CONCEPT **MAP**

THERMODYNAMICS

In thermodynamics, interaction between large ensembles of objects are studied and categorized. Central to this are the concepts of system and surroundings. A system is composed of particles whose average motions define its properties. Properties can be combined to express internal energy and thermodynamic potentials.

Class XI

Thermodynamic terms

Properties of system: Physical quantities which are used to define the system.

Intensive: These do not depend upon quantity of matter. *e.g.*, T, P.

Extensive: These depend upon quantity of matter, *e.g.*, mass, volume, energy.

Thermodynamic processes

- If $dq = 0$, process is adiabatic.
- If $dT = 0$ and $dE = 0$, the process is isothermal.
- If $dV = 0$, process is isochoric.
- If $dP = 0$, process is isobaric.

Heat (q) and heat capacity (C)

- Heat capacity, $C = dq/dT$
- $C_v = \left(\frac{\partial U}{\partial T}\right)_V ; C_p = \left(\frac{\partial H}{\partial T}\right)_P$
- When n_1 moles of gas A and n_2 moles of gas B are mixed.

$$(C_v)_{\text{mix}} = \frac{n_1C_{v_1} + n_2C_{v_2}}{n_1 + n_2}$$

- $C_p - C_v = nR$

Work (W)

- $W = -P_{ext}\Delta V$

[irreversible isothermal expansion]

- $W = -2.303nRT\log(P_1/P_2)$
- $W = -2.303nRT\log(V_2/V_1)$

[reversible isothermal expansion]

- $W = nC_v dT = \frac{nR}{\gamma - 1}(T_2 - T_1)$

[reversible adiabatic expansion]

where, $\gamma = C_P/C_V$

- $W = -P_{ext}R\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$

[irreversible adiabatic expansion]

Bond enthalpy

It is the enthalpy change accompanying the breaking of one mole of covalent bonds.

Bond enthalpy =

$\sum$ Bond enthalpies of reactants

$-\sum$ Bond enthalpies of products

Enthalpy(H)

Total heat of the system

- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V = C_P\Delta T$

$= \Delta U + \Delta n_g RT$ (at constant pressure)

- $\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$

$= -$ve (exothermic)

$= +$ ve (endothermic)

Gibbs Free Energy (G)

Useful work done by the system

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

(Gibbs - Helmholtz equation)

$$\Delta G^\circ = \sum G^\circ_{f(\text{product})} - \sum G^\circ_{f(\text{reactant})}$$

- $\Delta G^\circ = -2.303\,RT\log K_{eq}$.
- If $\Delta G = +$ve (Non-spontaneous)
- If $\Delta G = -$ve (Spontaneous)

Enthalpy of combustion, $\Delta_c H$

It is the enthalpy change when 1 mole of a substance burnt completely in air.

Hess's law of constant heat summation

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Enthalpy change of a reaction

It is the enthalpy change when a given reactant reacts completely.

Enthalpy of formation

It is the enthalpy change occurring during the formation of 1 mole of a substance from its elements.

Enthalpy of solution

$\Delta_{\text{sol}}H = \Delta_{\text{lattice}}H + \Delta H_{\text{hyd}}$

where, $\Delta_{\text{lattice}}H = S + I + \frac{1}{2}D - \Delta_f H + E.A.$

Thermodynamic laws

Zeroth law: System in thermal equilibrium with each other have same temperature.

First law: The total energy of the universe remains constant although it may undergo transformation from one form to the other.

$\Delta U = q + w$ (ΔU = internal energy)

Second law: In a spontaneous process total energy of the universe increases.

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

Entropy (S)

Measure of randomness or disorder

- $\Delta S = \frac{q_{rev}}{T}$ (reversible process)
- $\Delta S = 2.303nC_v\log\left(\frac{T_2}{T_1}\right) + 2.303nR\log\left(\frac{V_2}{V_1}\right)$
- $\Delta S = 2.303nC_p\log\left(\frac{T_2}{T_1}\right) + 2.303nR\log\left(\frac{P_1}{P_2}\right)$
- $\Delta S = 2.303nR\log\left(\frac{V_2}{V_1}\right)$
- $\Delta S = 2.303nR\log\left(\frac{P_1}{P_2}\right)$

Isothermal

- $\Delta S = 2.303nC_p\log\left(\frac{T_2}{T_1}\right)$ [isobaric]

Third law

- Entropy of all pure crystals is zero at the absolute zero temperature.
- $\lim_{T \to 0} S = 0$
- Residual Entropy

$S_R = k\ln W$

(W = thermodynamic probability)