# CHEMICAL ENERGETICS

## Preface

Every chemical reaction involves the exchange of energy. The study of exchange of energy between the chemical species is known as chemical energetics.
This chapter deals with the study of various laws of thermodynamics and thermochemistry, various types of heat of reaction, concept of entropy and free energy.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total number of questions in **Chemical Energetics** are :

| | | | |
|---|---|---|---|
| (i) | In chapter Examples | .......................... | 11 |
| (ii) | Solved Examples | .......................... | 15 |
| | Total no. of questions | ......................... | **26** |

## 1. INTRODUCTION

Chemical reactions involve the change in energy. Some reactions like oxidation, hydration etc. produce energy. Other like hydrolysis, ionisation, splitting of water into hydrogen and oxygen etc. use energy. These energy changes result due to breaking of bonds in reactant molecules (consume energy) and formation of bonds in product molecule (release energy) during a chemical reaction.

## 2. CHEMICAL ENERGETICS

The branch of science which deal with the energy changes associated with chemical reactions is called chemical energetics. While the study of heat energy and its transformation is known as thermodynamics.

## 3. ENERGY

Basically energy is the capacity of do work. or energy is the capacity of transfer heat It is basically of two types -

(i) Kinetic Energy : It is the energy of motion and its magnitude depends upon mass of an object 'm' and its velocity u.

$$\text{i.e.K.E.} = \frac{1}{2}mu^2$$

(ii) Potential Energy : An object can also possess energy by virtue of its position relative to other. This stored energy is known as potential energy.

### 3.1 Units of Energy

(i) The SI units of energy is the Joule (J) :

Let one joule is defined as the kinetic energy associated with a mass of 2 kg object moving with a velocity of 1m/s

then K.E. = 1 Joule .

(ii) Traditional unit of energy is calorie.

One calorie is the amount of energy required to raise the temperature of 1g water by 1ºC from 14.5ºC to 15.5ºC is –

1 calorie = 4.18 Joule

## 4. TERMS USED IN THERMODYNAMICS

### 4.1 System

A specified part of the universe with real or imaginary boundaries, on which studies of P, T etc are to be made

### 4.2 Surrounding

The rest part of the universe, adjacent to real or imaginary boundaries of the system .

Universe = System + Surrounding

### 4.3 Types of system

(i) Homogenous systems : A system having uniform nature throughout, made up of one phase only

(ii) Heterogeneous system : A system not uniform throughout, consists of more than one phase.

### 4.4 Another classification of system

(i) **Open system :** Those in which exchange of mass and energy is possible with surroundings

Example - Boiling of water in beaker.

(ii) **Closed system :** Those in which only exchange of energy (and not of mass) takes place with surrounding

Example : Heating of liquid in a sealed tube.

(iii) **Isolated system :** Those in which neither exchange of mass nor exchange of energy takes place with surrounding

Example : Liquid in a sealed thermos flask.

### 4.5 Properties of a system

It is of two types

(i) Intensive properties : The properties of a system which are independent of quantity of matter present in the system.

Example : Temperature, Pressure, Density etc.

(ii) Extensive properties : The properties of a system which depends upon the quantity of matter present in system.

Example : Mass, Volume, Energy etc.

### 4.6 State functions

The fundamental properties - Pressure, Volume, Temperature, Energy, Enthalpy, Entropy etc. which define the state of system are known as state functions.

## 5. THERMODYNAMIC PROCESS

### 5.1 Isothermal Process

(i) A process in which temperature of the system does not change throughout the studies.

(ii) Means $dT = 0$ and thus $dE = 0$

(iii) It can be achieved by using thermostatic both.

### 5.2 Adiabatic Process

(i) A process in which exchange of heat between system and surrounding does not take place.

(ii) Means $q = 0$

(iii) It can be achieved by insulating the system boundaries .

### 5.3 Cyclic Process

(i) In which initial state of system is required after a series of operation

(ii) For a cyclic process $\Delta E = 0$ and $\Delta H = 0$

### 5.4 Isochoric Process

(i) A process in which volume of the system remains constant throughout.

(ii) For an Isochoric process $\Delta V = 0$

### 5.5 Isobaric process

(i) A process in which pressure of the system remains constant

(ii) Means $\Delta P = 0$

### 5.6 Reversible Process

A reversible process is one in which all changes occurring at any part of the process are exactly reversed when change is carried out in opposite direction. It involves a slow change during operations and take place in either direction.

### 5.7 Irreversible Process

An irreversible process is one in which direction of the change cannot be reversed by small change in variables. It involves fast changes during operations and is unidirectional process.

### 5.8 Nature of work and heat

**Work :** It is expressed as the product of two factors i.e.

W = Intensity factor x Capacity factor

i.e. Mechanical work

= Force (F) × Displacement (d)

Electrical work

= Potential difference (E) ×Charge flown (Q)

Expansion work

= Pressure (P) × Change in Volume ($\Delta V$)

### 5.9 Units of Work

In C.G.S. = erg

M.K.S. = Joule or N × M

### 5.10 Sign Conventions

(i) Work done by the system is (– ve) Negative.

(ii) Work done on the system is (+ ve) positive.

**Note :**

(i) Work is not a state function because the amount of work performed depends upon the path followed.

(ii) Heat : It is a measure of quantity of energy transferred from one body to other

Heat absorbed by the system is positive ;

$$\Delta H = + ve$$

Heat evolved by the system is negative ;

$$\Delta H = - ve$$

## 6. INTERNAL ENERGY (E)

The internal energy is comprised of many energy terms such a translational, vibrational, rotational, potential, interaction energy etc.

Internal energy is a state function and thus depends upon the state of the system and not upon how the system attains this state.

Change in Internal Energy i.e. $\Delta E$

$$\Delta E = E_{final} - E_{initial}$$

A positive $\Delta E$ results when $E_{final} > E_{initial}$ indicating that the system has gained energy from its surrounding.

A negative $\Delta E$ is obtained when $E_{final} < E_{initial}$ indicating that the system has lost energy to its surrounding.

In a chemical reaction

$$\Delta E = E_{product} - E_{reactant}$$

for Example :

$$H_2 + ½ O_2 \longrightarrow H_2O$$

i.e. $\Delta E = E_{H_2O} - [E_{H_2} + ½ E_{O_2}]$

### 6.1 Characteristics of internal Energy

(i) It is an extensive property and depends upon the amount and physical state of substance.

(ii) Internal energy change during a cyclic process is zero.

### 6.2 Exothermic and Endothermic Reactions

Consider a Reaction - Reactant → Product

### 6.2.1 Exothermic Reactions

A reaction that results in the evolution of heat is exothermic i.e. heat flows out of the system into its surrounding.

Means $E_{Product} < E_{Reactant}$ i.e. $\Delta E = -$ ve

Example - Combustion reactions

### 6.2.2 Endothermic Reactions

A reaction that result in the absorption of heat is endothermic i.e. system absorb heat from its surrounding.

Means $E_{Product} > E_{Reactant}$ i.e. $\Delta E = +$ ve

Example - Melting of ice etc.

## 7. FIRST LAW OF THERMODYNAMICS

(i) The first law of thermodynamics is also called the law of conservation of energy.

(ii) The law was first of all stated by Meyer and Helmholtz.

(iii) It states that the generation of any kind of energy is impossible without the expenditure of an equivalent amount of another kind of energy.

or Energy of the universe is conserved.

or Energy can neither be created nor destroyed although it may be changed from one form to another.

Let the system be supplied Q amount of heat and $\Delta E$ is the change in internal energy associated with W work done then

$$Q = \Delta E - W$$

### 7.1 Enthalpy (H) and Enthalpy Change (ΔH)

It expressed as the sum of the internal energy and the pressure volume energy.

i.e. $H = E + PV$

but in other words, the heat changes of chemical reactions at constant pressure and constant temperature known as enthalpy.

Where H is enthalpy, E is internal energy, P is pressure, V is volume

According to F.L.O.T.

$$q = \Delta E + W$$

or $q = \Delta E + P\Delta V$

or $q = (E_2 - E_1) + P(V_2 - V_1)$

or $q = (E_2 + PV_2) - (E_1 + PV_1)$

or $q = H_2 - H_1 = \Delta H$

In chemical reactions

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

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

Thus the enthalpy change represents the heat change taking place during the process occuring at constant temperature and constant pressure.

### 7.2 Relationship between ΔH and ΔE

$$H = E + PV$$

or $\Delta H = \Delta E + \Delta(PV)$

at constant pressure :

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

or $\Delta H = \Delta E + (\Delta n) RT$

Where $\Delta n$ = Change in number of gaseous moles.

### 7.3 Enthalpies of Reactions

The enthalpy change for a chemical reaction is given by

(i) $\Delta H = H_{products} - H_{reactant}$

Case I : When $H_P > H_R$.

An equivalent amount of Heat i.e. $q_p = \Delta H =+$ ve is absorbed and the reaction is endothermic.

Case II : When $H_P < H_R$

An equivalent amount of heat i.e. $q_p = \Delta H = -$ve is evolved. $\Delta H = -$ ve

Exothermic reaction : $\Delta E$ or $\Delta H = -$ ve

Endothermic reaction : $\Delta E$ or $\Delta H = +$ ve

### 7.4 Characteristics of Enthalpy concept

(i) Enthalpy is an extensive property

(ii) The enthalpy change for a reaction is equal in magnitude but opposite in sign to $\Delta H$ for reverse reaction

$$C + O_2 \rightarrow CO_2 \ ; \ \Delta H = -94.3 \text{ Kcal}$$

$$CO_2 \rightarrow C + O_2; \ \Delta H = +94.3 \text{ Kcal}$$

## Examples based on First Law of Thermodynamics

**Ex.1** A sample of gas is compressed by an average pressure of 0.50 atmosphere so as to decrease its volume from 400cm$^3$ to 200cm$^3$. During the process 8.00 J of heat flows out to surroundings. Calculate the change in internal energy of the system.

**Sol.** Here $\Delta V = 200 - 400 = -200\ cm^3$

A we know 1 Litre = 1000 cm$^3$

$\Rightarrow$ $\Delta V = -\ 0.2$ Litre.

External Pressure (P) = 0.50 then

Work done $= -\ P\Delta V = +\ 0.50\ (0.2)$

$= +\ 0.1$ atm Litre

and 1 litre – atmosphere = 101.3 Joule

$\therefore$ W = + 10.13 Joule

According to F.L.O.T.

$q = \Delta E - W$

then $\Delta E = q + W$

Given $q = -\ 8.00$ J

$\Rightarrow$ $\Delta E = -\ 8 + 10.13 = 2.13$ Joule

**Ex.2** The heat of combustion of napthalene ($C_{10}H_8(s)$) at constant volume was measured to be – 5133 kJ mol$^{-1}$ at 298K. Calculate the value of enthalpy change (Given R = 8.314 JK$^{-1}$ mol$^{-1}$).

**Sol.** The combustion reaction of napthalene.

$C_{10}H_8(s) + 12O_{2(g)} \rightarrow 10CO_{2(g)} + 4H_2O_{(l)}$; $\Delta E = -\ 5133kJ$

$\Delta n = 10 - 12 = -\ 2$ mol.

Now applying the relation.

$\Delta H = \Delta E + (\Delta n)\ RT$

$= -\ 5133 \times 10^3 + (-2)\ (8.\ 314)\ (298)$

$= -\ 5133000J - 4955.14J$

$= -\ 5137955.\ 14$ Joule

**Ex.3** What is the true regarding complete combustion of gaseous isobutane -

(A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$

(C) $\Delta H = \Delta E = O$ (D) $\Delta H < \Delta E$

**Sol.** **(D)**

$C_4H_{10}(g) + 6.5O_2\ (g) \rightarrow 4CO_2(g) + 5H_2O_{(l)}$

$\Delta n = [4 - 7.5] = -3.5$

$\Delta H = \Delta E + \Delta n_g RT$

$\therefore$ $\Delta H < \Delta E$

## 8. THERMOCHEMICAL EQUATIONS

It is an equation which represents chemical as well as thermal changes taking place in a reaction.

Example :

A Chemical equation

$C + O_2 \longrightarrow CO_2$

A thermochemical equation

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ ; $\Delta H = -\ 943$ Kcal

reactants products Energy change.

### 8.1 Heat of Reaction

It is defined as the change in heat enthalpy or change in internal energy or amount of heat evolved or absorbed during the complete course of reaction as represented by a balanced thermochemical equation.

**Example :** $C + O_2 \rightarrow CO_2$ ; $\Delta H = -\ 94.3$ Kcal

It signifies that 12g of carbon on reaction with 32g $O_2$ gives 44g $CO_2$ along with 94.3 Kcal of heat evolution.

### 8.2 Factors Influencing Heat of Reaction

1. Physical nature of reactants and products : The heat of reaction varies for a given reaction with the change in physical nature of reactant or products.

   **Exmaple :** $C_{diamond} + O_2 \rightarrow CO_2$ ; $\Delta H = -\ 94.3$ Kcal

   $C_{amorphous} + O_2 \rightarrow CO_2$ ; $\Delta H = -\ 97.7$ Kcal

2. Reaction carried out at constant pressure or constant volume :

   At Constant

   $V.q_v = \Delta E$ Change in Internal Energy

   At Constant

   $P.q_p = \Delta H$ Change in Enthalpy

3. Temperature : Heat of reaction also depends on the temperature :

   In terms of Enthalpy

   $\Delta H_2 - \Delta H_1 = \Delta Cp\ (T_2 - T_1)$

   and In terms of Internal Energy

   $\Delta E_2 - \Delta E_1 = \Delta Cv\ (T_2 - T_1)$

When $\Delta C_P = \Sigma C_P$ of products – $\Sigma C_P$ of reactants

$\Delta C_V = \Sigma C_V$ of products – $\Sigma C_V$ of reactants

### 8.3 Types of heat reactions

**(a) Heat of formation or Enthalpy of formation**

It is the change in enthalpy when one mole of a substance is formed directly from its constituent element

Example :$C + O_2 \rightarrow CO_2$ ; $\Delta H = -94.3$ Kcal

$C + 2S \rightarrow CS_2$ ; $\Delta H = 22.0$ Kcal

**Standard Heat Enthalpy : ($\Delta H_f^0$)**

The heat enthalpy of a compound at 25ºC and one atmosphere pressure is known as standard heat enthalpy of that compound.

**Note :** Assuming the enthalpy of a pure element in its most stable state at 25ºC and 1 atm, is equal to zero.

**(b) Heat of combustion**

It is defined as the change in heat enthalpy when one mole of a substance is completely burnt in oxygen.

Example :$C + O_2 \rightarrow CO_2$ ; $\Delta H = -94.3$ Kcal

**(c) Heat of solution**

It is defined as the change in heat enthalpy when one mole of a substance is dissolved in excess of water so that further dilution does not involve any heat change.

Ex. :$KCl_{(s)} + aq. \rightarrow KCl_{(aq)}$ ; $\Delta H = 4.4$ KCal

**(d) Heat of Hydration**

It is defined as the change in heat enthalpy when one mole of an anhydrous is completely hydrated by combining with specific moles of water.

Ex. : $CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4.5H_2O$ ; $\Delta H = -15.8$ Kcal

**(e) Heat of Neutralisation**

It is defined as the change in heat enthalpy when one gram equivalent of an acid is completely neutralised by 1gram equivalent of a base in dilute solutions.

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$ ; $\Delta H = 13.7$ Kcal.

$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_3 + H_2O$ ; $\Delta H = -13.7$ Kcal.

Thus it is clear that heat of formation is -13.7 K cal

but in case when 1gm equivalent each of weak acid and strong base or a strong acid and weak base or weak acid and weak base are allowed to react, the apparent value of heat of neutralization is lesser than 13.7 K Cal

Example

$HCl_{(aq)} + NH_4OH_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_2O$ ; $\Delta H = -12.3$ K Cal

## Examples based on Thermochemical Equation

**Ex.4** How much heat is produced when 4.50g methane gas is burnt in a constant pressure system.

**Sol.** Given

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ ; $\Delta H = -802$ KJ

$\because$ 16g $CH_4$ on burning produces heat = – 802KJ

$\therefore$ 4.5 g $CH_4$ on burning produces heat

$$= \frac{-802 \times 4.5}{16} = 225.6 \text{ KJ} .$$

**Ex.5** $\Delta H_f^0$ for $Al_2O_3$ is –1670 KJ. Calculate the enthalpy change for the reaction

$4Al + 3O_2 \rightarrow 2Al_2O_3$

**Sol.** Given $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$ ;

$\Delta H = -1670$KJ

Multiplying it by 2

then $4Al + 3O_2 \rightarrow 2Al_2O_3$

$\Delta H = 2 \times (-1670)$

$= -3340$KJ

**Ex.6** The specific heats of iodine vapours and solid are 0.031 and 0.055 Cal/g respectively. If heat of sublimation of iodine is 24Cal/g at 200º, What is its value at 250ºC.

**Sol.** $I_{2\,(solid)} \rightarrow I_{2\,(vapour)}$ ; $\Delta H = 24$ Cal/g at 200ºC

$\Delta C_p = C_p$ of product $- C_p$ of reactant

$\Delta C_p = 0.031 - 0.055 = -0.024$ Cal/g

$\because$ $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

$\Delta H_2 - 24 = -0.024\ (523 - 473)$

$\therefore$ $\Delta H_2 = 22.8$ Cal/g

**Ex.7** Calculate the heat of neutralization by mixing 200ml of 0.1M $H_2SO_4$ and 200 ml of 0.2 M KOH if heat generated by the mixing is 2.3 KJ.

**Sol.** Meq of $H_2SO_4 = 200 \times 0.1 \times 2 = 40$

meq or KOH $= 200 \times 0.2 = 40$

$\because$ 40 Meq of $H_2SO_4$ and 40Meq of KOH on mixing gives heat 2.3 KJ

$\therefore$ 1000 Meq of $H_2SO_4$ and 1000 Meq of KOH on Mixing gives heat -

$$= \frac{2.3 \times 1000}{40} \text{ KJ} = 57.5 \text{ KJ}$$

## 9. ENERGETICS OF PHASE TRANSITION

### 9.1 Enthalpy of fusion

It is defined as the change in heat enthalpy (always increase i.e. $\Delta H = +$ ve). When 1 mole of a substance is completely converted from solid state into liquid state at its freezing point.

$$H_2O(s) \longrightarrow H_2O(\ell) \ ; \ \Delta H = +6.0 \text{ KJ}$$

The reverse of fusion i.e. conversion of liquid to solid is known as freezing and enthalpy change shows an equivalent amount of decrease during the process.

### 9.2 Enthalpy of Vapourisation

It is defined as the change in heat enthalpy (always decrease i.e. $\Delta H = -$ve) when 1 mole of a substance is completely converted from liquid state into vapour state at its boiling point.

$$H_2O_{(l)} \longrightarrow H_2O(g) \ ; \ \Delta H = +40.6 \text{ KJ}.$$

The reverse of vapourisation is known as condensation.

### 9.3 Heats of sublimation

It is defined as the change in heat enthalpy (always increase i.e. $\Delta H = +$ve) When one mole of a solid is directly converted into its gaseous state at a temperature below its melting point.

$$I_2(s) \longrightarrow I_2(g) \ ; \ \Delta H = +62.4 \text{ KJ}$$

### 9.4 Heats of Transition

It is defined as the change in heat enthalpy when one mole of a substance is completely converted from one allotropic form to other as its transition temperature.

Example $C_{diamond} \longrightarrow C_{graphite} \Delta H = -1.9 \text{KJ}$

## 10. LAWS OF THERMOCHEMISTRY

### 10.1 Lavoisier and Laplace law

The enthalpy of decomposition of a compound of that compound is numerically equal to the enthalpy of formation with opposite sign

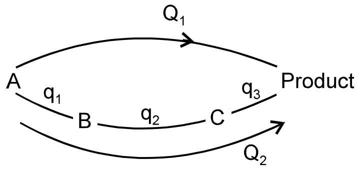
Example

$$C(s) + O_2(g) \longrightarrow CO_2(g) \ ; \quad \Delta H = -94.3 \text{ Kcal}$$

$$CO_2(g) \longrightarrow C(s) + O_2(g) \ ; \quad \Delta H = +94.3 \text{ Kcal}$$

### 10.2 Hess's Law of constant heat summation

It state that the total heat change during the complete course of a reaction is same whether the reaction is made in one step or in several steps.



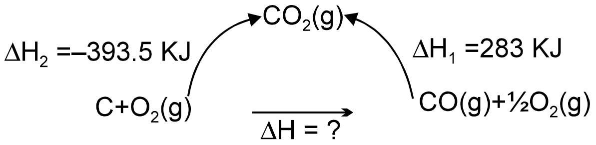
$$\Delta H = q_1 + q_2 + q_3 = Q_2.$$

Then According to Hess's Law $Q_1 = Q_2$.

#### 10.2.1 Significance of Hess's Law

1. **Calculation of enthalpies of reactions :**

   Example



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

$\Rightarrow \quad \Delta H = \Delta H_2 - \Delta H_1$ ,

$= -393.5 - (-283)$

$= -110.5$ KJ

2. **Calculation of Bond Energies :**

   The energy required to break a bond in a gaseous molecule is referred to as bond energy or bond dissociation Energy

   [Enthalpy of reaction] =

   [Sum of bond energies of reactants] – [Sum of bond energies of products]

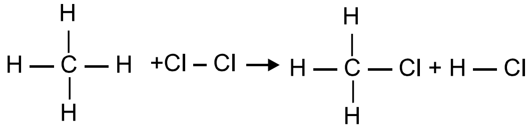
## Examples based on Bond energy

**Ex.8** Determine the enthalpy change for the reaction

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Bond energies for C – H, C – Cl, Cl – Cl, H – Cl are 412, 338, 242, 431 kJ/mol. respectively.

**Sol.**



$$H{-}\overset{H}{\underset{H}{C}}{-}H + Cl-Cl \rightarrow H{-}\overset{H}{\underset{H}{C}}{-}Cl + H-Cl$$

$$\Delta H = (\Sigma \text{ B.E})_{reactant} - (\Sigma \text{ B.E})_{product}$$

$$= 4(\text{B.E.})_{C-H} + 1(\text{B.E.})_{Cl-Cl} - 3(\text{B.E.})_{C-H}$$

$= [4(B.E.)_{C-H} + 1(B.E.)_{Cl-Cl} - \{3(B.E.)_{C-H} + 1(B.E.)_{C-Cl} + 1(B.E.)_{H-Cl}\}]$

$= 412 + 242 - 338 - 431$

$= -115$ kJ/ mol

**Ex.9** Calculate the enthalpy change ($\Delta H$) for the following reaction

$2C_2H_2 (g) + 5 O_2(g) \rightarrow 4CO_2 + 2H_2O (g)$

Given average bond energies of various bonds i.e. C – H, C≡ C , O = O, C = O, O – H as 414, 810, 499, 724 and 460 KJ/mole respectively

**Sol.** $2 [H - C \equiv C - H] + 5 (O = O) \rightarrow 4 (O = C = O) + 2(H - O - H)$

The reaction involves the breaking of 4 C – H bonds, 2 C ≡ C bonds, 5 O = O bonds and formation of 8 C = O bonds and 4 O – H bonds.

$\Delta H$ = [Total energy required to break bonds] – [Energy given out in forming the bonds]

$= [4\Delta H_{C-H} + 2\Delta H_{C\equiv C} + 5\Delta H_{O=O}] - [8\Delta H_{C=O} + 4\Delta H_{O-H}]$

$= (4 \times 414 + 2 \times 810 + 5 \times 499) - (8 \times 724 + 4 \times 460)$

$= 5771 - 7632$

$= -1861$ KJ

## 11. FUEL AND SOURCES OF ENERGY

(1) Fossil Fuels : Coal, oil and natural gas which are presently our major source of energy are known as fossil fuels.

(2) Hydroelectric power

(3) Geothermal Power

(4) Nueclear Energy

(5) Solar Energy

## 12. SPONTANEOUS PROCESS

In our daily life, we come across many natural processes which take place of their own in one direction but not in the other. For example, water flows down the hill without the help of external agency but water cannot flow up the hill of its own.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under a given set of conditions is known as spontaneous process.

**Example**

(i) Which need no initiation

(1) Evaporation of water $H_2O (\ell) \rightarrow H_2O (g)$

(2) Dissolution of sugar in water to form a solution. etc.

(ii) Which need initiation -

(1) Hydrogen react with oxygen gas to produce water. It is initiated by passing an electric discharge.

$$2H_2(g) + O_2(g) \xrightarrow[\text{discharge}]{\text{Electric}} 2H_2O(\ell)$$

### 12.1 Criterion of Spontaneity

(I) $\Delta H$ as criterion of spontaneity -

A process in which the enthalpy of the system decreases (or an exothermic process) may tend to occur spontaneously, because every system tends to change from higher energy level to lower energy level.

Examples: $C + O_2 \longrightarrow CO_2 \quad \Delta H = -$ ve

$H_2 + 1/2O_2 \longrightarrow H_2O \quad \Delta H = -$ ve

$N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = -$ ve

the enthalpy change of process is not enough, because the criteria of spontaneity on the basis of decrease in heat enthalpy fails in many of the examples.

Examples :

(i) Decomposition of Mercuric oxide

$2HgO (s) \longrightarrow 2Hg (\ell) + O_2 (g)$ ; $\Delta H = +$ ve

(ii) Formation of Water gas

$C_{(s)} + H_2O_{(steam)} \longrightarrow CO_{(g)} + H_{2\,(g)}$ ; $\Delta H = +$ ve

(II) Randomness criterion for spontaneity :

Spontaneity is the tendency of show maximum disorder.

Process in which the disorder of the system increase to occur spontaneously.

Spontaneity of some endothermic reactions in terms of randomness.

Example :

(i) Dissolution of $NH_4NO_3$ :-

During dissolution, the ions which were tightly held in crystal lattice are set free to move in all direction showing increase in randomness

(ii) Evaporation of water :

During evaporation, the liquid molecules having their motion restricted inside the liquid level, move freely in open space to increase disorder

## 13. ENTROPY (S)

Spontaneity is associated with an increase in randomness or disorder of the system. The randomness is impressed by a thermodynamic quantity called entropy.

### 13.1 Sailent Features of Entropy

(1) The change in entropy $\Delta S$ is given by

$\Delta S = S_{final} - S_{initial}$ and it depends only on the initial and final states of the system and not on the particular path way by which the system changes

(2) When $\Delta S$ = +ve (Positive)

- Increase in Randomness

$\Delta S$ = –ve (Negative)

- Decrease in Randomness

(3) For any substance

$S_{solid} < S_{liquid} < S_{gas}$

(4) At absolute zero temperature i.e. zero kelvin, the entropy of pure crystal is arbitrarily taken as zero.

(5) Mathematically, the entropy change

i.e. $\Delta S = \frac{q_{rev}}{T}$

Where $q_{rev}$ = Heat supplied to a system at temperature T.

(6) Unit of Entropy change J/K mol.

(7) Larger is the space available for motion of molecules, more is entropy

Example -Expansion of gas, dissolution

(8) An increase in the number of molecules also leads to an increase in entropy

Example - Decomposition of $NH_4Cl$ to $NH_3$ and HCl

(9) An increase in temperature increases entropy due to increase in motion which results in more disorder.

### 13.2 Overall criterion of spontaneity

There are two driving forces that determine the behaviour of molecular systems to show spontaneity

(1) Achieve the lowest possible state of energy ($\Delta H$ = minimum)

(2) Acquire the state of minimum disorder.

The overall tendency of a process to occur by itself is resultant of these two tendencies and is called driving force.

Gibbs gave a new state function (G). Known as Gibb's free energy by incorporating both H and S values in it.

i.e. $G = H - TS$

or the change in free energy. at constant temperature

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

Conditions:

(1) If $\Delta G$ is negative, the reaction is spontaneous in forward direction .

(2) If $\Delta G$ is zero, the reaction is at equilibrium.

(3) If $\Delta G$ is positive, the reaction in the forward direction is non spontaneous.

| **ΔH** | **ΔS** | **ΔG** | **Properties of reaction** |
|---|---|---|---|
| – | + | Always Negative | Reaction is spontaneous at all temperature |
| + | – | Always positive | Reaction is nonspontaneous at all temperature |
| – | – | Negative at low temperature but positive at high temperature | Spontaneous at low temp. & non spontaneous at high temperature |
| + | + | Positive at low temperature but negative at high temperature | Nonspontaneous at low temp. & spontaneous at high temperature |

### 13.3 Standard free energy changes

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

**Second law of Thermodynamics :**

It states that the entropy of the universe always increases in the course of every spontaneous (Natural) Change.

The energy of universe is conserved whereas entropy of universe always increases in any natural or spontaneous process.

**Third law of thermodynamics :**

It states that at absolute zero, the entropy of a perfectly crystalline substance is taken as zero.

$$\Delta S^\circ = \Sigma S^o_{(product)} - \Sigma S^o_{(reactant)}$$

## Examples based on On Entropy (E)

**Ex.10** The gaseous endothermic reaction :

$P + Q \rightarrow 3R$

at 327°C takes place spontaneously, because-

(A) $\Delta H < 0; \Delta S < 0$ (B) $\Delta H > 0; \Delta S > 0$

(C) $\Delta H < 0; \Delta S > 0$ (D) $\Delta H > 0; \Delta S < 0$

**Sol.** **(B)**

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

For an endothermic reaction $\Delta H = +$ ve

[less molecules → more molecules],

$\Delta S = +$ ve

$\therefore$ $T\Delta S > \Delta H$, and $\Delta G = -$ ve

Hence, the reaction occurs spontaneously.

**Ex.11** Calculate the standard free energy change for the reaction

$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3$ at 298K

Given $\Delta H^o = -92.4$ KJ and $\Delta S^o$

$= -1983 \text{ JK}^{-1}$

**Sol.** $\Delta G^o = \Delta H^o - T\Delta S^o$

$= -92.4 - 298 \times (-198.3) \times 10^{-3}$

$= -33.306$ KJ.

# SOLVED EXAMPLES

**Ex.1** A system does 100J work on surroundings by absorbing 150J of heat. Calculate the change in internal energy-

(A) 100 J (B) 50 J
(C) 25 J (D) 150 J

**(Ans. B)**

**Sol.** W = –100J , q = 150J

$\because$ q = $\Delta$E – W

$\therefore$ 150 = $\Delta$E – (–100)

= 150 – 100

$\Delta$E = 50 J

**Ex.2** A gas absorbs 200J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre to 1.0 litre, Calculate the change in internal energy-

(A) 124 J (B) 224 J
(C) 114 J (D) 154 J

**(Ans. 2)**

**Sol.** W = –P$\Delta$V

= –1.5 (1– 0.5)

= –0.75 atm-litre = – 0.75 × 101 Joule

q = 200 J

$\because$ q = $\Delta$E–W

200 = $\Delta$E–(–0.75 × 101)

$\Delta$E = 124.25 Joule

**Ex.3** Heat of reaction for

$C_6H_{12}O_6$ (s) + $6O_2$ (g) $\rightarrow$ $6CO_2$ (g) + $6H_2O$ (l)

at constant pressure is –651 Kcal at 17ºC. Calculate the heat of reaction at constant volume at 17ºC-

(A) – 554.5 Kcal (B) – 654.5 Kcal
(C) – 354.5 Kcal (D) – 154.5 Kcal

**(Ans. B)**

**Sol.** $\Delta$H = $\Delta$E + $\Delta$N RT

Given

$\Delta$H = – 651 x $10^3$ cal. , R = 2 cal,

T = 290 K and $\Delta$n = 6 + 6 – 6 = 6

$\therefore$ $\Delta$E = – 651 × $10^3$ – 6 × 2 × 290

= – 654480 cal

= – 654.5 Kcal

**Ex.4** A cooking gas cylinder is assumed to contain 112kg isobutane. The combustion of isobutane is given by-

$$C_4H_{10}\,(g) + \left(\frac{13}{2}\right) O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O(\ell)\ ; \quad \Delta H = -\,2658\ KJ$$

If a family needs 15000 KJ of energy per day for cooking, how long would the cylinder last?

(A) 22 days (B) 28 days
(C) 32 days (D) 34 days

**(Ans. D)**

**Sol.** $\because$ 58 g isobutane provides energy = 2658 KJ

$\therefore$ 11.2 × $10^3$ g isobutane provides energy

$$= \frac{2658 \times 11.2 \times 10^3}{58}\ KJ \quad = 513268.9\ KJ$$

The daily requirement of energy = 15000KJ

$$\therefore \text{ cylinder will last} = \frac{513268.9}{15000} = 34 \text{ days}$$

**Ex.5** Calculate the entropy change in melting 1 mole of ice at 273K, $\Delta H_f^o$ = 6.025 KJ/mole-

(A) 11.2 $JK^{-1}\ mol^{-1}$ (B) 22.1 $JK^{-1}\ mol^{-1}$
(C) 15.1 $JK^{-1}\ mol^{-1}$ (D) 5.1 $JK^{-1}\ mol^{-1}$

**(Ans. B)**

**Sol.** $$\Delta S_f = \frac{\Delta H_f}{T} = \frac{6025}{273} = 22.1\ JK^{-1}\ mol^{-1}$$

**Ex.6** Determine the standard free energy change for the following reaction at 298 K

$N_2$ (g) + $3H_2$(g) $\rightarrow$ $2NH_3$(g)

Given $\Delta G^o_f$ for $N_2$(g) , $H_2$(g) and $NH_3$(g) are 0, 0 and -16.66 KJ $mol^{-1}$

(A) – 11.22 KJ (B) – 22.22 KJ
(C) – 33.32 KJ (D) – 44.44 KJ

**(Ans. C)**

**Sol.** $\Delta G^o = 2 \times \Delta G^o_{NH_3} - \Delta G^o_{N_2} - (\Delta G^o_{H_2} \times 3)$

= 2 × (–16.66) – 0 – 0

= – 33.32 KJ

**Ex.7** For a gaseous reaction

$2A_2(g) + 5B_2(g) \rightarrow 2A_2B_5(g)$

at 27ºC the heat change at constant pressure is found to be –50160J. Calculate the value of internal energy change ($\Delta E$). Given that R = 8.314 J/K mol.

(A) –34689 J (B) –37689 J

(C) –27689 J (D) –38689 J

**(Ans. B)**

**Sol.** $2A_2(g) + 5B_2(g) \rightarrow 2A_2B_5(g)$; $\Delta H = -50160$ J

$\Delta n = 2 - (5 + 2) = -5$ mol.

$\Delta H = \Delta E + (\Delta n)RT$

$-50160 = \Delta E + (\Delta n)RT$

$\Delta E = -50160 - (-5)(8.314)(300)$

$= -50160 + 12471 = -37689$ J

**Ex.8** Calculate the standard enthalpy change for a reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ given that $\Delta H_f^0$ for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ as -393.5, -110.5 and -241.8 KJ/mol respectively.

(A) –31.2 KJ (B) –21.2 KJ

(C) –11.2 KJ (D) –41.2KJ

**(Ans. D)**

**Sol.**

$\Delta H^o = \Sigma \Delta H_f^o{}_{(products)} - \Sigma \Delta H_f^o{}_{(Reactants)}$

$= [\Delta H^0_{f(H_2O)} + \Delta H^0_{f(CO)}] - [\Delta H^0_{f(CO_2)} + \Delta H^0_{f(H_2)}]$

$\Delta H^o = [-241.8 - 110.5] - [-393.5 + 0]$

$= -352.3 + 393.5 = +41.2$ KJ

**Ex.9** Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25ºC from 15 to 50 litres.

**Sol.** We have,

$$W = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15}$$

$= -1436$ calories.

**Ex.10** At 25ºC for the combustion of 1 mole of liquid benzene the heat of reaction at constant pressure is given by,

$$C_6H_6(\ell) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$$

; $\Delta H = -780980$ cal.

What would be the heat of reaction at constant volume ?

**Sol.** We have,

$\Delta H = \Delta E + \Delta n_g RT$

Here, $\Delta n_g = 6 - 7.5 = -1.5$

Thus, $\Delta E = \Delta H - n_g RT$

$= -780980 - (-1.5) \times 2 \times 298$

$= -78090$ calories.

**Ex.11** From the following data of $\Delta H$ of the following reacts as,

$C(s) + ½ O_2(g) \rightarrow CO(g)$ ; $\Delta H = -110$ kJ

and $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ ; $\Delta H = 132$ kJ.

calculate the mole composition of the mixture of oxygen and steam on being passed over coke at 1273K, keeping the reaction temperature constant.

**Sol.** From the question we see that the first reaction is exothermic and the second one is endothermic. Thus, if a mixture of oxygen and steam ($H_2O$) is passed over coke and at the same time, temperature does not change, the composition should be such that $\Delta H$ of both the reactions are numerically equal.

In the first reaction, consumption of ½ mole of $O_2$ evolves 110 kJ of energy while in the second reaction, for 1 mole of steam ($H_2O$), 132 kJ of energy is obsorbed.

$\therefore$ Mole of $O_2$ needed to evolve 132 kJ = $\frac{0.5}{110} \times 132 = 0.6$

$\therefore$ Mole ratio of $O_2$ and steam ($H_2O$) = 0.6 : 1

**Ex.12** 200 ml of KOH and 200 ml of $HNO_3$ of same molarity are mixed together and liberated 3.426 kJ of heat. Determine the molarity of each solution.

**Sol.** Let the molarity of KOH and $HNO_3$ solution is x.

$\therefore$ 200 ml of x mole KOH solution

$$= \frac{200}{1000} \times x \text{ mole } OH^- \text{ ions}$$

$= 0.2\ x$ mole $OH^-$ ions

Similarly,

200 ml of x mole $HNO_3$ solution

$= \frac{200}{1000} \times x$ mole $H^+$ ions

$= 0.2\ x$ mole $H^+$ ions

$H+ (aq) + OH^- (aq) \rightarrow H_2O (\ell)$

0.2      0.2 x      0.2 x

Heat evolved during formation of 1 mole $H_2O$ = 57.1 kJ

∴ Heat evolved during formation of 0.2 x mole = 57.1 x 0.2 X x kJ

Heat evolved is = 3.426 kJ.

∴ $57.1 \times 0.2 \times x = 3.426$ kJ

or $x = \frac{3.426}{57.1 \times 0.2} = 0.3$ mole.

**Ex.13** Calculate the heat change in the reaction $4NH_3 (g) + 3O_2 (g) \rightarrow 2N_2(g) + 6H_2O (\ell)$ at 298 K given that the heats of formation at 298 K for $NH_3$ (g) and $H_2O$ (l) are – 46.0 and – 286.0 KJ $mol^{-1}$ respectively.

**Sol.** $\Delta H^\circ$ for the reaction

$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O (\ell) + 2N_2(g)$

$\Delta H^\circ = \Delta H^\circ_f$ (products) - $\Delta H^\circ_f$ (reactants)

$= \{6H^\circ_f [H_2O (\ell)] + \Delta H^\circ_f [N_2(g)\}$

$- \{4\Delta H [NH_3(g)] + 3\Delta H_f [O_2(g)]\}$

$\Delta H^\circ_f [H_2O (\ell)] = -286.0$ kJ $mol^{-1}$

$\Delta H^\circ_f [NH_2 (g)] = 0$ and $\Delta H^\circ_f [N_2 (g)]$ = 0 (by convention)

$\Delta H^\circ = \{6(-286) + 2 (0)\} - \{4(-46.0) + 3 (0)]$

$= -1716 + 184 = -1532$ kJ

**Ex.14** The heats of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4\ 5H_2O$ are – 66.5 and 11.7 kJ $mol^{-1}$ respectively. Calculate the heat of hydration of $CuSO_4$ to $CuSO_45H_2O$.

**Sol.** The required equation is :

$CuSO_4(s) + 5H_2O (l) \rightarrow CuSO_4.5H_2O(s)$

$\Delta H$ = ?

given that

$CuSO_4(s) + (aq.) \rightarrow CuSO_4. (aq)$

$\Delta H_1 = -66.5$ kJ

$CuSO_4 . 5H_2O(s) + aq. \rightarrow CuSO_4.(aq)$

$\Delta H_2 = +11.7$ kJ

The process of hydration may be expresed as

$$\begin{tikzcd} CuSO_4\ (s) \arrow[rr, "\Delta H_1"] \arrow[dr, dash, "\Delta H"'] & & CuSO_4(aq) \\ & CuSO_4.\ 5H_2O \arrow[ur, dash, "\Delta H_2"'] & \end{tikzcd}$$

According to Hess's law

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

$\Delta H = \Delta H_1 - \Delta H_2$

$= -66.5 - 11.7 = -78.2$ KJ

**Ex.15** Calculate the entropy change ($\Delta S$) per mole for the following reactions:

(a) Combusiton of hydrogen in a fuel cell at 298 K

$H_2(g) + ½\ O_2(g) \rightarrow H_2O (g)$

$\Delta H = -241.6$ kJ, $\Delta G = -228.4$ kJ

(b) Vaporisation of methanol at its normal boiling point.

$CH_3OH (l) \rightarrow CH_3OH (g)$

$\Delta H_{vap} = 23.9$ kJ , boiling point = 338 K

(c) Fusion of ice at its normal melting point,

Ice → Water

$\Delta H_{fusion} = 6.025$ kJ, melting point = 0°C

**Sol.**(a) According to the reaction .

$\Delta G = \Delta H - T\Delta S$ of $\Delta S = \frac{\Delta H - \Delta G}{T}$

Given that $\Delta G = -228.4$ kJ, $\Delta H = -241.6$ kJ and T = 298 K

Substituting the values, we get

$$\Delta S = \frac{(-241.6kJ) - (-228.4kJ)}{298K}$$

$= -0.0443$ kJ $K^{-1}$ or $= -44.3$ $JK^{-1}$

(b) Vaporisation represents a state of equilibrium between the liquid and the vapour state of the substance. At this state $\Delta G = 0$ so that

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

Here $\Delta H = 23.9$ kJ . T = 338 K

∴ $\Delta S = \frac{23.9kJ}{338K} = 0.070$ kJ $K^{-1}$ = 70 $JK^{-1}$

(c) Fusion represent a state of equilibrium between ice and water. At this state.

$\Delta G = 0$ so that

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

Here $\Delta H = 6.025$ kJ and T = 273 K

$\Delta S = \frac{6.025kJ}{273K} = 0.0220$ kJ $K^{-1}$ = 22 $JK^{-1}$