Chapter 6
Thermodynamics

Some Important Points and Terms of the Chapter

1. **System and the Surroundings**: A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The wall that separates the system from the surroundings is called **boundary**

2. **Types of the System:**
   - **Open System:** In an open system, there is exchange of energy and matter between system and surroundings.
   - **Closed System** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
   - **Isolated system** :In an isolated system, there is no exchange of energy or matter between the system and the surroundings

3. **State of a System**: The state of a system means the condition of the system which is described in terms of certain observable properties such as temp(T), pressure(p), volume (v), etc. of the systems. These properties of a system are called state variables.

4. **State Functions**: A physical quantity is solid to be state functions of its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.

5. **Internal Energy:** a quantity which represents the total energy of the system. It may be chemical, electrical and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system.

6. **Isothermal Process**: When a process is carried out in such a manner that the temp remains constant throughout this process, it is called an isothermal process.

7. **Adiabatic Process:** Process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa.

8. **Isochoric Process:** Process during which the volume of the system is kept constant.

9. **Isobaric Process:** Process during which the pressure of the system is kept constant. .

10. The positive sign expresses that Work (w_{ad}) is positive when work is done **on** the system. Similarly, if the work is done **by** the system, wad will be negative.

11. The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

12. **First law of Thermodynamics**: Statement: Energy can neither be created nor destroyed, however it may be converted from one form to another.

<u>or</u>

The total energy of the universe remains constant although it may undergo transformation from one to another.

Mathematical expression = $\Delta U = q + w$

13. A process or change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A **reversible process** proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as **irreversible processes**.

14. <u>**Difference between Reversible Process & Irreversible Process**</u>

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly	1. It is carried out rapidly
2. At any stage, the equilibrium is not disturbed	2. Equilibrium may exist only after the completion of the process.
3. It takes infinite time for completion.	3. It takes a finite time for completion.
4. Work obtained in this process is maximum.	4. Work obtained in this process is not maximum

15. **Enthalpy, *H***: The enthalpy *H* [Greek word *enthalpien*, heat content] is defined as : $H = U + pV$ For finite changes at constant pressure, we can write above equation as $\Delta H = \Delta U + \Delta pV$ Since *p* is constant, we can write $\boxed{\Delta H = \Delta U + p\Delta V}$ *since* $p\Delta V = \Delta n_g RT$,therefore $\boxed{\Delta H = \Delta U + \Delta n_g RT}$

16. **Extensive property**: An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

17. **Intensive property**: Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

18. **Specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, *q*, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as $q = c \times m \times \Delta T = C \Delta T$.

19. **Relationship between Cp and C$_V$ for an ideal gas:** $\boxed{C_p - C_V = R}$

20. **Bomb calorimeter:** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter . Here, a steel vessel (the bomb)

is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to qV, by using the known heat capacity of the calorimeter with the help of equation (18).

21. **Enthalpy Change of a reaction**: The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$.

    $\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants).

    $$\boxed{\Delta_r H = \sum a_i \, H_{Products} - \sum b_i \, H_{Reactants}}$$

22. The **standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar. Standard conditions are denoted by adding the superscript ^{o} to the symbol ΔH, e.g., ΔH^o

23. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called **standard enthalpy of fusion or molar enthalpy of fusion**, $\Delta_{fus} H^o$. e.g. $H_2O(s) \rightarrow H_2O(l); \Delta_{fus} H^0 = 6.00$ kJ mol^{-1} .

24. Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its **standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap} H^0$**. e.g. $H_2O(l) \rightarrow H_2O(g); \Delta_{vap} H^0 = 40.79$ kJ mol^{-1}

25. **Standard enthalpy of sublimation,** $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar). Sublimation is direct conversion of a solid into its vapour. Solid CO_2 (dry ice) sublimes at 195K with $\Delta_{sub}H^0=25.2$ kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H^0=73.0$ kJ mol^{-1}

26. .The **standard enthalpy change for the formation** of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^0$.

27. .Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

28. **Enthalpy of atomization (symbol: $\Delta_a H^0$):** It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen the enthalpy of atomization is also the bond dissociation enthalpy. In some cases, the enthalpy of atomization is same as the enthalpy of sublimation.

29. **Bond Enthalpy (symbol: $\Delta_{bond}H^0$):**

$$\Delta_r H = \sum bondenthapies_{reactants} - \sum bondenthapies_{products}$$

30. **Enthalpy of Solution (symbol : $\Delta_{sol}H^0$):** Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

31. **Lattice Enthalpy** The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.
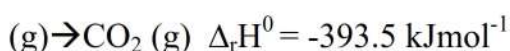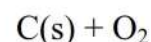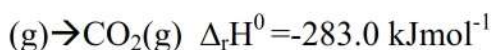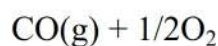
32. **Hess's Law**: Enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of: If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature. $\boxed{\Delta_r H^0}$

$\boxed{=\Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3}$ For example: $C(s) +$

$1/2 O_2 (g) \rightarrow CO(g)$ $\Delta_r H^0 = -110.5 \text{ kJmol}^{-1}$ $CO(g) + 1/2 O_2$

$(g) \rightarrow CO_2(g)$ $\Delta_r H^0 = -283.0 \text{ kJmol}^{-1}$ $C(s) + O_2$

$(g) \rightarrow CO_2 (g)$ $\Delta_r H^0 = -393.5 \text{ kJmol}^{-1}$

33. **Spontaneous Process**: A process which occurs by its ones i.e. Without the intervention of an outside agency.

34. **Non Spontaneous Process**: A process which can neither take place by itself nor by initiation is called a non spontaneous process.

35. Driving Force: The force which is responsible for spontaneity of a process is called the driving force.

36. Entropy(S): Entropy is a measure of randomness or disorder of the system.

37. Entropy change (ΔS): It is defined as the amount of heat (q) observed isothermally and reversibly divided by the absolute temp(T) at which the heat is absorbed.

$$\Delta S = \frac{q}{T}$$

38. Entropy of fusion : $\Delta S \text{ fusion} = \dfrac{\Delta H \text{ fusion}}{Tm}$

Where, ΔH fusion = Entropy of fusion per mole

T_m = Melting point

$$\Delta S_{VAP} = \frac{\Delta H_{VAP}}{T_b}$$

ΔH_{VAP} = Entropy of vaporization per mole

T_b = Boiling point

39. Second Law Of Thermodynamics

The entropy of universe is continuously increasing due to spontaneous process taking place in it.

ΔS system $+ \Delta S$ surrounding > 0

i.e. ΔS total > 0

40. <u>Gibbs Free Energy (G)</u> : It is defined as max^m amount of energy available to a system during the process that can be converted into useful work. It is a measure of capacity to do useful work.

$$\boxed{G = H - TS}$$ this equation is also known as Gibb's Helmholtz equation

G is a state function. ΔG is change in free energy.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

41. **If ΔG is negative, process is spontaneous** when $\Delta G = 0$, the process is in equilibrium if ΔG is positive, the process does not take place.

42. **Standard Free Energy Change (ΔG^0)** : It is defined as free energy change measured at 298 K and 1 atm Pressure.

43. **Standard Free energy of formation**: ($\Delta_f G^\circ$) It is free energy change when 1 mole of compound is formed from its constituting elements in their standard state.

$$\Delta_r G^\circ = \sum \upsilon_p \Delta_f G^\circ (\text{products}) - \sum \upsilon_R \Delta_f G^\circ (\text{reactants})$$

44. **Gibbs Energy Change and Work**

In case of galvanic cell, Gibbs energy change $\Delta_r G$, is related to the electrical work done by the cell.

Thus $$\boxed{\Delta_r G = -nFE_{cell}}$$

If reactants and products are in their standard states

$\Delta_r G^\circ = -nFE^\circ$ cell, Here E°_{cell} is the standard cell potential.

45. **Gibbs Energy Change and Equilibrium Constant**

$\Delta_r G^\circ = -RT \ln K$

$\Delta_r G^\circ = -2.303RT \log K$

Some Important Formulas(Thermodynamics)

- $\Delta U = q + w$

- $\Delta H = \Delta U + p\Delta V$

- $\Delta H = \Delta U + \Delta ng\mathrm{R}T$

- $\mathrm{Cp} - \mathrm{C_V} = \mathrm{R}$

- $\Delta_r H = \sum a_i\, \mathrm{H_{Products}} - \sum b_i\, \mathrm{H_{Reactants}}$

- $\Delta_r H = \sum bondenthapies_{reactants} - \sum bondenthapies_{products}$

- $.\Delta_r \mathrm{H}^0 = \Delta_r \mathrm{H}_1 + \Delta_r \mathrm{H}_2 + \Delta_r \mathrm{H}_3$

- $\Delta S\ \text{fusion} = \dfrac{\Delta H\ \text{fusion}}{\mathrm{Tm}}$

- $\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta \mathrm{S}$

- $\Delta_r \mathrm{G}^\circ = \sum \upsilon_p \Delta_f \mathrm{G}^\circ (\text{products}) - \sum \upsilon_R \Delta_f \mathrm{G}^\circ (\text{reactants})$

- $\Delta_r \mathrm{G} = -n\mathrm{FE_{cell}}$

- $\Delta_r \mathrm{G} = -2.303\mathrm{RT}\ \log \mathrm{K}$