



Subjective Matter : For Self Study

● 4.1 Introduction

- Energy is defined as capacity to do the work.
- Potential energy, kinetic, mechanical, electrical heat, chemical, work, etc. are the different forms of the energy. It can be converted one form to another form.
- Thermodynamics is a branch, in which study of energy and its changes, interms chemical and physical transformations.
- Macroscopic or easily measurable properties as P, V, T, E, H, S, G are studied in thermodynamics.
- It is not concerned with microscopic properties, internal structure, rate of the reaction, mechanism of the reaction etc.
- Thermodynamical properties depends on the initial and final states of the system.
- Thermodynamics gives information of feasibility of the chemical reaction, direction and upto which extent reaction is completed.
- Absolute value of macroscopic properties can not be determine.

● 4.2 Terms used in Thermodynamics

- **System** : It is part of universe under thermodynamic consideration. e.g. beaker.
- **Surrounding** : It is remaining part of the universe i.e. part of the universe other than system.
- **Universe** : System + Surrounding.

● Types of systems :

- Open system** : A system which can exchange both energy and matter with surrounding. e.g. Hot tea in a cup.
- Closed system** : A system which can exchange only energy and not matter with surrounding. e.g. Hot tea covered with dish on a cup.
- Isolated system** : A system which can neither exchange energy nor matter with the surrounding. e.g. Isolated flask or thermoflask

● Properties of systems

- Intensive property** : The properties which are independent to amount or course of the system. e.g. Temperature, density, surface tension.

- Refractive index, M.P., B.P., specific heat, molar heat capacities, C_p , C_v , pH, dielectric constant, pressure etc.

(ii) **Extensive property** : The property which depends on mass or amount of the system.]
e.g. Mass, weight, volume, area, energy, enthalpy, heat capacity, free energy, etc.

- Ratio of two extensive property is an intensive property.

● State function or Thermodynamic function

- The property which, depends on initial and final state of system and independent to path by which it operated.

e.g. Pressure, volume, temperature, no. of moles, energy, enthalpy etc.

- **Path functions** : The property which depends on path of the system.

e.g. Work and heat

● Thermodynamical equilibrium

- It is a state of equilibrium when the state functions of the system does not changes with time.

- **Process** : It is path of method by which system changes one state to another state.

1) Isothermal process

- Temperature remains constant. $\Delta T = 0$.

- Heat can exchange with surrounding i.e. system absorbs or evolved heat to maintain the constant temperature.

$$\Delta U = 0 \text{ or } \Delta E = 0$$

- System is not thermally isolated.

2) Adiabatic process

- $dq = 0$, $q = \text{constant}$.

$$\Delta T \neq 0$$

- In adiabatic expansion, temperature decreases i.e. **endothermic process**.

- In adiabatic compression, temperature increases of the system i.e. **exothermic process**.

$$\Delta U \neq 0$$

- System is thermally isolated.

3) Isochoric process

- Volume of the system remains constant. $\Delta V = 0$

- It occurs in a closed container.

4) Isobaric process

- Pressure of system remains constant, $\Delta P = 0$
- Reaction occurs in an open container with constant atmospheric pressure.

5) Reversible process

- It is a process in which driving force and opposing force differs infinitesimally small to each other and process can be reverse by increasing opposing force.
- It is infinitely slow process and occurs in number of steps.
- At the end of each step there is a mechanical equilibrium of system with the surrounding.
- Driving force infinitesimally smaller than opposing force.
- Maximum work can be obtained in such process.

● 4.3 Work and Heat

- Work means by which system exchange energy with surrounding.
- $W = f \times d$,
Where, f = force, d = displacement of a body
- When a gas expands or contracts against external pressure is nothing but PV type of work.
- Heat is one of the ways by which system exchange energy with the surrounding.
- $+W$ = Work done by the surrounding on system.
 $-W$ = Work done by the system on surrounding.
 $-q$ = Heat evolved by the system.
 $+q$ = Heat absorbed by the system.

● 4.4 Pressure-Volume type (P-V type) work at constant pressure

- $W = -P(V_2 - V_1) = -P(\Delta V)$
Where, P - Constant pressure, V_2 - Final volume of a gas, V_1 - Initial volume of gas.
- $V_2 > V_1$ ΔV +ve ,
 $-W$ i.e. work of expansion
- $V_1 > V_2$ ΔV -ve ,
 $+W$ i.e. work of compression.
- W can be expressed in J, Lit-atm or cal.
 $1 \text{ Lit-atm} = 101.3 \text{ J}$ $1 \text{ cal} = 4.184 \text{ J}$

● Work done in vacuum

- Expansion of a gas in a vacuum without opposing force called as free expansion.

- In vacuum opposing force i.e. $P = 0$. Thus work done in vacuum is zero.
- Work done in cyclic process may be positive or negative depending upon heat absorbed or evolved by the system.
- Cyclic process is one in which system can be brought to its initial state again.

● 4.5 Maximum work can be obtained in isothermal and reversible process

- $W_{\max} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$ or $\frac{P_1}{P_2}$
- $W_{\max} = -nRT \log_e \frac{V_2}{V_1}$
- $n = \text{no. of moles} = \frac{\text{Mass of substance}}{\text{Molar mass of substance}}$

● 4.6 Internal energy (u)

- Fixed or definite amount of energy associated in the system called as internal energy.
- It is sum of kinetic and potential energy. Electronic and nuclear also contribute internal energy.
- Absolute value cannot determine, in thermodynamics.
- $\Delta U = (U_2 - U_1)$
 $\therefore U_1$ = Internal energy of at initial state
 U_2 = Internal energy of final state
- Internal energy of system increases or decreases depending upon heat absorbed or evolved and work done on the system or work done by the system.

● 4.7 First law of Thermodynamics

- First law of thermodynamics is nothing but modification of law of conservation of energy.
- The total energy of system and surrounding remains constant although it may change one form to another form.
- Mathematical equation

$$\Delta U = q + W$$

Change in internal energy = Heat absorbed or evolved by the system + Work done

- > Total energy and mass of an isolated system remains constant (Modified form of first law of thermodynamics based on relation $E = MC^2$)

● Deductions

- 1) In isothermal process,

$$\Delta U = 0$$

$$\boxed{q = -W} \text{ OR } \boxed{W = -q}$$

- 2) In adiabatic process,

$$q = 0, \quad \text{i.e. } \boxed{\Delta U = W}$$

- 3) In isochoric process,

$$\Delta V = 0, \quad \text{i.e. } \boxed{\Delta U = q_V}$$

- 4) In isobaric process, $\boxed{\Delta U = q_p + W}$

● 4.8 Enthalpy or Heat Content (H)

- > Enthalpy is sum of internal energy and pressure-volume type of energy of the system.

$$\Delta H = U + PV$$

- > $\Delta H = \Delta U + P\Delta V$ P at constant pressure. It is enthalpy change equation.

- > At constant volume or in isochoric process (for solids / liquid systems) $\Delta V = 0$

$$\therefore \boxed{\Delta H = \Delta U} \text{ or } \boxed{q_p = q_V}$$

- > At constant pressure or in isobaric process for a gaseous system.

$$\boxed{\Delta H = \Delta U + P\Delta V} \text{ or } \boxed{q_p = q_V + P\Delta V}$$

$$\text{i.e. } \Delta H = q_p$$

- > $\Delta H = \Delta U + \Delta nRT$

$$\Delta n = (\text{No. of moles of gas products}) - (\text{No. of moles of gaseous reactants})$$

$$\text{i) } \Delta n = 0, \Delta H = \Delta U,$$

(a) Reaction in a closed container

(b) Reaction in solid or liquid phase

(c) For gaseous reaction $n_1 = n_2$.

$$\text{ii) } \Delta n = +ve, \Delta H > \Delta U$$

$$\text{iii) } \Delta n = -ve, \Delta H < \Delta U$$

- > Work done in chemical reaction, $W = -\Delta nRT$

$$\Delta n = (n_2 - n_1)$$

$$\text{If i) } n_2 > n_1 \quad W = -ve,$$

$$\text{ii) } n_1 > n_2 \quad W = +ve$$

$$\text{iii) } n_1 = n_2 \quad W = \text{No work done.}$$

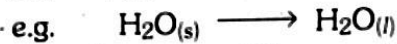
● 4.9 Enthalpies in physical transformation

1) Enthalpy in fusion (ΔH_{fusion})

- > It is enthalpy change in the fusion of 1 mole of solid without change in temperature at constant pressure.

$$\Delta H_{\text{fusion}} \rightleftharpoons \Delta H_{\text{freezing}}$$

$$\Delta H = +ve \quad \Delta H = -ve$$



$$\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$



$$\Delta H_{\text{freezing}} = -6.01 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$

2) Enthalpy of vapourisation (ΔH_{vap})

- > It is enthalpy change in the vapourisation of 1 mole of liquid without change in temperature at constant pressure.

$$\Delta H_{\text{vap}} = \Delta H_{\text{Condensation}}$$

$$\Delta H = +ve \quad \Delta H = -ve$$

(Endothermic) (Exothermic)



$$\Delta H_{\text{vap}} = 40.7 \text{ kJ mol}^{-1} \text{ at } 100^\circ\text{C}$$



$$\Delta H_{\text{con}} = -40.7 \text{ kJ mol}^{-1} \text{ at } 100^\circ\text{C}$$

3) Enthalpy of sublimation (ΔH_{sub})

- > The enthalpy of change when 1 mole of solid is directly converted into gas at constant temperature and pressure.



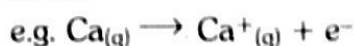
$$\Delta H_{\text{sub}} = 51.08 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$

$$\Delta H_{\text{sub}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}}$$

- > Sublimation is endothermic process.

4) Enthalpy of atomic or molecular changes (ΔH_{ion}) or Enthalpy of ionization

- > It is enthalpy change when an electron is removed from atom or ion to form 1 mole of gaseous atom or ion.



$$\Delta H_{\text{ion}} = 590 \text{ kJ mol}^{-1} \text{ (I}^{\text{st}} \text{ I.P.)}$$

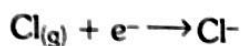


$$\Delta H_{\text{ion}} = 1150 \text{ kJ mol}^{-1} \text{ (II}^{\text{nd}} \text{ I.P.)}$$

- > Ist I.P. < IInd I.P. < IIIrd I.P. values.

- > Electron gain enthalpy (ΔH_{eg}) is a reverse of ionisation enthalpy.

- > It is enthalpy change when 1 mole of gases atom accept electrons to form gaseous anion.

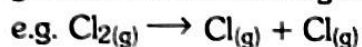


$$\Delta H_{\text{eg}} = -349 \text{ kJ mol}^{-1}$$

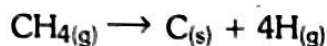
> ΔH_{eg} highest value for Cl.

5) Enthalpy of atomisation (ΔH_a)

> It is enthalpy change in dissociation of 1 mole of gaseous molecule into gaseous atoms.



$$\Delta H_a = 242 \text{ kJ mol}^{-1}$$



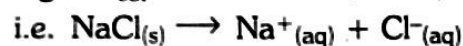
$$\Delta H_a = 1600 \text{ kJ mol}^{-1}$$

6) Enthalpy of solution ($\Delta_{\text{sol}}H$)

> It is enthalpy change when one mole of a substance is dissolved in a specific quantity of a solvent so as to form a particular concentration of solution at given temperature.

> $\Delta H_{\text{sol}} = \Delta H_{\text{lattice enthalpy}} + \Delta H_{\text{hydration}}$

> e.g. ΔH_{sol} of NaCl = 4 kJ/mol.



$$\Delta H = 4 \text{ kJ/mol}$$

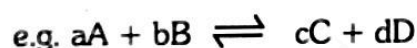
> ΔH_{sol} involves solute-solute, solute-solvent and solvent-solvent interactions.

> ΔH_{sol} of KCl = +17.2 kJ mol⁻¹.

● 4.10 Thermochemistry

1) Heat of reaction or enthalpy of reaction (ΔH)

> It is enthalpy of a reaction when number of moles of a balanced chemical reaction are reacted at their std. physical state and given temperature and pressure.



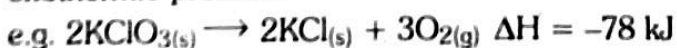
$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{Reactants}}$$

> ΔH may be positive or negative value.

i) If ΔH is positive indicates $H_P > H_R$. Heat is absorbed by the system from surrounding. It is endothermic process.



ii) If ΔH is negative value indicates $H_P < H_R$. Heat is evolved by the system to surrounding. It is exothermic process.



iii) Lower the enthalpy value that substance is more stable.

iv) Standard conditions are :

(a) 1 atm = $1.01325 \times 10^5 \text{ Pa}$ or N/M^2

(b) 25°C or 298 K

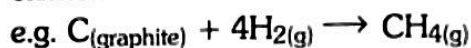
(c) 1 M concentration of the solution.

2) Standard heat of reaction (ΔH°)

> It is enthalpy change accompanying the reaction when all substance involved in it are in their standard state.

3) Standard enthalpy of formation (ΔH°_f)

> It is enthalpy change for a reaction when 1 mole of product or substance formed from their constituent elements at their standard state.



$$\Delta H^\circ = -74.8 \text{ kJ mol}^{-1}$$

> It may positive or negative value.

4) Standard enthalpy of combustion or Heat of combustion (ΔH°_c)

> It is enthalpy change when one mole of substance completely combusted (with excess of oxygen) at their standard state.

> ΔH°_c always negative or exothermic reaction.

> Combustion of hydrocarbon always produce $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$. Combustion of CS_2 gives $\text{CO}_{2(g)}$ and $\text{SO}_{2(g)}$



$$\Delta H_a = -283 \text{ kJ}$$



$$\Delta H^\circ_c = -3267 \text{ kJ}$$

5) Bond energy or Bond enthalpy

> It is an average amount of energy (in kJ/mol) required to break a particular bond to form free atoms or radicals in polyatomic molecules called as bond energy.

> For diatomic molecules,

Bond formation = Bond dissociation energy with opposite sign. But Bond dissociation energy is always positive. Bond formation may be positive or negative.

> For polyatomic molecule, average bond energy

$$= \frac{\text{Total bond energy}}{\text{No. of bonds in molecule}}$$

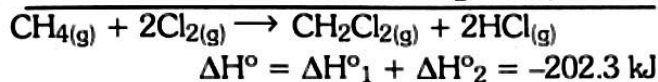
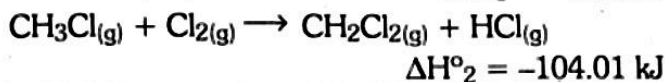
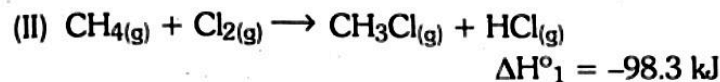
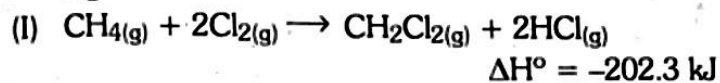
$$\Delta H^\circ = \sum H^\circ_{(\text{Reactant bonds})} - \sum H^\circ_{(\text{Product bonds})}$$

● **Hess's law of constant heat summation**

- Enthalpy change during a chemical reaction remains constant whether it involves one step or no. of steps.
- i.e. Enthalpy change during chemical reaction is independent to the path between initial and final state.
- It is an application of law of conservation of energy and state function.
- It is useful to calculate ΔH_C , ΔH_f , ΔH_R , ΔH_n . Heat of reaction which cannot calculate directly. Thermochemical equation can be added, subtracted, multiplied or divide.

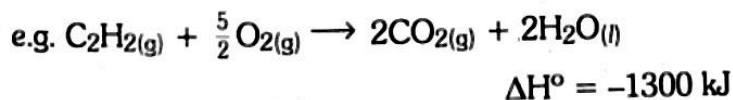
$$\Delta H_{\text{Total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots\dots\dots$$

➤ e.g.



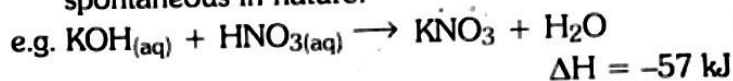
● **Thermochemical equation**

- It is a balanced chemical equation which gives enthalpy change, physical states and no. of moles of each component of the reaction.
- Equation must be balanced form of number of moles of reactants and products.
- ΔH° represented right hand side with proper sign. Negative sign indicates exothermic and positive sign indicates endothermic reactions.
- Physical states are mention, like (s), (l), (g), (aq.) etc.
- If reaction reverse sign of ΔH° also reverses.
- Enthalpy of elements at their std. state consider as zero value. e.g. Enthalpy of $\text{Na}(\text{s}) = 0$
- If reaction is multiple or divide by suitable value, same factor used for ΔH° value.



● **4.11 Spontaneous process (Irreversible process)**

- Spontaneous process is a process which occurs without the external influence or which takes place with its own occurred.
- Examples of spontaneous process
 - Flow of water from higher level to lower level.
 - Heat flows from hotter body to cold body.
 - KCl solid spontaneous in water.
 - Neutralisation of acid and base.
 Such process cannot reverse without external force.
- All the natural (spontaneous) processes occurs in a direction till equilibrium is reached.
- In spontaneous process energy decreases i.e. exothermic process. But endothermic processes also spontaneous in nature.



- Entropy is disorder in a reaction or degree of randomness of the system.
- Disorder increases entropy increases.
- In solid atoms or molecules are arranged orderly hence entropy is lowest. In liquid entropy increases and highest in gaseous state.
- In spontaneous process disorder increases then entropy change is positive.

➤ $\Delta S = \frac{q_{\text{reversible}}}{T}$

- It is expressed in JK^{-1} .
- Entropy is a state function and depends on initial and final state of the system.
 $\Delta S = (S_2 - S_1)$

● **Second law of Thermodynamics**

- The total entropy of system and surrounding (i.e. universe) always increases in a spontaneous process.

OR

Entropy of universe increases in all spontaneous process.

- $\Delta S_{\text{universe}} = \Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$
- $\Delta S_{\text{Total}} > 0$ Spontaneous process.
- $\Delta S_{\text{Total}} < 0$ Non-spontaneous process.

$\Delta S_{\text{Total}} = 0$ Process is at equilibrium.

> **Gibb's energy** : $G = H - TS$

Where G - Gibb's energy, H - Enthalpy, S - Entropy and T - Temperature. All are the state functions.

Thus,

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

> $\Delta G = -T\Delta S_{\text{Total}}$

i) For spontaneous process,

$$\Delta S_{\text{Total}} > 0, \text{ then } \Delta G < 0$$

ii) For non-spontaneous process,

$$\Delta S_{\text{Total}} < 0, \text{ then } \Delta G > 0$$

iii) At equilibrium,

$$\Delta S_{\text{Total}} = 0, \text{ then } \Delta G = 0$$

> At equilibrium,

$$\Delta G = 0,$$

$$\text{Thus, } \Delta H = T\Delta S \quad \text{OR}$$

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

> At standard state,

$$\Delta G^\circ = -RT \ln K \text{ or, } \Delta G^\circ = -2.303 RT \log_{10} K$$

Where, K is equilibrium constant.

ΔH	ΔS	ΔG	Nature of reaction
-ve	+ve	-ve	Spontaneous at all temperature
+ve	-ve	+ve	Non-spontaneous at all temperature
-ve	-ve	-ve	Spontaneous at low temperature
+ve	+ve	+ve	Non-spontaneous at low temperature
-ve	-ve	+ve	Non-spontaneous at high temperature
+ve	+ve	-ve	Spontaneous at high temperature

● Third law of thermodynamics

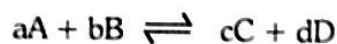
> The entropy of a pure and perfect crystalline substance is zero at absolute zero temperature.

$$\Delta S = S_T - S_0 = \int_0^T \frac{C_P}{T} dt$$

Where, S_T - absolute entropy at T K, S_0 - absolute entropy at 0 K, C_P - heat capacity of a constant pressure.

> The absolute entropy of a 1 mole of pure substance at 1 atm. pressure and 25°C is called as standard molar entropy (S°)

> For a reaction, standard entropy change ΔS° can be calculated



$$\Delta S^\circ = \sum_{(\text{Products})} S^\circ - \sum_{(\text{Reactants})} S^\circ$$

$$\Delta S^\circ = (cS_C^\circ + dS_D^\circ) - (aS_A^\circ + bS_B^\circ)$$