5. THERMODYNAMICS

1 VSAQ+ 1SAQ = 6 MARKS

CONCEPTS & DEFINITIONS

1. Thermodynamics means flow of heat. Thermodynamics deals with the study of heat energy changes in chemical processes.

2.1 **Heat(q) :** Heat is a form of energy. It flows between system and surroundings due to difference in temperatures.

Units : Calorie (cal), Joule (J).

2.2 **Specific heat (s):** The heat energy required to raise the temperature of 1 gram of a substance through 1°C is called specific heat.

3. **Types of systems :**

Isolated system: A system which can't exchange heat energy or matter with the surroundings is called isolated system.

Ex: Hot Coffee in a thermos flask.

Closed system: A system which can exchange heat energy but not matter with the surroundings is called closed system.

Ex: Chilled sealed Pepsi bottle.

Open system: A system which can exchange heat energy and matter with the surroundings is called open system. **Ex:** A cup of tea in a saucer.

4. **Properties of Systems:**

Extensive properties: The properties which depend on the total amount of the material present in the system are called extensive properties of the system.

These are mass dependent properties.

Ex: Weight,Volume, Internal energy, Heat

Intensive properties: The properties which donot depend on the total amount of the material present in the system are called intensive properties of the system.

These are mass independent properties.

Ex: Pressure, Temperature, Specific heat, Density, Refractive index, Viscosity, Surface tension.

5. **State Variables:** The fundamental characteristics that determine the state of gaseous system are pressure(P), temperature (T), volume (V), amount (n) .These are called State variables (functions). Their values depend only on the initial and final states of the system, but not on the path of the reaction.

State variables of thermodynamic system: Internal energy (E), Enthalpy(H), Entropy(S), Gibbs energy (G).

6. **Internal energy (U)**: The energy stored in the form chemical, electrical, mechanical or any other form in a system, at constant temperature and volume is called internal energy.

7.1 First law of thermodynamics (Law of conservation of energy):
"The energy in a process is neither created nor destroyed" but it may be transferred from one form into the other.

7.2 Mathematical form: $\Delta U = q + w$.

8. Enthalpy (H): The amount of heat exchanged by a system with its surroundings at constant pressure and temperature is called enthalpy.

(i) Enthalpy change measured at constant pressure is given by $q_p = \Delta H$.

(ii) Enthalpy change measured at constant volume is given by $q_v = \Delta U$.

9. Heat capacity (C): The amount of heat required to raise the temperature of a substance through one degree is called heat capacity.

Formula: $C = q/\Delta t$ ($\because q = C\Delta t$)

10.1 Heat capacity at constant volume (C_v): C_v measures the change in internal energy of a system corresponding to a change in temperature at constant volume.

10.2 Heat capacity at constant pressure (C_p): C_p measures the change in heat capacity when heat is absorbed by the system at constant pressure.

10.3 Relation between C_p and C_v: i) $C_p - C_v = R$ ii) $\frac{C_p}{C_v} = \gamma$

11.1 Exothermic reactions: The chemical reactions in which liberation of heat takes place are known as exothermic reactions. In exothermic reactions H_P is less than H_R .

Here ΔH is negative. **Ex:** $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286.2$ KJ

11.2 Endothermic reactions : The chemical reactions in which the absorption of heat takes place are known as endothermic reactions. In endothermic reactions H_P is greater than H_R.

Here ΔH is positive. **Ex:** Photosynthesis in plants.

12. Spontaneity: Spontaneity means having potential to proceed without the help of external agency.

A spontaneous process is an irreversible process and may only be reversed by some external agency.

Ex: Flow of water, Falling of rocks from hills.

13. Hess's law: The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps.

14. Entropy(S): Entropy is a measure of disorder or randomness of molecules of the substance.

Entropy is a thermodynamic property. Entropy is an extensive property.

ΔS is a state function.

Order of Entropy: $S_{vapour} > S_{liquid} > S_{solid}$

For a spontaneous change $\Delta S > 0$.

If the system is not isolated, the total entropy change (ΔS total) must be positive.

$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} > O$

The units of entropy change(ΔS) is J/K.

15. Statements of II law of thermodynamics:

1. Heat can not flow from a colder body to a hotter body on its own.
2. All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes.

16. Gibbs energy(G): Gibbs energy relates entropy and enthalpy change.

It is the amount of the energy available from a system which can be put to useful work at constant temperature and pressure. G= H–TS $\Rightarrow$ **$\Delta G = \Delta H - T\Delta S$.**

For a spontaneous change $\Delta G < 0$.(negative)

For a non-spontaneous change $\Delta G > 0$. (positive)

For equilibrium reactions $\Delta G = 0$.

17. Third law of thermodynamics: "The entropy of a pure and perfectly crystalline substance approaches zero, when the temperature approaches absolute zero."

TIPS

1. Enthalpy H = U+pV
2. Internal energy change(ΔU) is affected when
   i) Heat passes into or out of the system.
   $\Delta U = q + w$(For an open system)
   $\Delta U = q - w$(For a closed system)
   ii) Work is done on or by the system.
   $\Delta U = w_{ad}$(For an adiabatic system)
   $\Delta U = -q$(For thermally conducting system)
3. For an isolated system $\Delta U = 0$
4. For adiabatic change, $q = 0$ and $\Delta U = w_{ad}$
5. At constant volume $w = 0$ and $\Delta U = q_v$
6. At constant pressure $\Delta H = q_p$; $\Delta H = \Delta U + \Delta n_g RT$
7. In the expansion of gases $w = -p_{ex}\Delta V$
8. In a reversible process $w_{rev} = -p\Delta V$
9. For isothermal irreversible change $q = -w = P_{ext}(v_f - v_i)$
10. For isothermal reversible change $q = -w = nRT\, ln\, (v_f / v_i)$
11. Standard Gibb's energy change : $\Delta_r G^- = -RT lnK$.

☛ For **Chem Beats** of this chapter Refer Page **No. 247**

CONCEPT MAP OF THERMODYNAMICS

THERMODYNAMICS

(Study of energy transformation in chemical system)

Universe

System
Part of the universe under study
- **Open :** both mass and energy can exchange
- **Closed :** only energy can exchange
- **Isolated :** both can't exchange

Surroundings
(includes every thing other than system)

Types of Processes

- Isothermal (Temperature constant)
- Adiabatic (q = 0)
- Isobaric (Pressure constant)
- Isochoric (Volume constant)
- Reversible and Irreversible process

Laws

First Law

Energy conversion

$\Delta U = q + w$

ΔU = Charge in internal energy

q = heat

w = work

$W = -p_{ex}\Delta V$

- For isothermal reversible change

$w_{rev} = -2.303\, nRT \log \frac{V_f}{V_i}$

- For isothermal irreversible change

$q = -w = p_{ex}(V_f - V_i)$

For adiabatic change, q = 0,

$\Delta U = w_{ad}$

- **Extensive Property :** Whose value depends on its quantity.
Eg.: mass, V, U, H
Intensive Property : Whose value does not depends on its quantity.
Eg.: T, P, d

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

ΔH = Charge in enthalpy

ΔH = -ve exothermic

ΔH = +ve endothermic

$C_p - C_V = R$; $\frac{C_p}{C_V} = \gamma$

Second Law

Entropy increases in spontaneous process
- **Entropy (S):** Measure of disorder

$\Delta S = \frac{q_{rev}}{T}$

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

Third Law

At absolute zero temperature, entropy of pure cyrstalline substance is zero.

Application

Spontaneous and non-spontaneous
- ΔH = -ve spontaneous
- ΔH = +ve non-spontaneous
- ΔS = +ve spontaneous
- ΔS = -ve non-spontaneous

Gibbs energy from ΔS and ΔH
- $\Delta G = \Delta H - T\Delta S$
- ΔG = -ve spontaneous
- ΔG= +ve non-spontaneous
- ΔG = 0 equilibrium
- $\Delta G = -RT \ln K$
- K = Equilibrium constant