CHAPTER 4

THERMODYNAMICS

4.1 INTRODUCTION

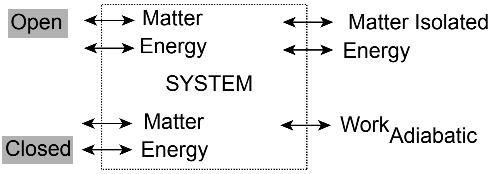
It is the study of energy changes associated with various physical and chemical processes. In thermodynamics, speed of change is not considered and it also does not consider the time element involved in transformation. Laws of thermodynamics are also not applicable at microscopic level.

- In a closed system, boundaries are impermeable.
- In an open system, boundaries are permeable.

4.1.1 Terms Used in Thermodynamics

System and surrounding: System is the specified portion of the universe in which we are observing physical or chemical change. It is surrounded by real or imaginary boundary. Rest of the universe outside the defined system is called surrounding.

4.1.2 Types of System



4.1.3 Thermodynamic Properties

(a) **Intensive properties:** Properties which are independent of quantity of matter, e.g., pressure, specific heat, surface tension, viscosity, boiling point, specific volume, etc.

(b) **Extensive properties:** Properties which depends upon quantity of matter, e.g., total mass, volume, number of moles, etc.

- All thermodynamic quantities whose name include prefix specific or molar are always intensive.
- Extensive properties are additives, whereas intensive properties are not additives.
- Ratio of two extensive variables are always intensive.
- An intensive property depends only on intensive variables, whereas extensive properties depend upon both intensive and extensive variables.

4.1.4 State Function or State Variable

A physical quantity is a state function if its value depends only upon the state of the system and not upon the path by which state is reached, e.g., temperature, pressure, volume, enthalpy, entropy, internal energy, etc.

4.1.5 Path Function and Path Variables

A quantity which depends not only on the state of the system but also on the path or route by which the state is reached, e.g., work done by heat supplied, etc.

4.1.6 Thermodynamic Process

(a) Isothermal (T = constant, i.e., $\Delta T = 0$)
(b) Isobaric (P = constant, i.e., $\Delta P = 0$)
(c) Isochoric (V = constant, i.e., $\Delta V = 0$)
(d) Adiabatic (in which no heat enters or leaves the system, i.e., $q = 0$)

Reversible or quasistatic or pseudostatic process: Thermodynamic process in which driving force is infinitesimally greater than that of restoring force and where direction of change can be reversed by increasing the restoring force by infinitesimal amount is called reversible or quasistatic process.

All slow processes are considered as reversible; however, perfectly reversible process is that which requires infinite number of steps for their completion.

4.1.7 Thermodynamic Equilibrium

Thermodynamic equilibrium in a system implies the existence of the following three equilibria simultaneously:

(i) Thermal equilibrium, i.e., no flow of heat from one part to another, i.e., T = constant
(ii) Mechanical equilibrium, i.e., no flow of matter from one part to another, i.e., P = constant
(iii) Chemical equilibrium, i.e., no change in composition of any part of the system with time.

4.2 FIRST LAW OF THERMODYNAMICS

According to this law, energy can neither be created nor it can be destroyed but it can be transformed from one form to another. Let a system was having E_1 as its internal energy and q amount of heat was supplied to it. Now if w amount of work is done over it then, lets say final internal energy becomes E_2.

$$E_2 = E_1 + q + w \qquad E_2 - E_1 = q + w \qquad \Delta E = q + w$$

Alternative statement of first law of thermodynamics is 'It is impossible to construct a perpetual motion machine, i.e., a machine which can produce energy without expenditure of energy'.

4.2.1 Internal Energy

The energy stored within a substance is called internal energy. Its absolute value cannot be determined, for it is the sum of various form of energies contained in the system.

i.e., $E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \ldots..$

In thermodynamics, we are concerned with energy change which occurs when a system moves from one state to another, i.e., $\Delta E = E_{\text{final (f)}} - E_{\text{initial (i)}}$.

Internal energy is a state function and is an extensive property, as $\Delta E = nC_v \Delta T$.

4.2.2 Work Done in Expansion or Compression

If a system changes its volume from V_1 to V_2 against external pressure, then $\Delta V = (V_2 - V_1)$

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

In case of expansion work done is negative, and in case of compression, work done is positive.

Work done appears at the boundary of the system.

4.2.3 Heat supplied

The energy which crosses the system boundary on account of temperature difference between the system and its surrounding is called heat supplied. It is a path function quantity.

4.2.4 Enthalpy

Heat content of the system at constant pressure and constant temperature is called enthalpy. It is represented by H.

$H = U + PV \quad \Rightarrow \quad \Delta H = \Delta U + \Delta(PV)$

$\Delta H = \Delta U + P\Delta V$ and at constant pressure $\Delta H = \Delta U + \Delta n_g RT$

4.3 MOLAR HEAT CAPACITY

It is defined as the amount of heat required to raise the temperature of one mole of substance by 1°C. It can be at constant volume (C_v) or at constant pressure (C_p). If heat is supplied at constant volume, then it causes change in the internal energy:

If dT rise in temperature is caused by heat supplied dE

$\therefore$ 1° rise in temperature is caused by heat supplied = dE/dT

$\therefore$ $C_v = dE/dT$

Similarly $C_p = dH/dT$

Meyer's equation, $C_p - C_v = R$

4.3.1 Special Case of First Law of Thermodynamics: Isothermal Expansion of an Ideal Gas

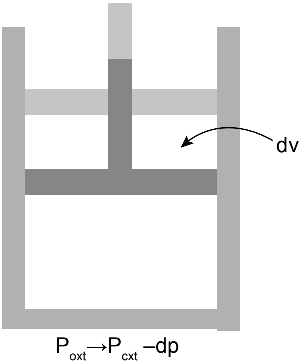
In isothermal expansion heat is allowed to flow in or out of system so that the temperature remains constant and if temperature is constant then ΔT and ΔE are zero. As there will not be any change in internal energy.

∴ From first law of thermodynamics, $\Delta E = q + w$

$$0 = q + w \Rightarrow q = -w$$

∴ Work will be done at the expense of heat absorbed but their magnitude depends upon whether the process is carried out reversibly or irreversibly.

4.3.2 Work Done in Reversible Isothermal Expansion



Let an ideal gas is enclosed in a cylinder fitted with a weightless and frictionless piston. It is not insulated and initially $P_{ext} = P$.

If external pressure fall by dP, then the gas will expand by small volume dV, till its pressure also becomes equal to external pressure (P – dP) and infinitesimally cooling produced by this expansion is compensated by absorption of heat from outside. The small work done in this expansion will be

$$dw = -(P_{ext} - dP)dV = -P_{ext}\, dV + dPdV$$

dPdV can be neglected as it is very small.

Therefore, $dw = -PdV$

If the gas expands from V_1 to V_2 then the total work done can be given by $w = -\int_{V_1}^{V_2} PdV$; We know that PV = n R T, i.e., $P = \frac{n\,R\,T}{V}$;

$$w = \int_{V_1}^{V_2} \frac{n\,RT}{V} dv = -nRT \int_{V_1}^{V_2} \frac{dv}{V};\ w = -\,2.303\ n\,R\,T\ \log \frac{V_2}{V_1} = -2.303\ n\,RT\ \log \frac{P_1}{P_2}$$

4.3.3 Work Done in Irreversible Isothermal Expansion

Irreversible isothermal expansion can be free expansion (in vacuum) or intermediate expansion (when external pressure is less than the pressure of gas). In free expansion, the work done is zero as there is no net pressure. In intermediate expansion, from volume V_1 to V_2, the work done is $w = -\int_{V_1}^{V_2} P_{ext} dV = -P_{ext}(V_2 - V_1)$

Work done in irreversible isothermal expansion is less than reversible isothermal expansion as P_{ext} is less than gas.

4.3.4 Adiabatic Expansion

In adiabatic expansion, no heat is allowed to flow into or out of the system. Therefore, q = 0.

∴ From $\Delta E = q + w$; We have $\Delta E = w$

∴ Work done accompanies the change in internal energy of the system, $dE = C_V\,dT$

∴ $w = \Delta E = C_V\Delta T$

(a) **Reversible Adiabatic Expansion:** If P is external pressure then work done will be $C_V\,dT = -P\,dV$

For 1 mole of gas $P = \frac{RT}{V}$; $C_V dT = -\frac{RT}{V}dV$

$\Rightarrow$ $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ $\Rightarrow$ $TV^{\gamma-1}$ = Constant; $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

∴ PV^{γ} = Constant $\Rightarrow$ $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$ We know that work done

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

(b) **Irreversible adiabatic expansion:** In free expansion, work done is zero.

∴ $\Delta E = 0$ and thus $\Delta T = 0$, $w = 0$ and $\Delta H = 0$.

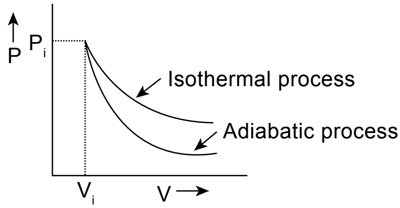
For intermediate expansion, $w = -P_{ext}(V_2 - V_1)$; $w = C_v(T_2 - T_1) = -P_{ext} \times R\left(\frac{P_1T_2 - P_2T_1}{P_1P_2}\right)$

Note:

Comparison between reversible isothermal and adiabatic expansion.

$\Rightarrow$ $P_{ISO} > P_{ADIA}$ $\Rightarrow$ $V_{ISO} > V_{ADIA}$

Area under P–V curve gives us work done. Therefore, work done during reversible isothermal expansion is greater than that of during adiabatic expansion.



4.4 JOULE–THOMSON EFFECT

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule–Thomson effect. The gas is compressed on the left-hand side. Thus, work is done on the gas. It is equal to P_1V_1.

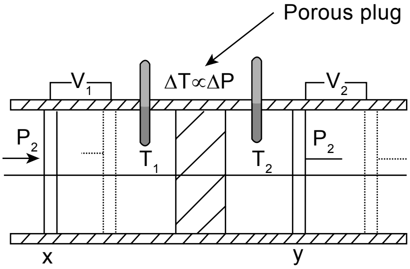
The work done on the right-hand side by the gas is equal to P_2V_2. Total work done by the gas = $P_1V_1 - P_2V_2$.

As q = 0, the work done by the gas lowers its internal energy and consequently temperature falls.

$\Delta E = P_1V_1 - P_2V_2$

$E_2 - E_1 = P_1V_1 - P_2V_2$

$(E_2 + P_2V_2) - (E_1 + P_1V_1) = 0$ or $H_2 - H_1 = 0$ or $\Delta H = 0$.



Note:

Joule–Thomson effect occurs at constant enthalpy; therefore, it is also called isoenthalpic process. When an ideal gas undergoes expansion under adiabatic condition in vacuum, no change takes place in its internal energy.

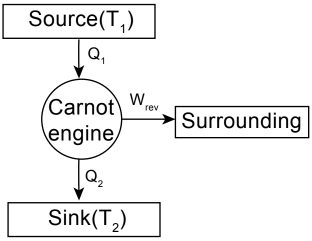
Alternatively, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e., $(\partial U/\partial V)_T = 0$

4.4.1 Joule-Thomson Coefficient

The number of degrees of temperature change produced per unit drop in atmospheric pressure under constant enthalpy condition when a gas is allowed to expand from a region of high pressure to a region of low pressure is known as Joule–Thomson coefficient. $\mu_{\pi} = \left(\frac{dT}{dP}\right)_H$

If μ is positive then gas cools on expansion and if μ is negative then gas warms on expansion. Every gas has a definite value of temperature where μ changes sign from negative to positive (as there is a temperature above which the forces of attraction among molecules become negligible) and that temperature is called inversion temperature. $T_i = \frac{2a}{Rb}$; where a and b are Van der Waal constants.

4.4.2 Carnot Engine



Thermodynamic efficiency, (η) = $\frac{\text{Work done output}}{\text{Heat input}} = \frac{W_{rev}}{Q_{input}}$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1} = \frac{Q}{T} = \text{Constant}$$

4.4.3 Spontaneous Process

A process which proceeds of its own accord without any external help is known as spontaneous process, e.g.,

1. Flow of heat from higher temperature to lower temperature
2. A ball rolling down the hill
3. Diffusion of various gases

It is considered that a process takes place because of its tendency to minimize energy but if it is so then exothermic reaction should only be spontaneous, but it is not so because endothermic reactions are also spontaneous. Therefore, decrease in energy is not the sole criteria for spontaneity. There is another criteria and it is increase in entropy (disorder) of system.

4.4.4 Second Law of Thermodynamics

Statement I: It is impossible to convert heat completely into equivalent amount of work done without compensation.

Statement II: Heat cannot transfer by itself from a cold body to a hot body.

Statement III: When-ever a spontaneous process takes place, then it is accompanied by total increase of entropy.

4.4.5 Entropy of the System

Entropy is the measurement of randomness or disorder of the system. It is a state function quantity and can be formulized as follows.

$$\Delta S = S_2 - S_1 = \frac{Q_2}{T_2} - \frac{Q_1}{T_1};\ \Delta S = \frac{Q_2 - Q_1}{T} \text{ if process is isothermal, } \Delta S = \frac{Q_{rev}}{T}.$$

(a) **Physical significance of entropy:**

  (i) In case of isothermal process, increase in entropy is directly proportional to amount of heat supplied.

  (ii) If heat supplied is kept constant, then increase in entropy is greater at lower temperature as compared to that at higher temperature.

(b) **Change in entropy of reversible process:**

Heat taken by system = Heat given by surrounding

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$.

$$\Delta S_{system} = \frac{Q_{rev}}{T};\ \Delta S_{surrounding} = -\frac{Q_{rev}}{T}$$

Entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero, i.e., $\Delta S = 0$; $\Delta S_{universe} = 0$ and for a reversible process, change in entropy of universe must be equal to zero.

(c) **Change in entropy of irreversible process:** In case of irreversible process, change in entropy of universe must be positive. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$

(d) **Determination of change in entropy:** If $dS = \frac{Q_{rev}}{T}$ and $Q_{rev} = dU - W_{rev}$

$dU = nC_V dT$ for ideal gas and $W_{rev} = -pdV$

$$\Rightarrow\ dS = \frac{nC_v dT + pdV}{T}$$

$$\Rightarrow\ dS = \frac{nC_v dT}{T} + nR\frac{dV}{V} \quad \text{For ideal gas } P = \frac{nRT}{V}$$

$$\Rightarrow\ \Delta S = 2.303n\left[C_v\ \log_{10}\frac{T_2}{T_1} + R\ \log_{10}\frac{V_2}{V_1}\right] = 2.303n\left(C_p \log_{10}\frac{T_2}{T_1} + R\ \log_{10}\frac{P_1}{P_2}\right)$$

Case I: For isothermal process: $\Delta S = 2.303nR\log_{10}\frac{V_2}{V_1} = 2.303\ nR\ \log_{10}\frac{P_1}{P_2}$

Case II: For isochoric process: $\Delta S = 2.303nC_V \log_{10}\frac{T_2}{T_1}$

Case III: For isobaric process: $\Delta S = 2.303nC_p \log_{10}\frac{T_2}{T_1}$

Case IV: For adiabatic process: $\Delta S = 0 = \frac{Q_{rev}}{T}\ \because Q_{rev} = 0$

In case of adiabatic process, change in entropy = 0. It is also called isoentropic process.

4.4.6 Entropy of Physical Changes

(a) **In case of fusion :**

Solid $\rightleftharpoons$ liquid, T_{mp} = melting point, $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{mp}} = \frac{Q_{fusion}}{T_{mp}}$

(b) **Sublimation:**

Solid $\rightleftharpoons$ Gas $\Delta S_{sub} = \dfrac{\Delta H_{sub}}{T_{sub}} = \dfrac{Q_{sub}}{T_{sub}}$; $T_{sub} < T_{mp}$

(c) **Vaporization:**

Liquid $\rightleftharpoons$ Gas $\Delta S_{Vap} = \dfrac{\Delta H_{Vap}}{T_{bp}} = \dfrac{Q_{Vap}}{T_{bp}}$

(d) **Transition:** Conversion of one allotropic form of a substance into another form is called transition.

$S_{\text{Monoclinic}} \rightleftharpoons S_{\text{Rhombic}}$

Diamond $\rightleftharpoons$ Graphite

Red phosphorous $\rightleftharpoons$ White Phosphorous

$$\Delta S_{Trans} = \frac{\Delta H_{Trans}}{T_{Trans}} = \frac{Q_{Trans}}{T_{Trans}}$$

4.4.7 Helmholtz Free Energy Change

Helmholtz free energy, $A = U - TS$

It is a state function quantity.

Decrease in Helmholtz free energy change = Maximum work done = Work function of process.

(a) Gibb's free energy change: Gibbs free energy, $G = H - TS$

It is a state function as $\Delta G = \Delta H - T\Delta S$.

ΔG = Useful work done.

(b) Maxwell's equations:

(i) $dU = TdS - PdV$ (ii) $dH = TdS + VdP$

(iii) $dA = -SdT - PdV$ (iv) $dG = -SdT + VdP$

If V is constant, then dV is zero. Then, equation (i) yields

$\Rightarrow \left(\dfrac{\partial U}{\partial S}\right)_V = T$. If S is constant, then $\left(\dfrac{\partial U}{\partial V}\right)_S = -P$.

4.5 THERMOCHEMISTRY

Thermochemistry is the branch of physical chemistry that deals with energy changes accompanying chemical reactions. In a chemical reaction, old bonds get broken with the absorption of energy and the formation of new bonds takes place with the release of energy. If there is net absorption of energy, then the reaction is called endothermic. Then, at constant pressure $H_P > H_R$; $\Rightarrow \Delta H = H_P - H_R = +ve$;

If there is net release of energy, then the reaction is called exothermic.

Then, $H_P < H_R$; at constant pressure, $\Delta H = H_P - H_R = -ve$;

Note:

Most of the reactions are carried out in open vessels so that the pressure remains constant during that process. So heat evolved or absorbed during the reaction will be equal to the enthalpy change in the reaction.

4.5.1 Heat of Reaction or Enthalpy of Reaction

It is defined as the amount of heat absorbed or evolved when the quantities of the substance indicated by balanced chemical equation have completely reacted, e.g.,

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$; ΔH = – 44 kcal

$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$; ΔH = + 31.4 kcal

4.5.1.1 Factors which influence the heat of reaction

(i) **Physical state of reactant and product:** Heat of reaction depends on the physical state of reactant and product.
e.g., Consider the following reaction $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$; ΔH = –57.8 kcal
$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)}$; ΔH = –68.32 kcal
More heat is released when water formed is in liquid state. It is because of the reason that heat is released during condensation of steam.

(ii) **Allotropic forms of the element:** The heat of reaction depends upon the allotropic forms of the element

e.g., $\underbrace{C_{(S)}}_{\text{Diamond}} + O_{2(g)} \rightarrow CO_{2(g)}$; ΔH = –394 KJ/ mol

$\underbrace{C_{(S)}}_{\text{Graphite}} + O_{2(g)} \rightarrow CO_{2(g)}$; ΔH = –393.5 KJ/ mol

This difference in the heat of reaction in two allotropic forms is due to the difference in the arrangement of atoms in these allotropic forms.

(iii) **Enthalpy of solvation:** The amount of enthalpy change when the substance reacts with each other in dry state will be different than when they react in solution
e.g., $H_2S_{(g)} + I_{2(g)} \rightarrow 2HI + S$; ΔH = –17.2 kcal
$H_2S_{(g)} + I_{2(Solution)} \rightarrow 2HI + S$; ΔH = –21.93 kcal
This difference is because of the reason that in solution there is involvement of energy in the form of solvation.

(iv) **Temperature:** The amount of enthalpy change depends upon temperature as the heat capacities of system varies with temperature. The standard temperature for the calculation of enthalpies of various reaction is 25° C or 298 K.

4.5.2 Enthalpy of Formation or Heat of Formation

It is defined as the amount of heat evolved or absorbed when 1 mole of a compound is formed from its constituent elements.

e.g., $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; ΔH = –97.5 kcal/mol

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$; ΔH = –44 kcal/mol

Since on formation of 2 moles of HCl, 44 kcal of heat is released. Therefore, in the formation of 1 mole of HCl, 22 kcal of heat will be released or we can say that the heat of formation of HCl is 22 kcal. Heat of a reaction can be calculated if the values of enthalpy of formation of reactants and products are known by using

$$\Delta H^\circ(\text{reaction}) = \Sigma\, \Delta H^\circ_f\,(\text{product}) - \Sigma\Delta H^\circ_f\,(\text{ reactants})$$

Note:

If the reaction is carried out at standard conditions (i.e., at 25°C and 1 atm. pressure), then the heat of formation is called standard heat of formation and it is denoted by ΔH°_f. For the determination of enthalpy of formation of compound, we take standard enthalpies of free elements as zero (arbitrarily).

4.5.3 Enthalpy of Combustion

It is defined as the amount of heat evolved when 1 mole of a substance is completely oxidized.

e.g., $C_{(s)} + 1/2 \rightarrow CO_{(g)}$; $\Delta H = -26$ kcal

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -94.3$ kcal

The enthalpy of combustion of carbon is 94.3 kcal and not 26 kcal, as the complete oxidation of carbon produces carbon dioxide.

4.5.4 Enthalpy of Solution

It is defined as the amount of heat evolved or absorbed when 1 mole of a substance is dissolved in that much quantity of solvent that further dilution does not cause any heat change.

e.g., $KCl + aq \rightarrow K^+(aq) + Cl^-$; $\Delta H = -4.4$ kcal

$KOH + aq \rightarrow K^+(aq) + OH^-(aq)$; $\Delta H = -13.3$ kcal

4.5.5 Enthalpy of Neutralization

It is defined as the heat evolved when 1 gram equivalent of an acid is neutralized by 1 gram equivalent of base in dilute solution.

e.g., Consider the neutralization of HCl with NaOH

$HCl \xrightarrow{(aq)} H^+(aq) + Cl^-(aq)$

$NaOH + aq \rightarrow Na^+(aq) + OH^-(aq)$

$H^+ + OH^- \rightarrow H_2O$

$HCl + NaOH \rightarrow Na^+ + Cl^- + H_2O$

Therefore neutralization reaction is the reaction between H^+ ion and OH^- ion and the heat evolved by using a strong base and strong acid will always be the same as they will ionize completely in the solution.

Note:

The heat evolved during the neutralization of weak acid by strong base or weak base by strong acid or weak acid by weak base will be less than 13.7 kcal as certain amount of heat is absorbed for the ionization of weak acid or weak base.

$$\underset{(strong)}{HCl_{(aq)}} + \underset{(weak)}{NH_4OH_{(aq)}} \rightarrow NH_4Cl + H_2O;\ \Delta H = -12.3 kcal$$

$$\underset{(weak)}{HCN_{(aq)}} + \underset{(strong)}{NaOH_{(aq)}} \rightarrow NaCN + H_2O;\ \Delta H = -11.5 kcal$$

$$H^+ + OH^- \rightarrow H_2O;\ \Delta H = -13.7\ kcal$$

4.5.6 Enthalpy of Fusion

It is defined as the heat absorbed when 1 mole of a substance changes its state from solid to liquid at its melting point.

$$H_2O(s) \xrightarrow{\text{melting}} H_2O(1); \Delta H = +10.5\text{kcal}$$

4.5.7 Enthalpy of Sublimation

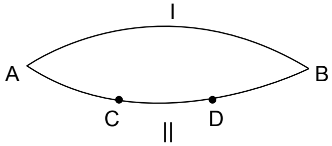
It is defined as heat absorbed when 1 mole of a substance changes into vapour state at a given temperature below its melting point, e.g., I_2 (s) → I_2 (g); $\Delta H = +14.9$ kcal.

It is equal to the sum of enthalpy of fusion and the enthalpy of vapourisation

$$\Delta H_{\text{Sublimation}} = \Delta H_{\text{Fusion}} + \Delta H_{\text{Vapourization}}.$$

4.6 HESS'S LAW OF CONSTANT HEAT SUMMATION

It states that the enthalpy of a reaction is dependent only on the initial and final stages whether it takes place in one step or in number of steps. Let us consider that a substance A is changed into B by two ways.



By the Ist way A is converted into B in one step and in the IInd step it is first converted into C and then into D and finally D is converted into B. Let us say that in the I step the heat evolved is more than IInd way, then we can go from A to B through the Ist way and then return to A through the IInd step. In this way the amount of energy released will be more than the energy absorbed in the cyclic process and as a result of which there is net production of energy which is in contradiction with law of conservation of energy.

Application of Hess's Law: Hess's law gave the following three indirect methods for the calculation of heat of reaction: $\Delta H_{\text{reaction}} = \sum$ Bond energy of reactants – $\sum$ Bond energy of products.

$\Delta H_{\text{reaction}} = \sum$ Heat of combustion of reactants – $\sum$ Heat of combustion of products.

$\Delta H_{\text{reaction}} = \sum$ Heat of formation of products – $\sum$ Heat of formation of reactants.

4.7 BOND ENERGY AND BOND ENTHALPY

The average bond dissociation energy required to break each bond in a compound is called bond energy.

e.g., $H_2O(g) \rightarrow H(g) + OH(g); \Delta H = 497.8 \text{ KJ mol}^{-1}$

$OH(g) \rightarrow H(g) + O(g); \Delta H = 428.5 \text{ KJ mol}^{-1}$

$$\text{Bond energy} = \frac{497.8 + 428.5}{2} = 463.15 \text{ KJ/mol}$$

The same amount of energy is released when the bond is formed between hydrogen and oxygen.

4.7.1 Applications of Bond Energy

(a) **Determination of heat of reaction:** In a chemical reaction old bonds get broken and formation of new bonds takes place among the reactant molecules, and the energy is absorbed to break the bonds and among product molecules the energy is released on the formation of new bonds. The net amount of energy absorbed or evolved is know as heat of reaction.

Note:

Heat of reaction = $\sum$ Bond energy of reactants – $\sum$ Bond energy of products.

(b) **Determination of resonance energy:** A compound which shows resonance has more stability and its heat of formation will be different than what we have calculated from bond energies. This difference is called resonance energy.

Note:

Resonance energy = Experimental or actual heat of formation or calculated heat of formation.

4.8 INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION

Heat of formation of reactants. We know that $\Delta H = H_P - H_R$

Differentiating the above equation w.r.t. T at constant $P = \left(\frac{d\,\Delta\,H}{dT}\right)_P = \left(\frac{d\,H_P}{dT}\right)_P - \left(\frac{d\,H_R}{dT}\right)_R$

$$\frac{d\Delta H}{dT} = (C_P)_{\text{products}} - (C_P)_{\text{Reactants}} \quad \text{....... (i)}$$

$d\,\Delta\,H = \Delta C_p\,dT$

On integrating equation (i) we have

$$\int_{T_1}^{T_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_P\,dT$$

$\Rightarrow \quad \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$; Kirchoff's equation at constant pressure:

Difference in the heat capacities of product and reactants is constant. If heat is supplied at constant volume, then $\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$.

Above equation is known as Kirchoff's equation at constant volume.