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 :**

(i) Open system : A system which can exchange both energy and matter with surrounding. e.g. Hot tea in a cup.

(ii) Closed system : A system which can exchange only energy and not matter with surrounding. e.g. Hot tea covered with dish on a cup.

(iii) Isolated system : A system which can neither exchange energy nor matter with the surrounding. e.g. Isolated flask or thermoflask

● **Properties of systems**

(i) 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.
- $\Delta U = 0$ or $\Delta E = 0$
- System is not thermally isolated.

2) Adiabatic process

- $dq = 0$, $q =$ 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, $\Delta P = 0$
- Reactions occurs in a open container with constant atmospheric pressure.

5) Reversible process

- It is 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 their is an mechanical equilibrium of system with the surrounding.
- Driving force infinitesimally smaller than opposing force.
- Maximum work can be obtained in such proces.

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 the way by which system exchange energy with the surrounding.
- +W = Work done by the surrounding on sytsem.
  –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 cals.
  1 Lit-atm = 101.3 J 1 cal = 4.184 J

Work done in vaccum

- Expansion of a gas in a vaccum without opposing force called as free expansion.
- In vaccum opposing force i.e. P = 0. Thus work done in vaccum 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 = no. of moles = $\frac{\text{Mass of substance}}{\text{Molar mass of substance}}$

4.6 Internal energy (v)

- 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.
- $\Delta U = (U_2 - U_1)$
  ∴ 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 workdone 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 althrough it may changes one form to another forms.
- Mathematical equation

$$\boxed{\Delta U = q + W}$$

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,
$\Delta U = 0$

$q = -W$ OR $W = -q$

2) In adiabatic process,
$q = U$, i.e. $\Delta U = W$

3) In isochoric process,
$\Delta V = 0$, i.e. $\Delta U = q_V$

4) In isobaric process, $\Delta U = q_P + W$

4.8 Enthalpy or Heat Content (H)

- Enthalpy is sum of internal energy and pressure-volume type of energy of the system.
- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V$ ..... P at constant pressure.
It is enthalpy change equation.
- At constant volume or in isochoric process (for solids / liquid systems) $\Delta V = 0$

$\therefore$ $\Delta H = \Delta U$ or $q_P = q_V$

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

$\Delta H = \Delta U + P\Delta V$ or $q_P = q_V + P\Delta V$

i.e. $\Delta H = q_P$.

- $\Delta H = \Delta U + \Delta nRT$
Δn = (No. of moles of gas products) – (No. of moles of gaseous reactants)
  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 $n_1 = n_2$.
  ii) $\Delta n = +ve$, $\Delta H > \Delta U$
  iii) $\Delta n = -ve$, $\Delta H < \Delta U$
- Work done in chemical reaction, $W = -\Delta nRT$
$\Delta n = (n_2 - n_1)$
If i) $n_2 > n_1$ $W = -ve$,
ii) $n_1 > n_2$ $W = +ve$
iii) $n_1 = n_2$ W = 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.
- $\Delta H_{fusion} \rightleftharpoons \Delta H_{freezing}$
$\Delta H = +ve$ $\Delta H = -ve$

e.g. $H_2O_{(s)} \longrightarrow H_2O_{(l)}$
$\Delta H_{fusion} = 6.01$ kJ mol^{-1} at 0°C

$H_2O_{(l)} \longrightarrow H_2O_{(s)}$
$\Delta H_{freezing} = -6.01$ kJ mol^{-1} at 0°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.
- $\Delta H_{vap} = \Delta H_{Condensation}$
$\Delta H = +ve$ $\Delta H = -ve$
(Endothermic) (Exothermic)
- $H_2O_{(l)} \longrightarrow H_2O_{(g)}$
$\Delta H_{vap} = 40.7$ kJ mol^{-1} at 100°C

$H_2O_{(g)} \longrightarrow H_2O_{(l)}$
$\Delta H_{con} = -40.7$ kJ mol^{-1} at 100°C

3) Enthalpy of sublmination (ΔH_{sub})

- The enthalpy of change when 1 mole of solid is directly converted into gas at constant temperature and pressure.
$H_2O_{(s)} \longrightarrow H_2O_{(g)}$
$\Delta H_{sub} = 51.08$ kJ mol^{-1} at 0°C

$\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$
- 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.
e.g. $Ca_{(g)} \longrightarrow Ca^{+}_{(g)} + e^{-}$
$\Delta H_{ion} = 590$ kJ mol^{-1} (Ist I.P.)

$Ca_{(g)} \longrightarrow Ca^{+2}_{(g)} + e^{-}$
$\Delta H_{ion} = 1150$ kJ mol^{-1} (IInd 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.

$Cl_{(g)} + e^- \longrightarrow Cl^-$

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

- 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.

  e.g. $Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)}$

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

  $CH_{4(g)} \longrightarrow C_{(s)} + 4H_{(g)}$

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

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

- 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.
- $\Delta H_{sol} = \Delta H_{\text{lattice enthalpy}} + \Delta H_{\text{hydration}}$
- e.g. ΔH_{sol} of NaCl = 4 kJ/mol.

  i.e. $NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

  $\Delta H = 4$ kJ/mol
- ΔH_{sol} involves solute-solute, solute-solvent and solvent-solvent interactions.
- ΔH_{sol} of KCl = $+17.2 \text{ kJ mol}^{-1}$.

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.

  e.g. $aA + bB \rightleftharpoons cC + dD$

  $\Delta H = \Sigma H_{products} - \Sigma H_{Reactants}$
- 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.

  e.g. $N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)}$ $\Delta H = 66.4$ kJ

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

  e.g. $2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$ $\Delta H = -78$ kJ

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

iv) Standard conditions are :

  (a) 1 atm = 1.01325×10^5 Pa or N/M^2

  (b) 25°C or 298 K

  (c) 1 M concentration of the solution.

2) Standard heat of reaction (ΔH^o)

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

3) Standard enthalpy of formation (ΔH^o_f)

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

  e.g. $C_{(graphite)} + 4H_{2(g)} \longrightarrow CH_{4(g)}$

  $\Delta H^o = -74.8 \text{ kJ mol}^{-1}$.
- It may positive or negative value.

4) Standard enthalpy of combustion or Heat of combustion (ΔH^o_C)

- It is enthalpy change when one mole of substance completely combusted (with excess of oxygen) at their standard state.
- ΔH^o_C always negative or exothermic reaction.
- Combustion of hydrocarbon always produce $CO_{2(g)}$ and $H_2O_{(l)}$. Combustion of CS_2 gives $CO_{2(g)}$ and $SO_{2(g)}$

  e.g. $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$

  $\Delta H_a = -283$ kJ

  $C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$

  $\Delta H^o_C = -3267$ 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 calld 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

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

- $\Delta H^o = \Sigma H^0_{(\text{Reactant bonds})} - \Sigma H^0_{(\text{Product bonds})}$

- **Hess's law of constant heat symmation**
- 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 calculated ΔH_C, ΔH_f, ΔH_R, ΔH_n. Heat of reaction which cannot calculate directly. Thermochemical equation can be added, subtracted, multiplied or divide.

  $\Delta H_{Total} = \Delta H_1 + \Delta H_2 + \Delta H_3$ ....
- e.g.

(I) $CH_{4(g)} + 2Cl_{2(g)} \longrightarrow CH_2Cl_{2(g)} + 2HCl_{(g)}$

$\Delta H^\circ = -202.3$ kJ

(II) $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

$\Delta H^\circ_1 = -98.3$ kJ

$CH_3Cl_{(g)} + Cl_{2(g)} \longrightarrow CH_2Cl_{2(g)} + HCl_{(g)}$

$\Delta H^\circ_2 = -104.01$ kJ

$CH_{4(g)} + 2Cl_{2(g)} \longrightarrow CH_2Cl_{2(g)} + 2HCl_{(g)}$

$\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 = -202.3$ kJ

- **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 $Na_{(s)} = 0$
- If reaction is multiple or divide by suitable value, same factor used for ΔH° value.

e.g. $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)}$

$\Delta H^\circ = -1300$ kJ

- **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
  - i) Flow of water from higher level to lower level.
  - ii) Heat flows from hotter body to cold body.
  - iii) KCl solid spontaneous in water.
  - iv) 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.

e.g. $KOH_{(aq)} + HNO_{3(aq)} \longrightarrow KNO_3 + H_2O$

$\Delta H = -57$ kJ

ice $\xrightarrow[0^\circ C]{\text{above}}$ $H_2O_{(l)}$ $\quad \Delta H = 6.01$ kJ mol^{-1}.

$NaCl_{(s)} + aq. \longrightarrow Na^+Cl^-_{(aq.)}$ $\quad \Delta H = 3.9$ kJ mol^{-1}.

- 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.
- $\Delta S = \dfrac{q_{reversible}}{T}$
- 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.
- $\Delta S_{universe} = \Delta S_{Total} = \Delta S_{System} + \Delta S_{Surrounding} > 0$
- $\Delta S_{Total} > 0$ ...... Spontaneous process.

  $\Delta S_{Total} < 0$ ...... Non-spontaneous process.

$\Delta S_{Total} = 0$ ...... 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, $\boxed{\Delta G = \Delta H - T\Delta S}$

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

i) For spontaneous process,
$\Delta S_{Total} > 0$, then $\Delta G < 0$

ii) For non-spontaneous process,
$\Delta S_{Total} < 0$, then $\Delta G > 0$

iii) At equilibrium,
$\Delta S_{Total} = 0$, then $\Delta G = 0$

- At equilibrium,
  $\Delta G = 0$,
  Thus, $\Delta H = T\Delta S$ **OR**

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

- At standard state,
  $\Delta G^o = -RT \ln K$ or, $\Delta G^o = -2.303\ RT \log_{10} K$
  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^0)

- For a reaction, standard entropy change ΔS^o can be calculated

  $aA + bB \rightleftharpoons cC + dD$

  $\Delta S^o = \Sigma S^0_{(Products)} - \Sigma S^0_{(Reactants)}$

  $\Delta S^o = (c S^0_C + d S^0_D) - (a S^0_A + b S^0_B)$