

- **Significance of  $\Delta H$  &  $\Delta U$ :**  $\Delta H = q_p$  and  $\Delta U = q_v$

- **Relation between  $\Delta H$  &  $\Delta U$ :**  $\Delta H = \Delta U + (n_p - n_v)RT$  for gaseous reaction

- (i)  $\Delta H = \Delta U$  if  $(n_p - n_v)$  is zero; e.g.  $H_2(g) + I_2(g) \longrightarrow 2 HI(g)$
- (ii)  $\Delta H > \Delta U$  if  $(n_p - n_v)$  is positive; e.g.  $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$
- (iii)  $\Delta H < \Delta U$  if  $(n_p - n_v)$  is negative; e.g.  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

- **Heat Capacity (C):** Amount of heat required to raise the temperature of a substance by  $1^\circ C$  or 1 K.

$$q = C \Delta T$$

### Types of Heat Capacities

$C_v$  – heat capacity at constant volume

$C_p$  – heat capacity at constant pressure

### For an ideal gas

$$C_v = \frac{dU}{dT} \text{ and } C_p = \frac{dH}{dT}$$

$$C_p - C_v = R \quad (\text{for 1 mole of an ideal gas})$$

### For $n$ moles

$$C_p - C_v = nR$$

- **Specific Heat Capacity ( $C_s$ ):** Amount of heat required to raise the temperature of 1 g of a substance by 1°C or 1 K.

$$q = C_s \times m \times \Delta T$$

- **Molar Heat Capacity ( $C_m$ ):** Amount of heat required to raise the temperature of 1 mole of a substance by 1°C or 1 K.

$$q = C_m \times n \times \Delta T$$

- **Standard State of a Substance:** The standard state of a substance at a specified temperature is its pure form at 1 bar.

- **Standard Enthalpy of Formation ( $\Delta_f H^\circ$ ):** Enthalpy change accompanying the formation of one mole of a substance from its constituent elements under standard condition of temperature (normally 298 K) and pressure (1 bar).

- $\Delta_f H^\circ$  of an element in standard state is taken as zero.
- Compounds with –ve value of  $\Delta_f H^\circ$  more stable than their constituents.
- $\Delta_f H^\circ = \sum a_i \Delta_f H^\circ (\text{products}) - \sum b_i \Delta_f H^\circ (\text{reactants})$ ; Where 'a' and 'b' are coefficients of products and reactants in balanced equation.

- **Standard Enthalpy of Combustion ( $\Delta_c H^\circ$ ):** Enthalpy change accompanying the complete combustion of one mole of a substance under standard conditions (298 K, 1 bar)

- **Hess's Law of Constant Heat Summation:** The total enthalpy change of a reaction remains same whether it takes place in one step or in several steps.

- **Bond Dissociation Enthalpy:** Enthalpy change when one mole of a gaseous covalent bond is broken to form products in gas phase.

For example,  $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g})$ ;  $\Delta_{\text{Cl-Cl}} H^\circ = 242 \text{ kJ mol}^{-1}$

- For diatomic gaseous molecules; Bond enthalpy = Bond dissociation Enthalpy = Atomization Enthalpy
- For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.
- $\Delta_f H^\circ = \sum \Delta_{\text{bond}} H^\circ (\text{Reactants}) - \sum \Delta_{\text{bond}} H^\circ (\text{Products})$

- **Spontaneous Reaction:** A reaction which can take place either on its own or under some initiation.

- **Entropy (S):** It is a measure of degree of randomness or disorder of a system.

- $$\Delta S_{sys} = \frac{(q_{rev})_{sys}}{\Delta T} = \frac{\Delta H_{sys}}{\Delta T}$$

- Unit of Entropy =  $\text{JK}^{-1} \text{ mol}^{-1}$

- **Second Law of Thermodynamics:** For all the spontaneous processes totally entropy change must be positive.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

- **Gibbs Helmholtz Equation for determination of Spontaneity:**

$$\Delta G = \Delta H - T\Delta S$$

- If  $\Delta G = -ve$ , the process is spontaneous
- If  $\Delta G = +ve$ , the process is non-spontaneous
- If  $\Delta G = 0$ , the process is in equilibrium

- **Relation between Gibbs Energy Change and Equilibrium Constant:**

$$\Delta G^\circ = -2.303 RT \log K_c$$

- **Third Law of Thermodynamics:** The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

### Standard Conditions

Pressure = 1 bar, Temperature = any specified temperature

- o - Standard conditions are denoted by adding the superscript O or Θ to the symbol. e.g.  $\Delta H^\circ$  /  $\Delta H^\Theta$

### - Standard enthalpy of a reaction $\Delta_r H^\Theta$ :

The enthalpy change accompanying the reaction when all the reactants and products are taken in their standard states (1 bar pressure and at any specified temperature, generally 298 K).

Depending upon the nature of the reaction, enthalpy of the reaction is named accordingly.

### - Enthalpy of combustion, $\Delta_c H$ :

the enthalpy change when one mole of a substance is burnt completely in excess of oxygen.

### - Enthalpy of formation $\Delta_f H$ :

the enthalpy change when one mole of a substance is formed from its elements under given conditions of temperature and pressure.

### - Enthalpy of neutralization $\Delta_{neut} H$ :

the enthalpy change when one gram equivalent of the acid is neutralized by a strong base.

### - Enthalpy of solution $\Delta_{sol} H$ :

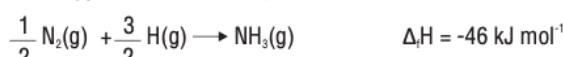
the enthalpy change when one mole of the substance is dissolved in a specified amount of the solvent.

The standard enthalpy of formation of  $\text{NH}_3$  is  $-46.0 \text{ kJ mol}^{-1}$ . If the enthalpy of formation of  $\text{H}_2$  from its atoms is  $-436 \text{ kJ mol}^{-1}$  and that of  $\text{N}_2$  is  $-712 \text{ kJ mol}^{-1}$ , the average bond enthalpy of N-H bond in  $\text{NH}_3$  is

a)  $-1102 \text{ kJ mol}^{-1}$       b)  $-964 \text{ kJ mol}^{-1}$   
 c)  $+352 \text{ kJ mol}^{-1}$       d)  $1056 \text{ kJ mol}^{-1}$

Solution : c

Enthalpy of formation of  $\text{NH}_3 = -46 \text{ kJ mol}^{-1}$



$$\Delta_f H = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}}$$

$$\Delta_f H = \frac{1}{2} \text{B.E.}(\text{N}_2) + \frac{3}{2} \text{B.E.}(\text{H}_2) - \text{B.E.}(\text{NH}_3)$$

$$-46 = \frac{1}{2} \times 712 + \frac{3}{2} \times 436 - 3(\text{N-H})$$

$$\text{B.E.}(\text{N-H}) = +352 \text{ kJ mol}^{-1}$$

\* There are 3 N-H bonds in  $\text{NH}_3$ , so average bond enthalpy will be (B.E. of  $\text{NH}_3$ )/3.