

## CHEMICAL THERMODYNAMICS

### 5.0 INTRODUCTION

Thermo (Heat/energy) + Dynamic (Flow/motion)

Thermodynamics is the branch of science which deals with the energy changes taking place in all physical and chemical processes but

Chemical thermodynamics is the branch of thermodynamic which deals with the study of energy changes taking place in chemical processes.

#### **Advantages of thermodynamics :**

- (i) It gives information about various thermodynamic laws.
- (ii) It helps us to predict whether a given chemical reaction will take place or not under the given set of conditions.
- (iii) It gives information about various energy changes.

#### **Limitations of thermodynamics :**

- (i) Thermodynamics deals with the properties like temperature, pressure, volume etc of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

Or

Thermodynamics deals with macroscopic models but not with microscopic models.

- (ii) It tells us whether a given chemical reaction will take place or not under the given set conditions but doesn't tell us anything about the rate of reaction.

### 5.1 SOME IMPORTANT TERMS :

- **System** : A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation.
  - **Surrounding** : The rest part of the universe excluding the system is called surrounding.  
Universe = System + Surrounding
  - **Boundary** : Anything which separates system and surrounding is called boundary/  
Types of boundary :
    - (i) Boundary can be conducting or non-conducting.
    - (ii) Boundary can be rigid or non-rigid.
    - (iii) Boundary can be real or imaginary.

#### **For example :**

A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and the anything which is outside the beaker is called surroundings.

### 5.2 TYPES OF SYSTEM

Systems are of 3 types

**Open system** : This type of system can exchange energy as well as matter with the surrounding. The boundary is neither sealed nor insulated. Total mass will not remain constant.

**Eg. 1.** Coffee in open glass. Hot water in open glass.

**Eg. 2** All living systems, human being, plants, animals.

**Eg. 3** Classroom, earth

**Closed system :** This type of systems can exchange energy, (in the form of heat, work or radiations) but not matter with its surrounding .the boundary is sealed but not insulated. Amount of the system will remain constant.

**Eg. 1** Coffee in closed vessel. Hot water in closed vessel.

**Eg. 2** Glowing bulb, tube light.

**Eg. 3** A satellite in orbit.

**Isolated system :** This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

**Eg. 1** Coffee in thermosflask.

### 5.3 STATE OF THE SYSTEM

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.
- The state of the system is defined by their measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

#### State Function :

- Those state variables which depend only upon initial and final state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

**Ex.** E, H, S, G, T, P, V etc.

#### Path Function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

**Eg.** Work done (w), heat (q)

#### Thermodynamic properties :

**(i) Intensive properties :** The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.

**(ii) Extensive properties :** The properties of the system which are dependent of matter (size and mass) present in system are called extensive properties.

Extensive Properties	Intensive Properties
Volume (V)	Molar volume ( $V_m$ )
Number of moles (n)	Density (d)
Mass (m)	Gibb's energy per mole ( $G_m$ )
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M, N)

Heat capacity (C)	Boiling point, freezing point ( $T_b$ , $T_f$ )
Force (F)	Cell potential ( $E_{\text{cell}}$ )
Surface Area (A)	Specific conductance ( $\kappa$ )
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure

### Special Points :

- (i) The ratio of two extensive property indicates the intensive property      Eg.  $d = \frac{\text{mass}}{\text{volume}}$
- (ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

**Eg.** Mass per unit volume = density ;  $d = \frac{m}{V}$

- (iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

Vessel	$\text{H}_2\text{O}$ A	$\text{H}_2\text{O}$ B	On adding
Mass	$m_1$	$m_2$	$m_1 + m_2$ (Total mass)
Moles	$n_1$	$n_2$	$n_1 + n_2$ (Total moles)
Volume	$V_1$	$V_2$	$V_1 + V_2$ (Total volume)
Density	$d$	$d$	Remains (d)
Boiling point	T	T	Remain same (T)

Extensive

Intensive

## 1.4 TYPES OF THERMODYNAMIC PROCESS :

When a system changes from one state to another, the operation is called a thermodynamic process. Thermodynamic process may be in form of expansion or compression.

### (a) Isothermal Process ( $n$ , $T = \text{constant}$ )

Isothermal process are those processes in which

- (a) Temperature remains constant i.e.  $\Delta T = 0$
- (b) Heat is exchanged with surrounding
- (c) System is placed at a constant temperature.
- For ideal gas in Isothermal process  $\Delta E = 0$  and  $\Delta H = 0$
- All phase transitions are isothermal process but  $\Delta E \neq 0$  and  $\Delta H \neq 0$

### (b) Isobaric Process ( $n$ , $P = \text{constant}$ )

Isobaric process are those processes in which

- (a) Pressure remains constant i.e.  $\Delta P = 0$
- (b) Volume & temperature are variable.
- (c) Process in open system is isobaric in nature.

### (c) Isochoric Process ( $n$ , $V = \text{constant}$ )

Isochoric process are those process in which

- (a) Volume remains constant i.e.  $\Delta V = 0$
- (b) Pressure & temperature are variable
- (c) Work,  $W = -P\Delta V$ ,  $\Delta V = 0$ ,  $\therefore W = 0$  (Zero)
- (d) Process in open system is isobaric in nature.

**(d) Adiabatic Process ( $n = \text{constant}$ ,  $q = 0$ )**

Adiabatic process are those processes in which

- (a) No exchange of heat takes place i.e.  $q = 0$
- (b) The temperature of the system varies.
- (c) The system is thermally insulated this can be done by keeping the system in an insulated container.

**(e) Cyclic Process**

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e.  $\Delta E = 0$ ,  $\Delta H = 0$ ,  $\Delta P = 0$ ,  $\Delta T = 0$

**(f) Reversible Process (quasi- static)**

- (1) Process in which all changes occurring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.
- (2) Driving force should be infinitesimally greater than opposing force.
- (3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.
- (4) It is an ideal process.
- (5) Work obtained in expansion is maximum.
- (6) System is in virtual equilibrium at any state.
- (7)  $P_{\text{ext}} = P_{\text{int}} \pm dP$ ;  $P_{\text{ext}}$  is variable.

**Irreversible Process**

- (1) Process in which direction of change cannot be reversed by small changes in variables.
- (2) Driving force is much greater than opposing force.
- (3) It takes place in short time
- (4) Process takes place in short time
- (5) All natural processes are irreversible
- (6) System is in equilibrium only at initial and final state.
- (7)  $P_{\text{ext}} = P_{\text{int}} \pm \Delta P$ ;  $P_{\text{ext}}$  is constant.

## 5.5 WORK AND HEAT

**(A) Work :** Product of force and displacement is known as work.

$$\text{Work (W)} = \text{force (F)} \times \text{displacement (}\lambda\text{)}$$

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose area of cross section of cylinder = A and pressure on the piston = P

Initial volume of the gas =  $V_1$  and final volume of the gas =  $V_2$

(By expansion) displacement of piston =  $\lambda$

Work done by the gas (in expansion) =  $W = F \cdot \lambda$

$$\ominus P = \frac{F}{A} \quad \therefore F = P \times A$$

$W = P \times A \times \lambda$  (Change in volume =  $A \times \lambda = V_2 - V_1$ )

$$W = P \times (V_2 - V_1)$$

$W = P\Delta V$  (According to Physics)

In general  $\boxed{W = -P_{\text{external}} \Delta V}$  (According to Chemistry)

### SIGN CONVENTIONS :

- According to latest sign conventions
  - (a) Work done is taken negative if it is done by the system since energy of system is decreased  
**Eg.** Expansion of gas.  
 $\ominus V_2 > V_1$  ;  $\Delta V = \text{positive}$ ;  $W = \text{negative}$
  - (b) Work done is taken positive if it is done on the system, since energy of system is increased.  
**Eg.** Compression work.  
 $\ominus V_1 > V_2$  ;  $\Delta V = \text{negative}$  ;  $W = \text{positive}$

### (B) Heat exchange (q)

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the thermodynamic system and its surroundings. It is a path function.

According to IUPAC convention heat given by the system is expressed with negative sign; heat given to the system is expressed with positive sign.

- Heat always flows from high temperature to low temperature.
- Heat flowing into the system  $q = \text{positive}$
- Heat flowing out of the system  $q = \text{negative}$

### Units of heat & work :

**Calorie :** It is defined as the quantity of heat required to raise the temperature of 1 g of water by  $1^\circ\text{C}$  (14.5 to  $15.5^\circ\text{C}$ )

$$1 \text{ cal} = 4.184 \text{ J} = 4.2 \text{ J}$$

$$1 \text{ L-atm} = 101.3 \text{ J} = 24.206 \text{ cal} = 101.3 \times 10^{-7} \text{ erg}$$

$$\boxed{1 \text{ L-atm} > 1 \text{ cal} > 1 \text{ J} > 1 \text{ erg}}$$

### GOLDEN KEY POINTS

- Molar properties like  $\Delta H_m$ ,  $\Delta G_m$ ,  $\Delta S_m$ ,  $\Delta U_m$  are intensive properties.
- In cyclic process change in all state functions will be equal to zero.  
 $\Delta E = 0$ ,  $\Delta H = 0$ ,  $\Delta P = 0$ ,  $\Delta T = 0$  etc.
- For ideal gases  $\Delta E = 0$  (For isothermal process)
- All natural processes are irreversible in nature
- Both  $q$  and  $w$  are (+) to system.
- Both  $q$  and  $w$  are (–) by the system.

## Illustrations

**Illustration 1.** Find the work done in each case :

(a) When one mol of ideal gas in 10 litre container at 1 atm. is allowed to enter a vacuum bulb of capacity 100 litre.

(b) When 1 mol of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

**Solution** (a)  $W = -P\Delta V$  but since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called free expansion and work done is zero.

**Note :-** work done in free expansion is always zero.

(b)  $W = -P\Delta V = -1(5 - 1) = -4 \text{ L-atm.}$

**Illustration 2.** A 5 litre cylinder contained 10 mol of oxygen gas at  $27^\circ\text{C}$ . Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmosphere pressure is 1.0 atm. Calculate the work done by the gas ?

( $R = 0.083 \text{ litre atm mol}^{-1} \text{ K}^{-1}$ )

**Solution**

$$V_{\text{initial}} = 5 \text{ L}$$

$$T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$V_{\text{final}} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 249 - 5 = 244 \text{ L}$$

$$W_{\text{exp}} = -P\Delta V = -1 \times 244 \text{ L-atm} = -244 \text{ L-atm}$$

### BEGINNER'S BOX-1

- Which of the following open system  
 (1) Animals and plants (2) A fridge  
 (3) A solar cooker (4) None of these
- One mole of gas occupying 3 litre volume is expanded against a constant external pressure of one atm to a volume of 15 litre. The work done by the system is :-  
 (1)  $-1.1215 \times 10^3 \text{ J}$  (2)  $+12.15 \times 10^3 \text{ J}$   
 (3)  $+121.5 \times 10^3 \text{ J}$  (4)  $+1.215 \times 10^3 \text{ J}$
- The work done during the expansion of a gas from a volume of  $4 \text{ dm}^3$  to  $6 \text{ dm}^3$  against a constant external pressure of 3 atm is :-  
 (1)  $-608 \text{ J}$  (2)  $+304 \text{ J}$  (3)  $-304 \text{ J}$  (4)  $-6 \text{ J}$
- The work done during the expansion of a gas from a volume of  $14 \text{ dm}^3$  to  $16 \text{ dm}^3$  against a constant external pressure of 2 atm is :-  
 (1)  $-405.2 \text{ J}$  (2)  $+304 \text{ J}$  (3)  $-304 \text{ J}$  (4)  $-6 \text{ J}$

### 5.6 INTERNAL ENERGY (E/U)

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translator, rotator and vibratory motion), electronic energy, nuclear energy etc.

$$E = E_{\text{PE}} + E_{\text{T}} + E_{\text{R}} + E_{\text{V}} + E_{\text{e}} + E_{\text{N}}$$

(i) Internal energy is an extensive property.



(ii) We can never find out the absolute value of internal energy (E) of system.

We can only calculate the change in internal energy of the system ( $\Delta E$ ) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a state function.

$$\Delta E = E_f - E_i$$

(In reaction)  $\Delta E = E_P - E_R$

$\Delta E$  is +ve if  $E_f > E_i$

$\Delta E$  is -ve if  $E_f < E_i$

## 5.7 LAWS OF THERMODYNAMICS

### GENERAL POINT :-

Laws of thermodynamics are based on human experiences there is no formal proof for them.

### FIRST LAW OF THERMODYNAMICS (FLOT) :-

- This law is based on law of conservation of energy and was given by Robert Mayer and Helmholtz.
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

$\Delta E = q + w$  : where q, are path function and E is state function.

Here q is the energy given to the system and w is the work done on the system ;  $\Delta E$  is change in internal energy.

**Note :** Put the value of q and w with proper sign.

### CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS :-

#### (a) During isothermal process of an ideal gas

During and isothermal process the temperature of the system remains constant and hence

$$\Delta E = 0$$

Therefore FLOT :  $\Delta E = q + w$

$$\therefore \boxed{+q = -w} \text{ or } -q = +w$$

In isothermal process –

(I) heat absorbed by the system is equal to work done by the system.

**OR**

(II) Heat evolved by the system is equal to work done on the system.

#### (b) During isochoric process

At constant volume  $V_1 = V_2$  i.e.  $\Delta V = 0$

Hence  $W = -P\Delta V = 0$ ..... No work done at constant volume therefore.

$$\text{FLOT : } \Delta E = q + w \quad \boxed{\Delta E = q_v}$$

(i) In isochoric process

- AT constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

**OR**

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume ( $q_v$ ) =  $\Delta E$

(iii) In isochoric process heat behaves as state function.

**(c) During adiabatic process**

During adiabatic process the system acts an isolated system and hence  $q = 0$  in such case. Therefore

**FLOT :**  $\Delta E = q + w$        $\ominus q = 0$        $\boxed{\Delta E = w}$

(i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

**OR**

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

(ii) In adiabatic process work behaves as state function

**(d) During Cyclic Process :**

$\Delta E = 0$       **FLOT :**  $\Delta E = q + w$        $\boxed{+q = -w}$

In cyclic process

(I) Work done by the system is equal to heat absorbed by the system.

**OR**

(II) Work done on the system is equal to heat evolved by the system.

**(e) During Isobaric process**

P – constant

**FLOT :**  $\Delta E = q + W$

$\Delta E = q + (-P\Delta V)$

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

$q_p = (E_2 - E_1) + P(V_2 - V_1)$

$q_p = (E_2 - PV_2) - (E_1 - PV_1)$

$\ominus$  Enthalpy  $H = E + PV$

$\therefore q_p = H_2 - H_1 \quad q_p = \Delta H$

(i) In isobaric process :

- At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system

**OR**

- At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

(ii) Heat at constant pressure ( $q_p$ ) =  $\Delta H$

(iii) In isobaric process heat behaves as state function.

## Illustrations



**Illustration 3.** 1 g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporization at this pressure is 540 cal/g. Find the increase in internal energy of water. (1 L atm = 101 J)

**Solution** Work done  $w = -PDV = -P(V_2 - V_1)$

$$= -1(1671 - 1) \times \frac{1}{1000} = \frac{-1670}{1000} \text{ L-atm}$$

$$= \frac{-1670}{1000} \times 101 \text{ J} = -168.67 \text{ J}$$

Given that  $q = 540 \text{ cal} = 540 \times 4.2 \text{ J} = 2268 \text{ J}$

$$\therefore \Delta E = q + w = 2268 - 168.67 = 2099.33 \text{ J}$$

**Illustration 4.** A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm calculate change in its internal energy.

**Solution**  $w = -P\Delta V = -1 \times (2.5 - 2) = -0.5 \text{ L-atm}$  or  $w = -0.5 \times 101.3 = -50.65 \text{ J}$

$$\Delta E = q + w = 300 + (-50.65)$$

$$\Delta E = 249.35 \text{ J}$$

**Illustration 5.** A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surroundings. Calculate the change in internal energy of the system.

**Solution** During the process,

$$q = 600 \text{ J}, \Delta V = 12 - 2 = 10 \text{ L}, P = 1 \text{ atm}$$

$$w = -P\Delta V$$

$$= -1 \times 10 = -10 \text{ L atm}$$

Now, 1 L atm = 101.3 J

$$\therefore w = -10 \times 101.3 = -1013 \text{ J}$$

According to first law of thermodynamics

$$\Delta E = q + w = 600 - 1013 = -413 \text{ J}$$

**Illustration 6.** Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant external pressure of 4 atm. Calculate q, w & ΔE. ( $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$ )

**Solution** Work done on the system

$$w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$$

$$V_f = \frac{nRT}{P}$$

$n = 2 \text{ mol}$  and  $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ,

$$T = 273 + 27 = 300 \text{ K}, P = 2 \text{ atm}$$

$$V_i = \frac{2 \times 0.082 \times 300}{2} = 24.6 \text{ L and } V_f = \frac{V_i}{2} = \frac{24.6}{2} = 12.3 \text{ L}$$

$$w = -4 \text{ atm} \times (12.3 - 24.6) \text{ L}$$

$$= 49.2 \text{ L atm} = 49.2 \times 101.3 \text{ J}$$

$$= 4984 \text{ J}$$

Since, it is isothermal compression,  $\Delta E = 0$

Now,  $\Delta E = q + w$

$$0 = q + 4984 \text{ J or } q = -4984 \text{ J}$$

**Illustration 7.** A system is provided with 100 J of heat. Work done on the system is 20 J. What is the change in internal energy.

**Solution**  $q = 100 \text{ J}$  and  $w = +20 \text{ J}$

$$\Delta E = q + w = 100 + 20 \text{ J} = 120 \text{ J}$$

**Illustration 8.** An insulated container is divided into two equal portions one portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect Vacuum. If a hole is opened between the two portions, Calculate the –

(i) Change in internal energy of the gas (ii) Change in temperature of the gas

**Solution** For insulated system,  $q = 0$

The gas is allowed to expand against vacuum, the process of free expansion and thus  $w = -P\Delta V = 0$  (for vacuum  $= P_{\text{ext}} = 0$ )

Thus from I law of thermodynamics,  $\Delta E = q + w$  or  $\Delta E = 0$

i.e., internal energy change is zero or internal energy of gas remains constant during free expansion. Also  $E \propto T$  and thus temperature of the gas will also remain constant.

### BEGINNER'S BOX-2

1. A system absorbs 300 cal of heat with the result of that, the volume of the system becomes double of its initial volume and temperature changes from 273 K to 546 K. The work done by the system on the surroundings is 200.0 cal. Calculate  $\Delta E$  :-  
 (1) 273 Kcal (2) 500 cal (3) 100 cal (4) -500 cal
2. One mol of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The  $\Delta E$  for the process is :-  
 (1) 163.7 cal (2) 1381.1 cal (3) 9 L-atm (4) Zero
3. In an adiabatic process which of the following is true :-  
 (1)  $q = +w$  (2)  $-\Delta E = -w$  (3)  $P\Delta V = 0$  (4)  $q = \Delta E$
4. In an isochoric process, the increase in internal energy is :-  
 (1) Equal to the heat absorbed (2) Equal to the heat evolved  
 (3) Equal to the work done (4) Equal to zero

## 5.8 ENTHALPY (H)

Mathematically it is heat contained in the system measured at constant pressure.

The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

$$H = E + PV$$

- It is impossible to determine absolute value of enthalpy so we determine change in enthalpy ( $\Delta H$ ).

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

- Enthalpy is an extensive property because E and V are extensive properties.
- It is a state function because E, P and V are state functions.

$$\ominus H = E + PV$$

$$\therefore \Delta H = \Delta E + \Delta(PV) \quad \dots(i)$$

(when P, V and T are variables)

$$\text{At constant pressure : } \Delta H = \Delta E + V.\Delta P \quad \dots(ii)$$

$$\text{At constant volume : } \Delta H = \Delta E + V.\Delta P \quad \dots(iii)$$

For chemical reactions at constant temperature and pressure

$$\ominus P.\Delta V = \Delta n_g RT$$

$$\text{So from equation (i)} \quad \Delta H = \Delta E + \Delta n_g RT \quad \dots(iv)$$

where  $\Delta H = q_p$  ; at constant P ;  $\Delta E = q_v$  ; at constant V

$$\text{So equation (iv) can be also written as } q_p = q_v + \Delta n_g RT \quad \dots(v)$$

### GOLDEN KEY POINTS

- If,  $\Delta n_g = 0 \rightarrow \Delta H = \Delta E$  eg.  $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If,  $\Delta n_g > 0 \rightarrow \Delta H = \Delta E$  eg.  $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If,  $\Delta n_g < 0 \rightarrow \Delta H = \Delta E$  eg.  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

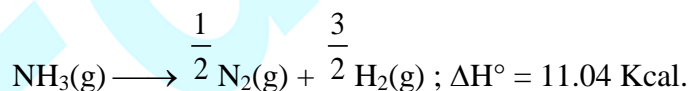
### Illustrations

**Illustration 9.** The heat of reaction for  $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$  at constant volume is  $-1228.2$  kcal at  $25^\circ C$ . Calculate the heat of reaction at constant pressure and at  $25^\circ C$ .

**Solution**

$$\begin{aligned} \Delta n_g &= [10] - [12] = -2 \\ \Delta H &= \Delta E + \Delta n_g RT \\ &= -1228.2 \times 10^3 + (-2)(2) \times 298 \\ &= -1229392 \text{ cal} \\ \Delta H &= -1229.392 \text{ Kcal} \end{aligned}$$

**Illustration 10.** For the reaction at  $25^\circ C$



Calculate  $\Delta E^\circ$  of the reaction at the given temperature.

**Solution**

$$\begin{aligned} \Delta H^\circ &= \Delta E^\circ + \Delta n_g RT \\ \Delta n_g &= 2 - 1 = 1 \text{ mol} \\ \Delta E^\circ &= \Delta H^\circ - \Delta n_g RT \\ &= 11.04 \text{ Kcal} - 1 \text{ mol} \times \frac{2}{1000} \text{ Kcal mol}^{-1} K^{-1} \times 298 K \\ &= 11.04 - 0.596 = 10.44 \text{ Kcal} \end{aligned}$$

**Illustration 11.** At  $27^\circ C$  the internal energy change of reaction  $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$  is  $2 \text{ cal}$ . What is the enthalpy change of this reaction.

**Solution**

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

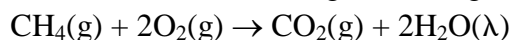
$$\Delta H = \Delta E + 0 \times RT$$

$$\Delta H = \Delta E$$

$$\Delta H = 2\text{cal}$$

**Illustration 12.** The heat of combustion of gaseous methane ( $\text{CH}_4$ ) at constant volume is measured in bomb calorimeter at 298K is found to be  $-885.4 \text{ kJ mol}^{-1}$ . Find the value of enthalpy change at the same temperature.

**Solution** Combustion of methane gives  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  as



$$\Delta E = -885.4 \text{ kJ mol}^{-1} = -885400 \text{ J mol}^{-1}$$

$$\Delta n_g = 1 - (1 + 2) = -2 \text{ mol}$$

$$T = 298\text{K}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} \text{Now, } \Delta H &= \Delta E + \Delta n_g RT \\ &= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298\text{K}) \\ &= -885400 - 4955 \\ &= -890355 = -890.355 \text{ kJ} \end{aligned}$$

**Illustration 13.** The enthalpy change ( $\Delta H$ ) for the reaction :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  is  $-92.38 \text{ kJ}$  at 298 K. What is  $\Delta E$  at 298 K ?

**Solution**  $\Delta H$  and  $\Delta E$  are related as  $\Delta H = \Delta E + \Delta n_g(\text{g})RT$   
for the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
 $\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$   
 $-92380 = \Delta E - 4955$   
 $\Delta E = -92380 + 4955$   
 $= -87425 \text{ J} = -87.425 \text{ kJ}.$

**Illustration 14.** The enthalpy change for the reaction  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  at 1000K is  $176 \text{ KJ mol}^{-1}$ . Calculate the change in internal energy.

**Solution**  $\Delta H = \Delta E + \Delta n_g RT$   
 $176 = \Delta E + (+1) \times 8.314 \times 10^{-3} \times 1000$   
 $\Delta E = 167.686 \text{ KJ}$

### BEGINNER'S BOX-3

- When a solid melts, there is :-  
 (1) No increase in enthalpy                      (2) Increase in enthalpy  
 (3) Decrease in enthalpy                        (4) Anything can happen
- For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  which of the following is valid :-  
 (1)  $\Delta H = \Delta E$                       (2)  $\Delta H < \Delta E$                       (3)  $\Delta H > \Delta E$                       (4) None of these
- Heat exchanged in a chemical reaction at constant pressure is called :-  
 (1) Internal energy                      (2) Enthalpy                      (3) Entropy                      (4) Free energy

4. Latent heat of vaporization of a liquid at 500 K and 1 atm pressure is 10.0 Kcal/mol. What will be the change in internal energy of 3 mol of liquid at same temperature and pressure  
 (1) 13.0 Kcal (2) -13.0 Kcal (3) 27.0 Kcal (4) -27.0 Kcal
5. What is the value of  $\Delta n_g$  if we consider the combustion of 1 mol of liquid ethanol if reactants and products are at 298 K :-  
 (1) -1 (2) -2 (3) +1 (4) +2
6. If a reaction involves only solids and liquids, which of the following is true  
 (1)  $\Delta H < \Delta E$  (2)  $\Delta H = \Delta E$  (3)  $\Delta H > \Delta E$  (4)  $\Delta H = \Delta E + RT\Delta n_g$
7. The value of  $\Delta H - \Delta E$  for the following reaction at 27°C will be,  $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$   
 (1)  $8.314 \times 273 \times (-2)$  J (2)  $8.314 \times 300 \times (-2)$  J  
 (3)  $8.314 \times 27 (+2)$  J (4)  $8.314 \times 300 (+2)$  J
8. At constant temperature for the reaction  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ ,  $\Delta E - \Delta H$  is  
 (1) +RT (2) -3RT (3) +3RT (4) -RT

### 5.9 HEAT CAPACITY / MOLAR HEAT CAPACITY / SPECIFIC HEAT CAPACITY

- (i) **Heat capacity (C)** : Amount of heat required to raise the temperature of given amount of a substance by 1°C or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

$$C = \frac{dq}{dT}$$

**Unit :-** JK<sup>-1</sup>, cal K<sup>-1</sup>, J °C<sup>-1</sup>, cal °C<sup>-1</sup>

- Heat capacity is extensive property.

- (ii) **Molar heat capacity (C<sub>m</sub>)**

Amount of heat required to raise the temperature of 1 mole of substance by 1°C or 1 K is called as molar heat capacity.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow C_m = \frac{C}{n}$$

**Unit :-** Jmol<sup>-1</sup> K<sup>-1</sup>, cal mol<sup>-1</sup> K<sup>-1</sup>, J mol<sup>-1</sup> °C<sup>-1</sup>, cal mol<sup>-1</sup> °C<sup>-1</sup>

- Molar heat capacity is an intensive property.

- (iii) **Specific heat capacity (c)**

Amount of heat required to raise the temperature of 1 gram of substance by 1°C or 1K is called as specific heat capacity.

$$c = \frac{C_m}{\text{molecular weight}}$$

**Unit :-** Jg<sup>-1</sup> K<sup>-1</sup>, cal g<sup>-1</sup> K<sup>-1</sup>, J g<sup>-1</sup> °C<sup>-1</sup>, cal g<sup>-1</sup> °C<sup>-1</sup>

- Specific heat capacity is an intensive property.

(iv) **Calorie :**

Amount of heat required to raise temperature of 1g of water of water by 1°C (14.5°C to 15.5°C) is called as calorie.

- If heat is supplied at constant pressure, then  $C_p = \left( \frac{dq}{dT} \right)_p = \frac{dH}{dT} \quad \dots(i)$
- If heat is supplied at constant volume, then  $C_v = \left( \frac{dq}{dT} \right)_v = \frac{dE}{dT} \quad \dots(ii)$

From equation (i) and (ii) :

	From equation (i)	Unit	From equation (ii)
$\gamma$	$\Delta H = C_p dT$ [Here $C_p$ is heat capacity at constant P]	$JK^{-1}$	$\Delta E = C_v dT$ [Here $C_v$ is heat capacity at constant V]
$\gamma$	For n moles $\Delta H = nC_p dT$ [Here $C_p$ is molar heat capacity at constant P]	$J \text{ mol}^{-1} K^{-1}$	$\Delta E = nC_v dT$ [Here $C_v$ is molar heat capacity at constant V]
$\gamma$	For m gram $\Delta H = mC_p dT$ [Here $C_p$ is gram specific heat (specific heat capacity) at constant P]	$J g^{-1} K^{-1}$	$\Delta E = mC_v dT$ [Here $C_v$ is gram specific heat (specific heat capacity) at constant V]

**Relation between  $C_p$  and  $C_v$  for 1 mole of an ideal gas :-**

$$\Theta \quad H = E + PV$$

for ideal gas,

$$PV = nRT$$

$$PV = RT \quad \text{for 1 mole}$$

$\therefore H = E + RT$  differentiate w.r.t. temperature

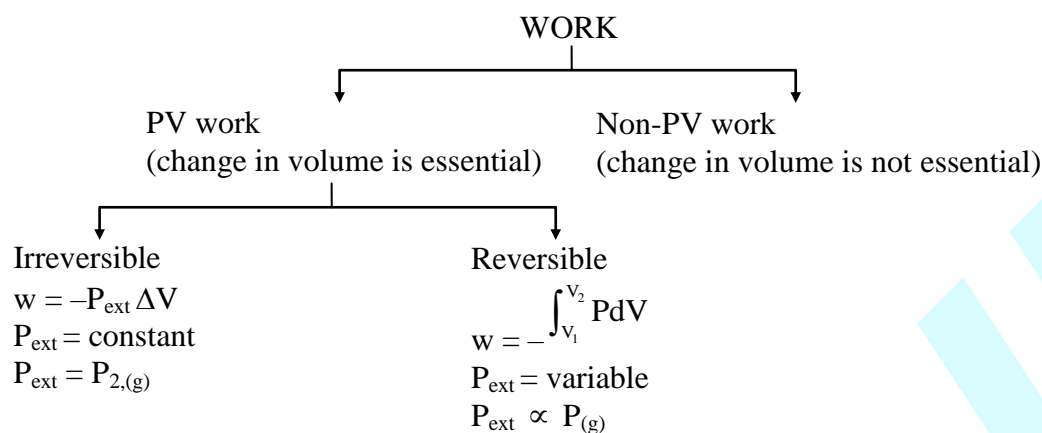
$$\left( \frac{dH}{dT} \right) = \left( \frac{dE}{dT} \right) + R$$

$$C_p = C_v + R$$

$$(i) \quad \boxed{C_p - C_v = R} \quad \text{Mayer's formula}$$

$$(ii) \quad \boxed{\frac{C_p}{C_v} = \gamma}, \gamma = \text{Poisson's ratio}$$

## 5.10 WORK DONE IN DIFFERENT PROCESS :-



**(a) Work done in reversible isothermal process :-**

$P_{\text{external}} = \text{Variable}$

For reversible process

$$P_{\text{ext}} = P_{\text{gas}} \pm dP$$

$$\ominus \quad W_{\text{rev}} = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$W_{\text{rev}} = - \int_{V_1}^{V_2} (P_{\text{ext}} \pm dV) \cdot dV$$

Both  $dP$  and  $dV$  are very small so,  $(dP \cdot dV)$  is negligible.

$$W_{\text{rev}} = - \int_{V_1}^{V_2} P_{\text{gas}} \cdot dV$$

$$W_{\text{rev}} = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$W_{\text{rev}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W_{\text{rev}} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

Or, 
$$W_{\text{rev}} = -2.303 nRT \log_{10} \left( \frac{V_2}{V_1} \right) \quad \dots\dots(1)$$

According to Boyle's law at constant temperature  $P \propto \frac{1}{V}$  or  $PV = \text{constant}$

$$\therefore P_1 V_1 = P_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W_{\text{rev}} = -2.303 nRT \log \left( \frac{P_1}{P_2} \right) \quad \dots\dots(ii)$$

**(b) Work done in reversible adiabatic process :-**

In adiabatic process  $q = 0$

**FLOT :  $DE = q + W$**

$$\Rightarrow \boxed{W = \Delta V} \Rightarrow W = NC_V \Delta T$$



$$\Theta \quad \boxed{W = nC_V(T_2 - T_1)} \quad \dots(i)$$

$$C_P - C_V = R$$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \quad \left( \text{Q } \gamma = \frac{C_P}{C_V} \right) \Rightarrow C_V = \frac{R}{\gamma - 1} \quad \dots(ii)$$

$$\text{From equation (i) and (ii)} \quad \boxed{W = \frac{nR}{\gamma - 1} (T_2 - T_1)} = \boxed{W = \frac{P_2 V_2 - P_1 V_1}{(\gamma - 1)}}$$

State equation of reversible adiabatic processes are :

$$PV^\gamma = \text{constant}$$

$$PV^{\gamma-1} = \text{constant}$$

$$P^\gamma V^{1-\gamma} = \text{constant}$$

### GOLDEN KEY POINTS

- Work in closed vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because  $P_{\text{ext}}$  is zero.
- Work in a chemical reaction  $w = -P\Delta V = \Delta n_g RT$

### Illustrations

**Illustration 15.** 5 mol of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas ? The molar heat capacity of oxygen at constant pressure,

$$C_p = 7.03 \frac{\text{cal}}{\text{mol K}} \text{ and } R = 2 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

**Solution** We know Mayer's relation is  $C_P - C_V = R$   
 $C_V = C_P - R = 7.03 - 2 = 5.03 \text{ cal mol}^{-1} \text{ K}^{-1}$   
 As we  $\Delta V = nC_V \Delta T = 5 \times 5.03 \times 10 = 251.5 \text{ cal}$

**Illustration 16.** At 27°C, one mole of an ideal gas compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate  $\Delta E$  and  $q$  in calorie.

**Solution** For isothermal process  $\Delta E = 0$  and  $w = -2.303 nRT \log_{10} \frac{P_1}{P_2}$

$$w = -2.303 \times 1 \times 2 \times 300 \times \log \frac{2}{10}$$

$$w = +2.303 \times 600 \times \log 5$$

$$w = +2.303 \times 600 \times 0.699$$

$$w = +965.87 \text{ cal}$$

For isothermal process

$$\Theta \quad w = -q$$

$$\therefore q = -965.87 \text{ cal}$$

**Illustration 17.** A gas expands from 3 dm<sup>3</sup> to 5 dm<sup>3</sup> against constant pressure of 3 atm. The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water (if specific heat of water is 4.184 J g<sup>-1</sup> K<sup>-1</sup>)

**Solution** Since work is done against constant P and thus, irreversible

$$\Delta V = 5 - 3 = 2 \text{ dm}^3 = 2 \text{ L}, P = 3 \text{ atm}$$

$$w = -P\Delta V = -3 \times 2 \text{ L-atm} = -6 \times 101.3 \text{ J} = -607.8 \text{ Joule}$$

Now this work is used up in heating water  $w = n \times C \times \Delta T$

$$607.8 = 10 \times (4.184 \times 18) \times \Delta T$$

$$\Delta T = 0.81 = T_2 - T_1$$

$$\text{Temperature} = T_1 + \Delta T = 290 + 0.81 = 290.81 \text{ K}$$

**Illustration 18.** A sample of 3 mol of an ideal gas at 200 K and 2 atm is compressed reversibly and adiabatically until the temperature reaches 250 K, given that molar heat capacity is  $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$  at constant volume, calculate w.

**Solution**  $C_V = 27.5 \text{ JK}^{-1} \text{ mol}^{-1}$

During reversible adiabatic process

$$W = nC_V(T_2 - T_1) = 3 \times 27.5 \times 50 = 4125 \text{ Joule}$$

**Illustration 19.** 10 moles of an idea gas at  $27^\circ\text{C}$  and 10 atm, pressure occupying a volume of 24.6 L undergoes the following changes.

(i) Isothermal & reversible expansion to 246 L

(ii) Isothermal and irreversible expansion to 246 L

(iii) Isochoric heating to  $177^\circ\text{C}$ .

Calculate the work done in each transformation in KJ.

**Solution** (i) Work done in isothermal reversible expansion

$$w = -2.303 \times nRT \log \frac{V_2}{V_1} = -2.303 \times 10 \times 8.31 \times 300 \times \log \frac{246}{24.6}$$

$$= -57413.79 \text{ J} = -57.41 \text{ KJ}$$

(ii) Work done in isothermal irreversible expansion

$$w = -P(V_2 - V_1) = -1(246 - 24.6) = -221.4 \text{ L-atm} = -221.4 \times 101.3 \text{ J} = -22.43 \text{ KJ}$$

(iii) Work done in isochoric change

$$\text{Since } \Delta V = 0 \quad \therefore w = 0$$

**Illustration 20.** Find the work done when 2 mol of a gas expands isothermally from  $5 \text{ dm}^3$  to  $40 \text{ dm}^3$  against a constant external pressure of 2 atm at 298 K. Also calculate  $w_{\text{rev}}$  for the change

**Solution** (i)  $w = -P\Delta V$

$$w = -2 \times (40 - 5)$$

$$w = -70 \text{ L atm} = -70 \times 101.3 \text{ J}$$

$$w = -7091 \text{ J}$$

$$(ii) w = -2.303nRT \log \frac{V_2}{V_1}$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \log \frac{40}{5}$$

$$W = -10.3 \times 10^{-3} \text{ J}$$

#### BEGINNER'S BOX-4

1. Calculate w for the isothermal reversible expansion of 1 mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K :-

- (1)  $-5227.2 \text{ J}$       (2)  $+5227.2 \text{ J}$       (3)  $-2257 \text{ J}$       (4)  $+2257 \text{ J}$

2. When 229 J of energy is supplied as heat at constant pressure to 3 mol Ar(g), the temperature of the sample is increased by 2.55 K. Calculate the molar heat capacity at constant volume :-

- (1)  $30 \text{ KJ}^{-1} \text{ mol}^{-1}$       (2)  $30 \text{ J K}^{-1} \text{ mol}^{-1}$   
 (3)  $21.7 \text{ JK}^{-1} \text{ mol}^{-1}$       (4)  $21.7 \text{ KJ K}^{-1} \text{ mol}^{-1}$

## 5.11 SPONTANEOUS PROCESS AND NON-SPONTANEOUS PROCESS

### (i) Spontaneous process :

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions
- All natural processes are irreversible and spontaneous process. The natural process take place of their own in one direction only.

### (ii) Non-spontaneous process :

- The process which does not occur of its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

### Examples of spontaneous process that need no initiation :

- Ex.1** Flow of water from high level to low level  
 Flow of heat form hot body to cold body  
 Flow of charge from high pressure to low pressure

- Ex. 2** Melting of ice at  $25^\circ\text{C}$   
 Evapouration of water at  $25^\circ\text{C}$   
 Dissolution of common salt in water

- Ex. 3** Mixing of different non reacting gases

### Examples of spontaneous process that need initiation :

- Ex. 1** Burning of fuel (coal, petrol)  
 $\text{C(s)} + \text{O}_2 \longrightarrow \text{CO}_2$   
 $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

- Ex.2** Lightning of candle

### Criteria for a process to be spontaneous :

- (i) Tendency to attain minimum energy or maximum stability (Energy Factor)  
 (ii) Tendency to attain maximum randomness (Entropy Factor)

## 5.12 ENTROPY (S)

- (i) The thermodynamic quantity, which is used to measure degree of randomness or disorderness of the system is called as entropy

Entropy (s)  $\propto$  Randomness or disorderness

- (ii) More is the disorderness, higher is the entropy

- (iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Where  $q_{\text{rev}}$  = heat absorbed by the system in a reversible manner at the temperature T

**Unit :** JK<sup>-1</sup> or Cal K<sup>-1</sup>

(iv)  $\Delta S = S_{\text{final}} - S_{\text{initial}}$

If  $S_{\text{final}} > S_{\text{initial}}$  : Then  $\Delta S$  = positive

If  $S_{\text{final}} < S_{\text{initial}}$  : Then  $\Delta S$  = negative

(v) Entropy is an extensive property and state function.

(vi) Entropy change in a chemical reaction  $\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$

(vii) Entropy change for a process :  $\Delta S = \frac{q_{\text{rev}}}{T}$   $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$  or

$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$

**Case I :** For an ideal gas reversible isothermal process :  $T_2 = T_1$

$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$

$\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 nR \log \frac{P_1}{P_2}$

**Case II :** For an isochoric process  $V_2 = V_1$

$\Delta S = nC_V \ln \frac{T_2}{T_1}$  ;

$\Delta S = 2.303 nC_V \log \frac{T_2}{T_1}$

(viii) For reversible adiabatic process :

Entropy remains constant so process is also known as isoentropic process.

### Factors affecting entropy of system :

(I) If  $\Delta n_g > 0$  then  $\Delta S > 0$

If  $\Delta n_g < 0$  then  $\Delta S < 0$

(II) Physical state :  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

**Ex.**  $\text{Fe(s)} \rightarrow \text{Fe(s)}$  ;  $\Delta S$  = positive

300 K    400K

(VI) Mixture :

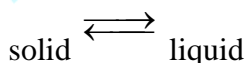
Solid + solid  
 liquid + liquid  
 gas + gas

}  $S \uparrow$

### Entropy change during phase transition

(I) Entropy of fusion [ $(\Delta S)_f$ ]

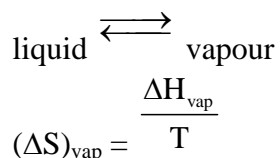
The entropy change, when 1 mol solid changes into liquid at its melting point temperature.



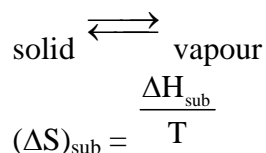
$$(\Delta S)_f = \frac{\Delta H_{\text{fusion}}}{T}$$

**(II) Entropy of vapourisation :  $[(\Delta S)_{\text{vap}}]$** 

The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.

**(III) Entropy of sublimation :  $[(\Delta S)_{\text{sub}}]$** 

The entropy change, when 1 mol solid changes into liquid at particular temperature.

**Some famous or extra ordinary examples of entropy change :**

(i) Entropy of graphite > Entropy of diamond.

(ii) In rusting of iron entropy increases.

(iii)  $\text{NH}_4\text{Cl (s)} + \text{aq} \longrightarrow \text{NH}_4^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$

In this process  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions are free to move in solution where as they are not free to move in solid  $\text{NH}_4\text{Cl}$ . Hence  $\Delta S$  is positive for this type of dissolution process.

(iv) On addition of  $\text{HCl}$  in the aqueous solution of  $\text{Ag}^+$  ions entropy decreases due to precipitation of  $\text{AgCl}$ .

(v) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(vi) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

**Total entropy change in reversible process :-**

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other. Let a system, releases  $q$  heat to the surroundings at temperature  $T$ .

$$\begin{aligned} \Delta S_{\text{system}} &= \frac{-q}{T} ; \Delta S_{\text{surroundings}} = \frac{+q}{T} \\ \text{⊕} \quad \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ \Delta S_{\text{total}} &= \frac{-q}{T} + \frac{q}{T} \Rightarrow \Delta S_{\text{total}} = 0 \end{aligned}$$

**Total entropy change in irreversible process :**

Let a system is at high temperature  $T_1$  and surroundings are at low temperature  $T_2$ .

Let  $q$  amount of heat is released by the system.

$$\begin{aligned} \Delta S_{\text{system}} &= \frac{-q}{T_1} ; \Delta S_{\text{surroundings}} = \frac{+q}{T_2} \\ \text{⊕} \quad \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{-q}{T_1} + \frac{q}{T_2} \\ \therefore \Delta S_{\text{total}} &= +ve \Rightarrow (\ominus T_1 > T_2) \end{aligned}$$

Total entropy change for irreversible spontaneous process is always greater than zero.

### Spontaneity of a process in terms of total entropy change :

If,  $\Delta S_{\text{total}} = +ve \Rightarrow$  spontaneous process

If,  $\Delta S_{\text{total}} = -ve \Rightarrow$  non spontaneous process

If,  $\Delta S_{\text{total}} = 0 \Rightarrow$  process is at equilibrium

## Illustrations

**Illustration 21.** The enthalpy change for transition of liquid water steam is  $40.8 \text{ kJ mol}^{-1}$  at  $373 \text{ K}$ . Calculate  $\Delta S$  for the process.

**Solution** The entropy change for the vapourization of water is given by  $\Delta S = \frac{\Delta H_{\text{vap}}}{T}$

Given  $\Delta H_{\text{vap}} = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 1000 \text{ J mol}^{-1}$  and  $T = 373 \text{ K}$

$$\Delta S = \frac{40.8 \times 1000 \text{ J mol}^{-1}}{373 \text{ K}} = 109.38 \text{ JK}^{-1} \text{ mol}^{-1}$$

**Illustration 22.** Calculate the change in entropy for the fusion of  $1 \text{ mol}$  of ice. The melting point of ice is  $273 \text{ K}$  and molar enthalpy of fusion of ice =  $6 \text{ kJ mol}^{-1}$

**Solution**  $\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.97 \text{ JK}^{-1} \text{ mol}^{-1}$

**Illustration 23.** The enthalpy of vapourisation of liquid diethyl ether  $(\text{C}_2\text{H}_5)_2\text{O}$ , is  $26.0 \text{ kJ mol}^{-1}$  at its boiling point ( $35.0^\circ\text{C}$ ). Calculate  $\Delta S$  for conversion of :-  
(i) Liquid to vapour and (ii) Vapour to liquid at  $35^\circ\text{C}$

**Solution** (i)  $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{26 \times 10^3}{308} = 84.41 \text{ JK}^{-1} \text{ mol}^{-1}$   
(ii)  $\Delta S_{\text{total}} = \frac{\Delta H_{\text{cond}}}{T} = \frac{-26 \times 10^3}{308} = -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

**Illustration 24.** Which of the following processes are accompanied by increase of entropy :

- (i) Disolution of iodine in a solvent  $[\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{aq})]$
- (ii)  $\text{HCl}$  is added to  $\text{AgNO}_3$  and a precipitate of  $\text{AgCl}$  is obtained.
- (iii) A partition is removed to allow two gases to mix.

**Solution** Increase of entropy : (i) and (iii)

## BEGINNER'S BOX-5

1. In any natural process, occurring in the universe :-
 

(1) Entropy is conserved	(2) Entropy increases
(3) Entropy decreases	(4) Entropy remains unchanged
2. The most random state of  $\text{H}_2\text{O}$  system is :-
 

(1) Ice	(2) $\text{H}_2\text{O}(\text{l})$ at $80^\circ\text{C}$ ; $1 \text{ atm}$
(3) Steam	(4) $\text{H}_2\text{O}(\text{l})$ at $25^\circ\text{C}$ ; $1 \text{ atm}$

3. Change in entropy is negative for :-  
 (1)  $\text{Br}_2(\text{l}) \longrightarrow \text{Br}_2(\text{g})$  (2)  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 (3)  $\text{M}_2(\text{g}, 10 \text{ atm}) \longrightarrow \text{M}_2(\text{g}, 1 \text{ atm})$  (4)  $\text{Fe} (\text{at } 400 \text{ K}) \longrightarrow \text{Fe} (\text{at } 300 \text{ K})$
4. Entropy change in spontaneous adiabatic process :-  
 (1) Zero (2)  $< 0$  (3)  $> 0$  (4) None of these
5. 5 mole of an ideal gas expand reversibly from a volume of  $8 \text{ dm}^3$  to  $80 \text{ dm}^3$  at a temperature of  $27^\circ\text{C}$ . The change in entropy is :-  
 (1)  $41.57 \text{ JK}^{-1}$  (2)  $-95.73 \text{ JK}^{-1}$  (3)  $95.73 \text{ JK}^{-1}$  (4)  $-41.57 \text{ JK}^{-1}$
6. The latent heat of vapourisation of water at  $100^\circ\text{C}$  is  $540 \text{ cal g}^{-1}$ . Calculate the entropy increases when one mole of water at  $100^\circ\text{C}$  is evaporated:-  
 (1)  $26 \text{ cal K}^{-1} \text{ mol}^{-1}$  (2)  $1.45 \text{ cal K}^{-1} \text{ mol}^{-1}$   
 (3)  $367 \text{ cal K}^{-1} \text{ mol}^{-1}$  (4)  $1.82 \text{ cal K}^{-1} \text{ mol}^{-1}$
7. Calculate enthalpy of vapourisation per mole of ethanol. Given  $\Delta S = 109.8 \text{ JK}^{-1} \text{ mol}^{-1}$  and B.P. of ethanol is  $78.5^\circ\text{C}$  :-  
 (1) Zero (2)  $38.594 \text{ KJ mol}^{-1}$   
 (3)  $3.85 \text{ KJ mol}^{-1}$  (4) None of these

### 5.13 SECOND LAW OF THERMODYNAMICS (SOLT)

- (i) Its states about the direction of flow of heat  
 (ii) All natural processes in universe are ir-reversible process or natural processes are spontaneous process.  
 (iii) Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

$$(\Delta S)_r = +ve \quad \text{or} \quad (\Delta S)_r > 0 \quad \text{or} \quad (\Delta S)_{\text{system}} + (\Delta S)_{\text{surr.}} > 0$$

### 5.14 GIBB'S ENERGY (G or F)

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.
- The term Gibb's energy was introduced to explain criteria of spontaneity in terms of system  
 Since ; energy = useful work + randomness energy

$$H = G + TS$$

$$\boxed{G = H - TS} \quad \dots\dots(i)$$

So the function that takes both enthalpy of system into account is called Gibbs energy

- Gibbs energy is an extensive property and state function.
- Absolute value of G can't be measured but change can be measured, So we discuss  $(\Delta G)$

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

From eq. (i)  $\boxed{\Delta G = \Delta H - T\Delta S}$

Where  $\Delta G = \text{Change in Gibb's energy}$



$\Delta H$  = Change in enthalpy

$\Delta S$  = Change in entropy

### Gibb's energy change and non expansion work or useful work :-

$$\text{FLOT : } \Delta E = q + W$$

If, work is done by the system, then,  $\Delta E = q - W$  .....(i)

$$\therefore W = W_{\text{expansion}} + W_{\text{non expansion}}$$

$$W = P\Delta V + W_{\text{non expansion}}$$

Put W in equation (i)

$$\Rightarrow \Delta E = q - (P\Delta V + W_{\text{non expansion}})$$

$$q = \Delta E + P\Delta V + W_{\text{non expansion}}$$

$$q = \Delta H + W_{\text{non expansion}} \quad (\ominus \Delta H = \Delta E + P\Delta V)$$

$$T\Delta S = \Delta H + W_{\text{non expansion}} \quad (\ominus \Delta S = q/T)$$

$$W_{\text{non expansion}} = T\Delta S - \Delta H \quad (\ominus \Delta G = \Delta H - T\Delta S)$$

$$\Rightarrow \boxed{W_{\text{non expansion}} = -\Delta G} \quad \text{or} \quad \boxed{W_{\text{useful}} = -\Delta G}$$

The decrease in Gibb's energy of system is equal to the non expansion work or useful work.

### Relation in between $\Delta G$ of system and $\Delta S_{\text{total}}$ or Gibb's energy change and spontaneity :

$$\ominus \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Let system releases heat at constant temperature T and pressure P.

$$\therefore q = q_p = \Delta H$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$

$$\Rightarrow \Delta H_{\text{system}} = -\Delta H_{\text{surroundings}}$$

$$\Delta S_{\text{surr.}} = \frac{\Delta H_{\text{surr.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys.}}}{T}$$

$$\ominus \Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \left( \frac{-\Delta H_{\text{system}}}{T} \right)$$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys.}} - \Delta H_{\text{sys.}}$$

$$T\Delta S_{\text{total}} = -(\Delta H_{\text{sys.}} - T\Delta S_{\text{sys.}})$$

$$T\Delta S_{\text{total}} = -\Delta G_{\text{sys.}}$$

$$\text{or} \quad \boxed{\Delta G_{\text{sys.}} = -\Delta G_{\text{sys.}}}$$

- (i) If,  $\Delta S_{\text{total}} = +ve \Rightarrow \Delta G_{\text{system}} = -ve \Rightarrow$  spontaneous process  
 (ii) If,  $\Delta S_{\text{total}} = -ve \Rightarrow \Delta G_{\text{system}} = +ve \Rightarrow$  non spontaneous process  
 (iii) If,  $\Delta S_{\text{total}} = 0 \Rightarrow \Delta G_{\text{system}} = 0 \Rightarrow$  process is at equilibrium

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description
-	+	-	Reaction spontaneous at all temperature
-	-	-	(at low T) reaction spontaneous at low temperature
-	-	+	(at high T) reaction spontaneous at high temperature
+	+	+	(at low T) reaction spontaneous at low temperature
+	+	-	(at high T) reaction spontaneous at high temperature

+	-	+	(at all T) reaction spontaneous at all temperature
---	---	---	--

Relationship between standard Gibbs energy change ( $\Delta G^\circ$ ) and Equilibrium constant (K)

For a reaction  $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium  $-\Delta G = 0$  and  $Q = K$

$$\therefore \Delta G^\circ = -RT \ln K \quad \dots (i)$$

$$\text{or } \Delta G^\circ = -2.303RT \log_{10} K \quad \dots (ii)$$

from equation (i)

$$\log K = -\frac{\Delta G^\circ}{RT}$$

$$\therefore K = e^{-\Delta G^\circ/RT} \quad \dots (iii)$$

## Illustrations

**Illustration 25.** For a certain reaction the change in enthalpy and change in entropy are  $40.63 \text{ kJ mol}^{-1}$  and  $100 \text{ JK}^{-1}$ . What is the value of  $\Delta G$  at  $27^\circ\text{C}$  and indicate whether the reaction is possible or not?

**Solution**

We know that :

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

$$T = 27 + 273 = 300\text{K}$$

$$\Delta H = 40.63 \times 10^3 \text{ J mol}^{-1} = 40630 \text{ J mol}^{-1}$$

$$\Delta S = 100 \text{ JK}^{-1}$$

$$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = +10630 \text{ J}$$

Positive value of  $\Delta G$  indicates that the reaction is not possible.

**Illustration 26.** For a reaction at  $25^\circ\text{C}$  enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) are  $-11.7 \times 10^3 \text{ J mol}^{-1}$  and  $-105 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. Find out whether this reaction is spontaneous or not.

**Solution**

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

$$= -11700 - 298 \times (-105)$$

$$= +19590 \text{ J}$$

$$\Delta G = +ve, \text{ so reaction is non-spontaneous.}$$

**Illustration 27.** Calculate the equilibrium constant for the reaction given below at  $400\text{K}$ .

$$\text{If } \Delta H^\circ = 77.2 \text{ kJ mol}^{-1} \text{ and } \Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$$



**Solution**

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 77200 - 400 \times 122 = 28400 \text{ J}$$

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$\text{or } 28400 = -2.303 \times 8.31 \times 400 \log K_c$$

$$\text{or } K_c = 1.958 \times 10^{-4}$$

**Illustration 28.** For the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ ;  $\Delta H = -95.4 \text{ kJ}$  and  $\Delta S = -198.3 \text{ J K}^{-1}$ . Calculate the temperature at which the reaction will proceed in forward direction.

**Solution**

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

⊖ At equilibrium  $\Delta G = 0$

$$\therefore \Delta H = T\Delta S \quad \text{so } T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ J K}^{-1}} = 481 \text{ K}$$

For this reaction  $\Delta H$  is -ve, so it will be spontaneous at low temperature.

$\therefore$  Below 481K the reaction would be spontaneous.

**Illustration 29.** Enthalpy and entropy changes of a reaction are  $40.63 \text{ kJ mol}^{-1}$  and  $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. Analyse the feasibility of the reaction at  $27^\circ\text{C}$ .

**Solution**  $\Delta H = 40.63 \text{ kJ mol}^{-1} = 40630 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$   
 Now  $\Delta G = \Delta H - T\Delta S$   
 $= 40630 \text{ J mol}^{-1} - (300 \text{ K}) \times (108.8 \text{ J K}^{-1} \text{ mol}^{-1})$   
 $\Delta G = 7990 \text{ J mol}^{-1}$   
 Since  $\Delta G$  is positive, the reaction is not feasible in the forward direction.

**Illustration 30.** For a certain reaction the change in enthalpy and change in entropy are  $40.63 \text{ KJ mol}^{-1}$  and  $100 \text{ JK}^{-1}$ . Show that the reaction at  $27^\circ\text{C}$  is possible or not.

**Solution**  $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = 40.63 - 300 \times 100 \times 10^{-3}$   
 $\Delta G = + 10.630 \text{ KJ}$   
 $\Delta G$  is positive so reaction is not possible.

**Illustration 31.** Zinc reacts with dilute hydrochloric acid to give hydrogen at  $17^\circ\text{C}$ . The enthalpy of the reaction is  $-12.55 \text{ KJ mol}^{-1}$  and entropy change is  $5 \text{ JK}^{-1} \text{ mol}^{-1}$  for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

**Solution** Given  $\Delta H = -12.55 \text{ KJ mol}^{-1}$  and  $\Delta S = 5 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $T = 17 + 273 = 290 \text{ K}$   
 Applying  $\Delta G = \Delta H - T\Delta S$

$$= -12.55 \frac{\text{KJ}}{\text{mol}} - 290 \text{ K} \times \frac{5}{1000} \frac{\text{KJ}}{\text{Kmol}}$$

$$= -12.55 - 1.45$$

$$= -14 \frac{\text{KJ}}{\text{mol}}$$

Since  $\Delta G$  is negative, the reaction will be spontaneous

**Illustration 32.** For a reaction both  $\Delta H$  and  $\Delta S$  are positive under what condition will the reaction occur spontaneously.

**Solution** The reaction will occur spontaneously only when  $T\Delta S > \Delta H$ .  
 $\Delta G = \Delta H - T\Delta S = (+) - T(+)$   
 For  $\Delta G$  to be negative,  $T\Delta S$  must be  $> \Delta H$

**Illustration 33.** Which of the following are state function ?

- (i)  $q$  (ii) Entropy (iii) Specific heat capacity

**Solution** (iv)  $D_fH$ . (v) w  
**Ans.** (ii), (iii) and (iv)

### BEGINNER'S BOX-5

- If  $\Delta G^\circ > 0$  for a reaction then :-  
 (1)  $K_p > 1$  (2)  $K_p < 1$  (3)  $K_p = 1$  (4) None
- For an endothermic reaction to be spontaneous :-  
 (1)  $\Delta G$  must be +ve (2)  $\Delta S$  must be  $> 0$   
 (3)  $T\Delta S$  must be -ve (4)  $T\Delta S$  must be equal to  $\Delta G$
- The value of  $\Delta G$  for the process  $H_2O(s) \longrightarrow H_2O(l)$  at 1 atm and 260 K is :-  
 (1)  $< 0$  (2)  $= 0$  (3)  $> 0$  (4) Unpredictable
- In a certain chemical reaction  $\Delta H = 150 \text{ KJ}$  and  $\Delta S = 10 \text{ J/K}$  at 300 K. The value of  $\Delta G$  would be :-  
 (1)  $-2850 \text{ J}$  (2) Zero (3)  $+2850 \text{ J}$  (4)  $147 \text{ KJ}$
- the standard Gibb's energy change for a gaseous reaction at  $27^\circ\text{C}$  is  $X \text{ Kcal}$ . If equilibrium constant for a reaction is 100 and  $R$  is  $2 \text{ cal K}^{-1} \text{ mol}^{-1}$ . Then  $X$  is :-  
 (1)  $-2.7636$  (2)  $+2.7636$  (3)  $+807$  (4)  $-807$
- The favorable conditions for a spontaneous reaction are :-  
 (1)  $T\Delta S > \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = +ve$  (2)  $T\Delta S > \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = -ve$   
 (3)  $T\Delta S = \Delta H$ ,  $\Delta H = -ve$ ,  $\Delta S = -ve$  (4)  $T\Delta S > \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = +ve$

### 5.15 THIRD LAW OF THERMODYNAMICS (TLOT)

At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

#### Exceptions :

- |                         |                |
|-------------------------|----------------|
| (i) NO, $N_2O$          | (2) CO, $CO_2$ |
| (3) Mixture of isotopes | (4) Ice        |

## ENERGETICS

### 5.16 INTRODUCTION

**Thermochemistry** is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system. Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

In this chapter we will introduce enthalpies of some specific reaction. Like, Enthalpy of formation ( $\Delta H_f$ ), Enthalpy of combustion ( $\Delta H_{\text{comb}}$ ), Bond dissociation enthalpy ( $\Delta H_{\text{BDE}}$ ) & Enthalpy of Neutralization ( $\Delta H_{\text{neutralization}}$ )

### THERMOCHEMICAL REACTION :

The balanced chemical reaction which gives information about the physical states of reactants & products and heat change is called as thermochemical reaction.



**Thermochemical reactions are 2 types.**

#### (i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.

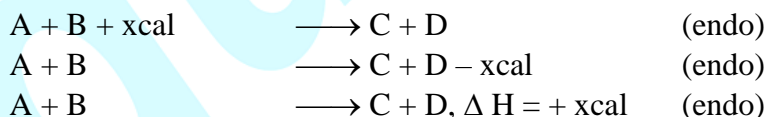
$$\Delta H = +ve$$

$$\Delta H = H_P - H_R = +ve \text{ i.e. } H_P > H_R$$

- (a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.
- (b) The product formed in the endothermic reaction is called an endothermic compound.
- (c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

**Figure.**

#### Representation of endothermic reaction :



#### Examples :

- (I) Dissociation reactions (mostly)
- (II) Fusion reactions
- (III) Vaporization reactions
- (IV) Sublimation reactions
- (V) Photosynthesis  $6\text{CO}_2 + 6\text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2, \Delta H = +ve$

#### (ii) Exothermic reaction :

The reaction which evolves heat is called as exothermic reaction.

$$\Delta H = -ve \quad \Delta H = H_P - H_R = -ve \text{ i.e. } H_P < H_R$$

**Figure**

- (a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.
- (b) The product formed in the exothermic reaction is called exothermic compound.
- (c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

### Representation of exothermic reaction.



### Examples :

(I) Combustion reactions

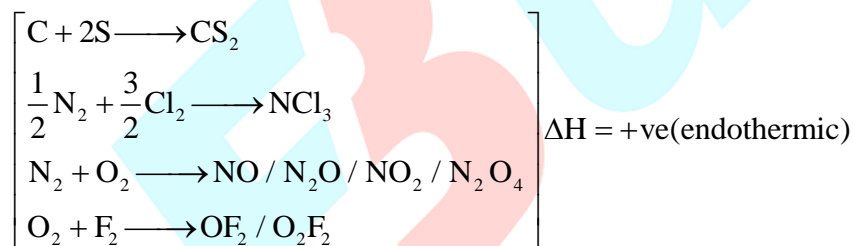
(II) Neutralization reactions

(III) Respiration reaction



(IV) Formation reaction  $\left\{ \begin{array}{l} \text{endo} \\ \text{exo (generally)} \end{array} \right.$

Exceptions of formation reaction :



## GOLDEN KEY POINTS

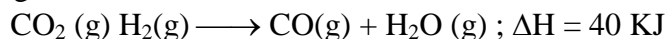
- (i) If conditions are not given then,  $\Delta H$  is considered to be  $\Delta H^\circ$ .
- (ii) If thermochemical reaction is multiplied by a coefficient then,  $\Delta H$  of reaction is also multiplied by that coefficient.
- e.g.  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -285 \text{ kJ/mol}$   
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -2 \times 285 \text{ kJ}$
- (iii) If reaction is reversed then numerical value of  $\Delta H$  remains same by sign is changed.
- e.g.  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -285 \text{ kJ/mol}$   
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = +285 \text{ kJ/mol}$

## BEGINNER'S BOX-7

- An endothermic reaction is one in which :
  - Heat is converted into electricity
  - Heat is absorbed
  - Heat is evolved
  - Heat is converted into mechanical work
- If heat of reaction  $A + 5B \longrightarrow 2C + 3D$ , is  $-50 \text{ KJ}$ . What is the heat of the reaction  $2A + 10B \longrightarrow 4C + 6D$ .
  - $-50 \text{ KJ}$
  - $-25 \text{ KJ}$
  - $-100 \text{ KJ}$
  - $+100 \text{ KJ}$
- The process  $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$ , Should be :
  - Exothermic

- (2) Endothermic
- (3) Neither exothermic nor endothermic
- (4) Exothermic or endothermic depending upon temperature

4. For the given reaction :

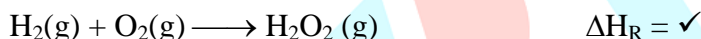
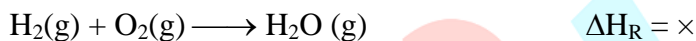
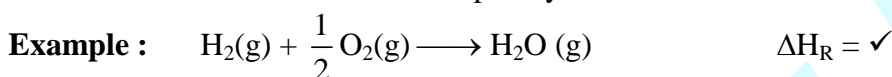


The  $\Delta H$  is specifically called

- (1) heat of formation of CO
- (2) Heat of combustion
- (3) Heat of reaction
- (4) Heat of hydrogenation of C=O bond

### 5.17 HEAT OF REACTION OR (ENTHALPY OF REACTION) OR ( $\Delta H_R$ ) :

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.



**Note :** Heat of reaction at constant pressure is  $\Delta H$  and heat of reaction at constant volume is  $\Delta E$ .

**Factors affecting heat of reaction :**

(i) **Reaction condition :**

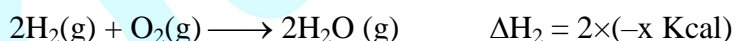
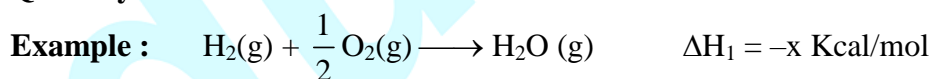
(a) The chemical reactions are carried out at constant temperature with either pressure or volume constant.

At constant pressure  $q_p = \Delta H_{\text{reaction}}$

At constant volume  $q_v = \Delta E_{\text{reaction}}$

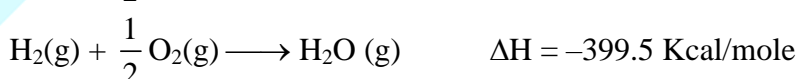
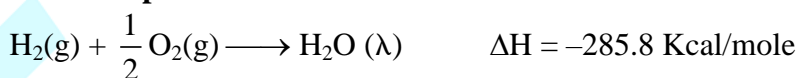
$$\Delta H = \Delta E + \Delta n_g \cdot RT$$

(ii) **Quantity of reactant :**



If equation is multiplied by coefficient then value of  $\Delta H$  is also multiplied by that coefficient.

(iii) **Physical state of products and reactants :**



If the physical state of product is different then the value of  $\Delta H$  is different

**Note :** For  $\text{H}_2\text{O}$  (liquid)  $\Delta H$  is more negative in comparison to the formation of  $\text{H}_2\text{O}$  (vapour) because when vapours convert into a liquid some heat is released.

(iv) **Allotropic form :** (Physical nature of reactant)



**(v) Temperature :**

Effect of temperature on heat of reaction is given by Krichoff equation

$$(i) \text{ at constant pressure : } \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{\text{Pm}}$$

$$\Delta C_{\text{Pm}} = \Sigma(C_{\text{Pm}})_{\text{P}} - \Sigma(C_{\text{Pm}})_{\text{R}}$$

$$\Delta H_{T_1} = \text{Heat of reaction } T_1 \text{ temperature}$$

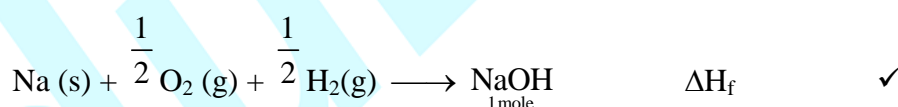
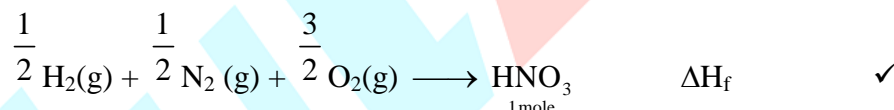
$$\Delta H_{T_2} = \text{heat of reaction at } T_2 \text{ temperature}$$

$$(ii) \text{ at constant pressure : } \frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{\text{Vm}}$$

$$\Delta C_{\text{Vm}} = \Sigma(C_{\text{Vm}})_{\text{P}} - \Sigma(C_{\text{Vm}})_{\text{R}}$$

**5.18 TPYS OF HEAT OF REACTION :****(A) Heat of formation, Enthalpy of formation ( $\Delta H_{\text{f}}$ ) or ( $\Delta_{\text{f}}H$ )**

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states). The reference state of oxygen, carbon and sulphur are  $\text{O}_2$  gas,  $\text{C}_{\text{graphite}}$  and  $\text{S}_{\text{rhombic}}$ , respectively some reaction with standard molar enthalpies of formation are:

**APPLICATION OF  $\Delta H_{\text{f}}$** **Calculation of  $\Delta H$  of any general reaction.**

Let us consider a general reaction  $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{f}}(\text{products}) - \Sigma \Delta H_{\text{f}}(\text{reactant}) = [c\Delta H_{\text{f}}(\text{C}) + d\Delta H_{\text{f}}(\text{D})] - [a\Delta H_{\text{f}}(\text{A}) + b\Delta H_{\text{f}}(\text{B})]$$

**GOLDEN KEY POINTS**

- Standard condition means,  $P = 1 \text{ atm}$ ,  $T = 25^\circ\text{C}$  or  $298 \text{ K}$   
Standard heat of formation is represented by  $\Delta H_{\text{f}}^\circ$ .
- If no condition is given then value of  $\Delta H_{\text{f}}$  is considered as  $\Delta H_{\text{f}}^\circ$ .
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

**Elements**  
C

**Reference state**  
 $\text{C}_{(\text{graphite})}$

S

P

O

H

Br

Metal

$S_{8(\text{Rhombic})}$  (Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)

 $P_{4(\text{white})}$  $O_{2(g)}$  $H_{2(g)}$  $Br_{2(l)}$  $M_{(s)}$  [except  $Hg_{(l)}$ ]

- The formation reaction may be exothermic or endothermic.

## Illustrations

**Illustration 34** Since enthalpy of elements in their natural state is taken as zero. The value of  $\Delta H_f^\circ$  of compounds

(1) is always negative

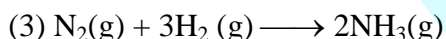
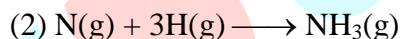
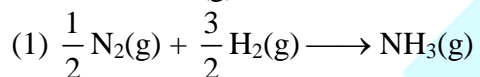
(2) is always positive

(3) may be positive or negative

(4) is zero

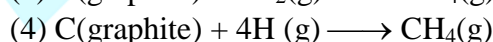
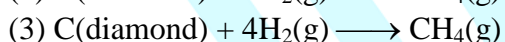
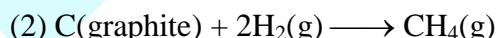
**Solution**      **Ans. (3)**

**Illustration 35** The enthalpy of formation of ammonia at 298 K is given as  $\Delta H_f^\circ = -46.11$  kJ per mol of  $NH_3(g)$ . To which of the following equation does this value apply?



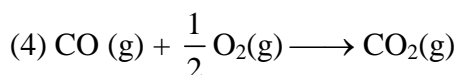
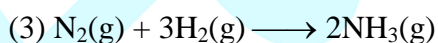
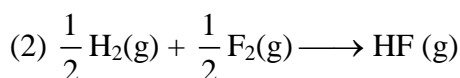
**Solution**      **Ans. (1)**

**Illustration 36** Which of the following equation represents the standard heat of formation :



**Solution**      **Ans. (2)**

**Illustration 37** Which of the following reaction defines  $\Delta H_f^\circ$



**Solution**      **Ans. (2)**

**Illustration 38** How much heat will be required at constant pressure to form 1.28 kg of  $CaC_2$  from  $CaO(s)$  &  $C(s)$ ?

Given :  $\Delta_f H^\circ (CaO, s) = -152$  kcal/mol

$\Delta_f H^\circ (CaC_2, s) = -14$  kcal/mol

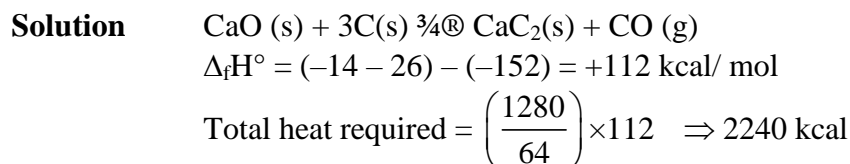
$\Delta_f H^\circ (CO, g) = -26$  kcal/mol

(1) +112 kcal

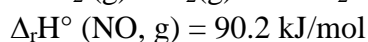
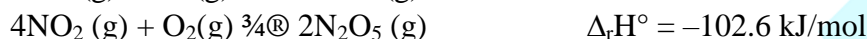
(2) 224 kcal

(3) 3840 kcal

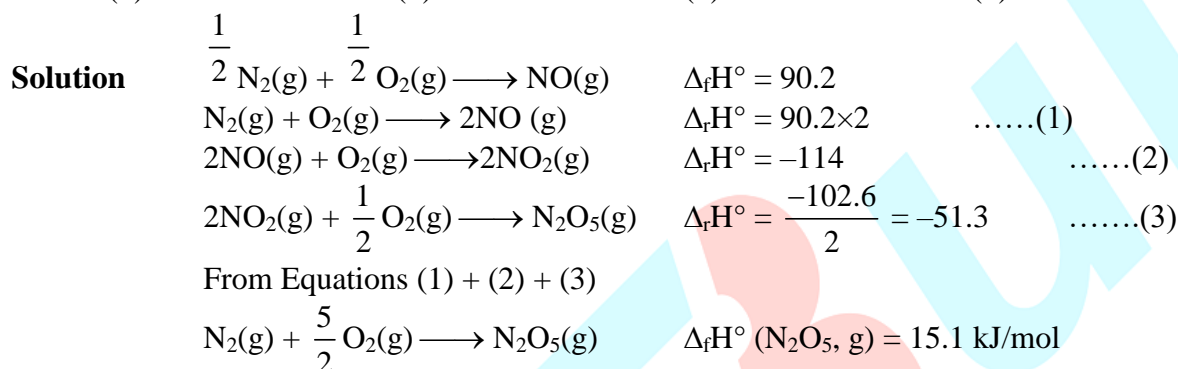
(4) 2240 kcal



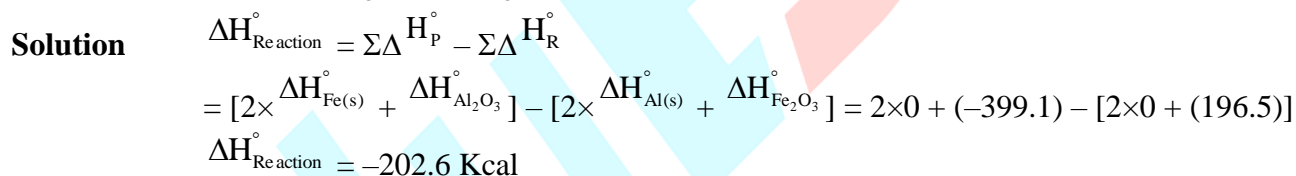
**Illustration 39** The  $\Delta_f H^\circ$  ( $\text{N}_2\text{O}_5$ , g) in kJ/mol on the bases of the following data is :



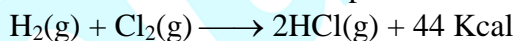
- (1) 15.1                      (2) 30.2                      (3) -36.2                      (4) None of these



**Illustration 40** Calculate  $\Delta H^\circ$  for  $2\text{Al(s)} + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{Fe(s)} + \text{Al}_2\text{O}_3$  given that standard enthalpy of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  are -196.5 and -399.1 Kcal.

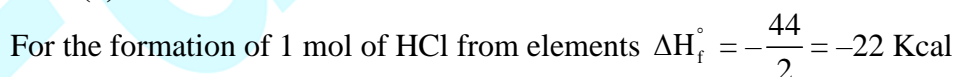


**Illustration 41** The heat of formation of the compound in the following reaction is :



- (1) -44 Kcal  $\text{mol}^{-1}$                       (2) -22 Kcal  $\text{mol}^{-1}$   
 (3) +11 Kcal  $\text{mol}^{-1}$                       (4) -88 Kcal  $\text{mol}^{-1}$

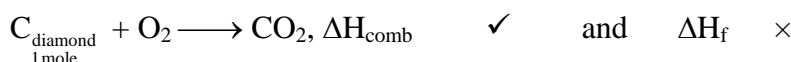
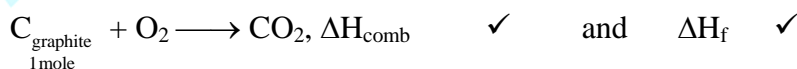
**Solution** **Ans. (2)**

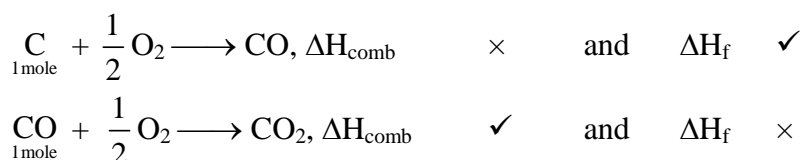


**(B) Heat of combustion ( $\Delta H_{\text{comb}}$ ) :**

Amount of heat evolved when 1 mole of substance is completely burnt or oxidised) in excess of oxygen.

**Example :**



**Note :**

(I) Heat of combustion reaction is always exothermic

(II) If conditions are not given then  $\Delta H_{\text{comb}}$  considered as  $\Delta H_{\text{comb}}^\circ$ .

(III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\Delta H = \Sigma(\Delta H_{\text{comb}})_R - \Sigma(\Delta H_{\text{comb}})_P$$

**APPLICATION OF HEAT OF COMBUSTION :**

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\text{Calorific value} = \frac{\Delta H_{\text{comb}}}{\text{Molecular weight}}$$

**Unit :-** KJ g<sup>-1</sup> or K cal g<sup>-1</sup>

**GOLDEN KEY POINTS**

- Heat of combustion reaction is always exothermic
- If conditions are not given then  $\Delta H_{\text{comb}}$  is considered as  $\Delta H_{\text{comb}}^\circ$ .
- Maximum value of calorific value = Maximum efficiency or best fuel
- H<sub>2</sub> has the highest calorific value (150 KJ/gm) but it is not used as domestic or industrial fuel due to some technical problems.

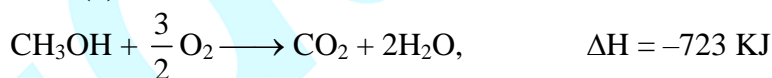
**Illustrations**

**Illustration 42** 1 mole of methanol, when burnt in oxygen, gives out -723 KJ mol<sup>-1</sup> heat. If 1 mole of oxygen is used what will be the amount of heat evolved?

- (1) 723 KJ                      (2) 964 KJ                      (3) 482 KJ                      (4) 241 KJ

**Solution**

**Ans. (3)**



$$\text{with 1 mole of O}_2, \quad \Delta H = -\frac{2}{3} \times 723 = -482 \text{ KJ}$$

**Illustration 43** Combustion of methane :

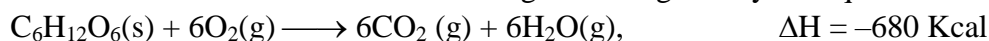
- (1) Is an exothermic reaction                      (2) Is an endothermic reaction  
(3) Requires a catalyst                      (4) Gives H<sub>2</sub>

**Solution**

**Ans. (1)**

Combustion is always exothermic

**Illustration 44** The heat evolved in the combustion of glucose is given by the equation



The wt. of  $\text{CO}_2(\text{g})$  produced when 170 Kcal of heat is evolved in the combustion of glucose is

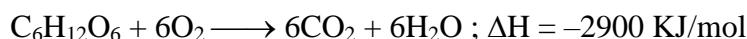
- (1) 264 g                      (2) 66 g                      (3) 11 g                      (4) 44 g

**Solution**      **Ans. (2)**

Evolution of 680 Kcal is accompanied by  $\text{CO}_2 = 6 \times 44 = 264 \text{ g}$

Evolution of 170 Kcal is accompanied by  $\text{CO}_2 = \frac{264}{680} \times 170 = 66 \text{ g}$

**Illustration 45** Find out the calorific value of Glucose



**Solution**

⊖ Heat evolved from 1 mol glucose = 2900 KJ

or Heat evolved from 180 gram glucose = 2900 KJ

∴ heat evolved from 1 gram glucose =  $\frac{2900}{180} = 16.11 \text{ KJ/gm}$

Or another method C.V. =  $\frac{\Delta H_{\text{comb}}}{M_w} = \frac{2900}{180} = 16.11 \text{ KJ/gm}$

**Illustration 46** Enthalpy of combustion of a substance is always :

- (1)  $> 0$                       (2)  $\geq 0$                       (3)  $\leq 0$                       (4)  $< 0$

**Solution**      **Ans. (4)**

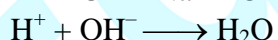
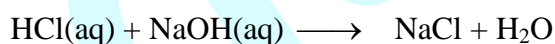
**Illustration 47** The heat change for a reaction :  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$  refers to

- (1) enthalpy of formation of carbon dioxide      (2) enthalpy of combustion of carbon dioxide  
(3) enthalpy of vapourisation                      (4) enthalpy of combustion of carbon monoxide

**Solution**      **Ans. (4)**

(C) **Heat of neutralization ( $\Delta H_{\text{neut}}$ ) :**

The heat evolved when one equivalent of an acid is completely neutralized by one equivalent of a base in dilute solution is called as heat of neutralization.



**Note :**

- (i) When one equivalent of SA is neutralized by one equivalent of SB then evolve heat remain constant and its value is  $-13.7 \text{ Kcal/equivalent}$  or  $-57.2 \text{ KJ/equivalent}$ .

eg.	SA		SB		
	$\text{HCl}(\text{aq})$	+	$\text{NaOH}(\text{aq})$	$\rightarrow$	$\text{NaCl} + \text{H}_2\text{O} + 13.7 \text{ Kcal}$
	$\text{NV} = 1 \text{ eq.}$		$\text{NV} = 1 \text{ eq.}$	$\rightarrow$	$\Delta H = -13.7 \text{ Kcal}$
	$\text{NV} = 2 \text{ eq.}$		$\text{NV} = 2 \text{ eq.}$	$\rightarrow$	$\Delta H = -13.7 \text{ Kcal}$
	$\text{NV} = 3 \text{ eq.}$		$\text{NV} = 3 \text{ eq.}$	$\rightarrow$	$\Delta H = -13.7 \text{ Kcal}$
	$\text{NV} = 4 \text{ eq.}$		$\text{NV} = 5 \text{ eq.} = (4+1)\text{eq.}$	$\rightarrow$	$\Delta H = -13.7 \text{ Kcal}$
	$\text{NV} = 5 \text{ eq.} = (3+2)\text{eq.}$		$\text{NV} = 5 \text{ eq.}$	$\rightarrow$	$\Delta H = -13.7 \text{ Kcal}$

- (ii) If one of the acid or base or both are weak then heat of neutralization is usually less than  $-13.7 \text{ Kcal eq}^{-1}$  or  $-57.3 \text{ KJ eq}^{-1}$  because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.



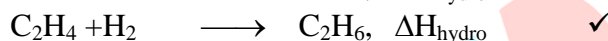
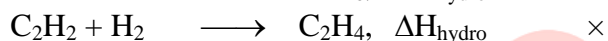
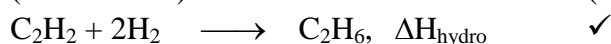
**Exception :**

For a reaction  $\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}; \Delta H = 16.7 \text{ Kcal}$ ; this is because of hydration of  $\text{F}^-$  ion.

**(D) Heat of hydrogenation ( $\Delta H_{\text{Hydrogenation}}$ ) :**

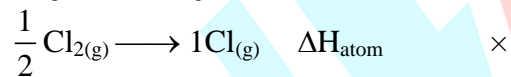
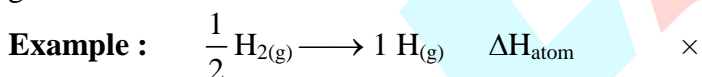
The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic  $\xrightarrow{\text{Change}}$  Saturated organic compound  
(= or  $\equiv$  Bond) (-Bond)



**Note :** Heat of hydrogenation is exothermic process.

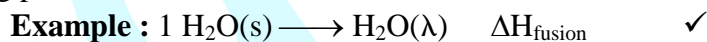
**(E) Heat of atomization ( $\Delta H_{\text{atom}}$ ) :** The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.



**Note :** It is an endothermic reaction.

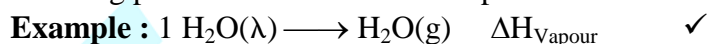
**(F) HEAT OF TRANSFORMATION**

- (i) **Heat of fusion ( $\Delta H_{\text{fusion}}$ ) :** The required amount of heat to convert 1 mol solid into liquid at its melting point is called as heat of fusion.



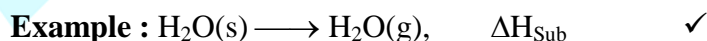
**Note :** Heat of fusion is always endothermic reaction i.e. ( $\Delta H = +\text{ve}$ )

- (ii) **Heat of vapourization ( $\Delta H_{\text{vapour}}$ ) :** The required amount of heat to convert 1 mol liquid into gas at its boiling point is called as heat of vapourization.



- (iii) **Heat of sublimation ( $\Delta H_{\text{sub}}$ ) :**

The required amount of heat to convert 1 mol solid into gas at a certain temperature is called as heat of sublimation.



**Note :** Heat of sublimation is always endothermic reaction i.e. ( $\Delta H = +\text{ve}$ )

## Illustrations

**Illustration 48** Heat of neutralization of an acid by a base is maximum when :

- (1) Both acid and base are weak (2) Both the acid and base are strong  
 (3) The acid is weak and the base is strong (4) The acid is weak and the base is strong

**Solution**      **Ans. (2)**

Heat of neutralization is maximum (57.2 KJ/eq. or 13.7 Kcal/eq.) when both acid and base are strong.

**Illustration 49** The enthalpy change for the process  $C(s) \longrightarrow C(g)$  corresponds to the enthalpy of

- (1) fusion (2) vapourization  
 (3) combustion (4) sublimation

**Solution**      **Ans. (4)**

Solid  $\longrightarrow$  gas, is sublimation.

**Illustration 50** If  $H^+ + OH^- \longrightarrow H_2O + 13.7 \text{ Kcal}$ , then heat of complete neutralization of 1 gm mol of  $H_2SO_4$  with base in excess will be :

- (1) -13.7 Kcal (2) -27.4 Kcal  
 (3) -6.85 Kcal (4) -3.425 Kcal

**Solution**      **Ans. (2)**

Moles of  $H_2SO_4 = 1 \text{ mol}$

Gm. eq. of  $H_2SO_4 = \text{moles} \times V.F. = 1 \times 2 = 2 \text{ gm eq.}$

Heat evolve due to 2 gm eq. =  $-13.7 \times 2 = -27.4 \text{ Kcal}$

**Illustration 51** 200 cm<sup>3</sup> of 0.1 M  $H_2SO_4$  is mixed with 150 cm<sup>3</sup> of 0.2 M KOH. Find the value of evolved heat.

**Solution**

$H_2SO_4$

KOH

eq. = NC =  $(0.1 \times 2) \times 0.2$   
 = 0.4

$(0.2 \times 1) \times (0.15)$   
 = 0.3

Heat liberated by 1 eq. = 57.2 KJ

So heat liberated by 0.3 eq. =  $57.2 \times 0.3 = 17.16 \text{ KJ}$

### BEGINNER'S BOX-8

- Enthalpy of neutralization of acetic acid with KOH will be numerically :  
 (1) = 57.2 KJ (2) > 57.2 KJ  
 (3) < 57.2 KJ (4) Unpredictable
- The vapourisation process is always :  
 (1) Exothermic (2) Endothermic  
 (3) Can be exothermic or endothermic (4) None of these
- One mol of  $H_2SO_4$  is completely neutralized with 2 mol of NaOH is dilute solution. The amount of heat evolved during the process is :  
 (1) 57.2 KJ (2)  $\frac{57.2 \text{ KJ}}{2}$   
 (3) 13.7 Kcal (4) 114.4 KJ
- Which of the following data represents the value of heat of neutralization of strong acid against strong base ?



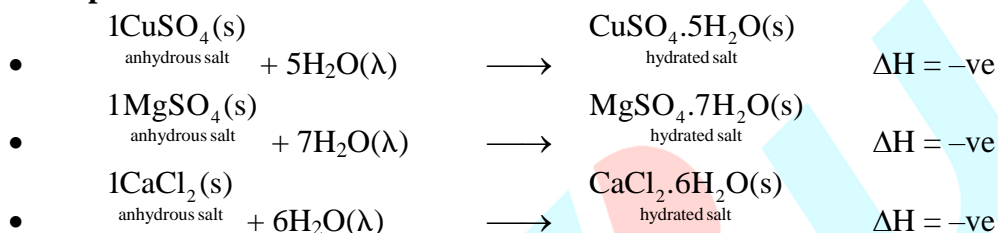
- (1)  $-13.7 \text{ Kcal}$       (2)  $-57.2 \text{ KJ}$       (3)  $-5.72 \times 10^4 \text{ J}$       (4) All the above

5. Fusion of ice is :  
 (1) Exothermic change  
 (2) Endothermic change  
 (3) A process that does not involve any heat change  
 (4) Unpredictable

**(G) Heat of hydration ( $\Delta H_{\text{hydra}}$ )**

Amount of heat evolved when one mol of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

**Example :**

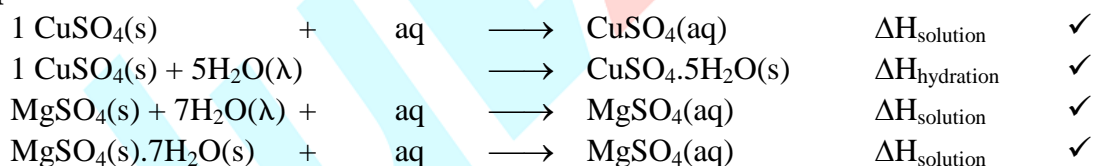


**Special Note :** Heat of hydration is exothermic

**(H) Heat of solution ( $\Delta H_{\text{sol}}$ )**

Amount of heat absorbed or evolved when one molar of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as 'Heat of solution'.

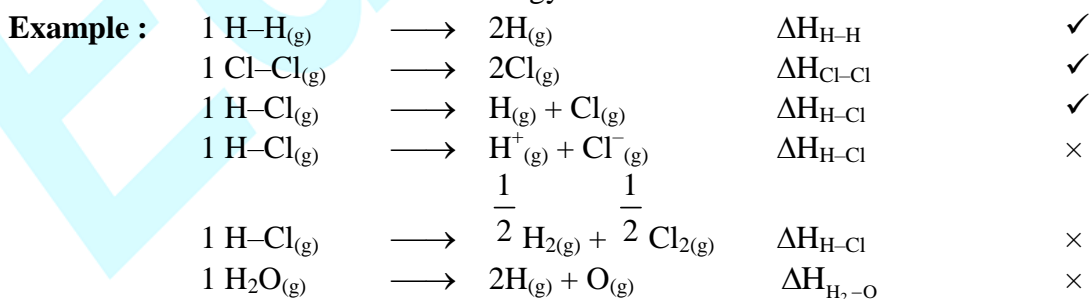
**Example 1 :**



**Special Note :** Heat of solution may be endothermic or exothermic

**(I) Bond energy / Bond dissociation energy :**

The required amount of energy to dissociate one mole gaseous bond into separate gaseous atoms is called as bond dissociation energy.



**GOLDEN KEY POINTS**

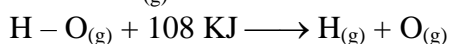
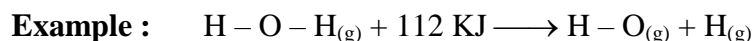
- The bond energy may be defined as the average amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.

- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then  $\Delta H$  of that reaction can be calculate as follows.

$$\Delta H = \Sigma(\text{B.E.})_R - \Sigma(\text{B.E.})_P$$

- In the case of poly atomic molecule we calculate the average bond energy.

$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}$$



$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{112 + 108}{2} = 110 \text{ KJ/mol}$$

## Illustrations

**Illustration 52** Given the bond energy of  $\text{N} \equiv \text{N}$ ,  $\text{H}-\text{H}$  and  $\text{N}-\text{H}$  bonds are 945, 436 and 391  $\text{KJ mol}^{-1}$  respectively, the enthalpy of the reaction  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \longrightarrow 2\text{NH}_{3(\text{g})}$  is :

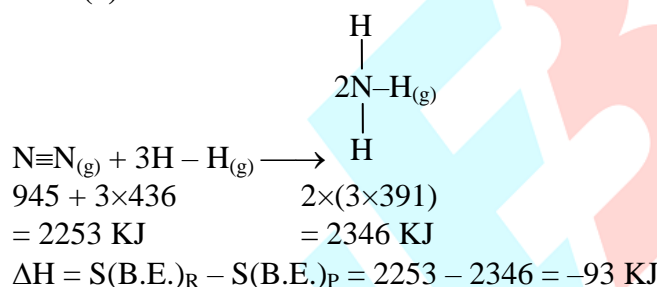
(1)  $-93 \text{ KJ}$

(2)  $102 \text{ KJ}$

(3)  $90 \text{ KJ}$

(4)  $105 \text{ KJ}$

**Solution**      **Ans. (1)**



**Illustration 53** The enthalpy changes at 298 K in successive breaking of  $\text{O}-\text{H}$  bonds of  $\text{H}-\text{O}-\text{H}$  are



The bond enthalpy of the  $\text{O}-\text{H}$  bond is

(1)  $498 \text{ KJ mol}^{-1}$

(2)  $463 \text{ KJ mol}^{-1}$

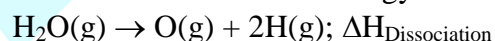
(3)  $428 \text{ KJ mol}^{-1}$

(4)  $70 \text{ KJ mol}^{-1}$

**Solution**      **Ans. (2)**

$$(\text{B.E.})_{\text{av}} = \frac{498 + 428}{2} = 463 \text{ KJ}$$

**Illustration 54** The required heat for dissociation of 1 mol  $\text{H}_2\text{O}$  into its atoms ( $\text{H}$  and oxygen) is  $\Delta H_{\text{Dis}}$ . Then calculate the bond energy of  $\text{O}-\text{H}$  bond.



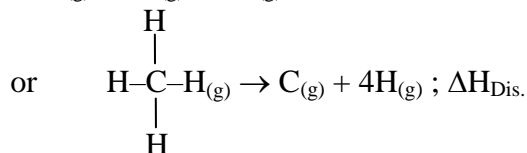
**Solution**  $\text{H}-\text{O}-\text{H}_{(\text{g})} \longrightarrow \text{O}_{(\text{g})} + 2\text{H}_{(\text{g})}; \Delta H_{\text{Dissociation}}$

$\ominus$  required energy for breaking the 2 mol  $\text{O}-\text{H}$  bond  $= \Delta H_{\text{Dis}}$ .

$$\therefore \text{required energy for 1 mole} = \frac{\Delta H_{\text{Dis}}}{2} ; \text{DH}_{\text{O-H}} = \frac{\Delta H_{\text{Dis}}}{2}$$

**Illustration 55** Calculate the bond energy of C–H bond in methane.

**Solution**  $\text{CH}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{H}_{(g)}; \Delta H_{\text{Dis.}}$



⊙ Bond energy of 4 mol C–H =  $\Delta H_{\text{Dis.}}$

$$\therefore \text{Bond energy of 1 mol C–H bond} = \frac{\Delta H_{\text{Dis.}}}{4}$$

**Illustration 56** The energy change of reaction  $\text{C}_2\text{H}_{6(g)} \longrightarrow 2\text{C}_{(g)} + 6\text{H}_{(g)}$  is X KJ. The bond energy of C–H bond is :

- (1)  $\frac{X}{6}$  KJ/mol  
(3) X KJ/mol

- (2)  $\frac{X}{3}$  KJ/mol  
(4) Unpredictable from data

**Solution** **Ans. (4)**

**Illustration 57**  $\text{CuSO}_4(\lambda) + 5\text{H}_2\text{O}(\text{s}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}); \Delta H = -x \text{ KJ}$

The value of  $\Delta H$  represents :

- (1) enthalpy of solution of copper (II) sulphate  
(2) enthalpy of hydration of copper (II) sulphate  
(3) enthalpy of hydrolysis of copper (II) sulphate  
(4) lattice energy of copper (II) sulphate

**Solution** **Ans. (2)**

**Illustration 58** The bond energy of hydrogen is  $103 \text{ Kcal mol}^{-1}$ . This means that :

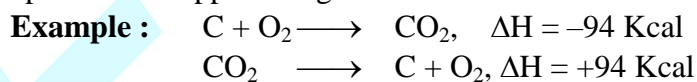
- (1) 103 Kcal are required to break  $6.023 \times 10^{23}$  gaseous  $\text{H}_2$  molecules into gaseous atoms  
(2) 103 Kcal are required to break the bonds in one gram of hydrogen  
(3) 103 Kcal are required to break one bond to form two atoms of hydrogen  
(4) 103 Kcal are required to break one mole of gaseous hydrogen molecules into ions.

**Solution** **Ans. (1)**

## 5.19 LAWS OF THERMOCHEMISTRY :

### (I) LAVOISIER AND LAPLACE LAW :

Enthalpy of formation of compound is numerically equal to the enthalpy of decomposition of that compound with opposite sign.



### (II) HESS LAW OF CONSTANT HEAT SUMMATION :

The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

**Example -1 : Figure**

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 \\ \text{or} \quad \Delta H &= \Delta H_3 + \Delta H_4 + \Delta H_5 \\ \text{or} \quad \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \end{aligned}$$

## Example :2: Figure

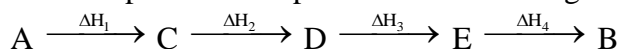
## GOLDEN KEY POINTS

- Heat change of a reaction does not depend on the number of steps used in the reaction.
- Heat change of a reaction does not depend on intermediate position, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on time of reaction.

## Illustrations

**Illustration 59** Single step reaction  $A \rightarrow B$ ;  $\Delta H = ?$

Multi step reaction to produce B from A is given



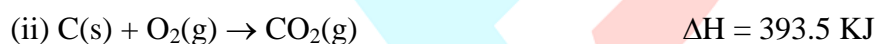
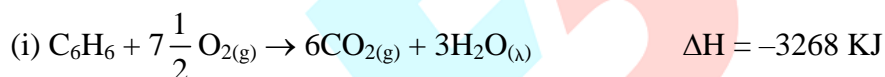
**Solution** According to Hess's law  $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

**Illustration 60** Calculate the heat of formation of Benzene. The reaction is given below :

$6C(s) + 3H_{2(g)} \rightarrow C_6H_{6(l)}$  and  $-3268$ ,  $-393.5$  and  $-285.8$  KJ/mol are the heat of combustion of benzene, heat of formation of  $CO_2$  and heat of formation of  $H_2O(l)$  respectively.

**Solution** Target reaction  $6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(l)}$

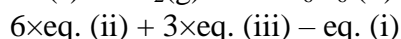
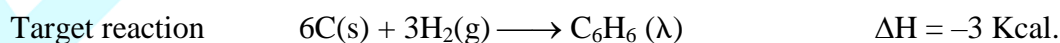
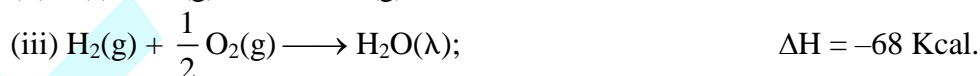
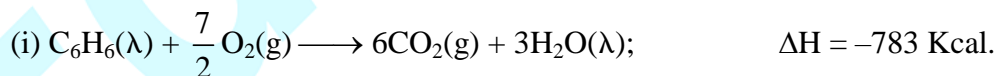
Given



$$\Delta H = 6 \times 1 - 393.5 + 3 \times -285.8 - (-3268) = +49.6 \text{ KJ/mol}$$

**Illustration 61** The heats of formation of  $CO_{2(g)}$  and  $H_2O_{(l)}$  are  $-97$  and  $-68$  kcal/mol. The heat of combustion of benzene is  $-783$  Kcal/mol. What will be the heat of formation of benzene?

**Solution** Given :

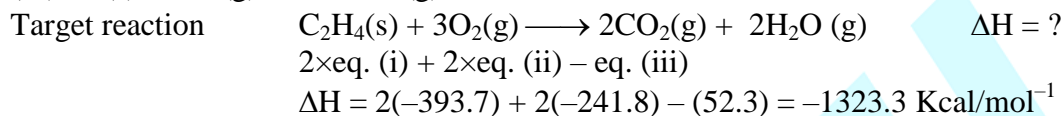
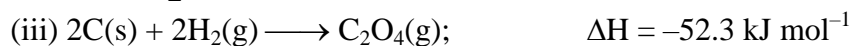
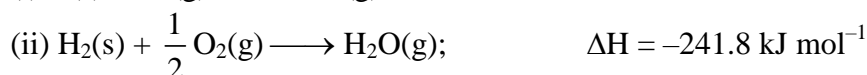


$$\Delta H = 6 \times -97 + 3 \times -68 - (-783) = -3 \text{ Kcal/mol}$$

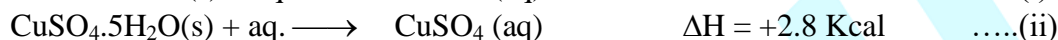
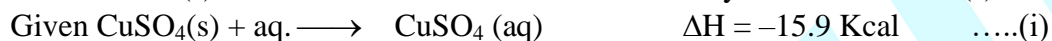
**Illustration 62** Calculate the enthalpy of combustion of ethylene (gas) to form  $CO_2$  (gas) and  $H_2O$  (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of  $CO_{2(g)}$ ,  $H_2O(g)$  and  $C_2H_4(g)$  are  $-393.7$ ,  $-241.8$ ,  $+52.3$  kJ per mol respectively.

**Solution**

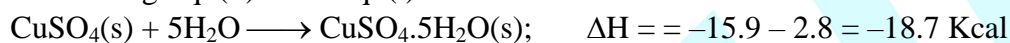
We are given :



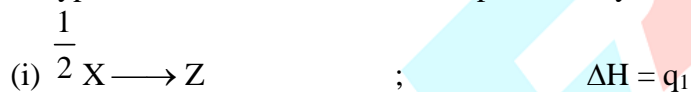
**Illustration 63** The heat of solution of anhydrous  $\text{CuSO}_4(\text{s})$  is  $-15.9 \text{ Kcal/mol}$  and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$  is  $2.8 \text{ Kcal/mol}$ . Calculate the heat of hydration of  $\text{CuSO}_4(\text{s})$ .

**Solution**

Subtracting Eq. (ii) from Eq. (i)

Heat of hydration of any  $\text{CuSO}_4 = -18.7 \text{ Kcal mol}^{-1}$ **BEGINNER'S BOX-9**

1. A hypothetical reaction,  $\text{X} \longrightarrow 2\text{Y}$  proceeds by the following sequence of steps

The value of  $\Delta H$  of reaction is :

2. Consider two paths of a certain reaction

**ANSWER KEY****BEGINNER'S BOX-1**

1. (1) 2. (1) 3. (1) 4. (1)

**BEGINNER'S BOX-2**

1. (3) 2. (4) 3. (2) 4. (1)

**BEGINNER'S BOX-3**

1. (2) 2. (2) 3. (2) 4. (3) 5. (1) 6. (2) 7. (4)  
8. (3)

**BEGINNER'S BOX-4**

1. (1) 2. (2)

**BEGINNER'S BOX-5**

1. (2) 2. (3) 3. (4) 4. (3) 5. (3) 6. (1) 7. (2)

**BEGINNER'S BOX-6**

1. (2) 2. (2) 3. (3) 4. (4) 5. (1) 6. (1)

**BEGINNER'S BOX-7**

1. (2) 2. (3) 3. (2) 4. (3)

**BEGINNER'S BOX-8**

1. (3) 2. (2) 3. (4) 4. (4) 5. (2)

**BEGINNER'S BOX-9**

1. (3) 2. (2)