THERMO CHEMISTRY

Some Basic Definitions

1. **Exothermic reaction:** The reaction in which heat is evolved, is called exothermic reaction.
2. **Endothermic reaction:** The reaction in which heat is absorbed, is called endothermic reaction.
3. **System:** It is that specified space of the universe which is under theromodynamic observation. It may be homogeneous or heterogeneous.
4. **Surroundings:** The remaining part of the universe that is outside the sytem, is called its surrounding. They are separated from each other by a real or imaginary boundary.

5. **State variables or state functions:** It is a measurable physical property of the system whose value depends only upon the state of the sytem and not upon the path followed to attain this state. Some common state functions are: pressure (P), volume (V), temperature (T), internal energy (E), entropy (S), enthalpy (H) and free energy (G). Out of these function, **two state functions are sufficient to describe the state of any thermodynamic system.**
6. **Isothermal process:** A process during which the temperature of the system remains constant, is known as isothermal process.
7. **Adiabatic process:** A process during which the total quantity of heat of the sytem remains constant i.e., the heat is not allowed to enter or leave the system, is known as adiabatic process.

8. **Isochoric process:** A process during which the volume of the system remains constant, is known as isochoric process.
9. **Isobaric process:** A process during which the pressure of the system remains constant, is known as isobaric process.
10. **Irreversible process:** A process in which the direction of the process can not be reversed, is known as irreversible process.
11. **Reversible process:** A process in which direction of the process can be reversed by an infinitesimally small change in the state of the system, is known as reversible process.
12. **Cyclic process:** A process in which a system after undergoing a number of changes returns back to its original state, is known as cyclic process.

First Law of Thermodynamics

It states that, energy can neither be created nor destroyed but can be transformed from one form to another form. The total energy of an isolated system remains constant. Mathematically,

$$\Delta E = Q + W \qquad \ldots(i)$$

Where ΔE = change in internal energy

Q = heat given to the system

W = work done on the system

But $W = -P.\ \Delta V$

So, $\Delta E = Q - P.\ \Delta V$ ...(*ii*)

$\Rightarrow$ $Q = \Delta E + P.\Delta V$

At constant volume, $\Delta V = 0$. So, $Q = \Delta E$

Hence, at constant volume, internal energy change is equal to heat of the system.

Enthaply (H) and Enthalpy Change (ΔH)

It is defined as the sum of internal energy and pressure-volume work of the system. So,

$$H = E + PV \qquad \text{...}(i)$$

Like internal energy, enthalpy is also a state function. Its absolute value cannot be measured hence it is measured as change between two states A and B of the process.

$$\Delta H = H_B - H_A$$

From eq. (*i*) $\Delta H = \Delta E + P.\ \Delta V + V.\ \Delta P$

$= Q + V\ \Delta P$

At constant pressure, $\Delta P = 0$. Hence $\Delta H = Q$

Hence, **at constant pressure, enthalpy change is equal to heat of the sytem.**

For an exothermic reaction, $\Delta H = -ve$

For an endothermic reaction, $\Delta H = +ve$

Its SI unit is J mol^{-1} or kJ mol^{-1}.

Characteristics of Enthalpy

(*i*) Enthalpy is a state function.

(*ii*) Enthalpy change is independent of the path followed.

(*iii*) Enthalpy is an extensive property and its value depends upon the amount of substace.

Entropy (S)

Entropy is a measure of the degree of disorder of a system. Disorder of a system is measured by the energy absorbed by the system to attain that disorder. Gaseous state is the most disordered and therfore has the highest entropy.

For a reversible process at constant temperature, the change in entropy is,

$$\Delta s = \frac{Q}{T}$$

where Q = heat absorbed or evolved
T = constant temperature

If heat is absorbed in the process, $\Delta s = +$ ve

If heat is evolved in the process, $\Delta s = -$ve.

SI unit of entropy is JK^{-1}.

Second aw of Thermodynamics

It states that the change in entropy for every spontaneous process must always be positive and hence the entropy of universe always increases.

Characteristic of Entropy

(*i*) Entropy is a state function. Hence entropy change

$$\Delta S = S_{\text{final state}} - S_{\text{initial state}}$$

(*ii*) Entropy change is independent of the path followed.

(*iii*) Entropy is an extensive property and its value depends upon the amount of substance.

(*iv*) Entropy of the universe alwasy increases.

(*v*) Entropy change for a cyclic process is zero.

(*vi*) Entropy change for a reversible process is zero.

(*vii*) Entropy change for an irreversible spontaneous process is always greater than zero. i.e. $\Delta S > 0$.

Free Energy (G)

Gibb's free energy or simply free energy (G) is defined as the maximum available energy of the system which can be converted into useful work.

$$G = H - TS$$

where, H = enthalpy of the system
S = entropy of the system
T = absolute temperature of the system

At constant temperature, free energy change is given by,

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

This is called is **Gibbs Helmholtz equation.**

Conditions for Spontaneous Processes (i.e. ΔG to be negative)

The conditions for spontaneous processes and the effect of temperature.

$$(\Delta G = \Delta H - T\,\Delta S)$$

	Sign of		Temperature	Nature of process
ΔH	$T\Delta S$	ΔG	(T)	
–ve (i.e. exothermic)	+ve	–ve		Spontaneous
–ve (i.e. exothermic)	–ve	–ve	Low ($T\,\Delta S < \Delta H$)	Spontaneous
		+ve	High ($T\,\Delta S > \Delta H$)	Non-Spontaneous
+ve (i.e. endothermic)	–ve	+ve		Non-Spontaneous
+ve (i.e. endothermic)	+ve	+ve	Low ($T\,\Delta S < \Delta H$)	Non-Spontaneous
		–ve	High ($T\,\Delta S > \Delta H$)	Spontaneous
Zero	+ve	–ve		Spontaneous
Zero	–ve	+ve		Non-Spontaneous

So, a process or reaction takes place in such a way that free energy is minimum.

Criterion for Feasibility of a Chemical Process

Only those chemical process are feasible or spontaneous in which free energy decreases i.e. ΔG is negative. There are three possibilities for ΔG :

(*i*) **ΔG is Zero.** In this case, the process does not proceed in any direction and is said to be in **equilibrium state**.

(*ii*) **ΔG is positive.** In this case, the reaction is non-spontaneous.

(*iii*) **ΔG is negative.** In this case, the reaction is spontaneous.

Characteristics of free energy

(*i*) Free energy is a state function. Hence free energy change
$\Delta G = G_{\text{final state}} - G_{\text{initial state}}$

(*ii*) Free energy change is independent of the path followed.

(*iii*) Free energy is an extensive property and its value depends upon the amount of substance.

(*iv*) $\Delta G_{\text{system}} = T\Delta S_{\text{universe}}$

(*v*) Free energy change gives the maximum useful work obtained from a process.

(*vi*) Free energy always decreases (or free energy change is always negative) during a spontaneous process.

Third law of thermodynamics

It states that, at absolute zero, the entropy of a perfectly crystalline substance may be taken as zero.

Standard entropy change ($\Delta S°$)

The entropy of one mole of substance at 298 K and 1 atm pressure is called as standard entropy ($S°$)

Standard entropy change in a reaction

= (sum of standard entropies of products)

– (sum of standard entropies of reactants)

or $\Delta S° = \Sigma\ S°\ (\text{products}) - \Sigma\ S°\ (\text{reactants})$

Limitations of thermodynamics

(*i*) It deals with microscopic systems and does not tell anything about macroscopic system.

(*ii*) It deals with only initial and final states of the sytem.

Some Importent Results

1. Intrinsic energy = – Heat of formation
   = Enthalpy change of formation
2. For exothermic reaction :
   $\Delta H = H_P - H_R = -Q$ i.e., $H_P < H_R$
3. For endothermic reaction :
   $\Delta H = H_P - H_R = +Q$ i.e., $H_P > H_R$
4. ΔH_V be heat of reaction at constant vol. and ΔH_P be heat of reaction at constant pressure, then : $\Delta H_P = \Delta H_V + \Delta nRT$

   where, Δn = change in no. of moles = no. of moles of gaseous products – no. of moles of gaseous reactants.

   If $\Delta n > 0$, then $\Delta H_P > \Delta H_V$
   If $\Delta n < 0$, then $\Delta H_P < \Delta H_V$
   If $\Delta n = 0$, then $\Delta H_V = \Delta H_P$
5. Kirchoff's equation : $\Delta H_P = \Delta C_P (T_2 - T_1)$